

**A STUDY OF CARBON CARBON BOND CLEAVAGE IN
STRAINED HYDROCARBON SYSTEMS.**

**A Thesis Presented By
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Abstract

This thesis is divided into three chapters. Chapter One discusses the current status of methods available for the activation of saturated carbon hydrogen and carbon carbon bonds. This is coupled with a critical overview of the recent literature concerning the use of novel homogeneous organotransition metal complexes in order to establish their potential in this area.

Chapter Two concerns the activation of strained carbon carbon bonds. The rearrangement of tricyclo[4.1.0.0^{2,7}]heptane by metallic species may yield ~~three~~ structurally different isomers. Product specificity is shown to be linked to the nature of the metallic catalyst, depending on the degree of Lewis acidity. A novel mechanistic pathway derived from these studies allows prediction of the product distribution and specificity for a given metallic catalyst.

Chapter Three reviews the techniques available for the vinyl cyclopropane-cyclopentene rearrangement. A novel radical approach to this transformation via α cyclopropyl carbinyl radicals is employed. The reagents diphenyl disulphide, dibenzyl disulphide and diphenyl diselenide have been investigated under photolytic conditions, and the introduction of cobalt(II) salen in this system is also discussed. Thiophenol and oxygen lead to opening of the vinyl cyclopropane ring system and the degree of ring cleavage is found to be dependent on the oxygen concentration. The reaction of tosyl iodide with suitably constructed vinyl cyclopropane derivatives yields novel functionalised adducts by an S_H2' mechanism. Anionic reactions of the derived product lead either via α -alkylation to a functionalised cyclopentene derivative or by γ -alkylation to functionalised vinyl cyclopropanes.

The anomalous reaction of tosyl iodide with the natural product thujopsene is rationalised by a carbonium ion rearrangement sequence.

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To Mum and Dad

Symbols and Abbreviations

Ac	acetyl
AIBN	azoisobutyronitrile
acac	acetyl acetate
bpy	bipyridine
n-BuLi	n-butyl lithium
Cp	cyclopentadienyl
Cp*	pentamethyl cyclopentadienyl
cy	cyclohexyl
cod	cyclooctadiene
dmpe	1,2- <i>bis</i> (dimethylphosphino)ethane
dppe	1,2- <i>bis</i> (diphenylphosphino)ethane
dipic	dipicolinate
DMSO	dimethylsulphoxide
L	ligand
LDA	Lithium Diisopropylamine
MVCl ₂	methyl viologen
pic	picolinate
py	pyridine
Pz	pyrazolyl
S	solvent
TPP	tetraphenylporphyrin
Ts	<i>p</i> -toluenesulphonyl(tosyl)
atmos	atmosphere
EWG	Electron Withdrawing Group

equiv.

equivalent

m.p.

melting point

nmr

nuclear magnetic resonance

r.t.

room temperature

S.C.E.

Saturated Calomel Electrode

tlc

thin layer chromatography

)))

ultrasound

CHAPTER 1

THE ACTIVATION OF SATURATED HYDROCARBONS

1. Introduction and Current Status of the Petrochemical Industry

Within the complex array of a petroleum refinery there is an increasing demand, not only for the production of quality fuels, but also for an expanding range of petrochemically derived molecules. This fact presents a viable possibility for a refinery designed with specific units to produce petrochemicals and/or petrochemical feedstocks.

The major constituents of petroleum are saturated alkanes (hydrocarbons); a class of compounds unfortunately notorious for their lack of reactivity. Alkanes are abundant in coal liquefaction procedures and also in natural gas. The conversion of alkanes to compounds such as methanol, related congeners or unsaturated species would provide starting materials, that is activated substances, for further chemical manipulations. This could in turn give rise to an large variety of petrochemically derived substances.

Thus the availability of alkane substrates and their cheapness has commanded a wealth of attention with respect to their functionalisation. Presently, activation methods range from the classical organic reactions of halogenation, nitration and ozonation, to the realms of high-valent metallic oxidants, both stoichiometric and catalytic, and the conceptually ideal, metallo porphyrin biomimetic systems. However, since the late 1970's, a new methodology for alkane activation has emerged, that of homogeneous, organotransition metal catalysis. The latter, as yet still in its infancy, is providing results that suggest that such reaction systems will be definite contenders for integration into new, large-scale, petrochemical-production units.

Before reviewing the problem of alkane activation, an insight into the petroleum

refining and petrochemical industries is instructive, both to highlight the petroleum activation techniques used and to consider the economic factors which dominate the refinery processes.

1.1. Petrochemicals and Petroleum Refining

A petrochemical may be defined as any chemical compound derived from petroleum or natural gas hydrocarbons and utilised in the chemical market. However in 1979 it was found that on average only six percent of a barrel of crude oil went into petrochemical production. The reason for this is quite simple; there is no economically feasible method for conversion of the crude oil fractions into useful activated feedstocks; the process would have to compete with the profitability of the alternative, fuel products.

The starting materials for petrochemicals are synthesis gas, olefins and benzene, toluene and xylene (the latter three are defined as BTX). The olefins can be considered as the main reactive link between the relatively inert paraffin hydrocarbons and consumer petrochemicals. They are obtained as a by-product of steam cracking of various feedstocks including ethane, naphtha gas and even crude oil.

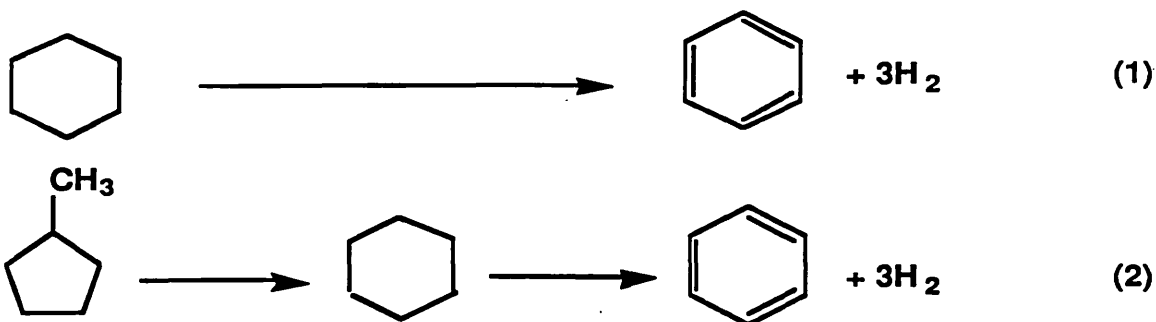
Refinery processes are either simple, such as those used to fractionate the crude oil, or more complex where chemical transformations occur. After any chemical process, physical processes are commonly involved for separation of the products.

The conversion processes are classified as thermal or catalytic and include, for example, catalytic reforming, hydrocracking, thermal cracking, catalytic cracking, isomerisation, dimerisation and demetallation. Though the primary consideration of each process is to produce the highest fuel output per barrel of crude oil, the processes of reforming and cracking are sources of reactive substrates for the petrochemical industry too.

(i) Catalytic Reforming

Reforming uses a feedstock of naphtha and stock from catalytic hydrocracking.

Reactions taking place in the reforming unit include dealkylation and transalkylation of aromatic compounds and, more significantly in our case, dehydrocyclisation of heptane and hexane (1). The cyclohexane thus formed will react further to produce benzene (Reaction 1). Methylcyclopentane also produces benzene (Reaction 2), this time by a two step procedure involving isomerisation and then dehydrogenation(2). Although reforming

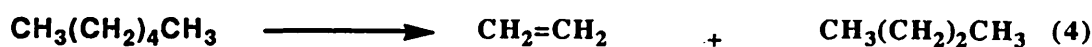
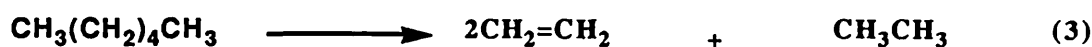


is the main source of BTX it is not economically acceptable for its sole production. Thus the reaction conditions are set such that BTX production takes second place to improvement of fuel product quality.

The catalysts used in petroleum reforming are usually bimetallic and bifunctional with an hydrogenation-dehydrogenation site and an acidic site. The latter commonly involves aluminium oxides and the former, bimetallic platinum/rhenium (called Rheniforming). More selective catalysts for BTX production are now being developed but are not yet employed industrially(3).

(ii) Catalytic Cracking

Petroleum cracking is the largest and perhaps most important area of petroleum processing. Some typical hydrocarbon cracking reactions are given in Equations (3)-(5).



In the early days of petroleum catalytic cracking, the industry employed mainly amorphous silica-alumina type catalysts. However, in the early 1960's, the discovery of the catalytic activity of zeolites in reactions of the carbonium ion type, led to their introduction as heterogeneous, hydrocarbon cracking catalysts too. In time, the zeolite based catalysts proved to have both greater reactivity and selectivity in comparison with the amorphous aluminosilicates, and thus established themselves firmly in the industry, eventually dominating it. For example, since 1976 all catalytic cracking in the United States and Canada has been done solely with zeolites as catalysts; furthermore a similar pattern for zeolite catalyst demand is now emerging on a worldwide scale.

The zeolite promoters used in the major processing unit for hydrocarbon cracking, that is the fluid catalytic cracking (F.C.C.) process, are zeolites X and Y. Both are structural analogues of the naturally occurring zeolite, faujasite (Figure 1). They differ in their alumina to silica ratio and are commercially available with a variety

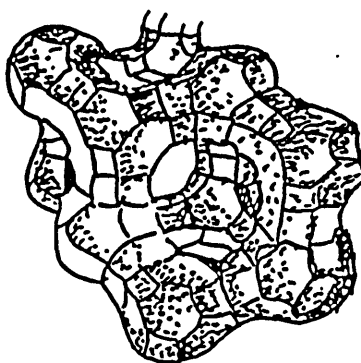


Figure 1: The Structure of Faujasite (X,Y)

of cations. Like faujasite, they have a three-dimensional pore system. The hydrocarbon is absorbed and, once in the cavities, the high acidity of the zeolite (which can be either Lewis or protonic) creates carbonium ions. The carbonium ions then rearrange to give lower molecular weight, often branched, hydrocarbons. These resulting hydrocarbons have the necessary combustion properties for use as an energy source (fuels-gasoline)

or the necessary chemical properties for use as feedstock in the petrochemical industry. The design of a commonly used F.C.C. process unit⁽⁴⁾ is shown in Figure 2. In this process the pre-treated oil (370°C), with the sulphur content removed, is combined with the hot regenerated catalyst; this causes an exothermic reaction raising the temperature to over 480°C. The resulting slurry is then passed through a reaction zone at between 480°C and 520°C to reach a disengaging area. At this stage the catalyst is isolated from the cracked products; the latter pass on to fractional distillation, and the former enters a "stripping section" where the catalyst is treated with steam to liberate it of absorbed hydrocarbons before continuing on into the regenerator. In this

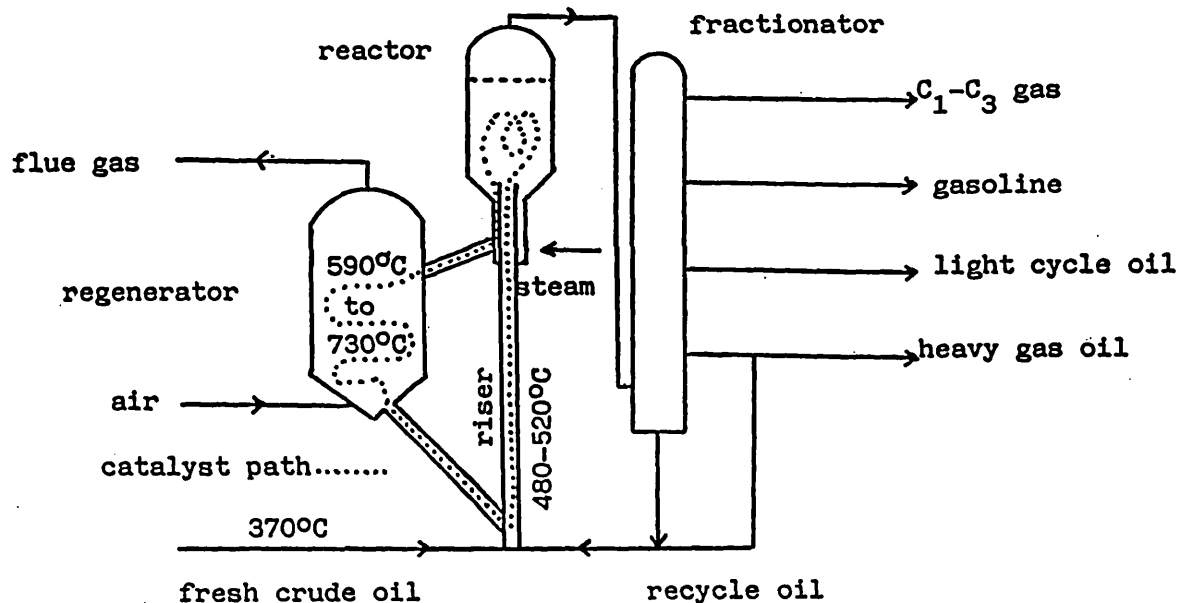


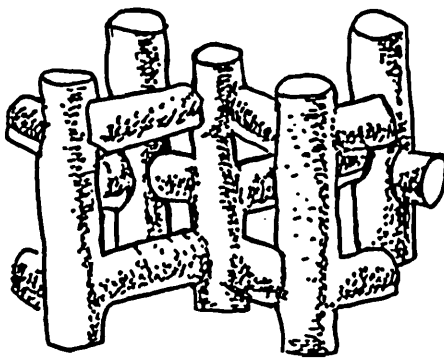
Figure 2: A Conventional Fluid Rise Cracking Design⁽⁴⁾

zone the carbonaceous layer deposited during the cracking reaction is burnt off thus reactivating the coke sensitive catalyst before re-entering the cycle.

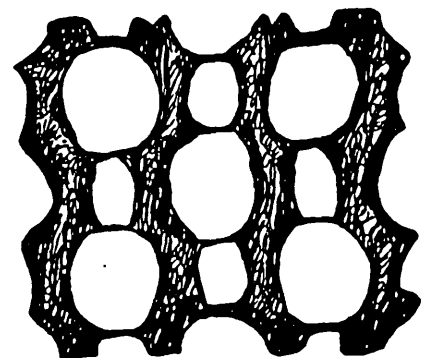
The high process temperatures and steam partial pressures have a destabilising effect on the zeolite. It is generally believed that the sodium level in the zeolite is the most important single factor influencing the catalyst's stability. Basically, the lower the sodium level the more likely is the zeolite to survive thermal treatment. For example,

most rare-earth exchanged promoters ($< 0.5\%$ by weight Na_2O) will survive temperatures of 815°C and high steam partial pressures up to 760°C without major degradation; above these temperatures structural collapse is rapid. At higher sodium levels degradation occurs more rapidly at lower temperatures. The nature of degradation may also change from straightforward lattice collapse to a more subtle reconstructive transformation resulting in ultrastabilisation, that is to say a significantly lower unit cell than the starting material where the three dimensional channel network is disrupted and thus catalytic activity is decreased. As the zeolites are often very hydrophilic, decoking by steam is unavoidably done at high temperatures so as to prevent hydration and therefore deactivation of the zeolite catalyst.

Though zeolites X and Y are used extensively, there are other commercially available zeolites used in other less highly developed cracking process units. These include ZSM5 and mordenite (Figure 3). The former has a two dimensional pore



ZSM-5



Mordenite

Figure 3

system, low acidity and hydrophobic properties. The latter, which is very acidic, is readily blocked by carbonaceous residues and this is due to its one dimensional pore system.

Zeolites are also employed in hydrocracking. This is similar to catalytic

cracking with hydrogenation superimposed. It is basically used to upgrade low value distillate feedstocks which are difficult or impossible to process by the two main refinery operations - catalytic cracking and reforming - since such feedstocks are characterised by either a high polycyclic aromatic content or by high concentrations of the two principal catalyst poisons, sulphur and nitrogen.

In effect, hydrocracking converts high boiling feedstocks to lower boiling products by cracking the feed hydrocarbons and hydrogenating the unsaturated compounds in the product mixtures. Thus the products will be unactivated but have a lower molecular weight. The products are mainly propane, butane, gasoline jet fuels, diesel or heating oils and sometimes lubricating oil. The area of hydrocracking is less interesting to us at this moment because, unlike catalytic cracking, the process by its nature does not provide functionalised compounds.

In conclusion, the petroleum refining industry can be seen to present great difficulties to the chemist in the provision of highly selective, though thermally stable, catalysts; and to the chemical engineer in the development of efficient process units. The necessity for high process temperatures features in all the refining procedures. It is not totally unexpected that energy consumption during these processes is colossal, and the expense hitherto monumental. In real terms, some 7 to 10% of the cost of refined oil is in direct consequence of the energy consumed during the execution of the chemical conversions and physical separations required.

If the petrochemical industry is to keep expanding, a thorough re-examination of the present petroleum refining industry is necessary. Novel processing units are needed with lower operating temperatures and more efficient catalysts specific for hydrocarbon activation. Only if these conditions are met, is there any strong possibility that the profits from petrochemicals will outweigh those of fuels, to result in petrochemicals becoming the major consumer products from crude oil.

1.2. Classical Organic Reactions for Hydrocarbon Functionalisation

Several alkane activation techniques have been in existence for many years and

are often generalised as fundamental organic reactions. Alas the systems included in this group generally have little regiospecificity in alkane activation, or require reaction conditions unacceptable for industrial-scale productions. It is therefore appropriate to discuss this group of reactions, and those of section 1.3., as evidence for the necessity for novel, homogeneous procedures; the latter to achieve a similar objective, that of alkane functionalisation, but in a more efficient and effective manner.

1.2.1. Halogenation

Methane can be chlorinated to give the mono-, di-, tri- and tetra-substituted species by reactions with gaseous chlorine under thermal or photolytic conditions. This radical-chain type reaction is initiated by the homolytic cleavage of chlorine (Reaction 6).



The chlorine atoms thus formed set off a chain reaction. The propagation steps for the mono-chlorinated species are given in equations (7) and (8). It is apparent from the enthalpy values of equations (7) and (8) that the overall reaction is noticeably exothermic.



The above system is not synthetically useful because it cannot be controlled to achieve selective mono-chlorination and, for higher alkanes, the product mixtures can be very complex indeed.

Halogenation with other halogens is presently seldom employed either synthetically or industrially. Fluorination is so highly exothermic that any selectivity is extremely difficult to achieve. The energy liberated is powerful enough to break other bonds in the substrate. Conversely, iodination is endothermic and so the iodine atoms which form tend to recombine and little or no reaction occurs with the substrate alkane.

Bromination is the most selective halogenation method. It is less exothermic than chlorination and follows the expected trend of radical forming reactions; brominating preferentially in the tertiary position, followed by secondary and then primary.

1.2.2. Nitration

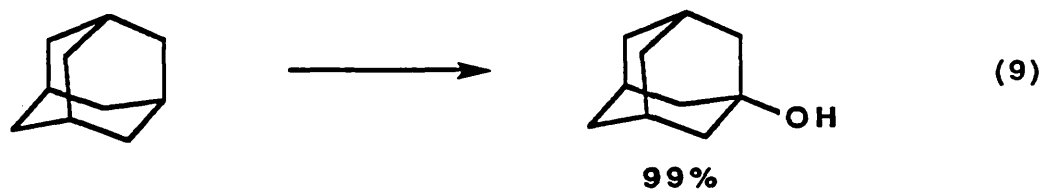
Alkanes react with nitric acid and dinitrogen tetroxide in the gas phase. The nitro derivatives are thought to be obtained by a radical-type mechanism. However, as with chlorination, there is little selectivity and complex mixtures of products are often obtained.

Nitration is also possible under conditions favouring ionic reaction mechanisms. In this case, nitration of ethane and also methane can be achieved using stable nitronium salts such as the hexafluorophosphate ($\text{NO}_2^+\text{PF}_6^-$) in aprotic solvents (5).

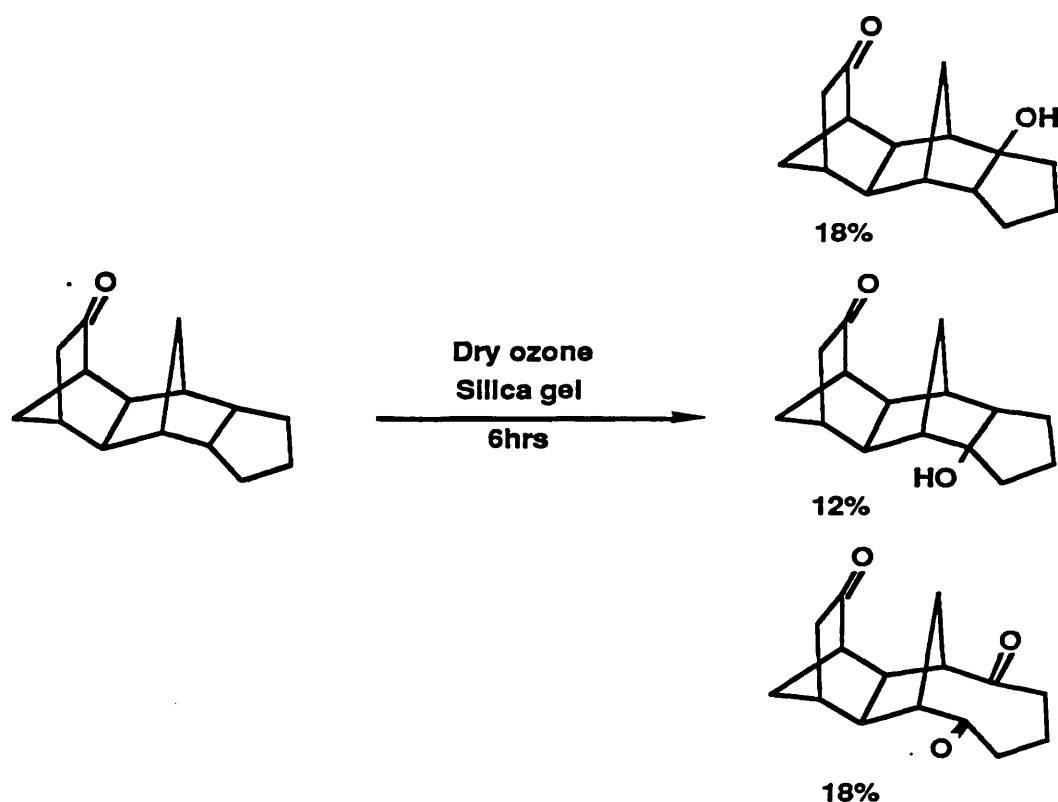
1.2.3. Ozonation

Ozone reacts slowly with saturated alkanes, inserting an oxygen atom into a C-H bond to provide alcohols from tertiary C-H bonds and ketones from secondary oxidation at methylene C-H entities (6,7). Reaction occurs preferentially at tertiary C-H centres and with retention of configuration.

The technique employed uses a silica gel matrix. Ozone absorbs efficiently onto silica at low temperatures ($\sim 4.5\%$ by weight at -78°C) and so the low solubility of ozone in organic solvents, a previous hindrance to this reaction method, is avoided. The method involves initial absorption of the hydrocarbon substrate onto the silica gel by direct mixing or by impregnation using a volatile solvent. A stream of ozone is then passed through the silica gel until the gel is saturated. The system is allowed to warm to room temperature and the organic product mixture is simply eluted from the silica. Generally conversions are quantitative (Reaction 9)(7). If a functional group is already present in the substrate,



oxidation occurs at the tertiary C-H centre most remote from the functional group (Scheme1)(6).



Scheme 1

The mechanism of reaction is thought to be similar to that of ozonolysis in solution. The reaction, though synthetically acceptable, is not commercially viable.

1.2.4. Peracid oxidations

Meyer *et al.* (8) use a solution of 30% hydrogen peroxide in trifluoroacetic acid to convert saturated, linear alkanes and cycloalkanes into a mixture of secondary

alcohols and their trifluoroacetate derivatives. The commanding feature of this system is its specificity for primary oxidation to alcohols; no trace of further secondary oxidation to ketone functionalities is observed. The active agent is trifluoroperoxyacetic acid and as hydroxylation occurs with retention of configuration, a cyclic, concerted reaction mechanism is proposed (Figure 4). As with Beckwith's ozonation method(6), if the substrate is already functionalised then activation occurs at the methylene centre most remote from the integral function.

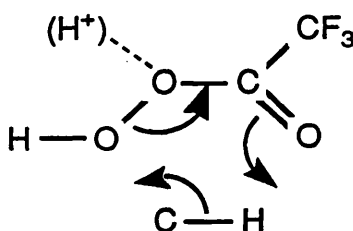
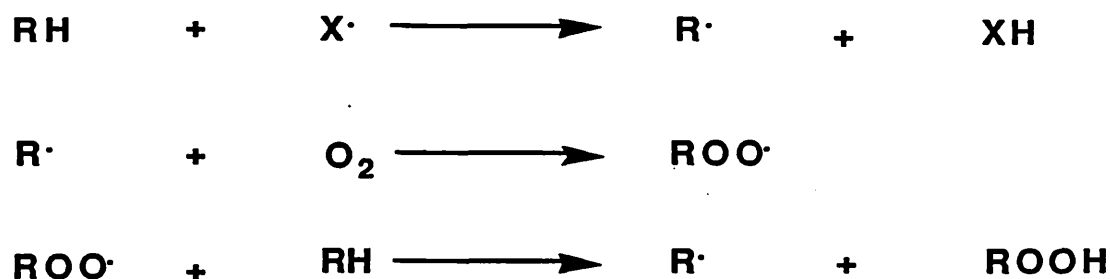


Figure 4

1.2.5. Gas phase oxidation and combustion

Gas phase oxidation of alkanes is commercially important for the production of acetaldehyde, methanol and formaldehyde from propane and butane. The technique requires an initiator to stimulate alkyl radical formation. The alkyl radical so formed reacts with dioxygen to provide an alkylperoxy radical which in turn is quenched by hydrogen atom abstraction from another alkane substrate molecule. As the latter step produces a new alkyl radical, the reaction is propagated and alkane oxidation continues (Scheme 2).



X=initiator

Scheme 2

Though not strictly functionalising, the combustion of natural gas, gasoline and fuel oils (Reaction 10) for the generation of thermal energy is a radical-multiplying reaction which leads to explosion under certain conditions. The mechanism is too complex to be certain, but again involves high energy alkylperoxy radicals. The reaction never goes to completion



and disposal of the residue is a major problem forever overshadowed by the necessity of this heat source both domestically and industrially.

1.3. Transition Metal Oxidants

Transition metal mediated oxidation of saturated alkanes is a popular approach to their functionalisation. In consequence, a plethora of transition metal oxidants has evolved including either stoichiometric or catalytic high-valent metallo species as integral components, or biomimetic, porphyrin-type system.

The mechanism by which hydrocarbon oxidation occurs can be divided into two general categories; namely homolytic and heterolytic oxidation. The characteristics of homolytic oxidation include free radical intermediates, outer sphere interactions, bimolecular steps (the substrate is generally not coordinated), low regio-and

stereospecificity, and one-electron oxidation and reduction steps of the metal. The metals commonly included in this category are first row transition metals, for example, vanadium(V)/(IV), chromium(VI)/(V), manganese(III)/(II), iron(III)/(II) and cobalt(III)/(II).

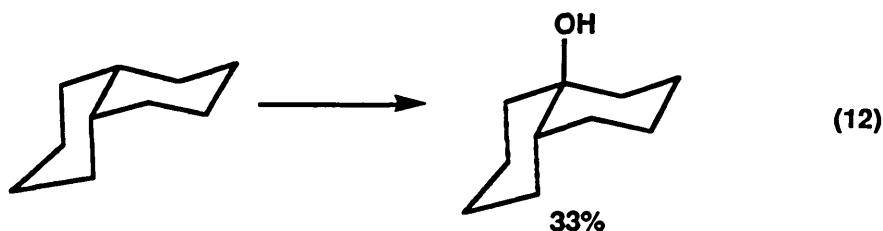
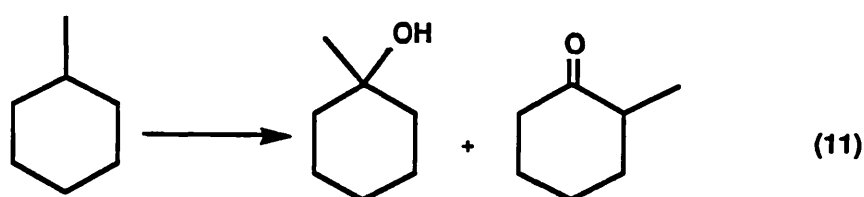
It is mainly second and third row transition metals which participate in heterolytic oxidation. In this case the substrate coordinates to the metal and thus high regio- and stereoselectivity is expected and obtained. This mechanism does not involve free radical intermediates and the transition metal centre either conserves its oxidation state or undergoes change by two-electron redox steps.

The above two categories are not rigorous and intermediate oxidation systems between homolytic and heterolytic reaction mechanisms occur. These intermediary systems include several enzymic oxygenases containing first row transition metals, for example iron and copper, as the active centre. Although homolytic in nature, the oxygenases act with a very high degree of regio- and stereocontrol. It is the protein cage network around the metal which orients the substrate at the active centre, and, in doing so, also permits the free radical intermediate to stay in close proximity to the metal centre and thus be oxygenated before inversion occurs.

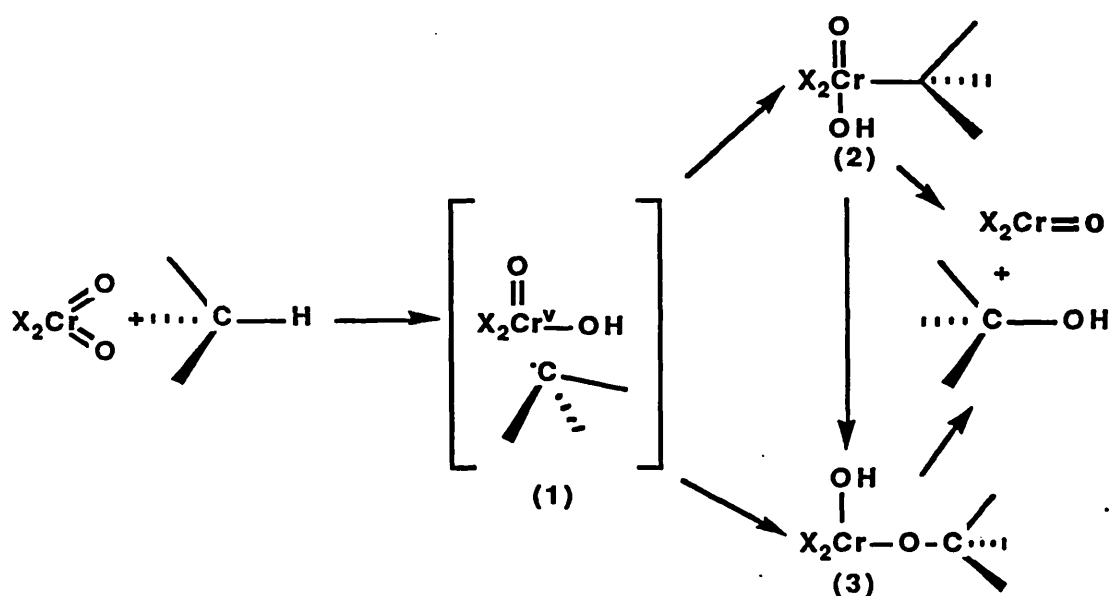
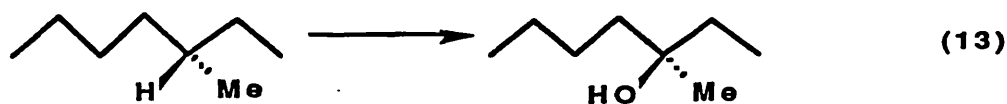
1.3.1. High valent transition metal oxidants; stoichiometric and catalytic system types

There are two main disadvantages of high valent transition metal oxidation systems. The first is the vigorous conditions often required with the metal oxide, for example, if using permanganate or chromium(VI) oxo species; the initial products of the carbon-hydrogen bond activation are alcohols but they are often susceptible to oxidation under milder conditions than the substrate, thus a considerable amount of secondary oxidation is often obtained. For example, oxidation of a methylene entity to a secondary alcohol is difficult as further oxidation to the ketone prevails. Tertiary C-H bonds can be converted to a tertiary alcohol selectively, however the acidic reaction conditions do not permit high yields as tertiary alcohol dehydration is prominent. The

second major problem which arises with transition metal oxidants is the solubility of the alkane substrate. Alkane oxidation by aqueous permanganate, MnO_4^- , requires the incorporation of an inert carboxyl or tertiary hydroxyl function into the alkane to allow substrate solubility; otherwise oxygen atom integration into the alkane molecule is unlikely. Alternatively, oxidation-resistant co-solvents can be employed such as acetic acid, acetone and crown ethers⁽⁹⁾, or tetra-alkylammonium and arsonium permanganate salts^(10, 11) can be used; Schmidt and Schafer⁽¹¹⁾ use benzyl(triethyl)ammonium permanganate in dichloromethane or glacial acetic acid to hydroxylate alkanes in reasonable yield (Reactions 11 and 12). Permanganate attacks the more nucleophilic C-H bond and thus the selectivity pattern is tertiary>secondary>primary. There is retention of configuration on oxidation of tertiary C-H bonds as is proved in the selective formation of *cis*-9-decalol from *cis*-decalin.

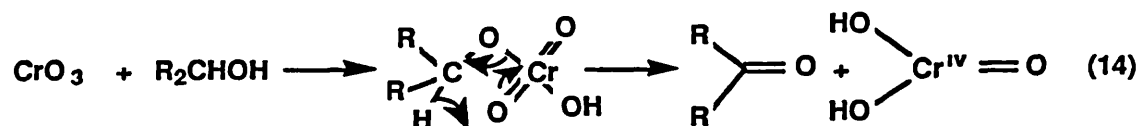


Chromium trioxide also preferentially hydroxylates at the more nucleophilic C-H bond and the relative affinity for tertiary: secondary: primary C-H activation is 7000:110:1, respectively⁽¹²⁾. Hydroxylation occurs with high stereoselectivity and is evident in Reaction 13, where hydroxylation of the chiral (+)-3-methylheptane to the chiral alcohol is achieved with 72-85% retention of configuration⁽¹³⁾.



Scheme 3

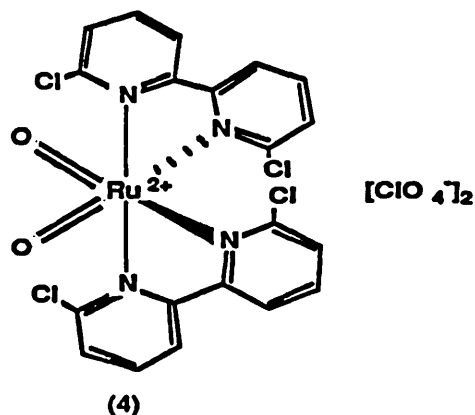
The mechanism of the reaction may involve initial hydrogen atom abstraction by the oxo reagent giving a chromium(V)-alkyl-carbon free-radical cage structure (1) (Scheme 3); this rapidly decomposes giving a chromium(VI)-alkyl intermediate (2) or a chromium(IV)-ester (3), which decompose to the alkyl alcohol and chromium (IV) (14). If chromium(VI)oxide reacts at a methylene centre, the chromate ester decomposition results in the secondary oxidation product, the ketone, plus a chromium(IV) species (Reaction 14).



In contrast with chromium species, the trioxo and *cis*-dioxo complexes of molybdenum and tungsten are quite stable. Consequently they are less reactive and have no affinity for saturated alkane oxidation.

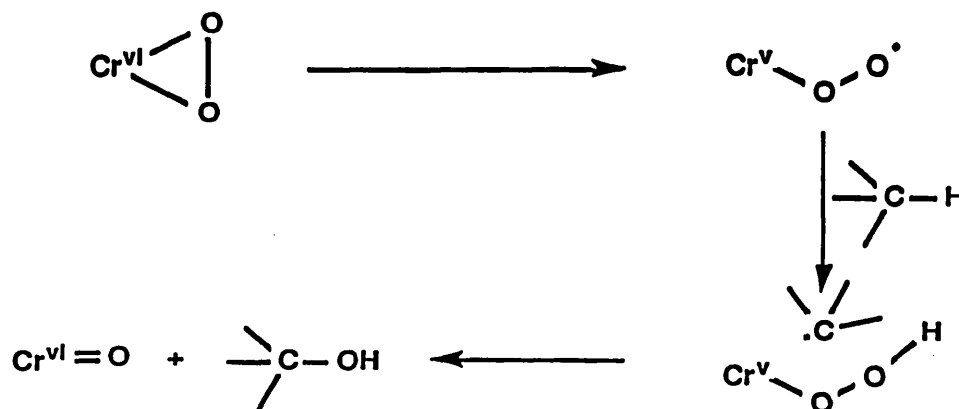
High valent iron-oxo complexes such as FeO_4^{2-} , FeO_3^{3-} and FeO_4^{4-} (15), do not normally activate saturated alkanes. The exception is the use of potassium ferrate in

the presence of oxalic acid. In this case, it is suspected that the oxalic acid produces an iron(IV)-oxo species capable of hydroxylating adamantane to 1-adamantol and 2-adamantone (16). Recently, a *cis*-dioxoruthenium (VI) complex $[\text{Ru}(\text{6,6'-Cl}_2\text{bpy})_2\text{O}_2][\text{ClO}_4]_2$ (4) has been used to oxidise cyclohexane to cyclohexanone

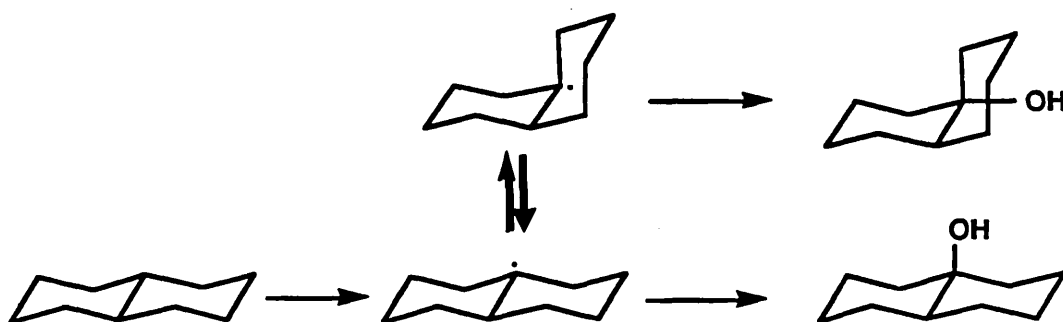


in 57% yield (based on the amount of metal complex used)(17). This reaction, though possibly of synthetic value, is of no industrial consequence due to the high and wasteful expense of the metal in a stoichiometric reaction system.

Chromium(VI)- and vanadium(V)-peroxo complexes are both applicable in alkane hydroxylation reactions. In the case of the chromium complexes, $\text{CrO}(\text{O}_2)_2\text{L}$ (L =basic ligand=py), cyclohexane is converted to a cyclohexanol-cyclohexanone mixture, adamantane is predominantly hydroxylated in the tertiary position, and oxidation of *cis*-decalin provides both *cis*- and *trans*-9-decanol in a non-stereoselective process (18).

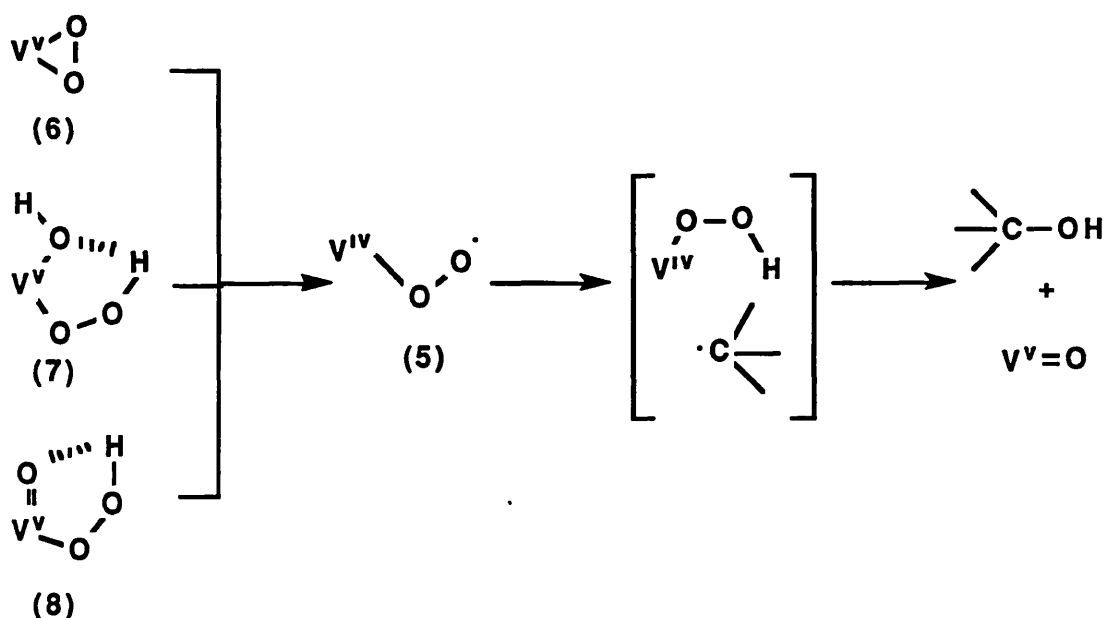


It is believed that the chromium(VI)-peroxo complex is acting exclusively as an alkane-hydrogen atom abstractor and this occurs when the peroxo ligand is in its homolytically dissociated form (Scheme 4)(18). The vanadium(V)-peroxo complexes of the formulae $\text{VO}(\text{O}_2)(\text{pic})\text{L}_1\text{L}_2$ ($\text{L}_1, \text{L}_2 = \text{H}_2\text{O}$ or basic ligand) and $[\text{VO}(\text{O}_2)(\text{pic})_2]\text{-A}^+$ ($\text{A}^+ = \text{H}^+, \text{PPh}_4^+$) both preferentially hydroxylate alkanes at the more nucleophilic C-H bonds. When cyclohexane is oxidised by $[\text{VO}(\text{O}_2)(\text{pic})_2]\text{-H}^+.\text{H}_2\text{O}$ in an acetonitrile-carbon tetrachloride (9:1) solvent system, the product obtained is cyclohexyl chloride. This is derived from radical abstraction of chlorine atoms from carbon tetrachloride and is evidence for a homolytic-type reaction mechanism (19). A disadvantage of the vanadium(V)-peroxo oxidants is that significant epimerisation occurs at the hydroxylated centre. This is exemplified in Scheme 5, where inversion to the *cis*-decalyl radical must be taking place at a faster rate than radical capture by the oxometalloid intermediate(19) to produce a mixture of the *cis*- and *trans*-decalols from *trans*-decalin. The active vanadium species in the initial hydrogen atom abstraction is generally accepted as the open form of the peroxy entity (5). The diradical system could be generated by the homolytic cleavage of the metal-peroxo metal-oxygen bond



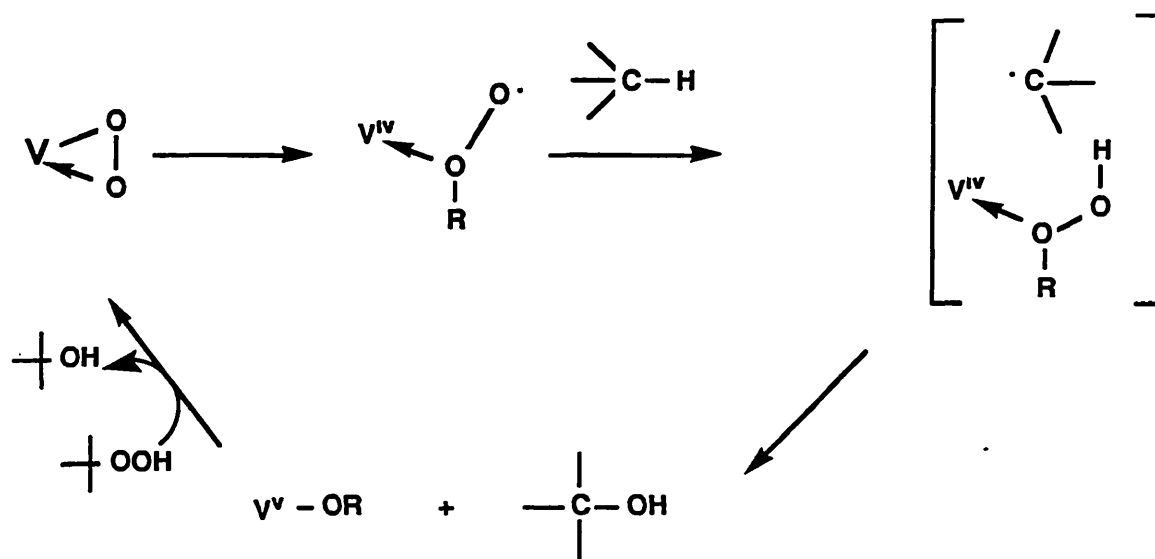
Scheme 5

(6) or by the rearrangement of the intramolecularly hydrogen bonded hydroxo-hydroperoxide (7) or oxo-hydroperoxide (8) (Scheme 6). The diradical abstracts a hydrogen atom from the alkane to give an intermediate carbon radical which is combined with a hydroxyl radical from the hydroperoxo ligand. This mechanism is very similar to that suggested for chromium(VI)-peroxo oxidations.



Scheme 6

The vanadium-alkylperoxides of the type $\text{VO}(\text{dipic})(\text{OOBu}^t)(\text{H}_2\text{O})(19)$, are also active alkane hydroxylation reagents. Oxidation generally occurs with epimerisation of the carbon centre activated, at the most nucleophilic C-H, and again by carbon radical intermediates. In the presence of an excess of *t*-butylhydroperoxide,

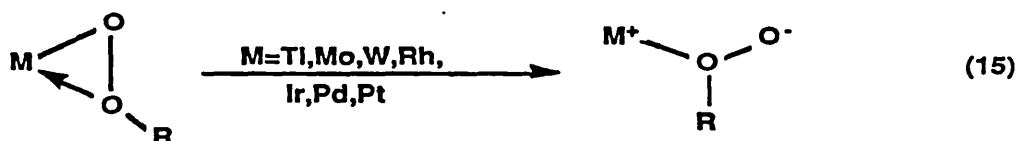


Scheme 7

this system becomes catalytic for alkane hydroxylation (Scheme 7)(20).

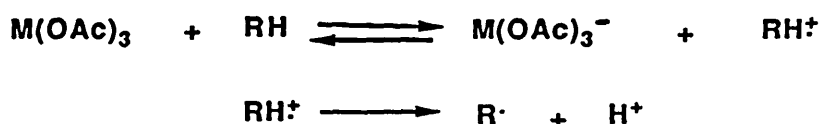
The key to hydroxylation by metal-alkylperoxides, hydroperoxides and

peroxides is the homolytic cleavage of the metal-peroxo metal-oxygen bond. In cases where this cleavage is heterolytic (Reaction 15), no alkane hydroxylation occurs.

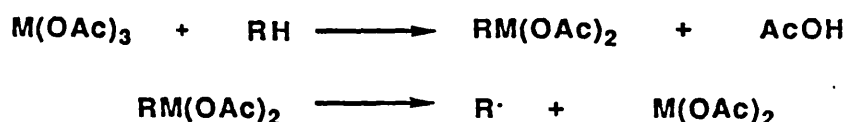


Alkanes can be hydroxylated catalytically by a variety of first row transition metal complexes. The reactions are often homolytic in nature and are generally characterised by one-electron oxidation-reduction steps. For example, in the case of cobalt(III) acetate or manganese(III) acetate promoted oxidation, the reaction is thought to proceed in two possible ways(21):-

(i) *Electron transfer reaction*



(ii) *Electrophilic substitution at the metal centre*

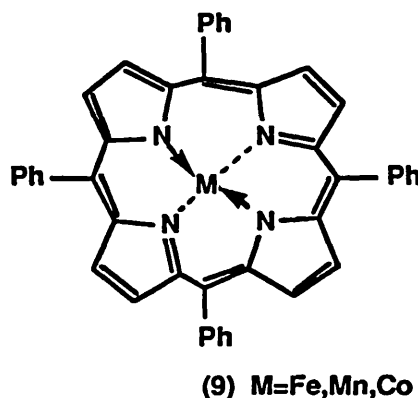


Processes (i) and (ii) both involve one-electron reduction of the metal with concomitant formation of an alkyl radical. The reactions depend on the redox potential of the metal [$E^\circ(\text{aq}) = 1.82\text{V}$ for $\text{Co(III)}/\text{Co(II)}$ and 1.5V for $\text{Mn(III)}/\text{(II)}$] and also the ionisation potential of the hydrocarbon(21). When dioxygen is used as the oxygen source the alkyl radical is quenched by the oxygen to produce an alkylperoxy radical. The peroxy radical then regenerates the Mn(III) or Co(III) catalysts by oxidation of the Mn(II) and Co(II) species, respectively. This provides primary oxygenated products and a catalytic cycle. Particularly the cobalt(III)acetate mediated oxidation of butane

leading (with several more steps) to acetic acid, and the transformation of cyclohexane to a cyclohexanol-cyclohexanone mixture, are reactions of significant industrial importance.

1.3.2. Biomimetic Systems

In nature, monooxygenase enzymatic systems such as the iron-porphyrin based cytochrome P-450(22) and the non-haem iron protein ω -hydroxylase(23) have evolved. As they are capable of catalysing alkane hydroxylation with both high stereo- and regioselectivity, a considerable amount of interest has arisen in creating related biomimetic systems. Most of these analogous systems (Table 1) use tetraphenylporphyrin (TPP) (9) as the quadridentate porphinato ligand.



Cytochrome P-450 enzymes functionalise alkanes by initially activating dioxygen. Then, in the presence of the hydrogen-donor NADPH cofactor, an oxygen atom can be incorporated into the alkane substrate molecule. Other oxygen sources which can be used biomimetically include iodosylbenzene and inexpensive hypochlorites.

In Tabushi's(26) biomimetic system, colloidal platinum is used to catalyse electron transfer to a (tetraphenylporphinato)manganese(III) to form a (tetraphenylporphinato)manganese(II) derivative. The latter then activates dioxygen (by its addition) to form a powerful oxidising agent capable of hydroxylating adamantane to predominantly 1-adamantol. Alternatively, Mansuy(27) chooses to use ascorbate as the

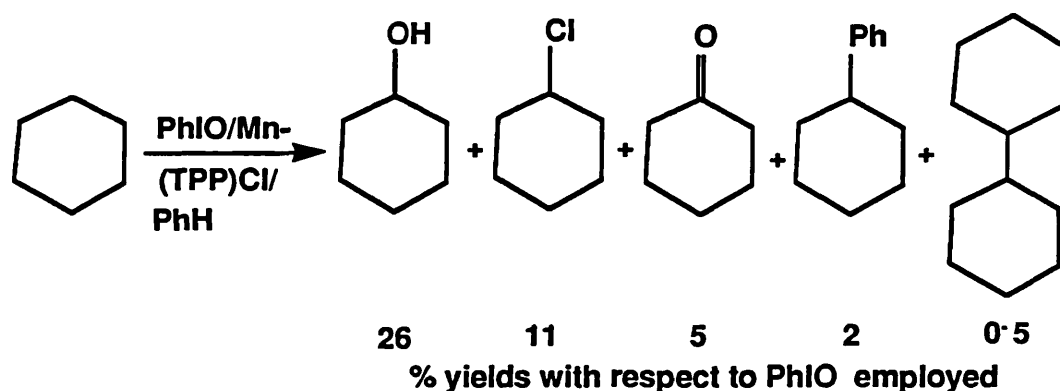
Table 1. Examples of Biomimetic Systems for Hydrocarbon Oxidation

Biomimetic System	Alkane hydroxylation Stereoselectivity:-			Reference
	High	Unknown	Low	
Mn(TPP)Cl/PhIO			+	24, 25
Mn(TPP)Cl/O ₂ /H ₂ /Pt		+		26
Mn(TPP)Cl/O ₂ /ascorbate		+		27
Mn(TPP)Cl/O ₂ /Zn/AcOH/py		+		28
Fe(II)O ₂ /H ⁺ /hydrazobenzene		+		29
Fe/AcOH/py/H ₂ O/O ₂		+		30
Fe(TPP)Cl/PhIO	+			31
Fe(TPP)Cl/O ₂ /Zn(Hg)/ MVCl ₂ /Ac ₂ O	+			32
Fe(II)/H ₂ O ₂ (Fenton)			+	31, 33
Fe(II)EDTA/O ₂ /ascorbate		+		34, 35
Co(TPP)/cumylhydroperoxide			+	36

reducing agent, hydroxylating under quite mild conditions. Surprisingly the stereospecificity of these reagents is not known in either case.

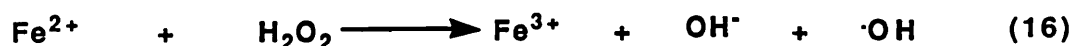
Mansuy⁽²⁸⁾ has also developed an activating system where a simple reducing agent, zinc, is used in the presence of a manganese porphyrin, imidazole, oxygen and acetic acid. The concept is very similar to the Gif system⁽³⁸⁾ $[\text{Fe}/\text{O}_2/\text{Zn}/\text{AcOH}/\text{py}]$, differing only by the use of manganese porphyrin as the catalyst instead of an iron cluster species. The latter is the more effective alkane hydroxylation method.

When iodosylbenzene is substituted for molecular oxygen, NADPH is no longer required by cytochrome-like oxidising systems⁽³⁷⁾. Groves⁽²⁵⁾ and Hill⁽³⁹⁾ reported simultaneously the oxidising properties of iodosylbenzene in the presence of the synthetic analogue $\text{Mn}(\text{TPP})\text{Cl}$. The hydroxylation reactions have the characteristics of a stepwise radical mechanism and alkane activation occurs preferentially at the more nucleophilic C-H bonds with little stereoselectivity. In the case of cyclohexane (Scheme 8)^(24, 39, 40), the alcohol, chloride and ketone are formed, along with minor amounts of coupling products.

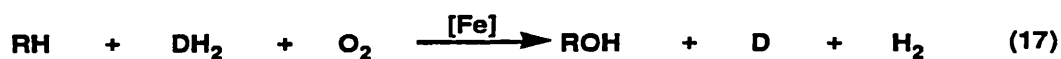


Scheme 8

In the realms of iron chemistry, Fenton's reagent⁽³³⁾ has been known since 1894. It is a powerful oxidising system containing hydrogen peroxide in the presence of iron(II) salts. Modification of this system, simply by using a non-aqueous co-solvent (acetonitrile), allowed Lindsay-Smith and Sleath to hydroxylate saturated alkanes, though without stereoselectivity. The generally accepted reaction mechanism involves formation of a hydroxyl radical produced by cleavage of the peroxide bond by the ferrous ion (Reaction 16) (41).

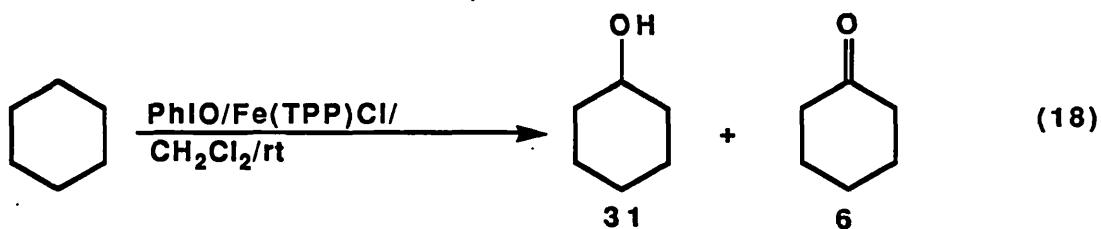


There are several iron-containing biomimetic systems in existence for the activation of dioxygen (Table 1) and, in the presence of a coreducing agent (D) and under an oxygen atmosphere, they can hydroxylate alkanes catalytically (Reaction 17). The first of these

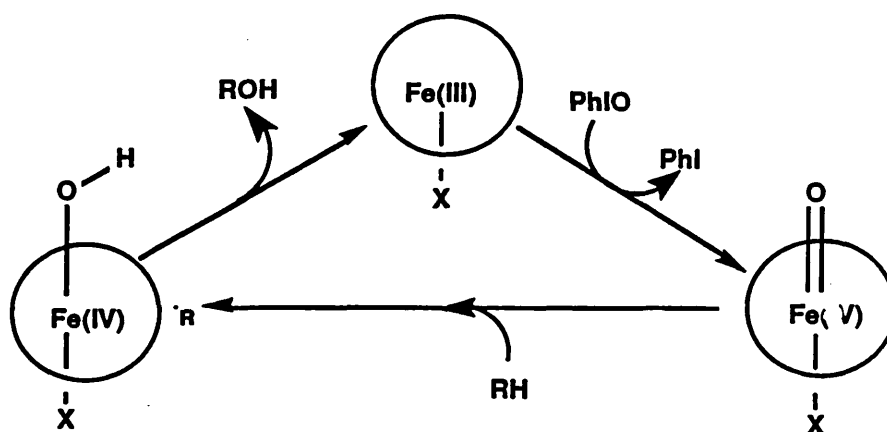


systems was described by Udenfriend^(34,42). It involves Fe(II)EDTA as the catalyst and ascorbate as the coreducing agent. Although in this particular case the hydroxylation was low yielding, it stimulated other chemists to screen related systems. Improvements in yields are obtained by using, for example, other reducing agents such as diaminopurine⁽⁴³⁾, 2-mercaptobenzoic acid⁽⁴⁴⁾, hydrazobenzene⁽²⁹⁾, 2-mercaptoethanol⁽⁴⁵⁾, zinc amalgam⁽³²⁾ and metallic iron powder^(30, 46). Although the yields are generally proportional to the concentration of the coreducing agent, competitive oxidation of this necessary "cofactor" is a serious problem. Hydroxylation of alkanes preferentially takes place at the tertiary C-H centre, the exceptions being when 2-mercaptoethanol⁽⁴⁴⁾ and metallic iron powder⁽⁴⁶⁾ are employed whence hydroxylation of adamantane favours methylene C-H activation. Not any of these systems hydroxylates *cis*-decalin with retention of configuration at the ring junction carbon atoms⁽³¹⁾.

Iron porphyrins may achieve alkane oxidation using iodosylbenzene as the oxygen source; alcohol formation gives the major reaction product with some secondary oxidation of the substrate also taking place (Reaction 18)^(31, 36, 47, 48). Hydroxylation of *cis*-decalin occurs with retention of configuration producing predominantly *cis*-9-decanol^(31, 47, 48). The proposed mechanism is given in Scheme 9 and is homolytic^(47,48).

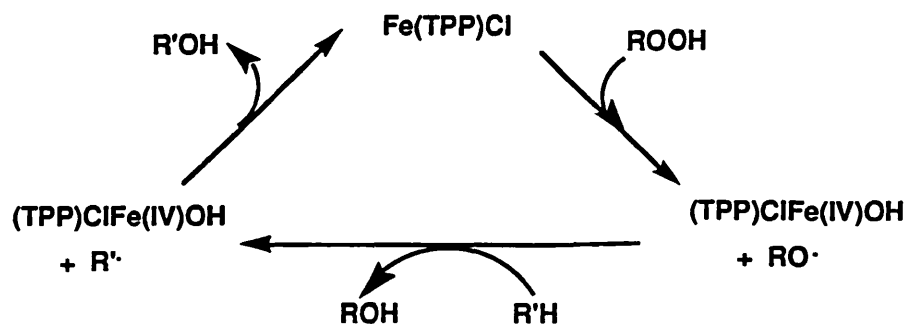


% yields with respect to PhIO employed



Scheme 9

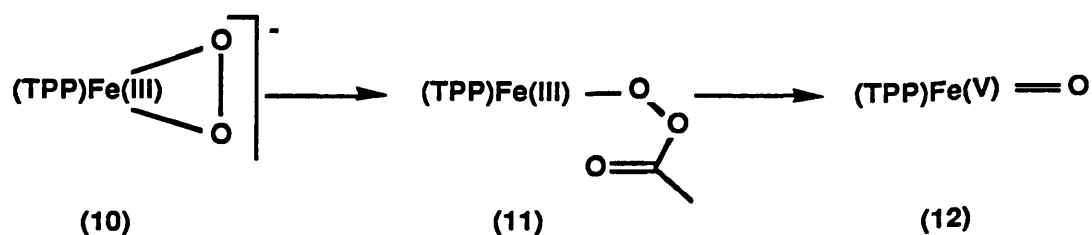
Iron porphyrins and also cobalt porphyrins can promote alkane oxidation using peroxides as the oxygen source; *t*-butylhydroperoxide and cumylhydroperoxide are commonly employed(36,49). The mechanism is again homolytic (Scheme 10), and the reaction is stereospecific.



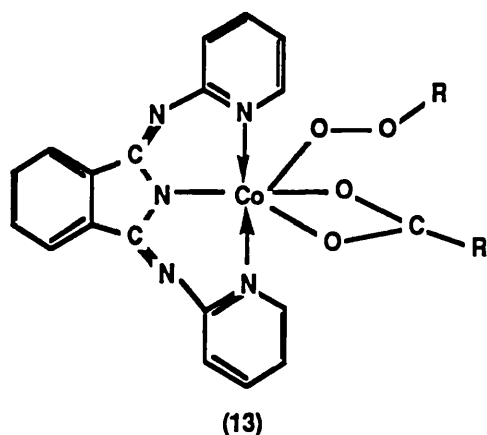
Scheme 10

The porphyrin-iron(III)-peroxo complex $[\text{Fe(TPP)O}_2]$ (10), in the presence of an excess of acetic anhydride, also promotes alkane hydroxylation(50). This reaction is presumed to proceed through acylation of the peroxo ligand, providing an iron

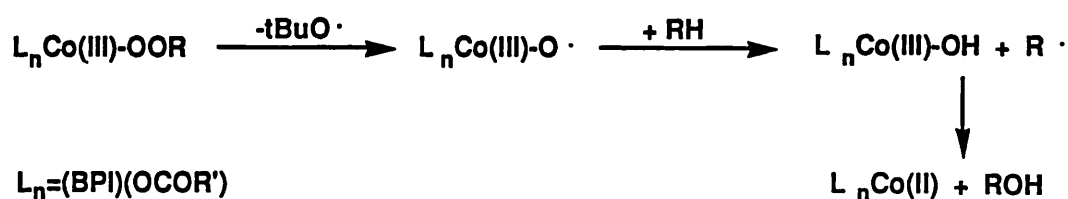
percarboxylate (11) which decomposes to the active Fe(V)-oxo species (12).



It is now possible to use cobalt(III)-alkylperoxo complexes of composition $[\text{Co}(\text{BPI})(\text{OOR})(\text{OCOR}')] \text{ (13)}$ ($\text{R} = t\text{-Bu}$, CMe_2Ph ; $\text{R}' = \text{Me}$, Ph , $t\text{-Bu}$) for the



homolytic oxidation of hydrocarbons producing alcohols, ketones and alkyl peroxide derivatives⁽⁵¹⁾. Hydroxylation is regioselective for the most nucleophilic C-H bond but extensive epimerisation occurs at the activated carbon centre. The suggested mechanism is given in Scheme 11.



Scheme 11

1.4 Alkane Activation by Homogeneous Organotransition Metal Species

A brief presentation of the area of homogeneous organometallic catalysis is instructive at this stage to appreciate the chemistry of the proceeding section. All organometallic promoters in homogeneous systems contain one or more of the following ligands (Figure 5).

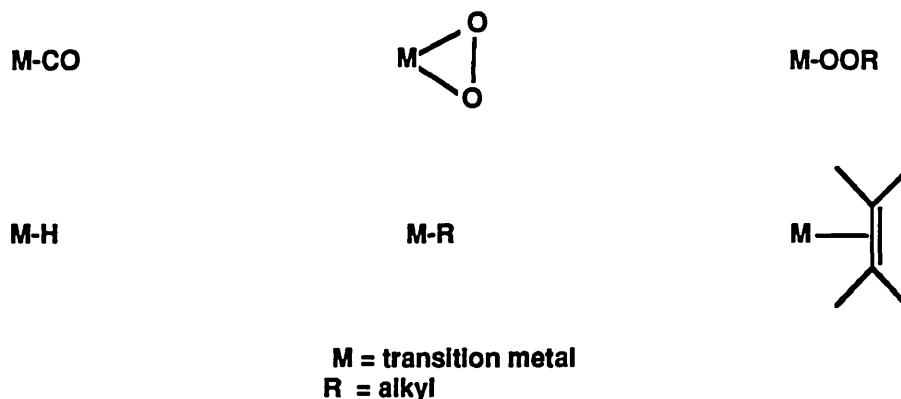


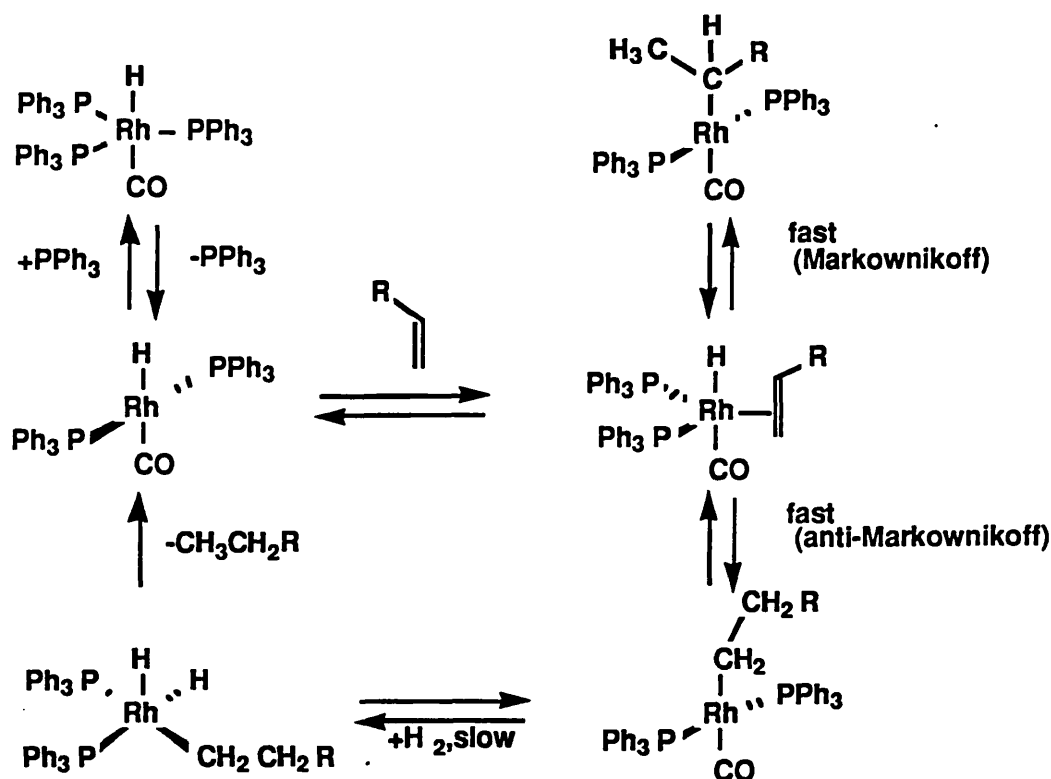
Figure 5

Transition metal alkyls are by far the most relevant system types when considering alkane activation as they could exist in the intermediates or in the products. Some general reactions of transition metal alkyls are given in Table 2. A homogeneous catalytic cycle can often be very complex; however, unlike heterogeneous systems, a homogeneous reaction can fortunately be studied mechanistically and spectroscopically. A cycle normally commences with an activated, coordinatively unsaturated transition metal species. Oxidative addition of a substrate follows, whence, according to the particular system involved, insertion reactions, attacks on coordinated ligands (including *cis* transfers and also reductive eliminations) can take place.

An example of a catalytic cycle is given in Scheme 12. In this case, a reactive sixteen electron species is generated by the reversible expulsion of a weakly bonded triphenylphosphine ligand. This triggers the catalytic cycle. The catalytic hydrogenation of alkenes can be considered as the reverse of one possible kind of hydrocarbon activation; i.e. alkane dehydrogenation to give alkenes.

Table 2: General Reactions of Transition Metal Alkyls

Reaction Type	Reaction
<i>Homolytic Fission</i>	$M-R \longrightarrow M\cdot + R\cdot$
<i>Hydrogen Transfer</i>	
α	$M-CH_3 \longrightarrow \begin{array}{c} H \\ \\ M=CH_2 \end{array}$ $M(CH_3)_2 \longrightarrow M=CH_2 + CH_4$
β	$M-CH_2CH_2R \longrightarrow M-H + CH_2=CHR$
γ	$M-CH_2Si(CH_3)_3 \longrightarrow \begin{array}{c} CH_2 \\ \diagup \quad \diagdown \\ M \quad \quad Si(CH_3)_2 \\ \diagdown \quad \diagup \\ CH_2 \end{array}$
<i>Reductive Elimination</i>	$\begin{array}{c} R \\ \diagup \\ M \\ \diagdown \\ R \end{array} \longrightarrow M + R-R$
<i>Insertions</i>	
CO	$M-R \longrightarrow M-COR$
O ₂	$M-R \longrightarrow M-OOR$
SO ₂	$M-R \longrightarrow M-SO_2R$
<i>Hydrogenolysis</i>	$M-R \longrightarrow M-H + RH$
<i>Halogenation</i>	$M-R \longrightarrow M-X + RX$
<i>Protolysis</i>	$M-R \longrightarrow M^+ + RH$
<i>Electron Transfer Cleavage</i>	$Et_2Ni(bipy) \xrightarrow{-e} [Et_2Ni(bipy)]^+$ $\downarrow$ $n-C_4H_{10}$



Scheme 12 ⁽⁵²⁾: Catalytic cycle of hydrogenation and isomerisation of 1-alkenes by $\text{RhH(CO)(PPh}_3)_3$ at 25 °C and 1atmos. of H_2

Homogeneous catalysis is used extensively in the chemical industry⁽⁵³⁾. It is involved in the production of inorganic reagents such as sulphuric acid and ammonia, and employed for the production of many organic compounds (Table 3)⁽⁵³⁾ including ethylene and toluene, but predominantly oxygenated species.

The main starting material for nearly all organic compounds is methanol. This is normally obtained from synthesis gas ($\text{CO} + \text{H}_2$) using copper on aluminium oxide as catalyst. The synthesis gas is itself obtained from the cracking of hydrocarbons, from coal, or from the somewhat wasteful burning of natural gas. The hydrogen content is often increased by homogeneous water gas shift reactions (Reaction 19) for



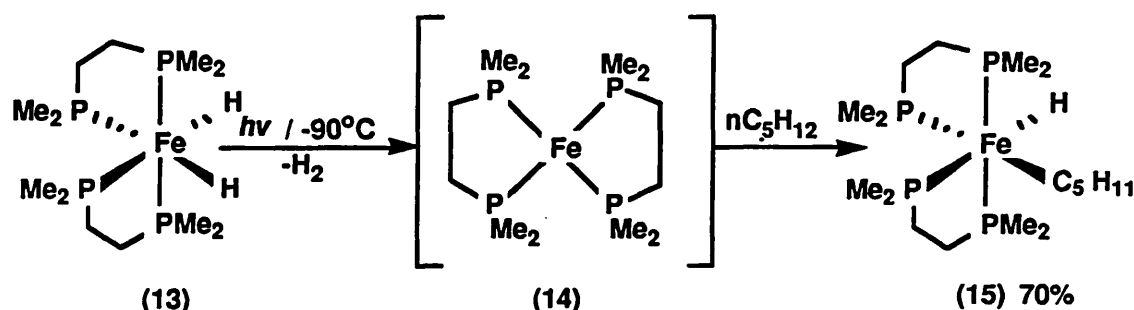
use in the Haber process. As seen in Scheme 13, an abundance of compounds can be prepared and almost all by virtue of homogeneous catalysis.

Table 3(53) : Major Applications of Homogeneous Catalysis in the U.S. Chemical Industry

Application	Approximate 1975 Capacity (c) or Production (p) (thousands of metric tons)
<i>Carbonylations</i>	
$\text{CH}_3\text{CH}=\text{CH}_2 + \text{CO} + \text{H}_2 \longrightarrow \text{C}_3\text{H}_7\text{CHO}$	650 p
$\text{RCH}=\text{CH}_2 + \text{CO} + 2\text{H}_2 \longrightarrow \text{RCH}_2\text{CH}_2\text{CH}_2\text{OH} (\text{R} > \text{C}_8\text{H}_{17})$	170 c
$\text{CH}_3\text{OH} + \text{CO} \longrightarrow \text{CH}_3\text{COOH}$	190 c
<i>Monoolefin reactions</i>	
$\text{CH}_2=\text{CH}_2 + \text{O}_2 \longrightarrow \text{CH}_3\text{CHO}$	410 p
$\text{CH}_3\text{CH}=\text{CH}_2 + \text{ROOH} \longrightarrow \text{CH}_3\text{CH}-\underset{\text{O}}{\text{CH}_2} + \text{ROH}$	250 c
$\text{CH}_2=\text{CH}_2$ Polyethylene (excludes oxide-supported catalysts)	150 c
$\text{CH}_2=\text{CH}_2 + \text{CH}_3\text{CH}=\text{CH}_2 + \text{diene} \longrightarrow \text{EPDM rubber}$	85 p
<i>Diene reactions</i>	
$3\text{CH}_2=\text{CHCH}=\text{CH}_2 \longrightarrow \text{cyclododecatriene}$	10 p
$\text{C}_4\text{H}_6 + \text{CH}_2=\text{CH}_2 \longrightarrow 1,4\text{-hexadiene}$	2 p
$\text{C}_4\text{H}_6 + 2\text{HCN} \longrightarrow \text{NC}(\text{CH}_2)_4\text{CN}$	70 c
$\text{C}_4\text{H}_6 \longrightarrow \text{cis-1,4-polybutadiene (all catalysts)}$	290 p
<i>Oxidations</i>	
$\text{c-C}_6\text{H}_{12} \longrightarrow \text{c-C}_6\text{H}_{11}\text{OH} + \text{c-C}_6\text{H}_{10}=\text{O} \longrightarrow \text{Adipic acid}$	610 p
$\text{c-C}_{12}\text{H}_{24} \longrightarrow \text{c-C}_{12}\text{H}_{23}\text{OH} + \text{c-C}_{12}\text{H}_{22}=\text{O} \longrightarrow \text{Dodecanedioic acid}$	10 c
$p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_3 \longrightarrow \text{Terephthalic acid and esters}$	2100 p
$n\text{-C}_4\text{H}_{10} \longrightarrow \text{CH}_3\text{COOH}$	470 p
$\text{CH}_3\text{CHO} \longrightarrow \text{CH}_3\text{COOH}$	335 p
<i>Other reactions</i>	
$\text{CH}_2=\text{CHCHClCH}_2\text{Cl} \longrightarrow \text{ClCH}_2\text{CH}=\text{CHCH}_2\text{Cl}$	270 p
$\text{ClCH}_2\text{CH}=\text{CHCH}_2\text{Cl} + 2\text{NaCN} \longrightarrow \text{NCCH}_2\text{CH}=\text{CHCH}_2\text{CN}$	125 c
$p\text{-COORC}_6\text{H}_4\text{CO.OR} + \text{HOCH}_2\text{CH}_2\text{OH} \longrightarrow \text{Polyester}$	1900 p

1.4.1. First Row Transition Metals

The first row transition metal series has so far offered little scope in the area of organometallic mediated alkane activations. It was not until 1987, that such metal complexes were found effective in intermolecular, alkane sp^3 C-H bond activation in solution⁽⁵⁴⁾. Field and coworkers⁽⁵⁴⁾ found that *bis*(diphosphine) complexes of iron when generated photochemically could insert selectively into the terminal C-H bond of a straight chain alkane (Scheme 14). The active 16 electron species (14) is formed by

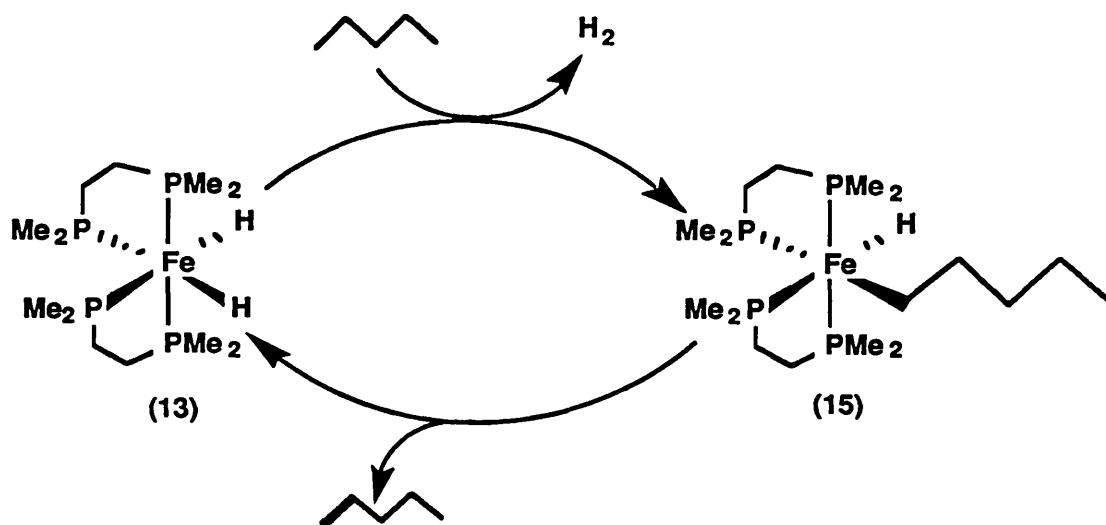


Scheme 14

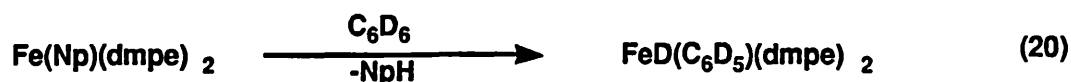
photoextrusion of dihydrogen from $\text{FeH}_2(\text{dmpe})_2$ (13) (dmpe =1,2-bis(dimethylphosphino)ethane) in a homogeneous *n*-pentane solution. The alkane adduct *cis*-(1-pentyl) $\text{FeH}(\text{dmpe})_2$ (15) which was characterised by proton nmr, provided 1-bromopentane on treatment with bromine gas at -78°C . At higher temperatures (-30°C), irradiation of the dihydride (13) in dilute *n*-pentane solution (the dilution factor was not given) produced 1-pentene, presumably by β -hydride elimination from the alkyl moiety in complex (15). This of course offers the possibility of a catalytic cycle (Scheme 15); however, the active iron species (14), under the conditions used, preferably reacts with the olefinic products rather than the alkane substrate, and so the catalytic nature of the reaction is swiftly terminated.

Previous to the above work, $\text{Fe}(\text{dmpe})_2$ was produced by the reductive elimination of naphthalene from $\text{Fe}(\text{H})(\text{Np})(\text{dmpe})_2$ (Np =2-naphthyl) at room temperature⁽⁵⁵⁾. Though activation of arene C-H bonds was possible in this system

(Reaction 20), intermolecular sp^3 C-H activation was never detected.



Scheme 15



Several reasons for the latter should be considered; firstly an alkane substrate would have to compete with free naphthalene for the unsaturated sites of the active metal species and secondly a photochemically excited state may be a necessary feature for alkane activation by 16 electron iron species. In the case of arene C-H activation, the low ionisation potential of Fe(dmpe)_2 is generally believed to be the important factor favouring oxidative-addition; however Crabtree⁽⁵⁶⁾ suggests that the oxidative addition reaction of alkanes is not very oxidising and such properties for the active metal species are not a requirement.

The cationic species $[\text{FeH(dppe)}_2]\text{BF}_4$ ($\text{dppe} = 1,2$ -bis(diphenylphosphino)ethane) generated thermally from *trans*- $[\text{FeH}(\eta\text{-H}_2)(\text{dppe})_2]\text{BF}_4$ ⁽⁵⁷⁾ and isoelectronic with Fe(dmpe)_2 , does not activate aliphatic or arene C-H bonds⁽⁵⁸⁾. This could be because the coordination number in this species is 5 and not 4, because it is not in an excited state or because the phosphine ligands are not electron releasing enough to stabilise the R-H adduct species in the necessarily higher oxidation level. Steric factors may also dominate, as intermolecular C-H activation is favoured by low steric hindrance around the metal centre.

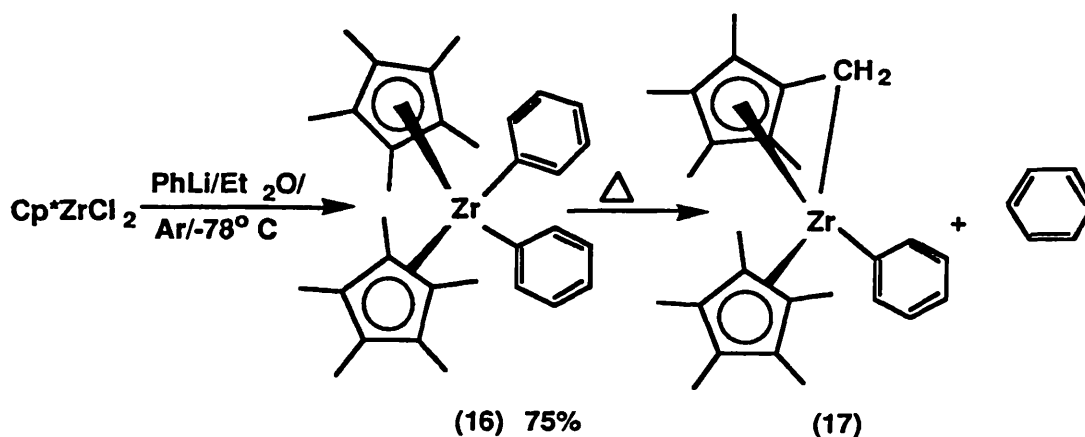
Other metals of the first transition series have not been successful in C-H

activation reactions in solution. Studies have mainly been of gas phase reactions of the naked metal cations⁽⁵⁹⁾, heteronuclear diatomic cluster ions⁽⁶⁰⁾, photochemically excited metal atoms both in the gas phase⁽⁶¹⁾ and matrix-isolated in frozen methane and ethane⁽⁶²⁾, and of unsaturated, anionic metal carbonyls in the gas phase⁽⁶³⁾. These studies are important because, for example, a naked metal cation in the gas phase is a guide to the possible behaviour of a coordinatively unsaturated cationic species of the same metal in a homogeneous solution. They suggest which metals may be C-H bond activators and which would prefer C-C bond oxidative addition.

1.4.2. Second and Third Row Transition Metals

1.4.2.1. Zirconium and Hafnium

Zirconium and hafnium offer exceedingly similar chemistry. This is due to the pronounced effect of the lanthanide contraction which renders both the atomic and ionic radii of the metals essentially identical. Organometallic complexes of either zirconium or hafnium cannot successfully achieve intermolecular C-H activation, but complexes of each may intramolecularly cleave sp^3 C-H bonds. During Marks's synthesis of $Cp^*Zr(C_6H_5)_2$ (16) ($Cp^* = C_5Me_5$), it was discovered that thermolysis clearly yielded a mononuclear $\eta^6-Me_4C_5CH_2$ zirconium complex (17) (Scheme 16)⁽⁶⁴⁾. The driving

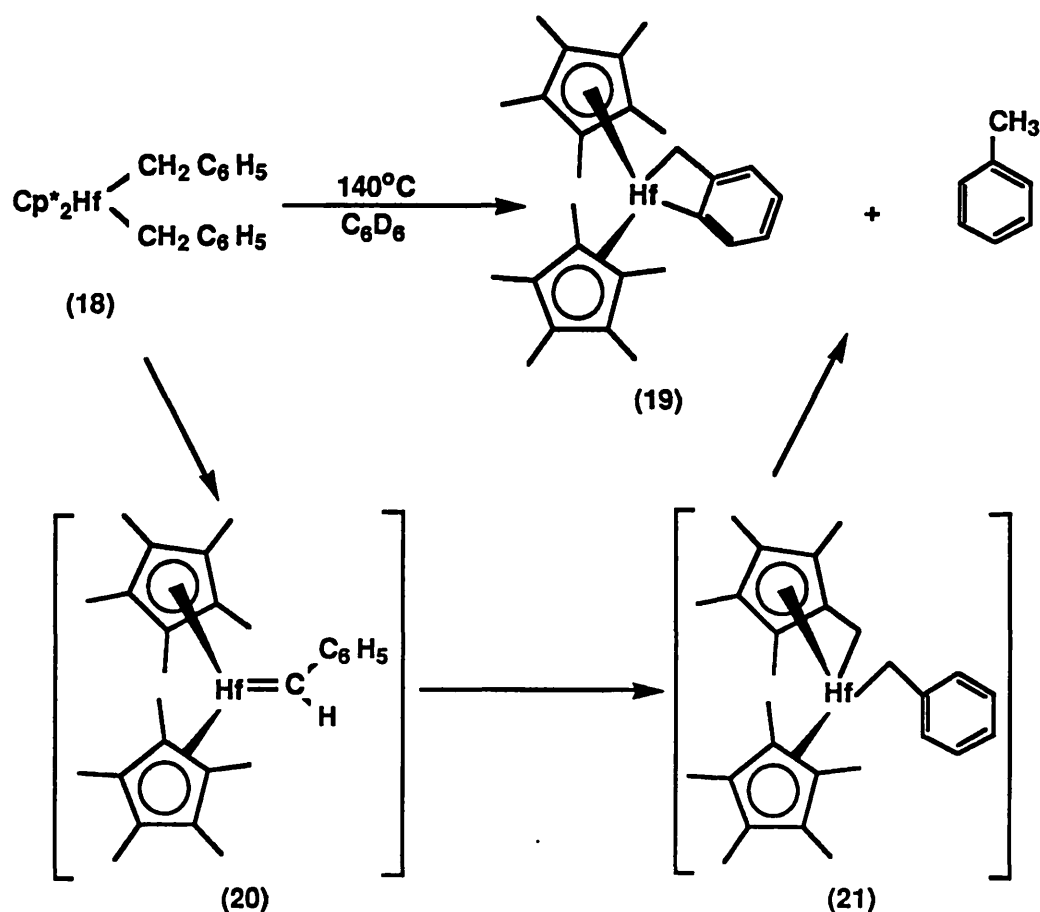


Scheme 16

force of this reaction can in part be attributed to the crowding in (16), whilst (17), though presumably of a strained nature, is less sterically hindered. It is believed that

scission of the zirconium-aryl bond is the rate limiting step rather than metallation of the Cp* -methyl group.

Bercaw *et al.*(65) have used the dibenzyl complex of permethylhafnacene (18) dissolved in benzene or toluene to yield the hafnabenzocyclobutene (19). They believe that the major mechanistic pathway (Scheme 17) involves the hafnium benzylidene complex (20) which produces (21) by pentamethylcyclopentadienyl ring hydrogen abstraction. The intermediate (21) then provides the cyclometallated product (19) by a



Scheme 17

highly ordered, four-centered transition state. The latter is a feature commonly expected for group IV metals and also the lanthanides and actinides, where C-H bond cleavage is achieved by formally d^0 or d^{0n} complexes(66).

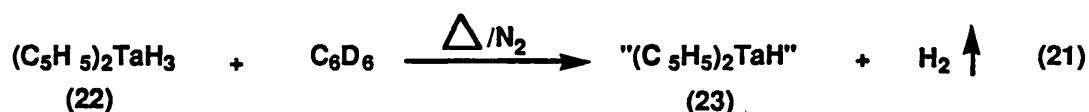
A possible route to intermolecular C-H activation of sp^3 centres by zirconium and hafnium would be to decrease the steric bulk around the metal, for example, exchanging pentamethylcyclopentadienyl ligands for cyclopentadienyl, this could be

difficult though as such species may be too unstable to synthesise resulting in dimers, clusters or decomposition to the metal.

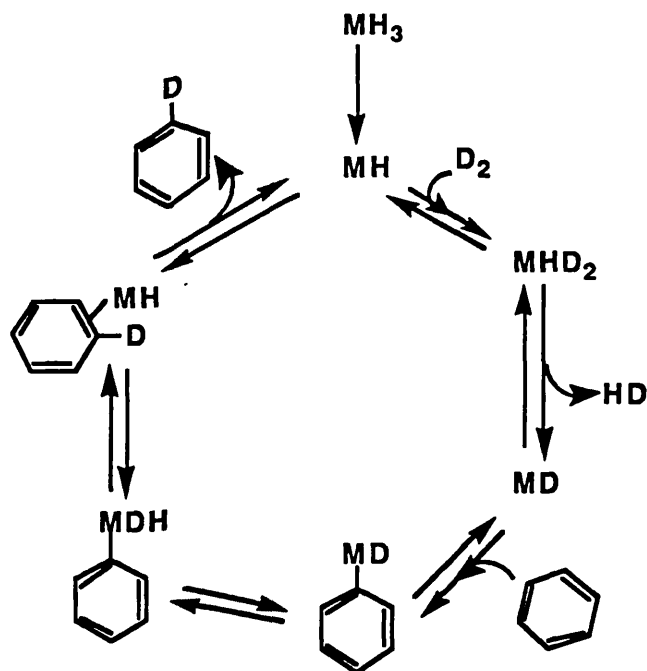
1.4.2.2. Niobium and Tantalum

The C-H activation chemistry of niobium and tantalum, like most of the early transition metals, mainly involves either intermolecular activation of aromatic C-H bonds or intramolecular activation of alkyl C-H bonds in the coordinated ligand.

In 1970, the tantalum trihydride complex, $\text{TaH}_3(\text{C}_5\text{H}_5)_2$ (22), and also the iridium pentahydride, $\text{IrH}_5(\text{PMe}_3)_2$, were found to effect catalytic exchange of benzene protons with deuterium (1-2atmos., 80-100°C)(67). Essentially when a benzene solution of the tantalum species is heated under a closed atmosphere of benzene and deuterium, HD and H_2 appear in the gas phase; this was conclusive evidence of catalytic exchange as the amount of hydrogen produced could only have come from the solvent, benzene. The active catalyst is generated by the thermal extrusion of dihydrogen from (22) producing a 16 electron species (23); this theory was suggested by the results of Reaction 21, where dihydrogen was again detected in

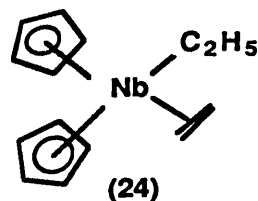


the gas phase. Later, it was discovered that other group V hydrides such as $\text{NbH}_3(\text{C}_5\text{H}_5)_2$ (68) and $\text{TaH}_5(\text{dmpe})_2$ (69) could duplicate the same H/D exchange process. The proposed mechanism for these reactions, is given in Scheme 18 (70).



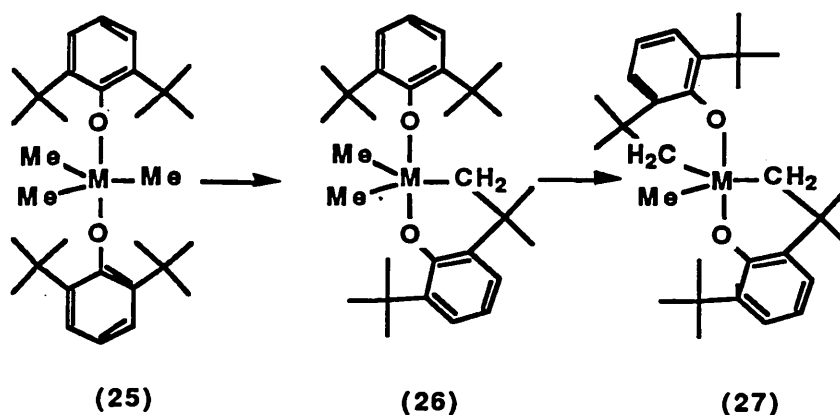
Scheme 18

Nonhydridic niobium catalysts can also be used in arene C-H activation. For example, when a solution of ethylbis(cyclopentadienyl)(ethylene)niobium (24) in



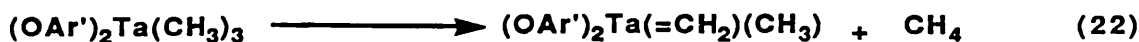
benzene- d_6 is heated over extended periods, substantial amounts of deuterium are incorporated into the reclaimed complex⁽⁷⁰⁾. The active species is thought to be that resulting from the expulsion of ethylene producing $NbH(C_2H_4)(C_5H_5)_2$. None of the above mentioned complexes will however mediate H/D exchange with alkanes.

The recent work of Rothwell has concentrated on the intramolecular activation of alkyl sp^3 C-H centres and comprehending such reaction systems leads ultimately to a better understanding of the related intermolecular reactions. Rothwell uses bulky 2,6-di-*t*-butylphenoxide (OAr') ligands in complexes of type $M(OAr')_2Me_3$ ($M = Ta, Nb$) (25) where thermolysis generates the loss of first one and then two equivalents of

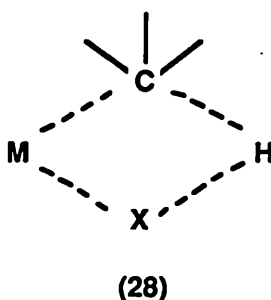


Scheme 19: M=Ta,Nb

methane to provide the mono-cyclometallated (26) and *bis*-cyclometallated (27) compounds (Scheme 19)(71). Labelling studies showed that the methane eliminated results from direct loss of the leaving group with the activated hydrogen(72). In contrast to thermolytic conditions, photolysis of the trimethyl complex gives initially a methyldene complex with loss of one equivalent of methane (Reaction 22). In the



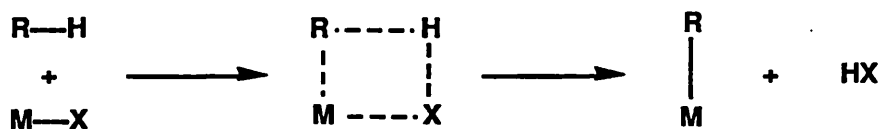
latter case a hydride abstraction is preferred to the distal C-H bond activation of the aryloxide ligand observed in the former example. The methyldene complex will however further react to form the cyclometallated product (26) if heated further(66). It



is now generally accepted that C-H bond activation, at least in intramolecular reactions and at d^0 -metal configurations, occurs by a four-centre transition state (28). This of course is not the case for metal complexes of higher d electron configuration occurring later in the transition series where three-centre transition states or homolytic mechanisms are more likely. Evidence for the four membered transition state hypothesis is being accumulated in studies particularly by Marks(73), Whitesides(74)

and Rothwell(66).

For an intermolecular C-H activation to occur at a d^0 -metal centre the C-H bond has first to enter the coordination sphere of the metal. Interaction with a metal orbital must follow to permit formation of a new M-C bond and subsequent loss of the hydrogen atom with the leaving group (Scheme 20).



Scheme 20: X=leaving group

Although this is possible for the comparable reaction with dihydrogen(75), successful intermolecular hydrocarbon activation reactions are few in number and tend to occur mainly for the lanthanide and actinide metals (Section 1.4.3.). Hydrogenolysis is often compared to the C-H activation problem of alkanes although such a comparison can be quite misleading; for instance, the rehybridisation energies differ (two s orbitals versus one s and one sp^3 orbital), ionisation potentials differ (H_2 is higher than C-H), bond strengths may differ, and finally the steric differences between H_2 and alkane C-H may reflect unfavourably in certain systems.

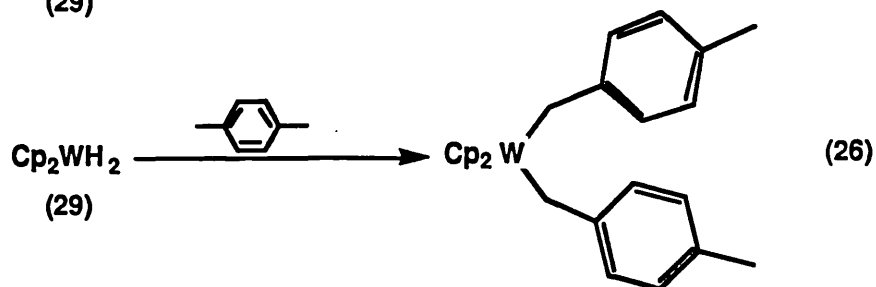
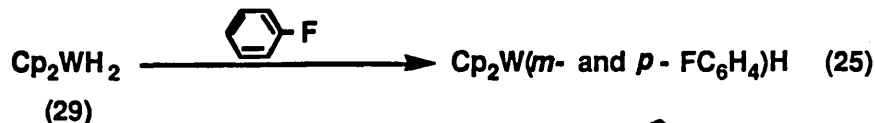
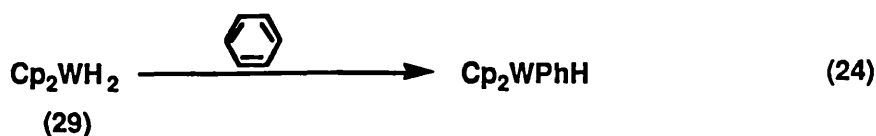
1.4.2.3. Molybdenum and Tungsten

The group VI metal, tungsten, played a major role in the area of C-H activation during the early 1970's; Green (76) discovered the photoextrusion reaction of dihydrogen from the dihydride (29) of *bis*(cyclopentadienyl)tungsten to provide the reactive 16 electron intermediate tungstenocene (30) (Reaction 23). This reaction was

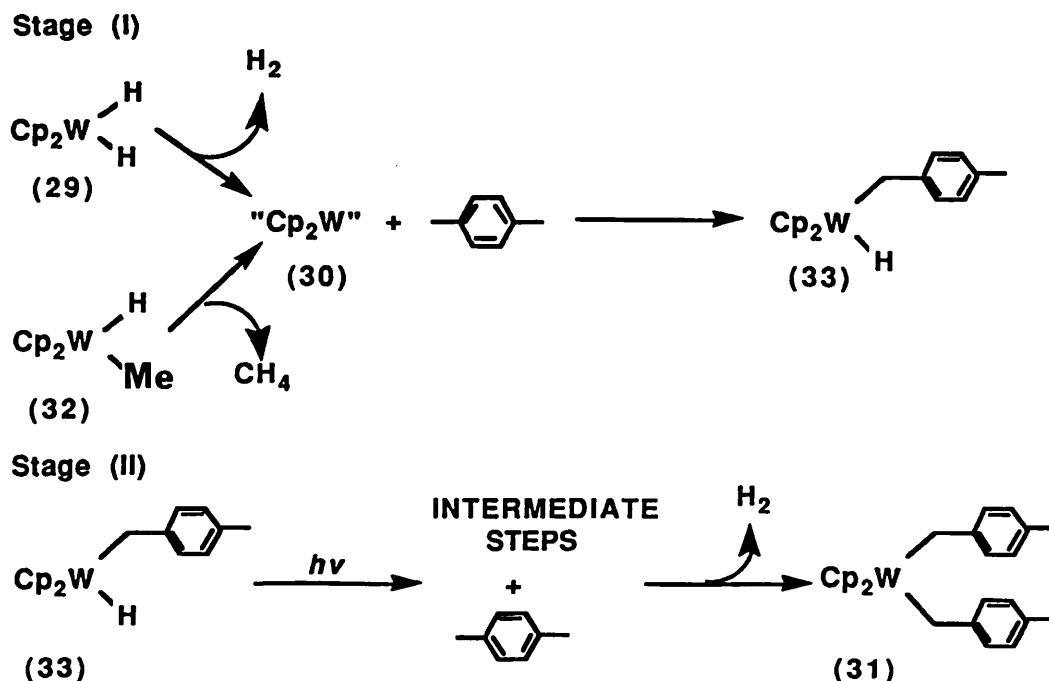


employed in the activation of both sp^2 and sp^3 C-H bonds (Reactions 24-27) and it was found that when the substrate was too unreactive (Reaction 27) the tungstenocene tended to dimerise. Similar results have also been acquired for the photoextrusion of carbon monoxide from $\text{Cp}_2\text{W}(\text{CO})$ (77). It must be reiterated that very low

concentrations of the metal are required if alkane activation is to be permitted before destruction of the active catalyst.

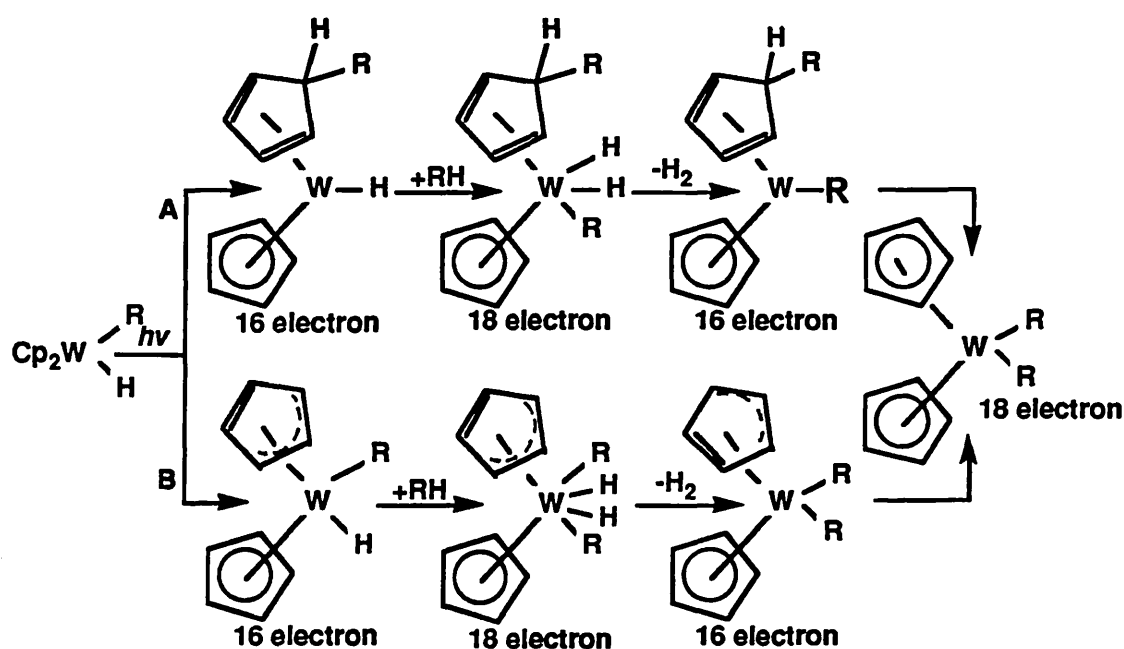


Green(78) has compared the reactions of tungstenocene when formed photochemically with those when formed thermally, both by extrusion of dihydrogen from (29) or methane from the methylhydride complex $\text{Cp}_2\text{WH}(\text{Me})$ (32). The results obtained were almost identical. The exception was Reaction 26; under thermal conditions (50-60°C), only the monoalkylhydride (33) was provided. However if (33) was then irradiated, the *bis*-alkyl derivative (31) formed. These observations



Scheme 21

gave rise to a possible reaction pathway (Scheme 21) consisting of two stages. Stage I is identical whether thermal or photolytic conditions are used. However the monoalkyl complex (33), unlike the aryl complexes of Reactions 24 and 25, is photochemically unstable so on irradiation proceeds to stage II yielding the disubstituted product (31). As stage II must involve intermediates with the potential to insert into sp^3 C-H bonds, Green has suggested two likely mechanistic routes (Scheme 22)⁽⁷⁹⁾. Route A



Scheme 22

involves the metal-to-ring migration of R to produce a 16 electron species. The latter oxidatively adds R-H, photochemical extrusion of dihydrogen from the *cis*-dihydride occurs followed by ring-to-metal transfer. A precedent for this mechanistic proposal is the reversible metal-to-ring migration of ethyl in the complex Cp_2WEtCl (80). Sequence B includes a reversible $\eta^3-C_5H_5-\eta^5-C_5H_5$ ring shift which occurs to prevent twenty electron intermediates. Twenty electron complexes, though apparently possible, for example nickelocene, are not really plausible in a C-H activation reaction mechanism where electron deficiency at the metal centre and low valency species help drive the oxidative addition reaction onwards.

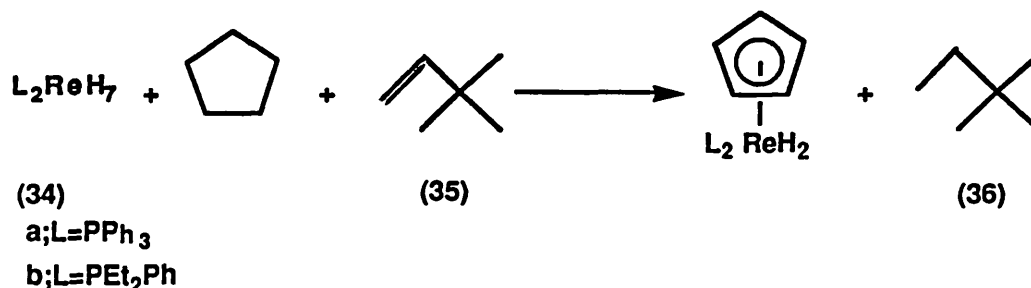
Little information has been accumulated on organometallic chemistry of molybdenum with respect to the C-H cleavage problem; this is quite puzzling as molybdenum chemistry does tend to reflect that of tungsten in many instances. The majority of studies of molybdenum have concentrated on the nitrogen fixation

problem(81).

1.4.2.4. Technetium and Rhenium

Whilst several rhenium complexes are emerging as very powerful tools for C-H and C-C bond cleavage reactions, a similar chemistry for technetium is unknown. This is because all technetium isotopes are unstable towards β -decay or electron capture, and so only traces are found in Nature and those arise from the spontaneous fission of uranium.

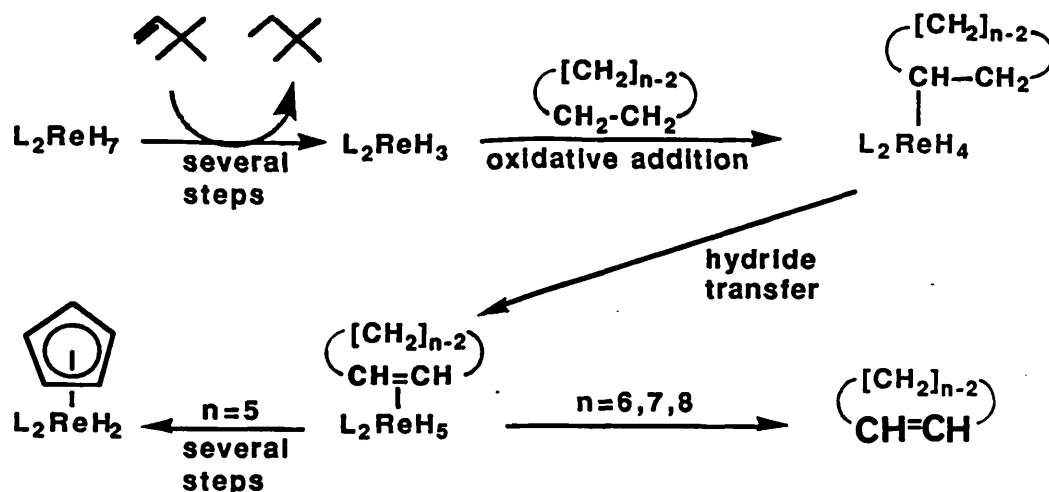
The rhenium heptahydride, $\text{ReH}_7(\text{PPh}_3)_2$ (34a) was used by Chatt and Coffey(82) in 1969 to catalyse H/D exchange between the substrate benzene- d_6 and hydrogen. It was not until the late 1970's when Felkin (83) commenced work on rhenium polyhydrides that it was discovered that they were worthy sp^3 C-H activators as well. The *bis*(phosphine)rheniumheptahydrides (34) were found to activate C-H bonds of cyclopentane under very mild conditions (Scheme 23)(83). Neohexene (35)



Scheme 23

is employed as the hydrogen acceptor producing neohexane (36); the efficiency of this hydrogen acceptor was originally discovered by Crabtree(84) for use in his iridium-based alkane activation systems.

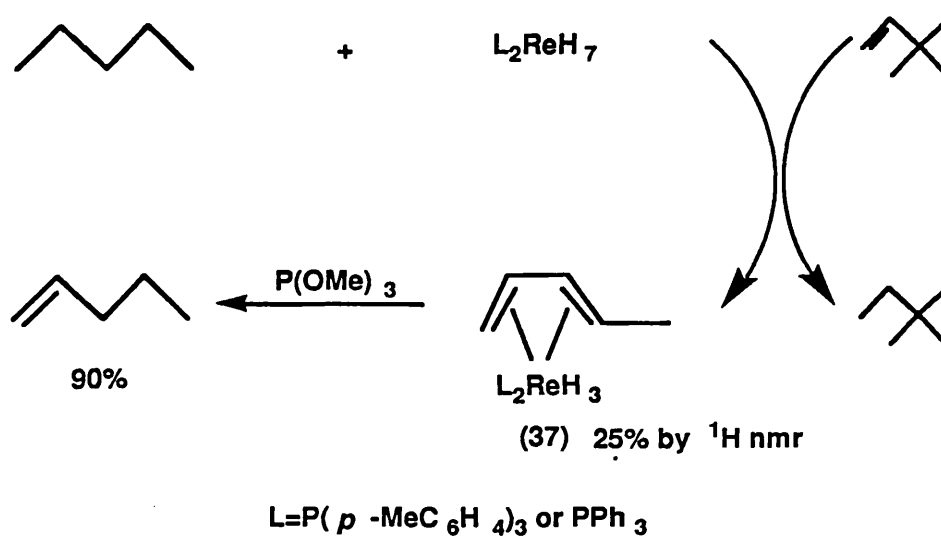
When Felkin's activation system was applied to the higher homologues cyclohexane, cycloheptane and cyclooctane, it directly afforded the corresponding cycloalkenes (Scheme 24)(85). A general trend towards more efficient alkane



Scheme 24

dehydrogenation with more electron-releasing phosphine ligands in the heptahydride was observed. The fact that larger cycloalkanes ($n > 5$) lead to the cycloalkene and do not undergo further dehydrogenations may well be because the former are more labile as ligands than cyclopentene, and so dissociate from the metal before further reaction can occur.

Treatment of *n*-pentane with heptahydrido*bis*(triarylphosphine)rhenium and neohexene was found to provide the trihydrido(*trans*-penta-1,3-diene)*bis*(triarylphosphine)rhenium species (37)(86). This complex when treated with trimethyl phosphite releases the diene ligand to produce pent-1-ene (Scheme 25) in 90% isolated

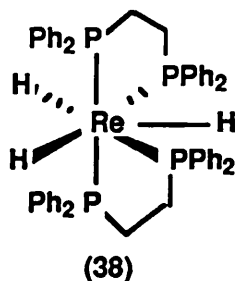


Scheme 25

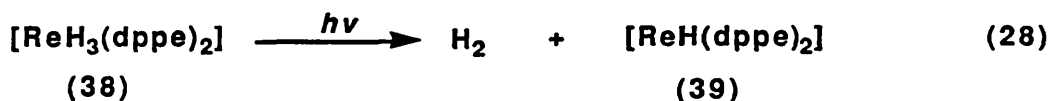
yield. Further work showed that the same procedure could also be applied to higher n-alkanes converting them in >95% yield and with >89% selectivity to the corresponding 1-alkene(87).

By 1983, Felkin(88) had made the rhenium system catalytic (up to 9 turnovers) for the case of cycloalkane conversion to cycloalkene. This was accomplished simply by using very low concentrations of the rhenium reagent (3.3mM) and neohexene (50mM) in the alkane as both solvent and substrate. The results established for the first time that the selective, non-radical catalytic functionalisation of unstrained saturated alkanes by means of a homogeneous transition metal species is a feasible process. The highest catalytic turnovers were obtained at temperatures of around 80°C.

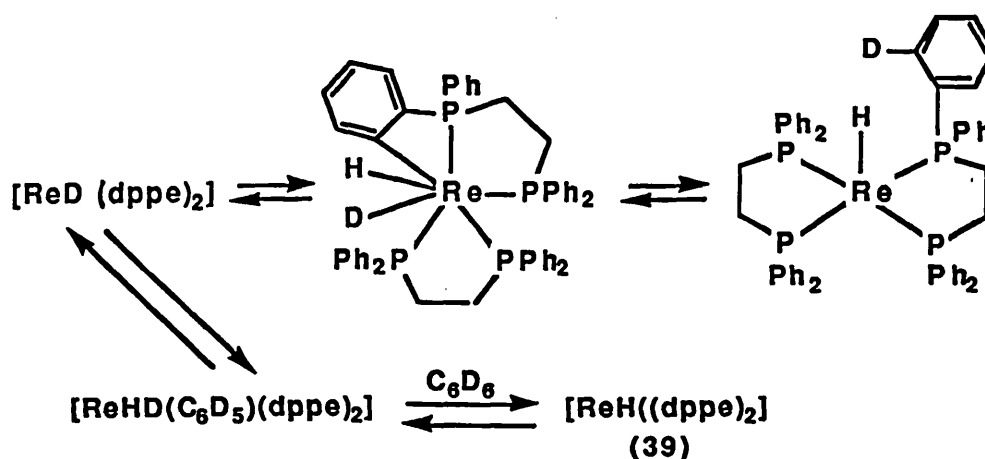
Geoffroy(89) has used the principle of dihydrogen photoextrusion(76) on the trihydridorhenium complex $\text{ReH}_3(\text{dppe})_2$ (38). This complex, although having *cis*-orientation of two of the hydrides, is stable to dihydrogen reductive elimination under thermal conditions. Photolysis results in an overall d^{16} species (39) (Reaction 28)



which undergoes reversible insertion into the C-H bonds of benzene and also the



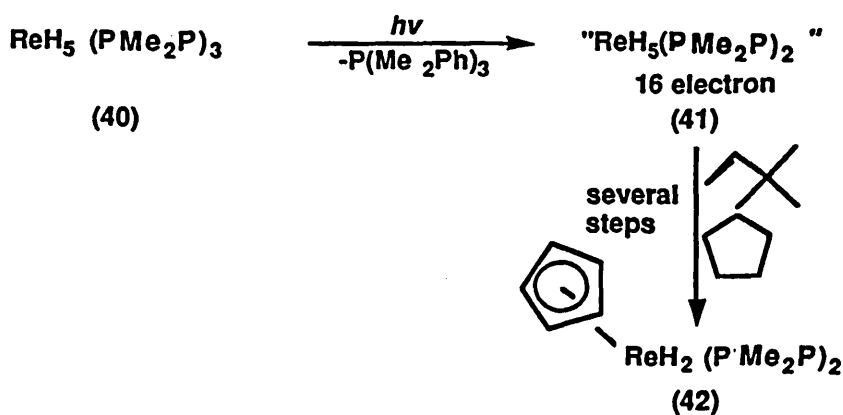
phenyl groups of the bidentate phosphine ligand (Scheme 26). Successful attempts to use the active species (39) for insertion into sp^3 C-H bonds intermolecularly have not yet appeared in the literature. It is likely that the reaction may not be possible due, in part, to steric hindrance around the rhenium centre by the four phosphorus entities and also to the presence of two bidentate phosphine ligands which are generally more



Scheme 26

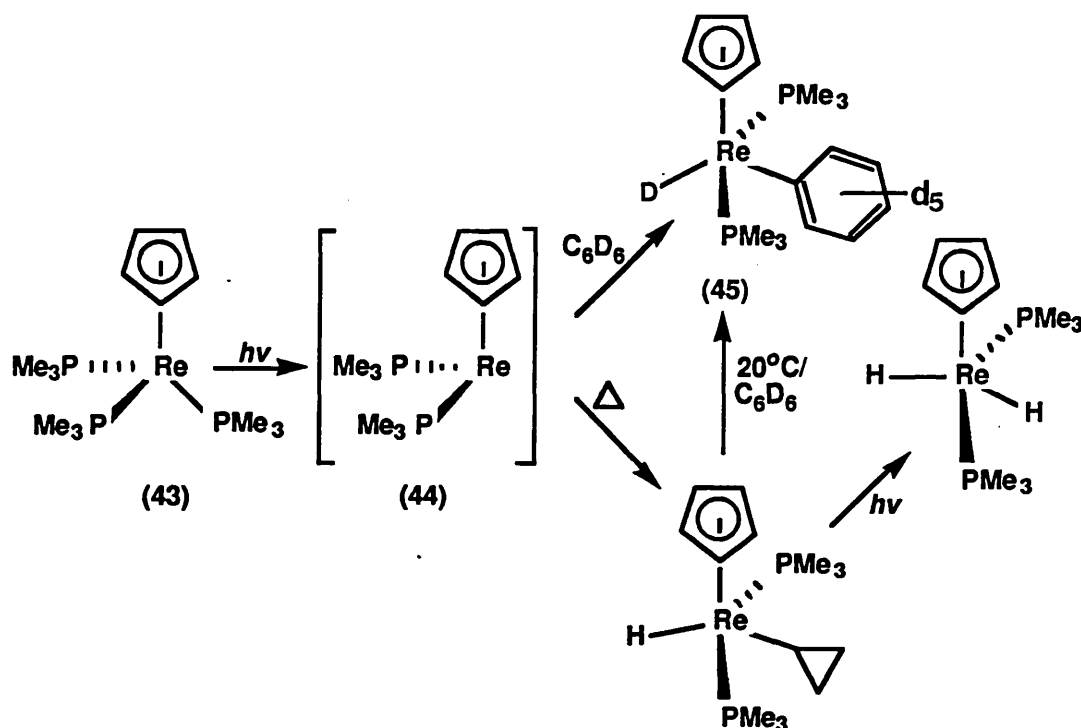
effective in stabilising the metal centre than, for example, two monodentate phosphine ligands as used in Felkin's work⁽⁸⁵⁾. These two points render Geoffroy's 16 electron intermediate (39) less reactive than ReH_3L_2 , and hence less prone to alkane C-H activation.

Caulton *et al.*⁽⁹⁰⁾, have used the *tris*(dimethylphenylphosphine)rhenium complex, $ReH_5(P(Me_2Ph)_3)_3$ (40), in a solution of cyclopentane and in the presence of neohexene as a hydrogen acceptor to effect formation of the cyclopentadienyl complex (42). The active metal species (41) is generated by phosphine dissociation upon irradiation of (40) (Scheme 27). It would be interesting to apply this system further, using the same substrates employed by Felkin⁽⁸⁵⁻⁸⁷⁾, to determine whether comparable or perhaps contrasting results are obtained for the same active rhenium intermediate, with the same phosphine ligands, but in a photochemically excited state.



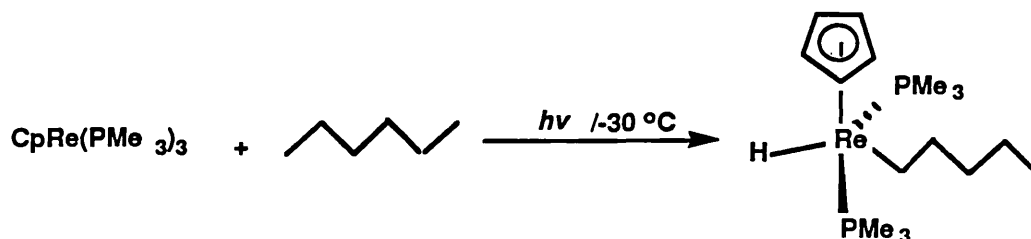
Scheme 27

Bergman⁽⁹¹⁾ also uses photolysis as a technique to provide the C-H insertion-sensitive cyclopentadienyl species (44) from $\text{CpRe(PMe}_3)_3$ (43) (Scheme 28).

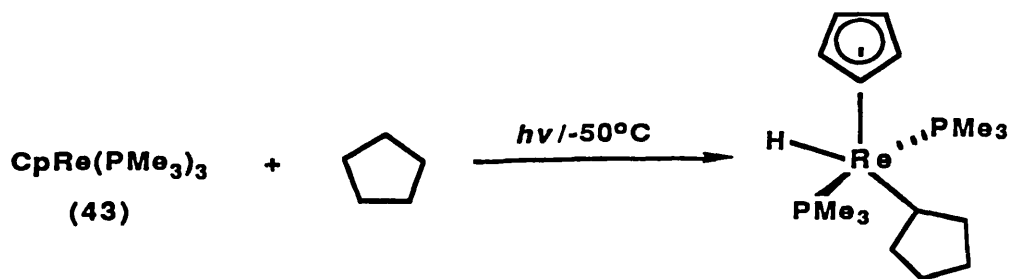


Scheme 28

Although a benzene solution of (44) is readily reactive towards C-H bonds of strained cyclopropane (Scheme 28) the same system does not activate n-alkane or cycloalkane C-H bonds as efficiently. This in part is because the adducts of the latter are not thermally stable and decompose rapidly at low temperatures, reforming the saturated alkane; reactions are most successful at -30°C (Scheme 29) and -50°C (Scheme 30), respectively. The cycloalkane and n-alkane insertion products are in fact so unstable, that the respective substrates may function as inert reaction solvents at 5°C to produce the benzene adduct (45) (Scheme 31). One problem of this system is dimerisation of the unsaturated metal species produced by the initial loss of the phosphine. Another is

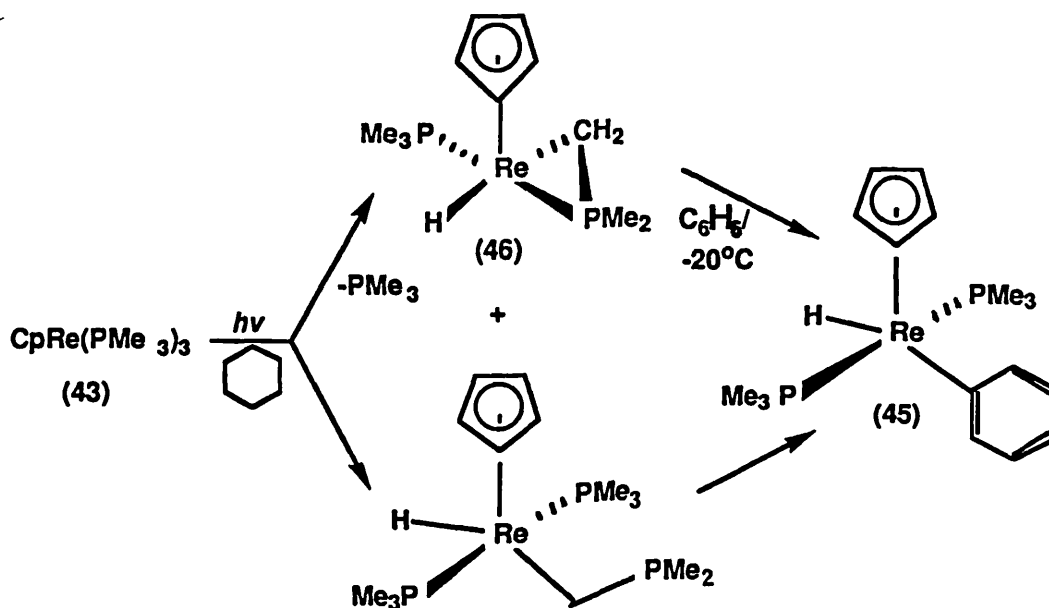


Scheme 29



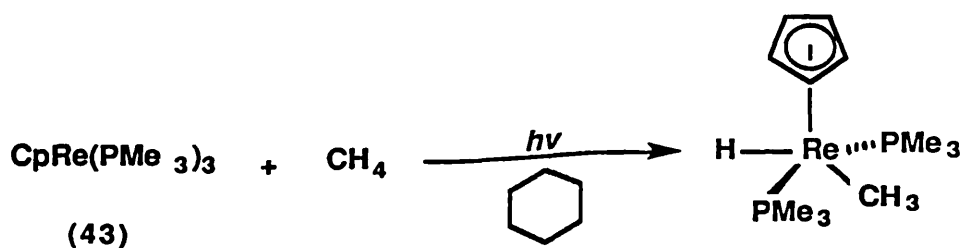
Scheme 30

the tendency for cyclometallation of the phosphine ligands to occur; this is prominent when cyclo- or n-alkanes are used as substrates. The major virtue, though, is the



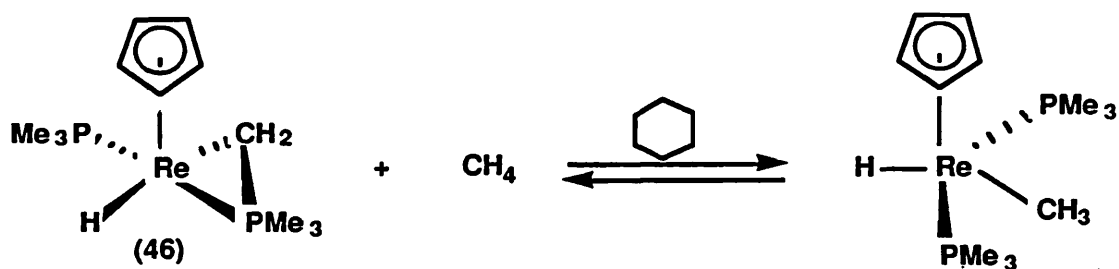
Scheme 31

ability to insert into the C-H bonds of methane. This can be achieved by irradiation of (43) in cyclohexane at $5\text{--}10^\circ\text{C}$ under 25 atmospheres of methane (Scheme 32) or by



Scheme 32

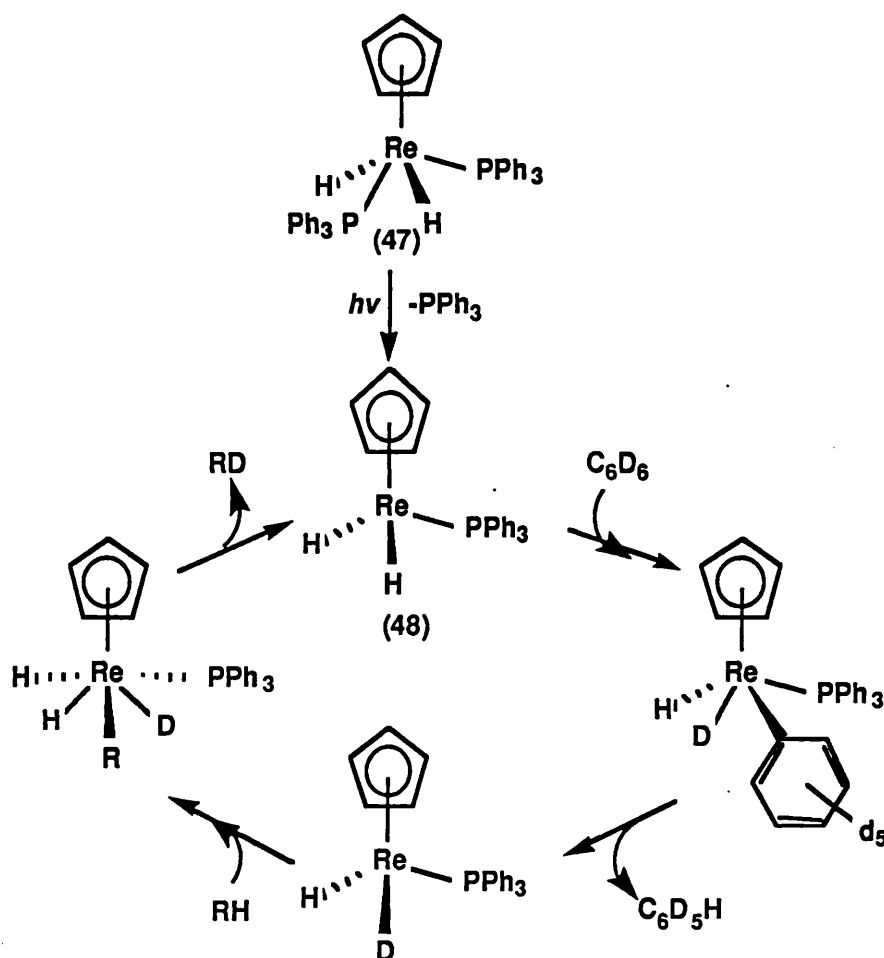
thermolysis of the cyclometallated species (46) at 20°C under 25 atmospheres of methane (Scheme 33).



Scheme 33

The above method, though activating alkanes, has yet to functionalise them by, for example, carbon monoxide insertion. However, this is very recent work and attempts to make the system functionalise alkanes catalytically may well be reported in the near future.

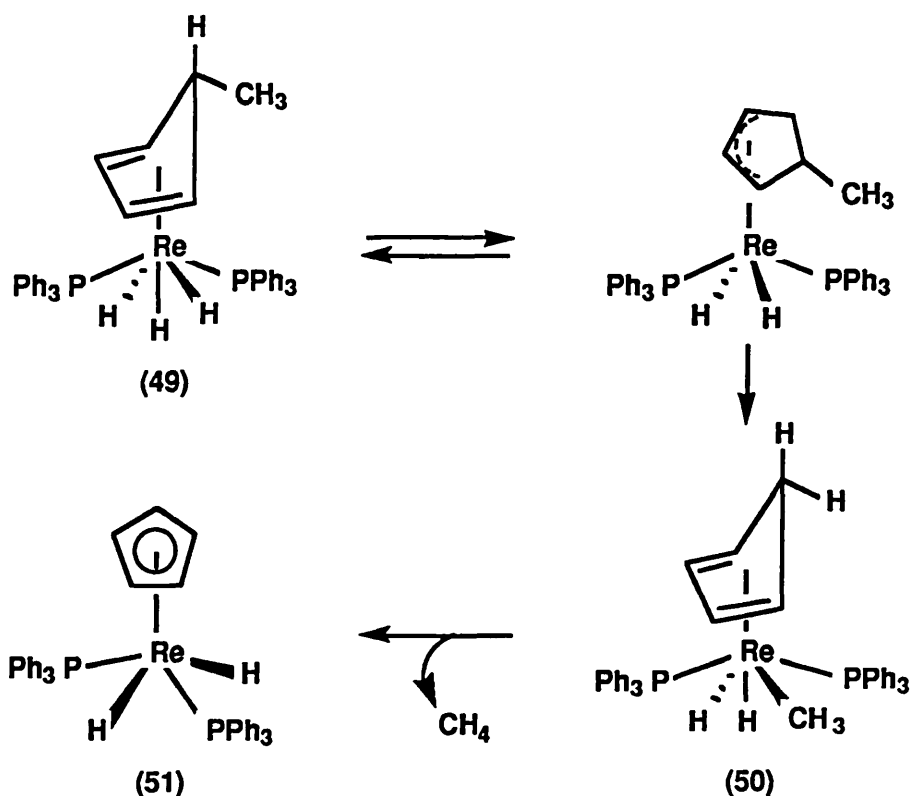
Jones⁽⁹²⁾ has also been able to use a rhenium complex to activate methane and other alkanes (Scheme 34). Photochemical extrusion of a triphenylphosphine ligand



Scheme 34

from $\text{CpRe}(\text{PPh}_3)_2\text{H}_2$ (47) produces the 16 electron dihydrido species (48); dihydrogen is not eliminated during irradiation as the hydride ligands are *trans*

disposed. The intermediate species (47) stimulates catalytic exchange of deuterium from benzene- d_6 and tetrahydrofuran- d_8 into alkanes. Other rhenium complexes of the general formula $HRe(P)_2L_3$ ($P=PPh_3, PMe_3$; $L=PMe_3, CO, CNR$; $R=Me, Et, i-Pr, t-Bu, neopentyl$) have been synthesised from the substrate $(\eta^4-C_5H_6)Re(P)_2H_3$ by ligand substitution of cyclopentadiene⁽⁹³⁾. The complexes were prepared in an effort to make new species which were capable of C-H activation and that also possessed a ligand suitable for functionalisation of the activated bond. Though the compounds have been used to catalytically exchange H/D, with benzene- d_6 as the deuterium source, reports of alkane activation and functionalisation have not yet been published. An interesting C-C bond cleavage reaction has been observed for *endo*-($\eta^4-C_5H_5Me$) $Re-(PPh_3)_2H_3$ (49) (Scheme 35) ⁽⁹⁴⁾ resulting in the expulsion of methane gas.



Scheme 35

The reaction is believed to proceed by initial migration of hydrogen from the metal to the C_5H_5Me ring followed by migration of the *endo*-methyl group to the metal. The resulting methyl hydride complex (50) then quickly eliminates methane providing (51). This type of reaction has been previously observed in, for example, Green's work on tungsten complexes (Scheme 22)⁽⁷⁹⁾. Even though the complex (49) is biased towards C-C bond cleavage, it does prove that homogeneous rhenium species can stimulate C-C

bond cleavage; this concept may well develop to include cases where the thermodynamic driving force is not so overwhelmingly strong.

1.4.2.5. Platinum Metals

Platinum metal chemistry is an exceedingly active area of research, and has offered many examples of complexes capable of C-H bond cleavage in arenes and alkanes. Cases of C-C bond cleavage are, alas, rare.

(i) Platinum

As early as 1967, Garnett and Hodges⁽⁹⁵⁾ discovered a platinum-based (PtCl_4^{2-}) catalytic H/D exchange system between arenes and a $\text{D}_2\text{O}/\text{CH}_3\text{COOD}$ solvent medium. Moreover, they found that in the presence of H_2PtCl_6 , chlorination of arenes takes place⁽⁹⁶⁾. For each case, Shilov^(97,98) showed that alkanes could be activated and functionalised in the same manner. The reaction system is formally electrophilic and for alkanes Shilov⁽⁹⁹⁾ believes that the mechanism involves oxidative addition of the C-H bond across the metal, and that H^+ is then rapidly lost from the Pt(IV)(R)(H) product producing a Pt(II)alkyl . The latter is oxidised to a Pt(IV)alkyl species, by excess Pt(IV) in the system, and then produces the chlorinated alkane. The reactions involving arenes may well involve classical electrophilic aromatic substitution.

(ii) Palladium

More recently, Hiraki *et al.*⁽¹⁰⁰⁾ have developed a palladium(II) acetate-dialkyl sulphide system for the functionalisation of benzene to benzoic acid under a carbon monoxide atmosphere. The system is so far stoichiometric and has not yet been applied to alkanes. The ability of palladium to activate aromatic C-H bonds has been exploited in a novel synthesis of 1-naphthol derivatives from cinnamyl compounds (Figure

6)(101). The method involves treatment of cinnamyl acetate (52) with triethylamine (2 equiv.) and acetic anhydride (> 1 equiv.) under a positive pressure of carbon monoxide.

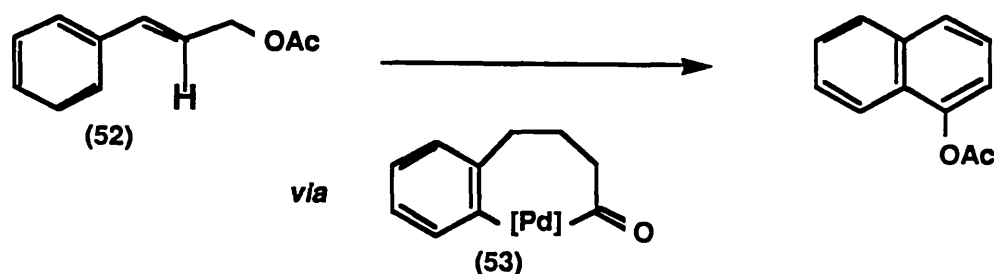
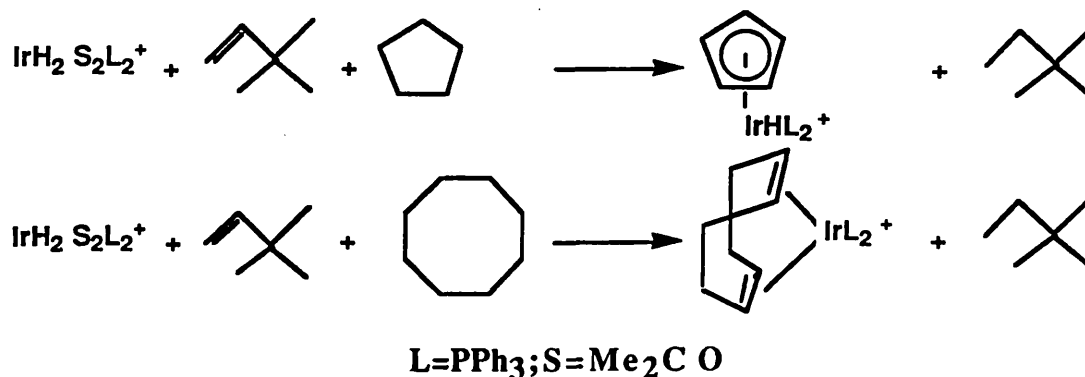


Figure 6

and in the presence of a catalytic amount of $\text{PdCl}_2(\text{PPh}_3)_2$. The reaction possibly proceeds by oxidative addition of (52) to a palladium(0) species followed by CO insertion and *ortho*-palladation providing the cyclometallated species (53). The main virtue of the palladium and platinum systems shown above is their functionalising ability as well as activation. This advantage may, in the future, provide very useful transformations if it can be applied to the more inert alkanes as well as BTX.

(iii) Iridium

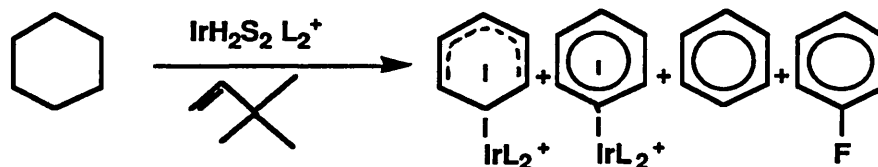
Pioneering advances in the activation of alkanes by soluble organoiridium species were made by Crabtree(84,102) in 1979. It was found that $[\text{IrH}_2(\text{Me}_2\text{CO})_2\text{L}_2]\text{BF}_4$ ($\text{L} = \text{PPh}_3$) and neohexene could dehydrogenate a number of alkanes in weakly-coordinating solvents, such as acetone and dichloromethane (Scheme 36). The initial active agent performing these multiple dehydrogenation steps is



Scheme 36

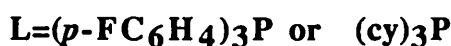
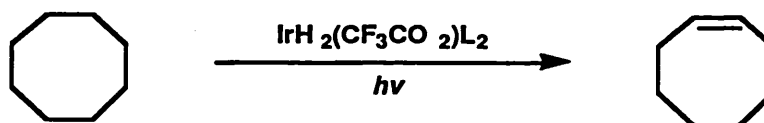
believed to be $[\text{IrL}_2]^+$, a 12 electron species. This is possible because the complex $[\text{IrH}_2\text{S}_2\text{L}_2]^+$ has not only two labile hydride ligands which can be removed by

neohexene but also two labile acetone ligands, thus revealing multiple coordination sites at the iridium centre. The same active species is also accessible from $[\text{IrH}(\eta^5\text{-C}_6\text{H}_7)\text{L}_2]^+$, $[\text{Ir}(\text{diene})\text{H}_2\text{L}_2]^+$ and $[\text{Ir}(\eta^4\text{-naphthalene})\text{L}_2]^+$, by extrusion of benzene, alkene and naphthalene, respectively⁽¹⁰³⁾. The activation of cyclohexane



Scheme 37

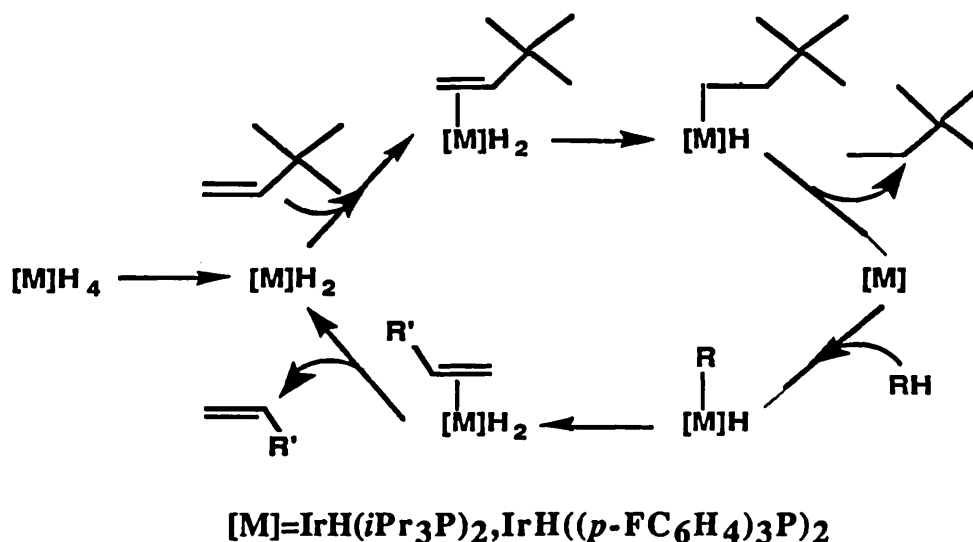
was unsuccessful until cyclohexane was employed as the solvent (Scheme 37)⁽⁵⁶⁾. This provided free benzene in stoichiometric amounts but deactivation of the metal species was a competing reaction providing fluorobenzene by hydrogenolysis of the P-C bond of the phosphine ligand; this problem is quite common and its relevance to homogeneous catalyst deactivation has recently been discussed by Garrou⁽¹⁰⁴⁾. Crabtree believes that the above systems are not catalytic because they involve multiple dehydrogenations producing a thermodynamic cascade⁽⁵⁶⁾ and iridium products with strongly bound ligands that hesitate to dissociate and recycle the active species. With this knowledge, the "masked 14 electron" species $[\text{IrH}_2(\text{CF}_3\text{CO}_2)_2\text{L}_2]$ was tested and found to positively undergo catalytic transformations of cyclic alkanes to their respective alkenes (Scheme 38)⁽¹⁰⁵⁾. The reaction can take place under thermal or



Scheme 38

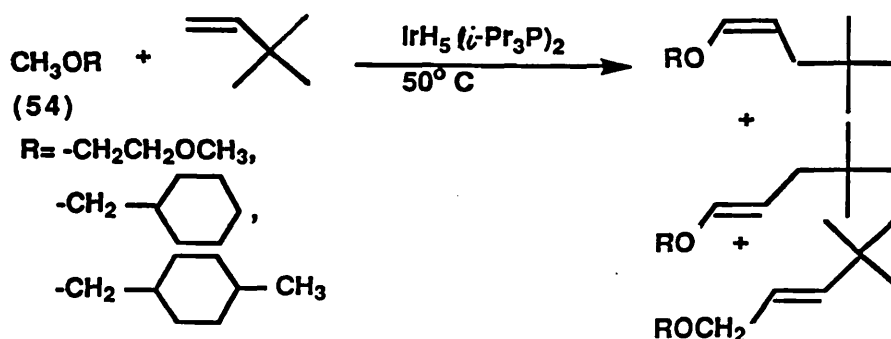
photolytic conditions and with or without neohexene for the latter. When *tris*(cyclohexyl)phosphine was used as the ligand, greater catalytic efficiency (up to 28 turnovers) was achieved by irradiation rather than thermal inducement (2 turnovers). Independently, Felkin's group^(105,106) also produced a catalytic iridium-based dehydrogenating system using $[\text{IrH}_5(\text{PPh}_3)_2]$ in the presence of acetic acid; they

considered that $[\text{IrH}_2(\text{MeCO}_2)(\text{PPh}_3)_2]$ was involved. Alternatively, using the complexes $[\text{IrH}_5(i\text{-Pr}_3\text{P})_2]$ and $[\text{IrH}_5((p\text{-FC}_6\text{H}_4)_3\text{P})_2]$ in the presence of



Scheme 39

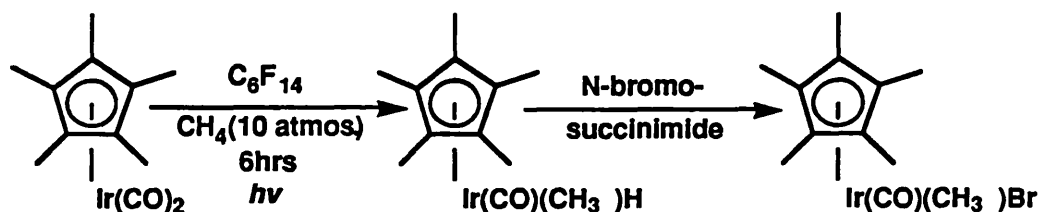
neohexene, in a solution of the substrate and at a temperature of 150°C , 45-70 catalytic turnovers could be achieved for the transformation of cyclooctane to cyclooctene. The postulated catalytic cycle is given in Scheme 39. Incidentally, this system is more efficient than the corresponding rhenium one⁽⁸⁸⁾. Also for straight chain alkanes and methylcyclohexane the $[\text{IrH}_5(i\text{-Pr}_3\text{P})_2]$ complex has been found to be reasonably selective towards attack of the strongest C-H bonds, functionalising at the methyl C-H bonds preferentially⁽¹⁰⁷⁾. Interestingly, *bis*(triisopropylphosphine)iridium pentahydride has been used to catalyse the formation of C-C bonds by initial C-H bond activation in methyl ethers (54) followed by olefin insertion into the Ir-C bond (Scheme 40)⁽¹⁰⁸⁾. This is a very important result which aspires to be the first documented example of the insertion of an olefin into a metal-hydrogen bond formed *in situ* by



Scheme 40

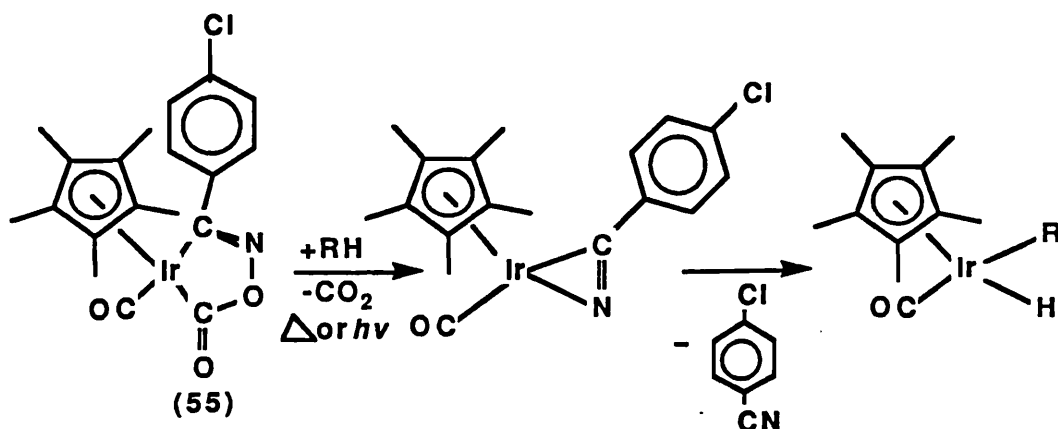
an intermolecular activation of an sp^3 C-H bond; if this was deemed possible for alkanes it would be an even more significant breakthrough.

Bergman's(109) iridium-centered activation systems use the pentamethylcyclopentadienyl complex $[Cp^*Ir(PMe_3)H_2]$. Though this was one of the first complexes to achieve intermolecular C-H activation, and inspired many other workers, the alkylhydrido insertion adducts could not be functionalised further and would only permit reductive elimination back to the alkane substrate or with bromoform replace hydride for bromine in the product complex. Oxidative addition of C-H bonds is believed to occur across the photogenerated, 16 electron complex, $[Cp^*Ir(PMe_3)]$, and a thermochemical study of the reaction has recently been forwarded(110). Similar complexes of formula $[Cp^*Ir(CO)]$, produced by photoextrusion of carbon monoxide from the corresponding dicarbonyl species, have also produced positive alkane C-H activation results, including cleavage of methane C-H bonds (Scheme 41)(111).



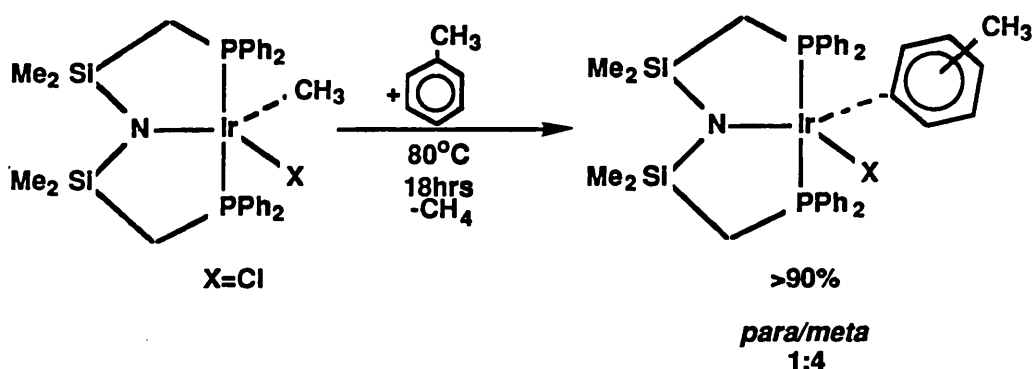
Scheme 41

As Bergman once suggested(109), the active iridium species in these systems do not require a photochemically excited state for the oxidative addition reaction but only require photochemistry to expel a ligand in order to provide a low valent species. Evidence for this theory was supplied by Hawthorne(112) who, using the iridium metallacycle (55), produced the active species $[Cp^*Ir(CO)]$ under both thermal and photochemical conditions. Corresponding products of oxidative addition were observed for benzene and cyclohexane (Scheme 42) from each initiation technique used, thus conclusively proving Bergman's remarks to be true.



Scheme 42

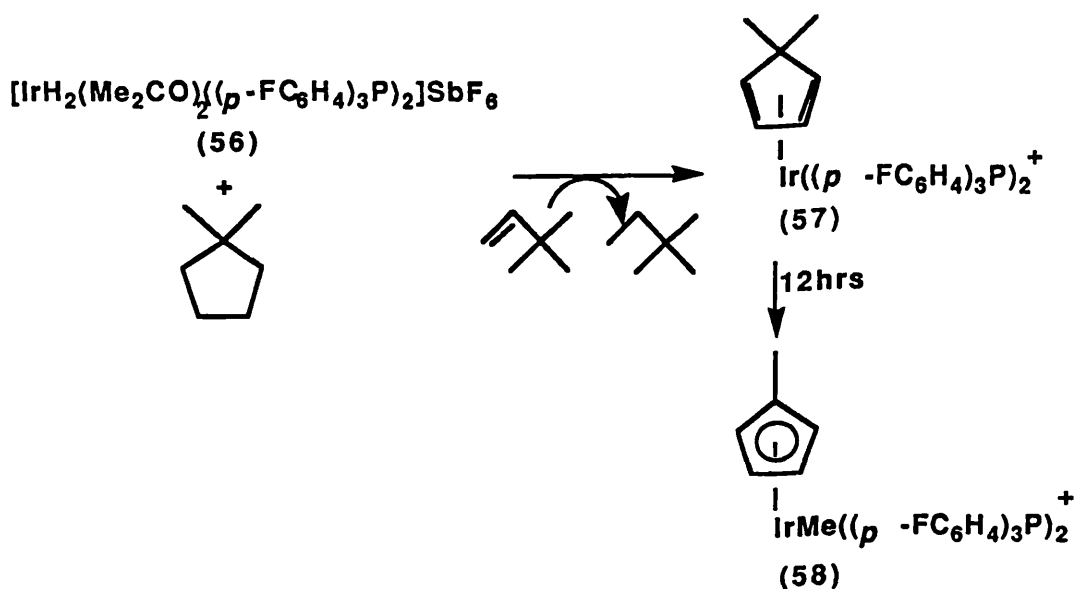
Another approach to C-H activation was attempted by Fyzuk and coworkers⁽¹¹³⁾ using iridium amide complexes. Unlike the above iridium species, the complex used in this case does not activate sp^3 C-H bonds but surprisingly is specific for arene C-H bond insertion (Scheme 43). If the metal is changed to rhodium the



Scheme 43

reaction system becomes specific for sp^3 C-H bonds of toluene⁽¹¹³⁾.

Examples of C-C bond cleavage in unstrained alkanes by iridium complexes have been provided by Crabtree⁽¹¹⁴⁾. It was found that the reaction of 1,1-dimethylcyclopentane with $[\text{IrH}_2(\text{Me}_2\text{CO})_2\{(p\text{-FC}_6\text{H}_4)_3\text{P}\}_2]\text{SbF}_6$ (56) at 150°C over eight hours produces the complex (57) in 50% yield. When the reaction mixture was heated further, the methyliridium complex (58) formed essentially quantitatively *via* the Green-Eilbracht^(80, 115) reaction (Scheme 44).



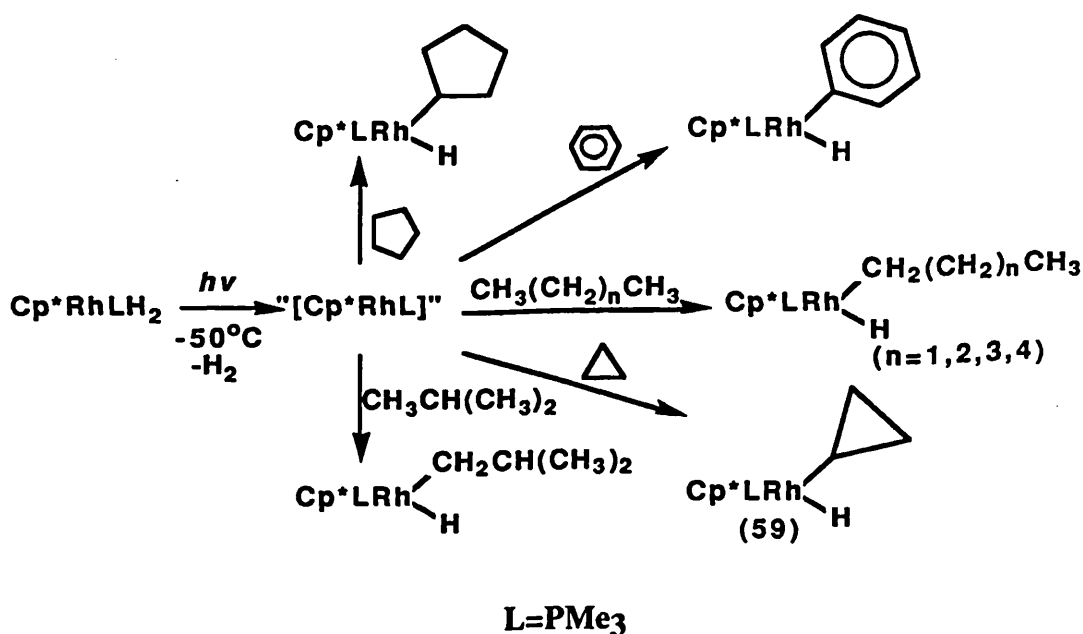
Scheme 44

Unfortunately the reaction system could not be applied to 1,1-dimethylcyclohexane; although a 12 electron iridium species is acceptable for aromatisation of cyclopentane, a 10 electron intermediate would be required for aromatisation of cyclohexyl derivatives. Research in the area of alkane C-C bond activation is still very much in its infancy.

(iv) Rhodium

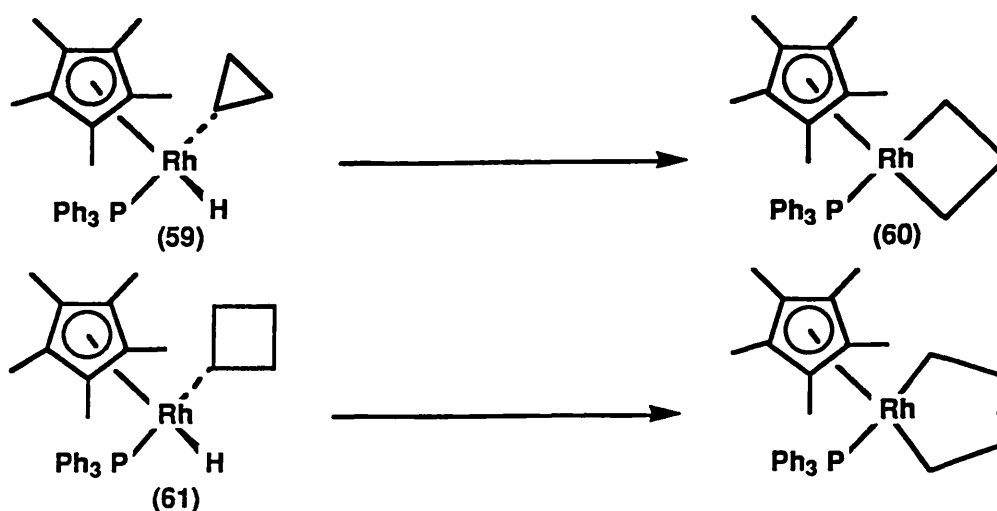
Rhodium, like iridium, is popular in the area of C-H activation. Generally the active metal species are generated by photoextrusion of labile ligands such as *cis*-orientated dihydrides or a phosphine moiety.

Jones and Feher⁽¹¹⁶⁾ studied the rhodium complex $\text{Cp}^*\text{Rh}(\text{PMe}_3)_2\text{H}_2$ and found that photolysis gave insertion products with both arenes and alkanes. For example, irradiation in liquid *n*-propane at -55°C gave the *n*-propyl rhodium hydride which decomposed at temperatures above -15°C unless converted to the bromide complex by bromoform; the alkane adducts of rhodium appear to be far less stable than the corresponding iridium ones⁽¹⁰⁹⁾. Bergam^(117,118) has also studied the same system (Scheme 45) obtaining similar, stoichiometric reactions. However, the



Scheme 45

cyclopropane adduct (59) has been found to react further to produce the rhodacyclobutane (60) (Scheme 46)(119) in 65% yield. A similar reaction occurs

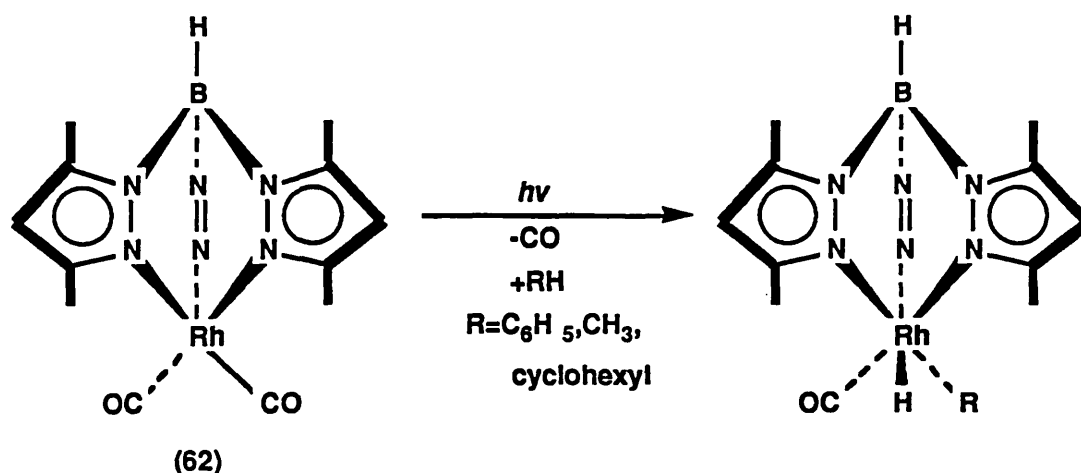


Scheme 46

for the adduct of cyclobutane (61) although in rather modest yields (12-13%). Neither of these cyclometallations can be duplicated in the analogous iridium systems(109).

Three novel rhodium-based methods have so far appeared in the literature in 1987. In the first case, Bianchini *et al.*, (120) used the *ortho*-metallated complex $[\{(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{N}(\text{CH}_2\text{CH}_2\text{PPhC}_6\text{H}_4)\}\text{RhH}](\text{SO}_3\text{CF}_3)$ under thermal conditions to reductively eliminate the substituted phenyl group thus producing the $\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\text{Rh}^+$ fragment. The latter complex can then undergo oxidative

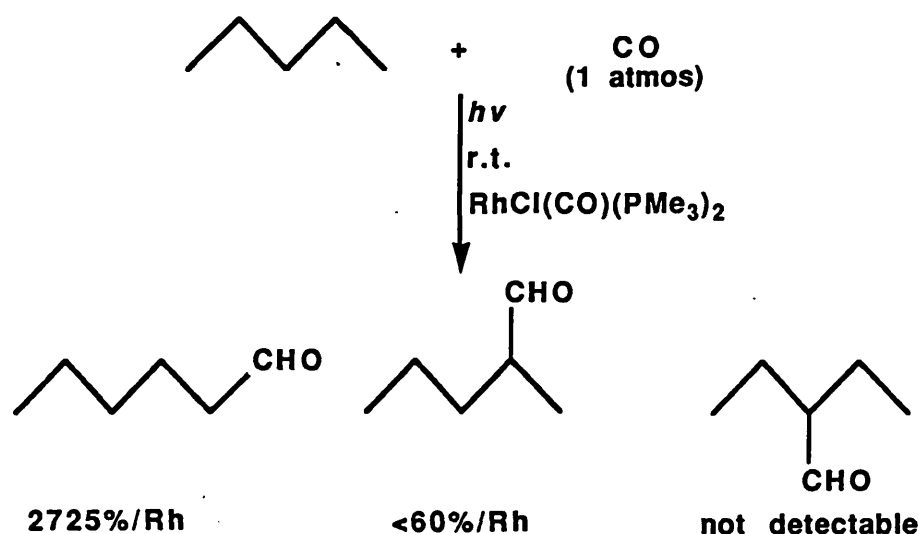
additions of H₂ and C-H bonds from arenes, alkynes and aldehydes. Activation of alkane sp³ C-H bonds was not mentioned and may or may not be possible. Graham and Ghosh⁽¹²¹⁾, have employed a *tris*(dimethylpyrazolyl)borato complex (HBPz*₃)Rh(CO)₂ (62) (Pz*=3,5-dimethylpyrazolyl) (Scheme 47) under



Scheme 47

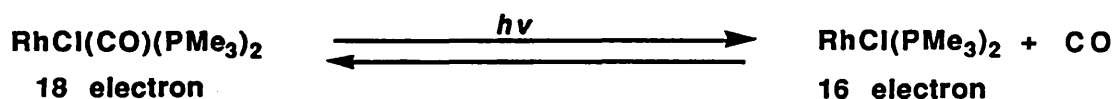
photochemical conditions to activate aromatic and saturated hydrocarbons, including methane, at room temperature. The system is more reactive to aromatic C-H oxidative addition than the corresponding Cp*Ir(CO)₂ species⁽¹¹¹⁾ and again forms thermally unstable alkane adducts^(109, 117, 118) where the hydride ligand has to be immediately exchanged with chlorine from carbon tetrachloride to obtain a reasonably stable complex.

Perhaps the most surprising results of this year have been obtained by Sakakura and Tanaka⁽¹²²⁾. They have achieved regioselective carbonylation of the terminal methyl group of n-pentane by the use of RhCl(CO)(PMe₃)₂ under one atmosphere of carbon monoxide and irradiation (Scheme 48). They believe the active species to be RhCl(PMe₃)₂, a sixteen electron intermediate resulting from photoextrusion of carbon monoxide. This undergoes oxidative addition of n-pentane to afford (n-C₅H₁₁)(H)RhCl(PMe₃)₂, followed by CO insertion and then reductive elimination. If the carbon monoxide was delivered to the reaction system under a higher pressure, then the oxidative addition step, if occurring by a 3-centered transition state, would increase in rate⁽¹²³⁾. However, Tanaka and Sakakura use only one atmosphere of carbon



Scheme 48

monoxide presumably to avoid a shift in the equilibrium (Scheme 49) which would favour the 18 electron complex totally.



Scheme 49

It is predicted that use of a Wilkinson-type catalyst, for example $\text{RhCl(PMe}_3)_3$ or $\text{RhCl(PPh}_3)_3$, under similar conditions, but with an increased pressure of carbon monoxide, would produce the same reaction products and possibly with higher catalytic turnovers; not only can carbon monoxide ligands be photochemically eliminated, but phosphine ligands as well,^(90, 91, 92) and elimination of a phosphine ligand would not be effected by a positive carbon monoxide pressure.

(v) Ruthenium

A ruthenium complex offered the first case of interaction between benzene and a soluble transition metal compound. The discovery was made by Chatt and Davidson in 1965⁽¹²⁴⁾ and the same publication also provided the first example of intramolecular sp^3 C-H bond activation *via* cyclometallation; when the complexes *cis*- or *trans*- $[\text{RuCl}_2(\text{dmpe})_2]$ were reacted with arene anions in tetrahydrofuran the complexes *cis*-

$[\text{Ru(II)H(aryl)(dmpe)}_2]$ (aryl=phenyl, 2-naphthyl) were produced. These compounds on pyrolysis reductively eliminated aryl-H and the resulting 16 electron species oxidatively inserted into a phosphine methyl C-H bond.

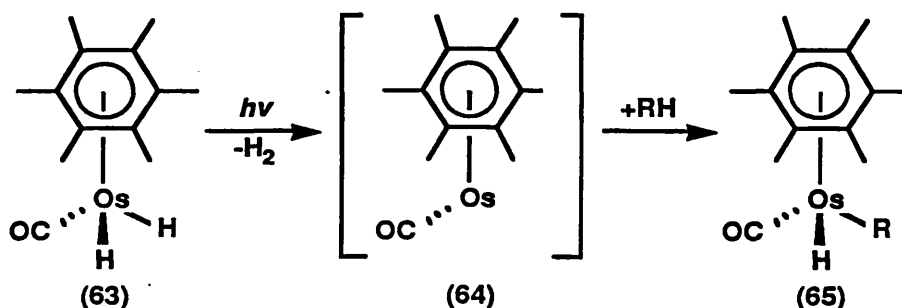
The isoelectronic species $[\text{RuH(dppe)}_2]^+$ produced by thermal extrusion of labile dihydrogen from $[\text{RuH(dppe)}_2(\eta\text{-H}_2)]^+\text{BF}_4^-$ has apparently not been used in comparable C-H activation, however it does oxidatively add into the C-H of acetonitrile⁽⁵⁷⁾. In this example, the phosphine ligands may not be electron releasing enough to stabilise the higher oxidation state necessarily produced.

Felkin and coworkers⁽¹⁰⁶⁾ in their work on soluble 18 electron transition metal polyhydride systems found the complexes $\text{RuH}_4(\text{PPh}_3)_3$ and $\text{RuH}_4\{(\textit{p}\text{-FC}_6\text{H}_4)_3\text{P}\}_3$ converted alkanes into alkenes catalytically (see Scheme 39 for the iridium analogues). The latter was found to be the most effective producing 44-45 catalytic turnovers during the dehydrogenation of cyclooctane to cyclooctene. Evidence is emerging which implies that the use of second and third row transition metal polyhydride complexes, in the presence of a hydrogen acceptor, may be a general approach for the activation of alkane sp^3 C-H bonds.

Although the monohydride, $\text{RuHCl(PPh}_3)_3$, catalyses the exchange between benzene and deuterium gas under vigorous conditions⁽⁷⁰⁾, Felkin's ruthenium tetrahydrides⁽¹⁰⁶⁾ seem to be the only ruthenium species capable of catalytic activation of alkane substrates intermolecularly.

(vi) Osmium

Little information has been published for the use of osmium complexes in the area of C-H bond activation. However Felkin and coworkers⁽¹²⁵⁾, have produced an osmium polyhydride system that is successful, and Graham *et al.*⁽¹²⁶⁾, have used the hexamethylbenzene osmium complex (63) to achieve C-H activation in alkanes (Scheme 50). Photolysis reductively eliminates dihydrogen from (63) to produce the



Scheme 50

16 electron species (64) which undergoes stoichiometric insertion into a C-H bond giving (65).

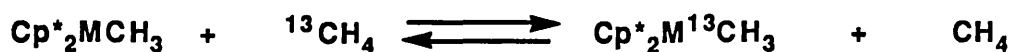
1.4.3. Lanthanides, Actinides; also Scandium and Yttrium

Lanthanides are strictly the fourteen elements that follow lanthanum in the Periodic Table and in which the fourteen 4f electrons are successively added to the lanthanum configuration. The electrons of the 4f shell are relatively uninvolved in bonding, resulting in these electropositive elements having a prime oxidation state of III. Actinides are much more prone to complex formation than the lanthanides due to spatial overlap of their higher atomic orbitals (5f, 6d, 7s and 7p), which allows a variety of coordination numbers and oxidation states.

The second row element, scandium, has a much smaller ionic radius than other metals classed in this group. Its organometallic chemistry is duly restricted and it has not been known to activate C-H bonds.

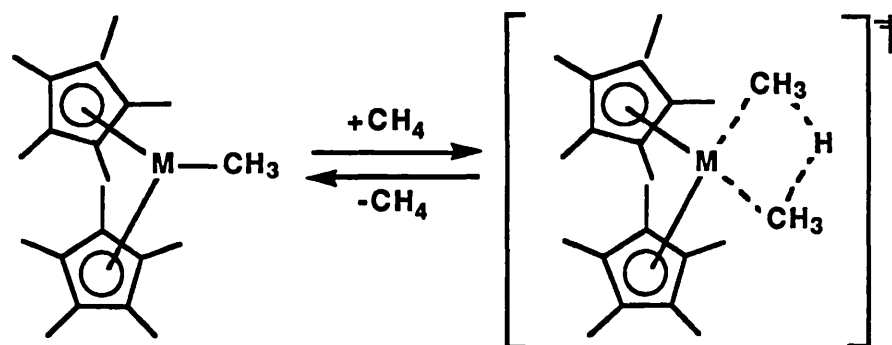
C-H activator species of this section are all thought to proceed by four-centered transition states (see section 1.4.2.2.) and although intramolecular examples are now well known, information on intermolecular activations are still sparse.

The yttrium complex $Cp^*_2YCH_3$ (66)⁽¹²⁷⁾ provided the first well-characterised example of the reaction of methane with a homogeneous organometallic complex. The probable mechanism for this bimolecular exchange reaction is given in

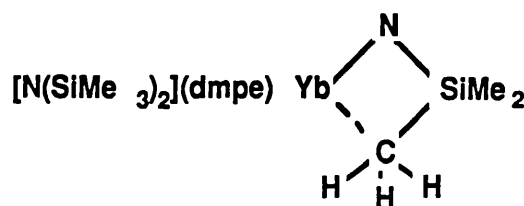
Reaction

(66) M=Y

(67) M=Lu

Mechanism**Scheme 51**

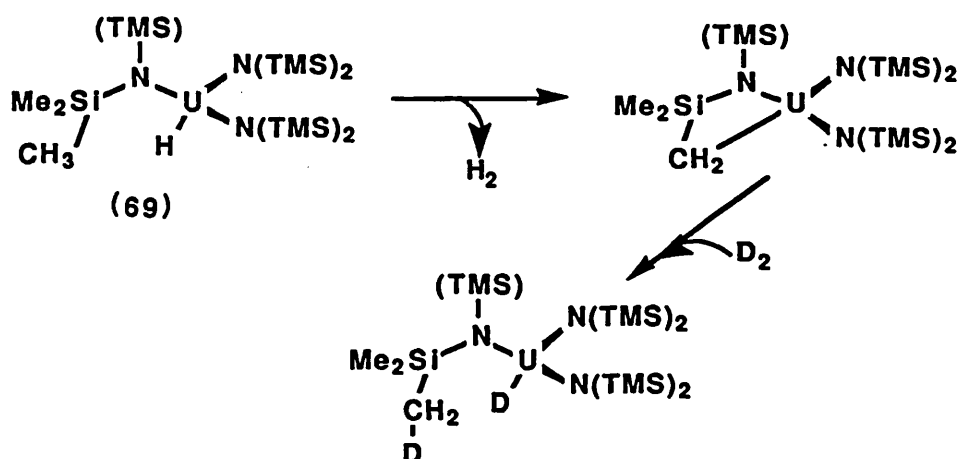
Scheme 51. The same complex can undergo exchange reactions with benzene, and the analogous lutetium species $(\text{Cp}^*)_2\text{LuCH}_3$ (67) is also active. The lanthanides are known to form strong metal-carbon bonds and a recent X-ray study of the ytterbium compound, $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{dmpe})$ (68)(128) has shown a definite interaction between one of the methyl groups and ytterbium in the ground state. The hydrogen atoms of the respective methyl group were apparently pointing away from the metal



(68)

centre; a contrasting situation to that with d block metals where $\text{M}\cdots\text{HC}$ type interactions are prevalent. This could mean that we may have to start looking more towards the lanthanide series for C-C bond cleavage reactions.

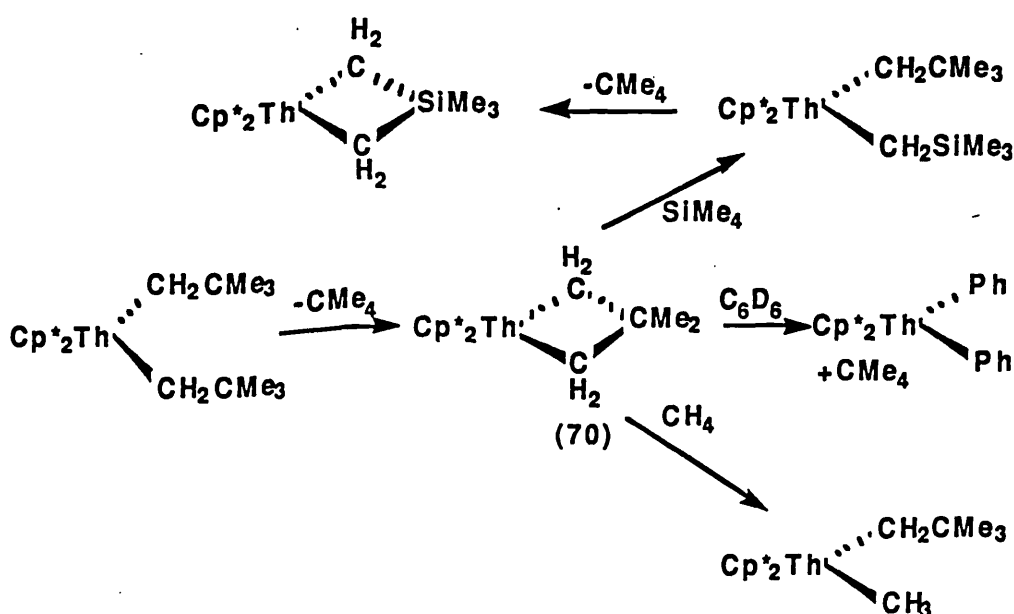
In the actinide group, both thorium and uranium have been used for C-H activation reactions. In the uranium complex (69), it has been shown that it is possible to catalytically deuterate the SiMe_3 group using D_2 (Scheme 52)(129). The cycle



Scheme 52

involves a hydride ligand as a leaving group for the cyclometallation reaction, coupled with the reverse hydrogenolysis of the metal-carbon bond so formed. Marks *et al.*(130), have found that the uranium complex $\text{Cp}^*_2\text{U}(\text{C}_6\text{H}_5)_2$, by virtue of thermally labile phenyl ligands, will produce $(\text{Cp}^*)_2\text{U}(\text{C}_6\text{H}_4\text{D})(\text{C}_6\text{D}_5)$ in the presence of benzene- d_6 , the deuterium being incorporated into the *ortho*-position. Direct exchange of the aromatic groups was ruled out, the mechanism presumably involving benzyne intermediates.

Marks(73, 131) has demonstrated that neopentyl derivatives of thorium (70) may undergo a number of intermolecular reactions with hydrocarbons (Scheme 53), including methane. The transition state for both cyclometallation and intermolecular C-

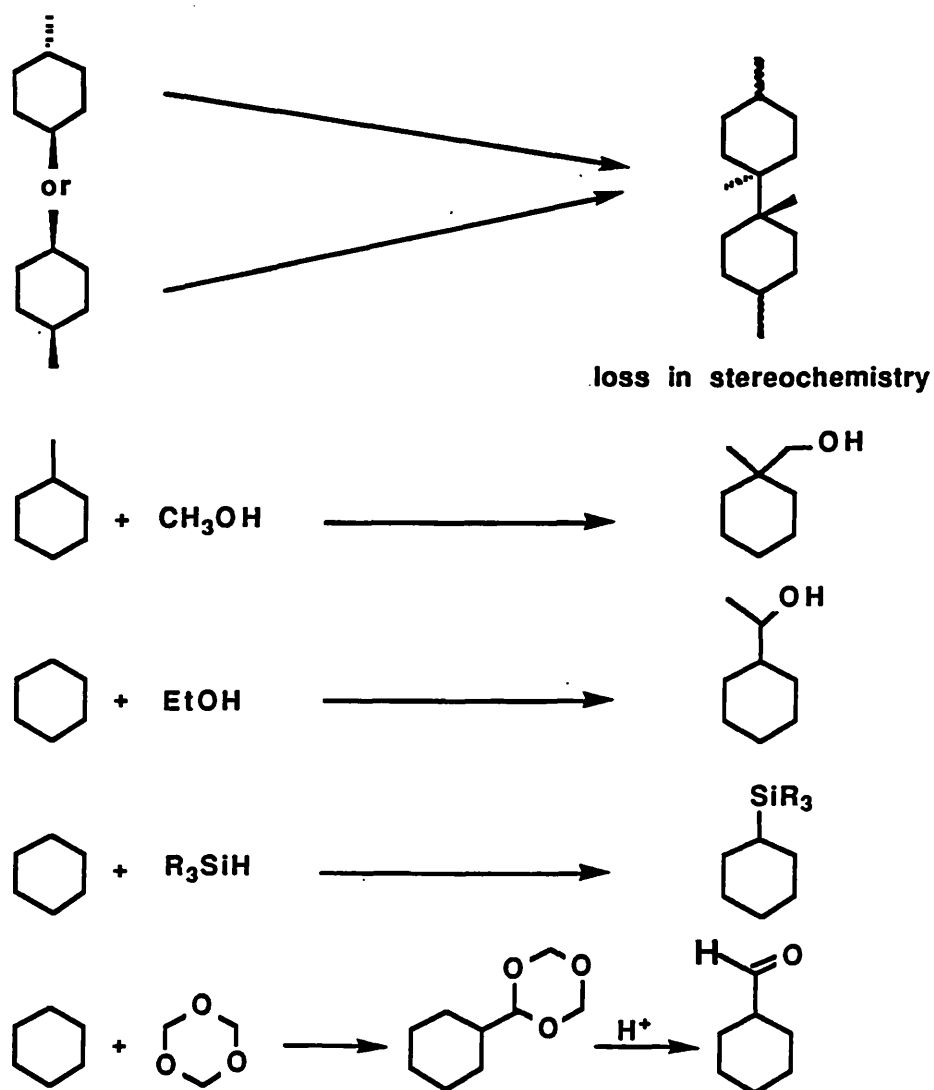


Scheme 53

H activation is believed to have stringent spatial requirements, since it is probably four-centered and heterolytic in nature⁽¹³²⁾. Such transition states offer a means to effect homogeneous C-H activation on saturated hydrocarbons with high intrinsic regioselectivity; related studies are now in progress.

1.5. Mercury Cross Dimerisation⁽¹³³⁾

Many of the techniques described above employ phosphine ligands; however this places the complexes concerned at a disadvantage due to decomposition of the active species by inter- and intramolecular interactions with phosphines⁽¹⁰⁴⁾. Crabtree⁽¹³³⁾ has solved this problem by removal of all ligands in the starting catalyst.

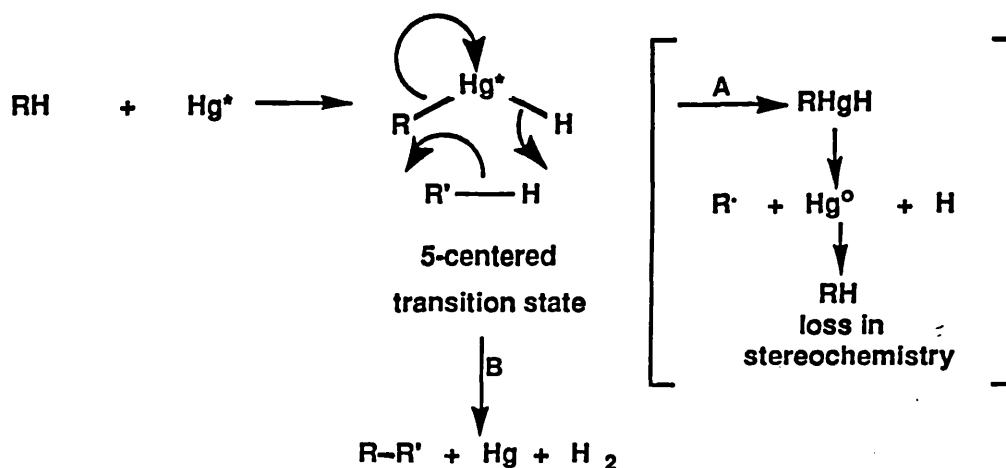


Scheme 54

Using the presence of mercury in a reaction system to test for homogeneity

(102), a versatile cross coupling reaction has unfolded for alkanes by virtue of the mercury alone (Scheme 54). The system was further applied to heteroatomic species, resulting in selective functionalisation of alkanes on preparatively useful scales and in excellent yields (90-95%). The technique has recently been extended to envelop reactions with thioethers, amines and even methane(134).

A mechanism (Scheme 55) has been proposed by Motherwell(135), which explains the loss in stereochemistry, high regioselectivity and the high deuterium isotope effect, 11, of this dimerisation process. Mercury in an excited, high energy state, reacts specifically with the most nucleophilic C-H bond of the substrate R-H. In most instances, relaxation of the intermediate follows leading to elimination of the respective alkyl radical ($R\cdot$) and an hydrogen atom. Before recombination to form R-H, loss in stereochemistry may prevail (Route A). Alternatively, the excited alkyl hydride adduct reacts with a second substrate molecule ($R'-H$) *via* a highly ordered, five membered transition state. This leads to production of a dimerised species ($R-R'$), dihydrogen, and ground state mercury (Route B). Hence, route A explains the observed loss of stereochemistry and route B accounts for the high regioselectivity and unusually large deuterium isotope effect.



Scheme 55

The reaction procedure simply involves photolysis of the substrate mixture under reflux temperatures, the products being separated by their differing boiling points or polarities.

1.6. Conclusions

Hydrocarbons are attractive feedstocks for the chemical industry. However, to increase their use would require considerable changes in petroleum refining encompassing novel, economical, hydrocarbon functionalisation techniques and the subsequent modification of engineering units. Among other drawbacks, classical functionalisation methods are not sufficiently selective or controlled; high-valent metal oxidants are acceptable for certain crude oil fractions but overall are of little use; the problem of biomimetic systems is scaling-up and the functionalisation of high alkanes (steric factors). The solution is most likely to emerge from the area of low valent transition metal chemistry.

The pleasing aspect is that unifying principles are emerging for this chemistry. Succinctly, it may be concluded that a coordinatively unsaturated, electron deficient and sterically uncongested metal species is required; although configurations of d^8 or d^{10} are preferred at metal centres for oxidative addition reactions, overall electron configurations of d^{10} , d^{12} or d^{14} are required to attempt catalytic processes.

We now know that alkane activation is viable at many metal centres. The quest now at hand is catalytic functionalisation of the alkane adducts before reductive elimination to the saturated alkane substrate dominates.

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CHAPTER 2

2. METAL ASSISTED CLEAVAGE OF THE CARBON CARBON BOND

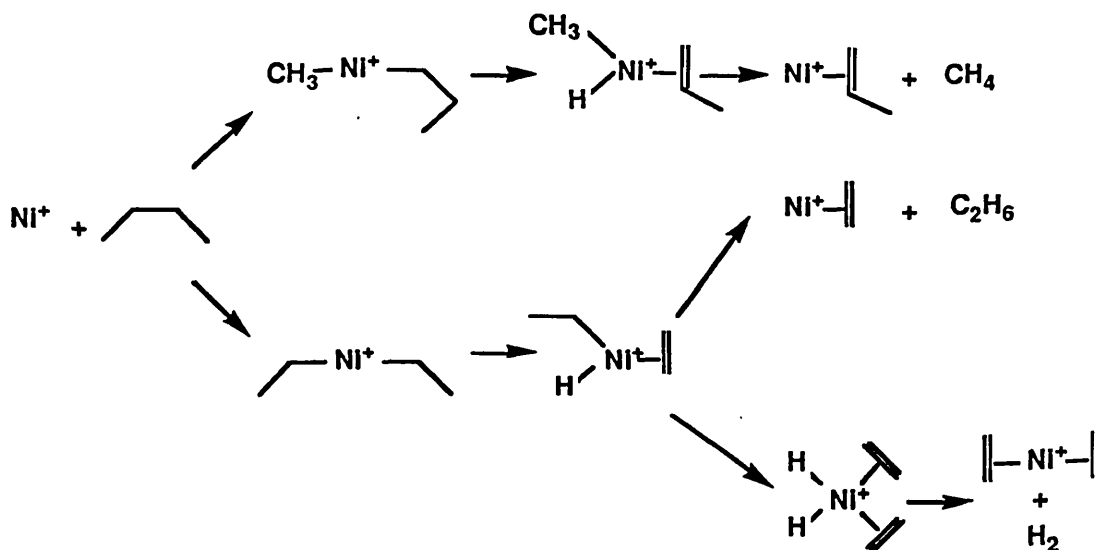
As outlined in the review section, the last five years has witnessed an explosive growth in the activation of saturated alkanes by coordinatively unsaturated transition metal complexes. However, the vast majority of reactions have involved activation of the C-H bond, and it is only within the last twelve months that carbon carbon bond activation has become a viable proposition.

This latter area was the initial focus of our intention, and the strategy adopted stemmed from observations made by Beauchamp⁽¹⁾ on the behaviour of isolated nickel cations in the gas phase which are discussed below. Additional impetus for our research came from the fact that relatively little information has been accumulated on the properties of coordinatively unsaturated cationic first row group VIII transition metal complexes.

2.1. Ion beam and ion cyclotron resonance studies

In 1982, the ion beam and ion cyclotron resonance studies conducted by Beauchamp *et al.*⁽¹⁾, showed that gaseous naked nickel cations demonstrated an unusual preference for insertion into C-C bonds, rather than C-H bonds, in the substrates butane, pentane and some higher homologues. The conditions employed generally produced the nickel cation at a temperature of $\sim 1400\text{K}$ and mainly in the ground state configuration, $3d^9$ ($< 2\%$ in the first excited state, $4s^1 3d^8$). In the case of n-butane (Scheme 1) C-C bond activation is exclusively preferred; this oxidative insertion process is somewhat unusual in that it is thermodynamically favoured over C-H bond cleavage. Moreover, the metal alkyl species thus formed are more prone to β -

hydride elimination to give the olefin and diolefin complexes, rather than to reductive elimination reforming the substrate. A qualitative potential energy diagram for the



Scheme 1

reaction of Ni^+ with n-butane to form the products $\text{Ni}(\text{C}_2\text{H}_4)^+$ and $\text{Ni}(\text{C}_2\text{H}_4)_2^+$ is given in Figure 1(1). The overall process is substantially exothermic, rendered so by the stability of the metal-alkene products. Latter studies by Radecki and Allison(2)

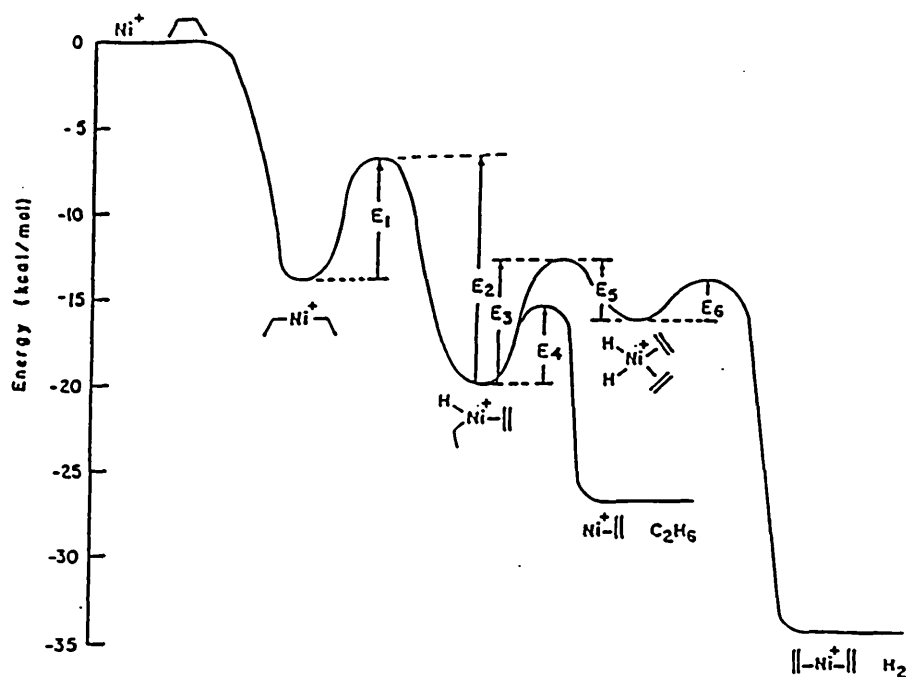


Figure 1

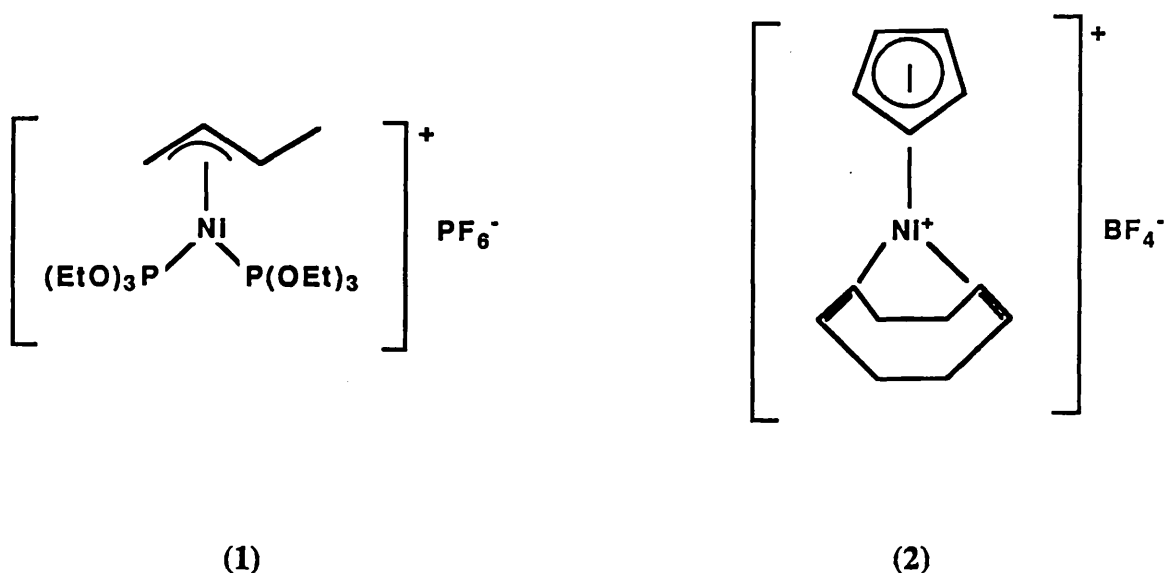
noted a correlation between the preference of gas phase Ni^+ for insertion into a particular skeletal bond and the ionisation potentials (IP's) of the alkyl radicals formed

when the C-C bond is cleaved. The correlation suggested a relationship between $IP(C_nH_{2n+1})$ and $D^0(M^+-C_nH_{2n+1})$ (D^0 = groundstate bond energy) with IP decreasing and bond energy increasing as n increases. Consequently, it can be generalised that the preferred intermediates involve those in which the (M^+-R) bonds which are formed are the strongest. This understanding enables products and branching ratios to be predicted *a priori*, at least for gas phase reactions; reactions in solution would of course provide more complications and hence less predictability. A report by Michl and coworkers(3), has provided evidence suggesting that only mononuclear cationic nickel species can undergo C-C insertion reactions and that polynuclear species are ineffective, causing dehydrogenation of butane only.

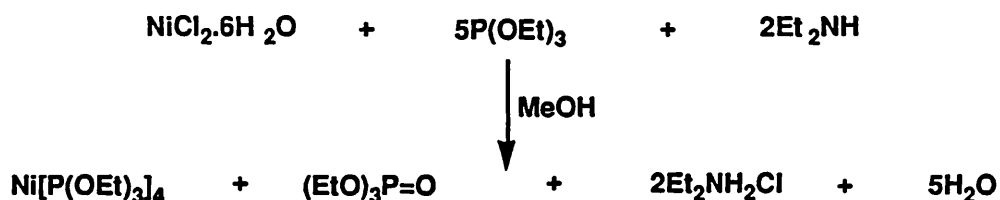
By analogy with the elegant studies of Crabtree, and Felkin, our objective was to reproduce the characteristic activation reactions of gaseous, naked nickel cations through the use of electron deficient, coordinatively unsaturated, cationic, organonickel complexes possessing weakly coordinating ligands such as acetone and dichloromethane. In order to facilitate carbon carbon cleavage initial studies were concentrated on the use of strained cycloalkanes as substrates. Moreover, although some understanding of the behaviour of such substrates with several homogeneous transition metal complexes had previously been acquired, if not specifically for nickel complexes, the exact role of the metal in determining the nature of the products certainly required clarification.

2.2. Generation of coordinatively unsaturated nickel species in solution

Initial studies concentrated on the complexes (1) and (2). Complex (1) is a sixteen electron species and it was hoped that removal of the masking labile crotyl



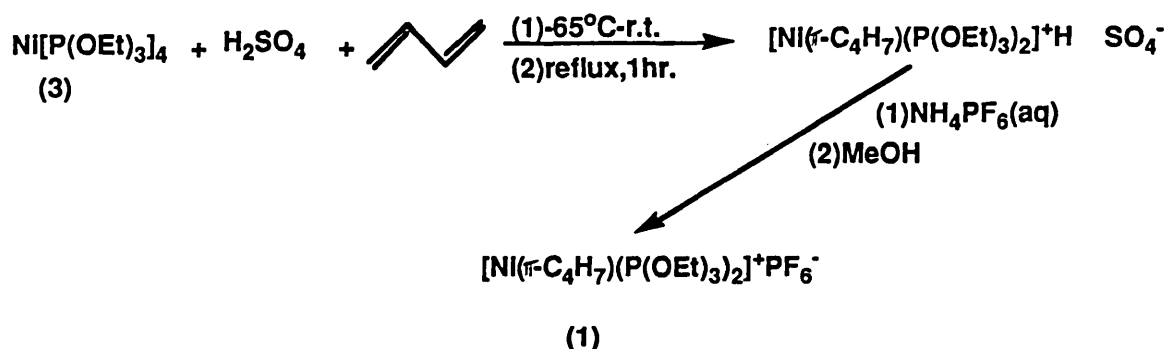
ligand *in situ* would reveal a low valent, effectively 15 electron species, $\text{LNi[P(OEt)}_3\text{]}_2^+$ ($\text{L} =$ acetone or dichloromethane), or derivative. The starting complex (1) was synthesised from *tetrakis*-(triethylphosphite)nickel(0), $\text{Ni[P(OEt)}_3\text{]}_4$ (3). The latter was prepared according to a literature procedure (4) (Scheme 2) but with a vastly improved yield of 82% compared to 30-40%. The yield was enhanced by careful



Scheme 2

dropwise addition of diethylamine to the nickel chloride/triethyl phosphite mixture following a colour change of purple to pale yellow in the system; since addition of excess diethylamine appeared to catalyse the decomposition of the nickel(0) product to nickel(II) compounds. The system also provided better yields when performed under an inert, argon atmosphere. The Ni(0) complex was always freshly prepared and dried *in vacuo* before use in the synthesis of (1). The synthesis of (1) (Scheme 3), using the method of Tolman⁽⁵⁾, required rigorously anaerobic conditions; all solutions being deoxygenated before submitting to the inert atmosphere of the reaction system. Again,

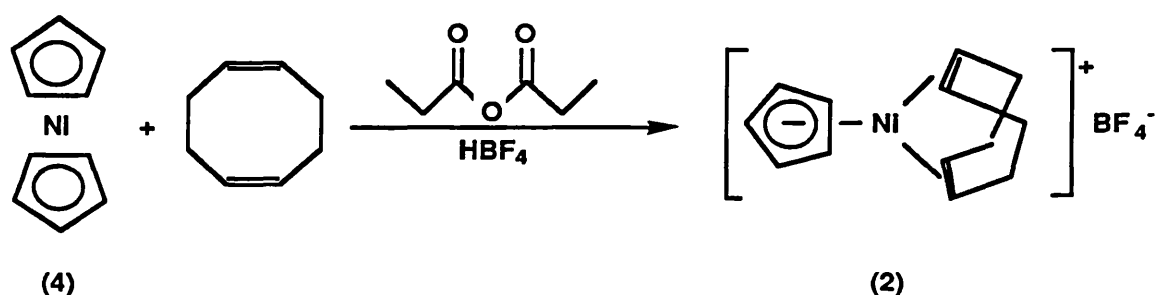
as in the case of *tetrakis*(triethyl phosphite)nickel synthesis, decomposition of the product appeared to be autocatalytic on exposure to even a trace of free oxygen. The



Scheme 3

product (1) was obtained as a bright yellow solid, readily decomposing to a red oil even on storing at -20°C under an argon atmosphere. Several attempts to synthesise the complex, (1), by the substitution of butadiene for 3-buten-2-ol and also 2-buten-1-ol, although in principle acceptable (the acidic conditions leading to the crotyl cation), in practice did not provide the required product. Reasons for the failure of these reactions include the possibilities of (a) catalytic deactivation initiated by attack of protons on the intermediate $[\text{HNi}(\text{P(OEt)}_3)_3]^+$ giving dihydrogen by reductive elimination; (b) phosphine ligand decomposition; (c) low valency in the product complex being increased to a coordination number of 5; and (d) the reaction conditions producing a water molecule. The former problems would also be prevalent when using butadiene as the crotyl ligand precursor and account for the low yields always observed.

The 18-electron nickel complex (2), chosen for the likely lability of the 1,5-cyclooctadiene ligand, was synthesised from nickelocene (4) according to the literature procedure presented in Scheme 4 (6). It is a dark green solid and can be obtained



Scheme 4

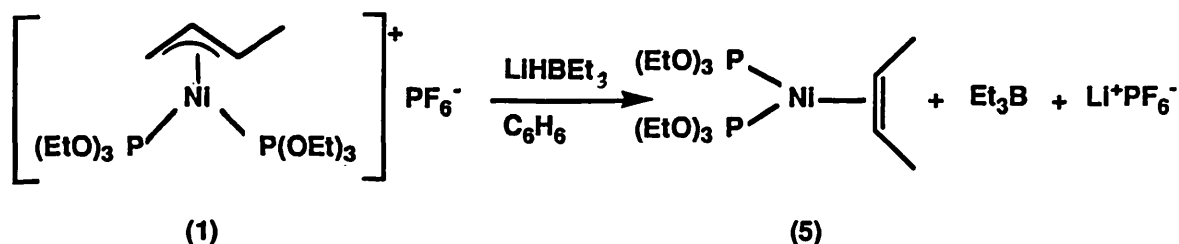
analytically pure. Once again the synthesis requires deoxygenation of all solvents, anaerobic transfers and the permanent maintenance of an argon atmosphere. Propionic anhydride is present to 'mop-up' the water of the aqueous tetrafluoroboric acid that is added. Cyclooctadiene was used in excess to avoid the competitive formation of the species $\text{Ni}_2(\text{C}_5\text{H}_5)_3$, a triple-decker sandwich complex.

Initially, we envisaged, as in the work of Crabtree⁽⁷⁾, that hydrogenolysis of the crotyl ligand would furnish a cationic dihydrospecies suitable for further elaboration. However, in practice removal of the crotyl ligand in (1) proved to be very difficult, in fact impossible in the reaction systems chosen, without the formation of colloidal nickel.

Bubbling hydrogen gas through a yellow coloured, dilute solution of (1) in dichloromethane at -60°C provided no colour changes in the system even after two hours, and the complex (1) was reclaimed intact. Dichloromethane was chosen as the solvent in these reactions as it is capable of acting as a weakly coordinating ligand and therefore could stabilise any low valent nickel species forming. This approach parallels the work of Crabtree⁽⁷⁾ on the activation of C-H bonds using $[\text{Ir L}_2\text{S}_2\text{H}_2]^+\text{A}^-$ (L=phosphine; S=weakly coordinating solvents; A^- =non nucleophilic counter anion) where the iridium species is formally 6 coordinate but realistically 4 coordinate owing to the lability of the S ligands i.e. the solvent is sufficiently coordinating to help prevent deactivation but not so much as to exclude the substrate. Increasing the hydrogen pressure to 5.5 atmospheres at -60°C again had no effect on the crotyl complex. Raising the temperature slowly to room temperature did not afford any colour changes and the complex (1) was again reclaimed. At this point we concluded that hydrogenolysis of the nickel-crotyl complex could not occur. In retrospect, however, the addition of a catalytic amount of *bis*(1,5-cyclooctadiene)nickel(0) may stimulate hydrogenolysis or autocatalytic hydrogenolysis to release the crotyl ligand.

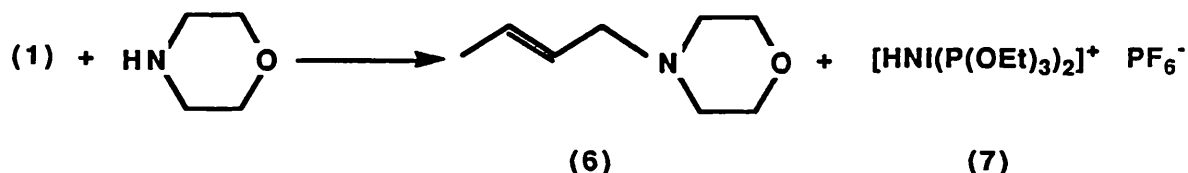
The generation of a neutral coordinatively unsaturated organonickel complex (5) was then attempted using 1 equivalent of super-hydride (Scheme 5); however, (5)

could not be isolated. On warming the reaction mixture from -80°C to room



Scheme 5

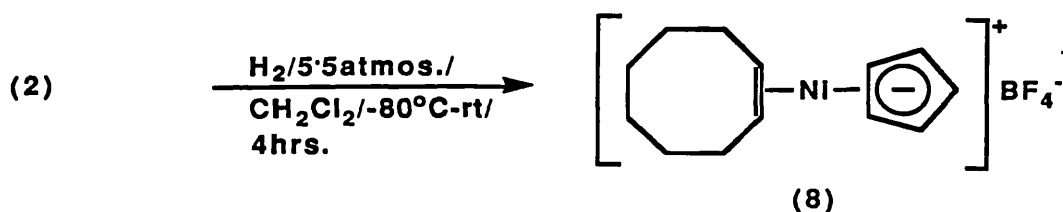
temperature, deposition of metallic nickel was observed. Using 8 equivalents of lithium borohydride or super-hydride provided only decomposition to colloidal nickel products and no nickel-hydride complexes were detected by high field proton nmr. Evidently, the product complexes are too reactive to be isolated before decomposition. A method of efficiently removing the crotyl ligand *in situ* could well be developed using the reaction of Scheme 6(8) as precedent. In this work, excess morpholine was used to produce 1-(N-morpholino)-2-butene (6) in 35% yield from (1) at 80°C over 15 hours. The organometallic product (7) of this reaction was not characterised



Scheme 6

by the authors but was presumed to be formed. If this 14 electron species was present in the reaction mixture, then its production could be enhanced through use of the more nucleophilic reagent, hydrazine.

We then turned our attention to removal of the 1,5-cyclooctadiene ligand in (2), again attempted under hydrogenolysis conditions. Autocatalytic hydrogenation of (2) under high pressure (5.5 atmos.) provided (8) (Scheme 7), identified by ^1H nmr and

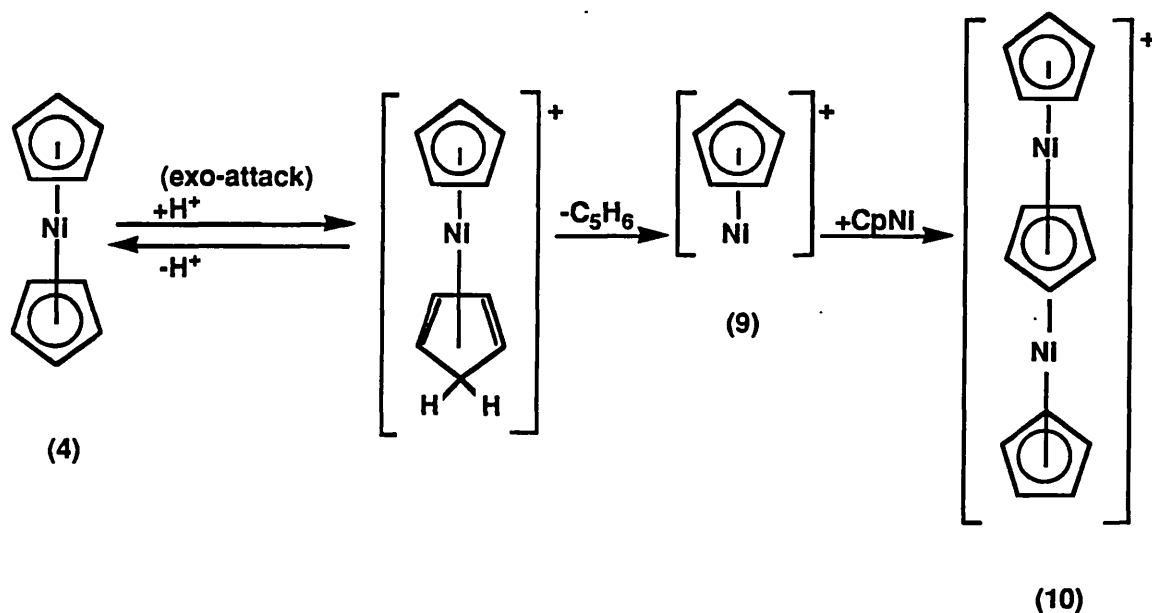


Scheme 7

microanalysis, and no metal-hydrides were detected by high field ^1H nmr. The 16 electron species (8) was provided by hydrogenation of one metal-alkene bonding system. Further hydrogenolysis of (8) to provide the 14 electron species $\text{CpNi}^+\text{BF}_4^-$ (9) (Cp = cyclopentadienyl) may arise under more forcing conditions. However, at this stage we started to look at the synthesis of (9) as opposed to its generation *in situ*.

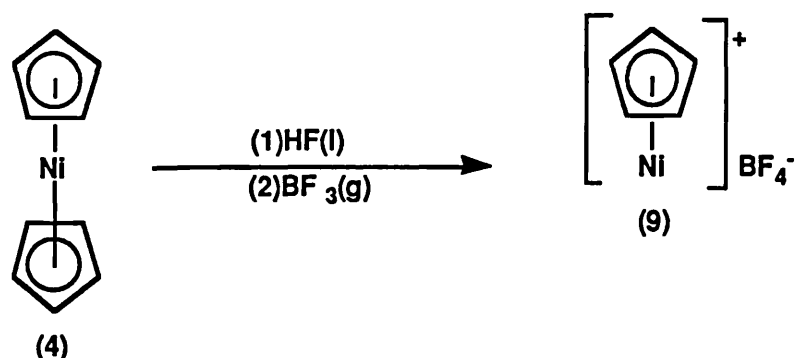
2.3. Synthesis of cyclopentadienylnickel tetrafluoroborate (9)

In 1974, Court and Werner⁽⁹⁾, in a study of the reaction pathway for the formation of the triple-decker sandwich complex (10) from nickelocene (4) under acidic conditions, discovered the existence of the cyclopentadienylnickel species (9) (Scheme 8). They noted that they had been able to isolate (9) by bubbling boron trifluoride gas



Scheme 8

through a hydrofluoric acid solution of (4) (Scheme 9) and hence we duly repeated the



Scheme 9

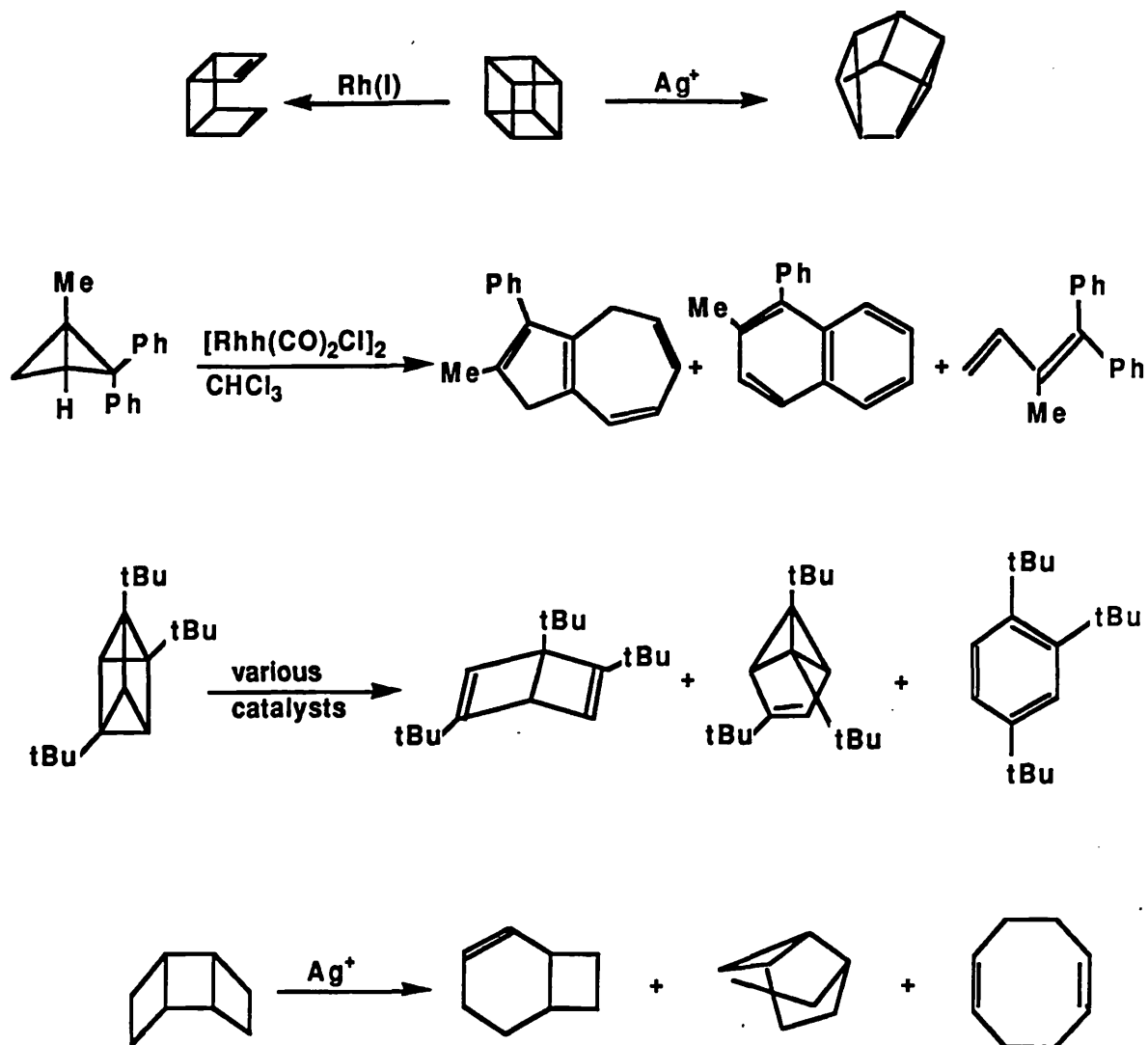
reaction. The reaction proved both difficult and dangerous to perform. As hydrofluoric acid was involved the reaction vessels were necessarily made of polytetrafluoroethylene. The vessels had specially made screw tops so they could be attached to a very low pressure (10^{-5} mm Hg) vacuum line. As liquid hydrofluoric acid has a vapour pressure of just over 1 atmosphere it had to be ensured that there were no leaks in any chamber, either in the vacuum line or in the reaction vessels; this was checked by pressure monitoring a closed, evacuated chamber for 3 days, if no pressure increase occurred then the system was considered adequate and safe. The vacuum line itself was made from stainless steel and aluminium joints and had both a rough vacuum pump, containing a chemical trap, and a mercury diffusion pump, for the attainment of very low pressures, attached. A cylinder of hydrofluoric acid was attached to the line, from which the acid was directly condensed into the graduated reaction vessel containing the substrate (4). The major problem arose in the use of borontrifluoride gas. The gas is notorious for blocking and corroding joints. Thus once a cylinder is opened it can be impossible to close it and, as borontrifluoride has a vapour pressure of greater than 200 atmospheres at room temperature, it is often a practical impossibility to gauge the amount of gas accumulated in a closed chamber, the amount excelling that which is measurable. With an unknown quantity of gas in an adjacent chamber to hydrofluoric acid, the impending danger due to very high vapour

pressures is quite obvious. However the synthesis of (9) successfully reproduced the observations reported by the Werner group and the identity of (9) was surmised by the colour of the compound and more importantly by its proton nmr in acetonitrile- d_3 which showed just one broad resonance at δ 5.54 ppm. That the resonance was broad suggested the presence of a paramagnetic impurity (possibly the starting material, nickelocene). Unfortunately an x-ray crystal structure determination of (9) proved to be impossible since some decomposition occurred on recrystallisation or attempted sublimation, and the originally prepared batch of (9) was produced microcrystalline due to the high vacuum applied to it to remove all traces of free hydrofluoric acid.

2.4. Carbon-carbon bond cleavage studies on tricyclo[4.1.0.0^{2,7}]-heptane.

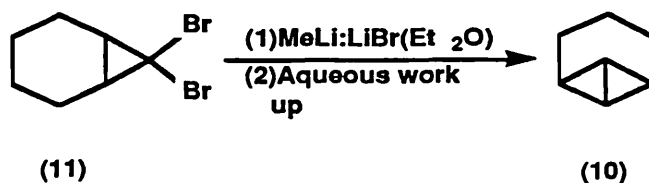
During the early 1970's, a number of remarkable σ -bond rearrangements in highly strained, polycyclic, saturated alkanes were found to be promoted by variety of transition metal cations or their complexes (Scheme 10)(10). The driving force for these isomerisation reactions is the relief of the high ring strain energy.

The requirement of the transition metals is to provide a low activation pathway otherwise inaccessible owing to the constraints of orbital symmetry. We concluded that it was most instructive to concentrate our initial studies with the nickel species (9) in this area of strained polycyclic hydrocarbons, simply because knowledge of various reaction systems was accessible and because simple C-C bond cleavage reactions for unstrained, saturated hydrocarbons are, as yet, unknown. The chosen strained substrate was tricyclo[4.1.0.0^{2,7}]heptane (10) often referred to as Moore's hydrocarbon(11).



Scheme 10

Moore's hydrocarbon (10) was synthesised from dibromonorcarane (11) (Scheme 11) using a modification of Gassman's⁽¹²⁾ procedure - itself based on Moore's⁽¹¹⁾ method involving a methyllithium promoted carbenoid insertion reaction. The volatile hydrocarbon is, of course, exceedingly prone to rearrangement under acidic conditions and hence all glassware used was silylated (HMDS) or base-washed



Scheme 11

(KOH/IPA or $\text{NH}_3(\text{aq})$) and oven dried before use. The species is purified by several

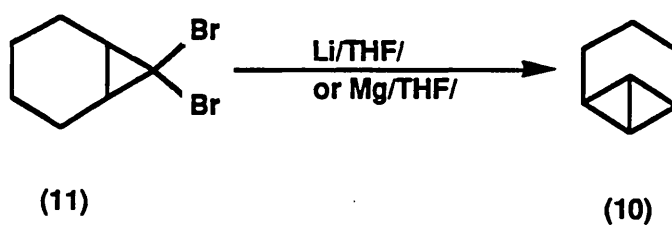
distillations, the most important being a trap to trap distillation, under a static vacuum removing Moore's hydrocarbon from the non-volatiles in the crude product mixture. It is very frustrating to record that this very significant fact has never previously been recorded in the literature. If the vacuum distillation is not carried out, the hydrocarbon swiftly decomposes at the necessarily higher distillation temperatures required. Though (10) could be obtained microanalytically pure, G.C.-M.S. analysis of the same sample suggested only 92% purity; the remaining 8% being mainly C_7H_{10} isomers of which 50% is (12). This fact was taken into account when measuring yields of rearrangement



(12)

products and on determining the amount of catalyst employed.

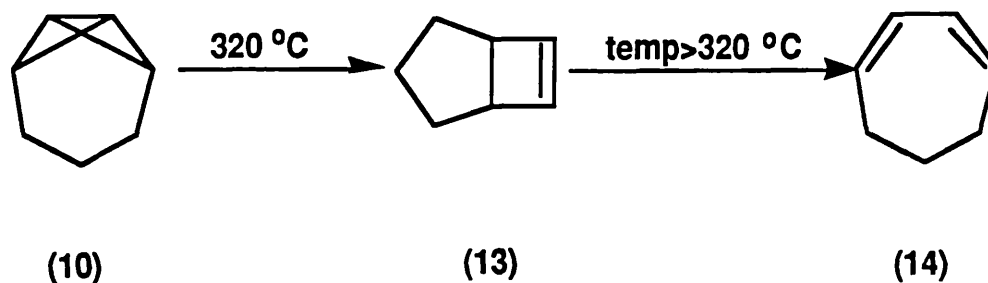
When attempts to synthesise (10) by a more recently published method (13) using ultrasonic radiation and magnesium or lithium metal to produce the carbene intermediates (Scheme 12), all reactions failed. The starting material (11) was not



Scheme 12

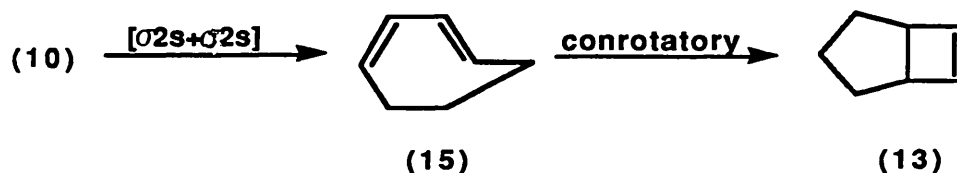
consumed even after very long periods under the reproduced reaction conditions, and formation of (10) was detected by gas chromatography, but only in a minimal amount.

Moore's hydrocarbon has received considerable attention since the discovery, by Wiberg⁽¹⁴⁾ of the thermal opening of the bicyclo[1.1.0]butane entity (Scheme 13) to provide bicyclo [3.2.0]hept-6-ene (13). At higher temperatures than 320°C, 1,3-



Scheme 13

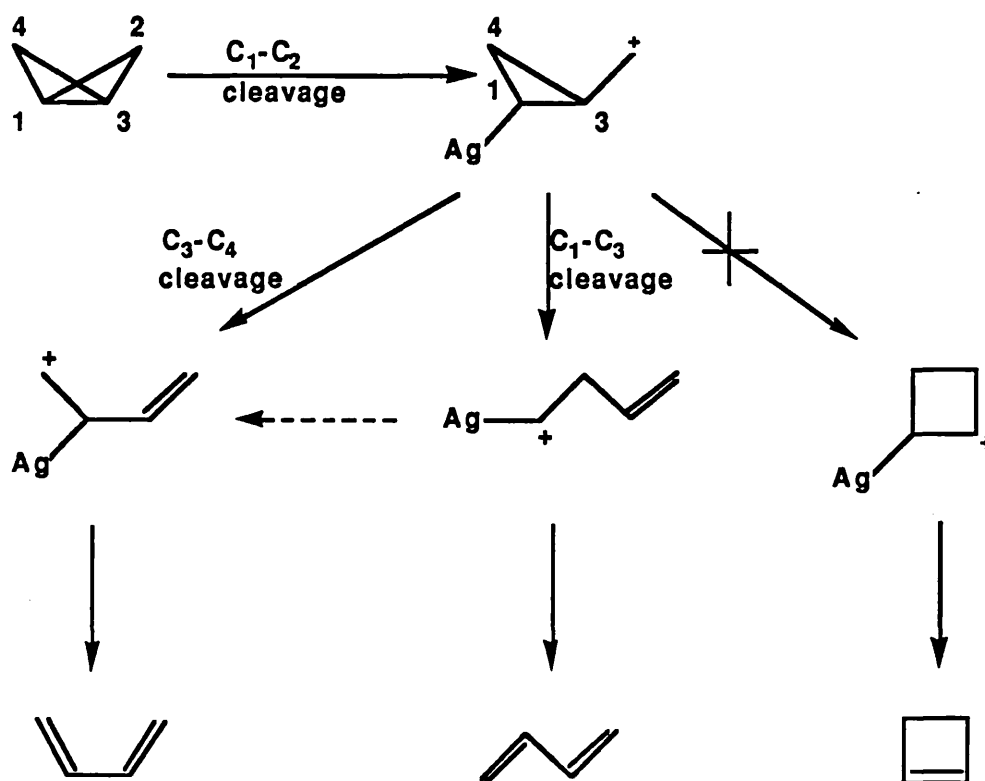
cycloheptadiene (14) formation prevailed. A concerted reaction pathway is believed to occur (Scheme 14) by providing (13) from the intermediate *cis,trans*-



Scheme 14

-cycloheptadiene (15) by an allowed thermal conrotatory process. Electronic factors clearly out-weigh thermodynamic considerations in determining the stereochemistry of the diene product (15). In 1970, Paquette⁽¹⁵⁾ cleaved the strained bicyclobutane system of (10) using silver (I) as a catalyst; conversion of (10) into (14) occurred exclusively

and in quantitative yield. Kinetic studies⁽¹⁵⁾ suggested that bicyclobutane-silver complexes were definitive intermediates. Masamune⁽¹⁷⁾ forwarded the idea that carbenoid intermediates may not be involved but rather that a heterolytic cleavage of the C₁-C₂ bond was occurring, followed by a cyclopropylcarbinyl-allylcarbinyl type rearrangement (Scheme 15). Cleavage of the C₁-C₃ bond was thought not to occur due to steric interference from the dimethylene bridge hydrogens. We consider, however, that the cyclopropylcarbinyl-allylcarbinyl rearrangement is much more typical

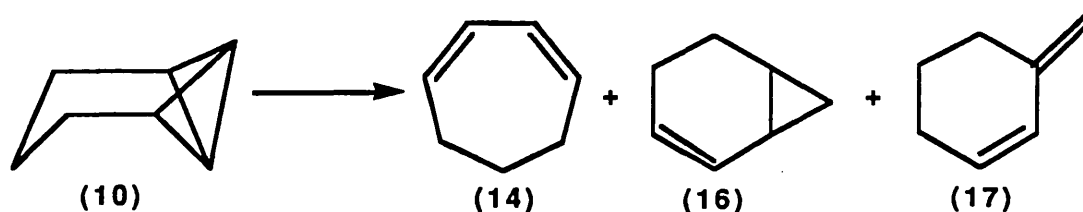


Scheme 15

of a radical process, particularly since Wagner Meerwein rearrangement to cyclobutanes is a facile pathway in the cationic series.

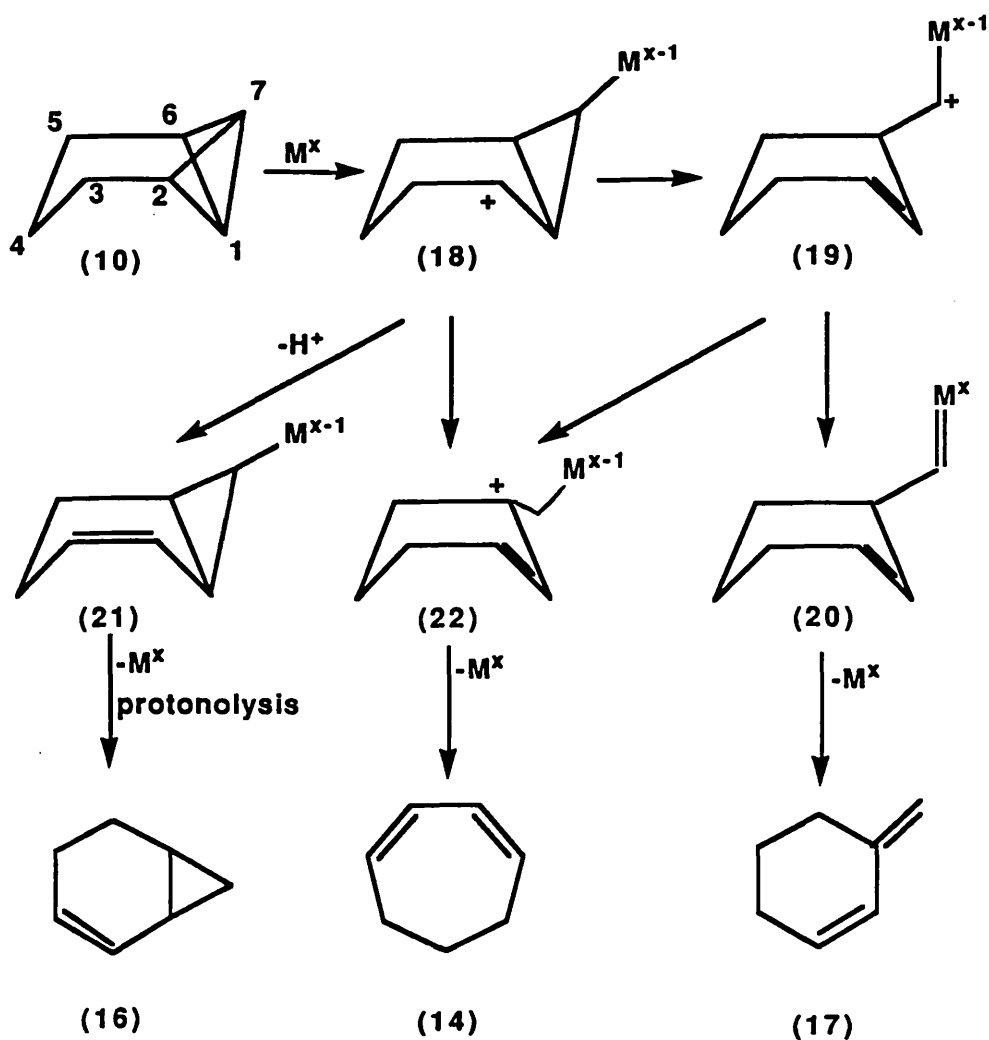
Gassman⁽¹⁸⁾, provided an extensive study of the σ -bond rearrangement reactions of (10) using a variety of transition metal catalysts. Three C₇H₁₀ products

were obtained (Scheme 16) jointly or severally, depending on the conditions employed.



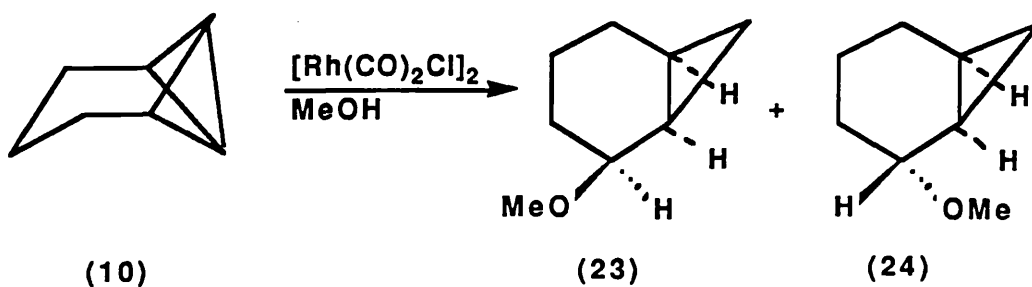
Scheme 16

All the isomers were purported to derive from the common intermediate, (18) (Scheme 17), which was likewise suggested by Masamune⁽¹⁷⁾ for silver(I) catalysis. The mechanism was suggested as being stepwise, initiated by attack of the transition metal catalyst, acting as a Lewis acid, producing (18) by heterolytic cleavage of the C₂-C₇ bond. Subsequent scission of the C₁-C₇ bond produces an intermediate designated in its carbonium ion (19) and carbenoid (20) resonance forms. From this intermediate a [1,2] hydride shift or carbenoid insertion then gives 3-methylenecyclohexene (17) and the regenerated catalyst. Elimination of a proton from (18) yields (21) which undergoes protonolysis providing bicyclo[4.1.0]hept-2-ene (16). 1,3-Cycloheptadiene (14) is believed to be produced by either cleavage of the C₁-C₆ bond in (18) or by vinyl migration in the (19)-(20) hybrid, both of which provide the carbonium ion species (22) as a precursor to (14).



Scheme 17

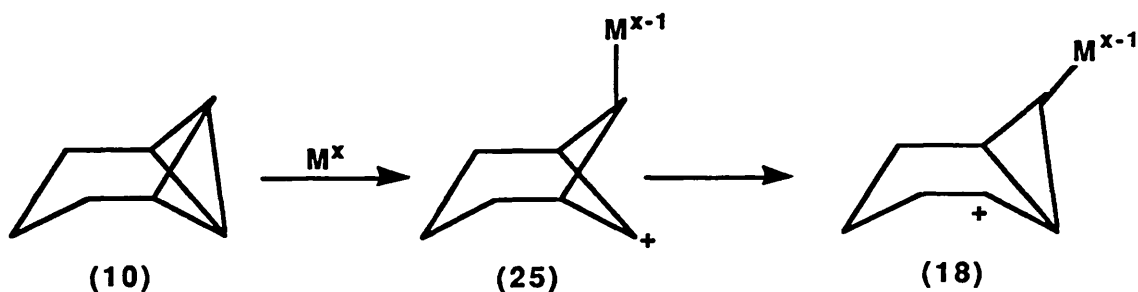
Evidence for the common intermediate hypothesis was provided by trapping the intermediate (18) whilst employing methanol as the nucleophilic, reaction solvent



Scheme 18

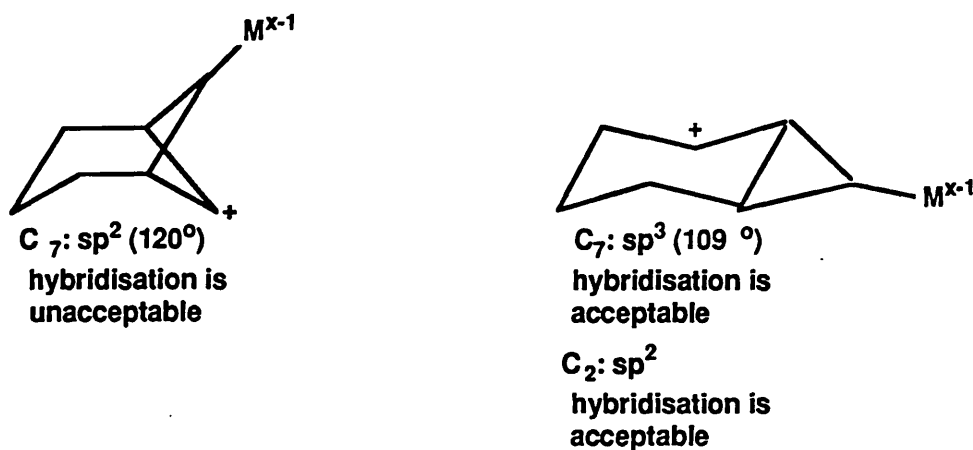
(Scheme 18)(18). This gave a 4:1 mixture of adducts (23) and (24), respectively, in

overall 75% yield. Trapping of the common intermediate however, did not conclusively prove which C-C bond of the bicyclobutane function was involved in the initial cleavage. The same intermediate could possibly be considered as being derived from C₁-C₇ bond scission to give (25) followed by alkyl migration to give (18) (Scheme 19). However alkyl migration seems unlikely compared to hydrogen transfer, for example.



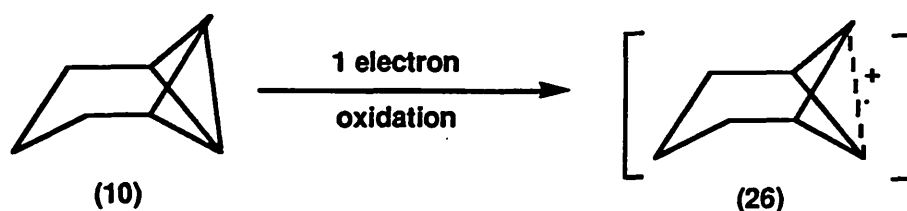
Scheme 19

Fellow workers in this area have never actually stated why they assume C₂-C₇ bond scission to occur in preference to C₁-C₇ bond cleavage. However, if we consider the two opposing products (Scheme 20), we can see that a carbonium ion centered at C₇ would not be possible: sp^2 hybridisation at a strained centre like this is less plausible, and sp^3 is preferred.



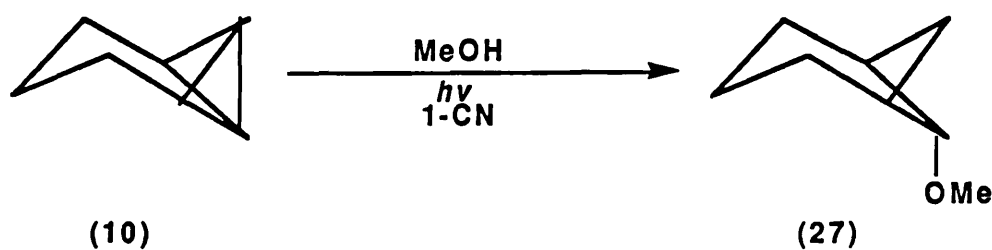
Scheme 20

More recently, Gassman⁽¹⁹⁾ has begun to forward the idea of the one-electron C-C bond. Moore's hydrocarbon can be very easily oxidised; this, as shown in Table 1, is a characteristic feature of strained, polycyclic hydrocarbons. If the hydrocarbon (10) loses one electron from the highest occupied molecular orbital, that is the C₁-C₇ bond, a radical cation (26) is produced (Scheme 21), or in other words a



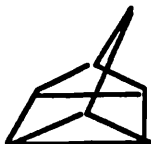
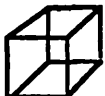
Scheme 21

two centre, one-electron bond between carbon 1 and carbon 7. Under metal promoted conditions an initial C₁-C₇ bond cleavage step cannot be detected; however under photolytic conditions the radical cation (26), can be efficiently trapped in methanol to form ether (27) (Scheme 22). Calculations on species (10) and (26) have shown that the partial bond in (26) is only 0.10Å longer than in the ground state and that the jaw is opened by a further 2° compared to (10).



Scheme 22

Table 1: Specific Examples and Ranges of the First Redox Potential of Hydrocarbons

Substrate	$E_{1/2}$ [V versus S.C.E. in CH_3CN]	Oxidised bond
	0.91	C-C
	1.50	C-C
	1.73	C-C
Unstrained alkane	2.5-3.2	C-H
Unstrained alkene	2.0-2.6	C=C
Strained alkane	0.4-2.1	C-H

A priori, a spectrum of possible mechanisms exists for the so called oxidative addition of a coordinatively unsaturated transition metal species into the carbon carbon bond. These range from one electron transfer to the metal and the evolution of the resultant radical cation type intermediates, through to a concerted insertion reaction with resultant metallocyclobutane formation which may be similar in concept to the edge protonation of cyclopropanes(16). Moreover the nature of the metal almost certainly plays a determining role in the evolution of the initial intermediates to the range of isomerised products (14), (16), and (17), and hence the overall picture is necessarily

complex. Our initial objective was therefore to gain some clearer understanding of the role of the transition metal catalyst in such processes.

Although Moore's hydrocarbon has been quite extensively studied previous to our work, the lack of concise experimental procedures both for its synthesis and for its metal mediated rearrangement reactions required lengthy calibration checks and the development of an efficient practical procedure for the catalysis reactions and product identification. It was decided that each experimental run should be repeated at least twice to check the validity; this involved the use of 5 molar percent of the catalyst with respect to (10) and use of consistent molarity (50mM) in a deuterated solvent. Due to the high volatilities of solvent, substrate and products, the reaction systems had to be sealed to prevent evaporation. The progress of a reaction was monitored by removal of the volatiles from the catalytic systems by trap to trap distillation under a static vacuum followed by proton nmr analysis of the distillate. The reactions were found to proceed quite well under an oxygen (air) atmosphere but better yields were obtained of the respective products if the system was rigorously deoxygenated. As low boiling solvents were employed, the products could be efficiently detected by gas chromatography too, with the isomers emerging from the column after the solvent. An OV1 carbowax column, suitable for non-polar hydrocarbons, was employed, and the hydrocarbons were eluted in the expected order of increasing boiling point (Table 2), and were recorded by a flame ioniser detector. A fairly low injection temperature of 60°C was used to rule out any initial thermal rearrangements of the products. G.C.-M.S. analysis proved to be an invaluable tool, in identifying the products by both their retention time and their mass spectrum. As can be seen in Table 2, the mass spectra of the C₇H₁₀ isomers are very similar, all having a base peak of 79 (M⁺-CH₃); hence an eight peak index was required and used to avoid any tentative assignments of product identity.

Authentic samples of the products were prepared for comparison purposes. 1,3-Cycloheptadiene was conveniently synthesised by Paquette's⁽¹⁵⁾ method using silver cation promoted rearrangement of (10). Bicyclo[4.1.0]hept-2-ene (16) was obtained as a mixture with Moore's hydrocarbon by the stannous chloride⁽¹²⁾ mediated

Table 2: Analytical Characteristics of C₇H₁₀ Hydrocarbons for Identification Procedures

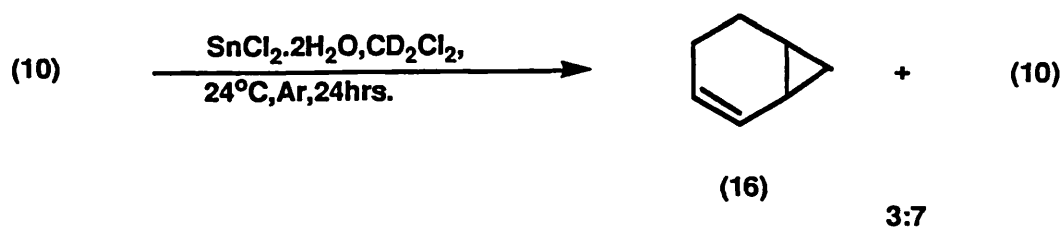
C ₇ H ₁₀ Hydrocarbon	b.p.(°C/760 mm Hg)	Ret.time ^a (mins.)	Eight peak M.S.index: % of base peak ^b	Proton nmr (250MHz) ^c
(10)	110-112	3.46	79(100),77(54), 39(48),66(33), 91(19),41(16), 65(15),94(13).	(CDCl ₃) 1.34(6H,br.m, 3-CH ₂ ,4-CH ₂ ,5-CH ₂), 1.42(2H,br.m,1-CH,7-CH), 2.24(2H,br.m,2-CH,6-H).
(17)	100-105	3.18	79(100),77(36), 94(35),39(21), 91(18),93(10), 66(10),65(9).	(CDCl ₃) 1.64(2H,m,5-CH ₂) 2.08(2H,m,6-CH ₂),2.33 (2H,m,4-CH ₂),4.74(2H,d, =CH ₂),5.82(1H,m,1-CH), 6.12(1H,m,2-CH).
(16)	115	3.74	79(100),39(53), 41(45),77(45) 94(26),40(26) 66(20),91(16)	(CD ₂ Cl ₂) 0.70(2H,m,7- CH ₂),1.25(2H,m,1-CH, 6-CH),1.85(4H,m,4-CH ₂ , 5-CH ₂)5.45(1H,m,3-CH), 5.90(1H,m,2-CH).
(14)	121	3.89	79(100),77(42) 39(40),94(34), 66(25),91(16), 41(12),93(11)	(CDCl ₃)1.82(2H,br.m, 6-CH ₂),2.40(4H,br.m, 5-CH ₂ ,7-CH ₂),5.7 (4H,m,olefinic-H).

(a) OV1 carbowax column, oven temperature 60-200°C (4°C per minute).

(b) Obtained using a Finnigan 4021 Quadrupole mass spectrometer linked to a gas chromatograph.

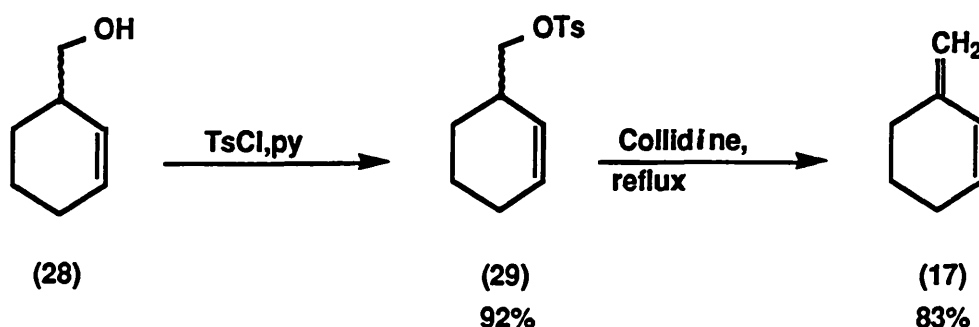
(c) Measured in δ/ppm using tetramethylsilane as an internal standard.

isomerisation of (10) (Scheme 23). Although (16) was not obtained in analytically pure



Scheme 23

form, the combination of G.C.-M.S. and proton nmr was sufficiently distinctive for analysis since the only contaminant was the unrearranged starting material. 3-Methylenecyclohexene (17) was synthesised using a modification of Blancou's(20) procedure. The tosylate (29) of 3-hydroxymethyl-cyclohexene (28) was refluxed in collidine overnight (Scheme 24) and the product isolated by means of its volatility.



Scheme 24

Purification was achieved by washing with an aqueous, saturated solution of copper(II)sulphate to remove all the collidine and finally by a second distillation through a Vigreux column. Once the three isomeric C_7H_{10} products were adequately characterised (Table 2) the metal promoted rearrangements of Moore's hydrocarbon could be studied.

A variety of catalysts were employed under various conditions (Table 3). The ruthenium complex, $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ (30), was synthesised according to the method of Griffith and Cleare(21) (Scheme 25) and the rhodium complex, $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}$

Table3: Metal Promoted Isomerisation of Tricyclo[4.1.0.0^{2,7}]heptane (10)

Catalyst	Conditions	Products of catalytic isomerisation (Yields %) ^a			
		(14)	(17)	(16)	(10)
AgBF ₄	CDCl ₃ /40°C/Ar/5mins	100	-	-	-
AgBF ₄	CDCl ₃ /40°C/minutes	(100) ^b	-	-	-
ZnI ₂	Et ₂ O/25°C/16hrs	88	11	-	-
ZnI ₂	CDCl ₃ /25°C/Ar/70hrs	75	8	15	-
HgBr ₂	Et ₂ O/50°C/48hrs	(85) ^c	(8) ^c	-	-
[Rh(CO) ₂ Cl] ₂	CH ₃ CN/25°C/15mins	-	(98) ^c	-	-
[Ir(CO) ₂ Cl] ₂	CHCl ₃ /25°C/14hrs	-	(91) ^c	-	-
[(π -allyl) ₂ PdCl] ₂	CHCl ₃ /25°C/30min	-	(94) ^c	-	-
[C ₆ F ₅ Cu] ₄	CHCl ₃ /25°C/2hrs	-	(74) ^c	-	-
[Ru(CO) ₃ Cl] ₂	CD ₃ CN/24°C/Ar/40hrs	-	12	-	88
(30)					
[Ru(CO) ₃ Cl] ₂	CD ₃ CN/24°C/Ar/90hrs	-	100	-	-
(30)					

continued.....

[Ru(CO) ₃ Cl ₂] ₂ (30)	CH ₃ CN/25°C/40hrs	-	(44) ^c	(12) ^c	-
[Ru(CO) ₃ Cl ₂] ₂	CD ₃ Cl/55-60°C/Ar/ 24hrs.	-	19	81	-
[Ru(CO) ₃ Cl ₂] ₂	CD ₂ Cl ₂ /24°C/Ar/44hrs	-	-	-	reclaimed
Rh(PPh ₃) ₂ (CO)Cl (31)	CH ₃ CN/65°C/48hrs	-	(92) ^c	(5) ^c	-
Rh(PPh ₃) ₂ (CO)Cl (31)	CD ₃ CN/55-60°C/Ar/ 48hrs	-	81	19	-
Rh(PPh ₃) ₂ (CO)Cl (31)	CDCl ₃ /55-60°C/Ar/ 90hrs	-	70	30	-
Rh(PPh ₃) ₂ (CO)Cl (31)	CD ₂ Cl ₂ /24°C/Ar/ 68hrs	-	45	-	55
Rh(P(π-OMePh) ₃) ₂ - (CO)Cl (32)	CD ₃ CN/55-50°C/Ar/ 48hrs	-	61	6	37
Rh(P(π-OMePh) ₃) ₂ - (CO)Cl (32)	CDCl ₃ /55-60°C/Ar/ 90hrs	-	90	10	-
Rh(PPhMe ₂) ₂ (CO)Cl (33)	CD ₃ CN/55-60°C/Ar/ 92hrs	-	78	4	18
Rh(PPhMe ₂) ₂ (CO)Cl (33)	CD ₃ CN/24°C/Ar/8hrs/)	-	-	6	94

continued.....

Rh(PPhMe ₂) ₂ (CO)Cl (33)	CDCl ₃ /55-60°C/Ar/ 72hrs	-	91	9	-
Rh(PPhMe ₂) ₂ (CO)Cl	CD ₂ Cl ₂ /24°C/Ar/92hrs	-	-	-	reclaimed
PtO ₂	CH ₃ CN/65°C/48hrs	-	(62) ^c	(24) ^c	-
SnCl ₂ .2H ₂ O	CHCl ₃ /60°C/25hrs	-	-	(40) ^c	-
	CDCl ₃ /55-60°C/Ar/ 24hrs	-	12	88	-
	CD ₂ Cl ₂ /24°C/Ar/ 24hrs	-	-	32	68
	CD ₃ CN/55-60°C/Ar/ 24hrs	-	-	100	-
AlCl ₃	Et ₂ O	-	-	(+) ^c	-
—	CH ₂ Cl ₂ /24°C/Ar/ 48hrs	-	-	-	reclaimed
—	CD ₃ CN/55-60°C/Ar/ 90hrs	-	-	-	reclaimed
—	CDCl ₃ /55-60°C/Ar/ 48hrs	-	-	-	reclaimed
—	CDCl ₃ /55-60°C/Air/ 48hrs	-	-	-	reclaimed
CpNiBF ₄ (9)	CD ₃ NO ₂ /0°C/Ar/ 24hrs	-	-	-	reclaimed

continued.....

CpNiBF ₄	CD ₃ NO ₂ /25°C/Ar/	-	-	-	reclaimed
(9)	24hrs/))				
CpNiBF ₄	CD ₃ NO ₂ /55-60°C/Ar/	-	-	-	reclaimed
(9)	24hrs				
CpNiBF ₄	CD ₂ Cl ₂ /25°C/Ar/	-	-	-	reclaimed
(9)	24hrs				
CpNiBF ₄	CD ₃ CN/25°C/Ar/	-	89	11	-
(9)	5hrs/))				
Cp ₂ Ni	CD ₃ CN/25°C/Ar/5hrs	-	-	-	reclaimed
(4)					

(a) Literature yields are given in parenthesis

(b) References 16 and 17

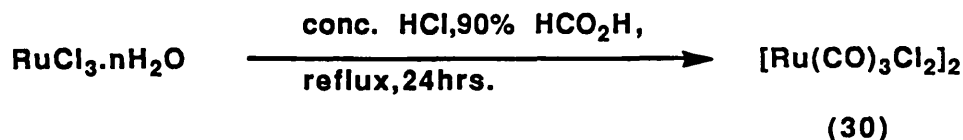
(c) Reference 18

(d) Laboratory yields were determined as a percentage of the C₇H₁₀ isomers formed during the reaction and of the starting material(10) (if still present). Yields were confirmed by repetition of each reaction at least twice and derived from proton nmr and G.C.-M.S. analysis.

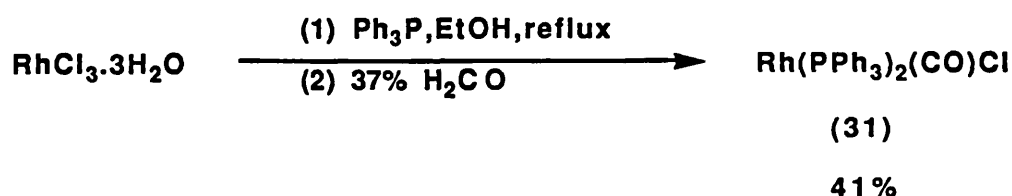
(31) by the procedure shown in Scheme 26(22).

Other transition metal promoters employed, except the nickel species (9), were purchased or available in the laboratory.

Initially it was of prime importance to perform blank experiments involving the



Scheme 25



Scheme 26

hydrocarbon (10) and each of the various solvents employed. This was particularly significant in the use of chloroform- d_3 , which in the absence of ethanol stabiliser is slightly acidic. The blank experiments served to demonstrate that no rearrangement reactions were occurring by means of solvent alone.

2.4.1. Observations concerning the role of the solvent and ancillary ligands

Changing the solvent had quite a remarkable effect, especially in the case of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ catalysis: using chloroform as solvent both (16) and (14) were obtained; however, use of acetonitrile led exclusively to the vinyl cyclopropane (16). Dichloromethane, necessarily used at a lower temperature, also exclusively provided (16) but in an overall lower yield. The inefficiency of the dichloromethane medium is believed to be due, in this particular case, to the decreased reaction system temperature rather than direct solvent effects. The differences observed in the chloroform and acetonitrile mixtures may be explained by either of two arguments. Chloroform could

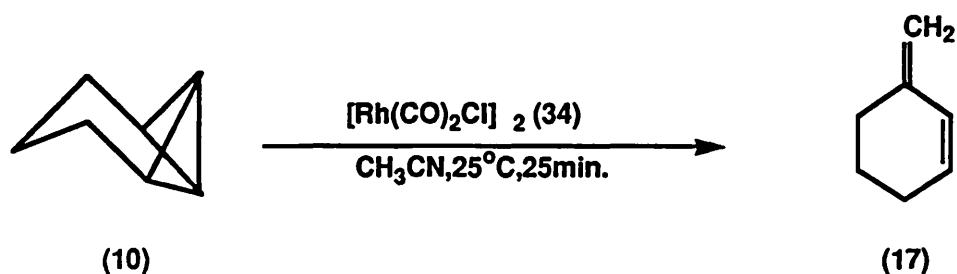
react with the catalyst to form a novel catalyst. Alternatively, coordination of the acetonitrile with the stannous centre could lead to action of the catalyst reaction to form (16) only. Dichloromethane is also a weakly coordinating solvent. Alternatively, in the case of the tricarbonyldichlororuthenium species (30), a dimerised d^{16} complex, the use of a weakly coordinating solvent such as acetonitrile led exclusively to the product (17). However, dissolved in chloroform, catalysis by (30) provided an 81:19 mixture of (16) and (17) respectively. In conclusion, the rearrangement products are not only determined by the type of catalyst employed but also equally, at least in the case of the ruthenium dimer, by the solvent used. It is possible that the coordinating acetonitrile solvent aids cleavage of the chloro-bridges of the ruthenium dimer yielding the 14 electron monomer $Ru(CO)_2Cl$. π -Bonding of acetonitrile solvent to produce an 18 electron species $Ru(CO)_2Cl(CD_3CN)_2$ will then form a new catalyst of decreased electrophilicity. This could account for the change in product distribution.

The rhodium catalysts appeared to have reasonable specificity for predominant formation of (17) independent of the solvent; it was the efficiency of the catalyst that suffered with change of solvent. Only in the case of $Rh(PPh_3)_2(CO)Cl$ (31) in dichloromethane was there no observable trace of (16). (31) has greatest efficiency in acetonitrile, whilst the *bis*(*p*-methoxytriphenylphosphine) derivative (32), where the phosphine ligands are more electron releasing and thus stabilise the rhodium(I) centre, was applied most successfully in chloroform solution. The same applied in the relatively electron rich species $Rh(PMePh_2)_2(CO)Cl$. The inefficiency of the rhodium catalysts in dichloromethane solvent systems is again thought to be more dependent on the lower reaction temperatures that are necessary, rather than on solvent effects. For the rhodium catalysts it may be suggested that as the Lewis acidity of the species decreases, the necessity for a coordinating solvent also decreases for the specific formation of (17), in fact the increasing coordination ability of the solvent tends to hinder the efficiency of the catalyst.

Assuming that the mechanism of rearrangement proceeds initially by an oxidative addition reaction to a strained C-C bond, either C_1-C_2 or C_1-C_7 , it may also

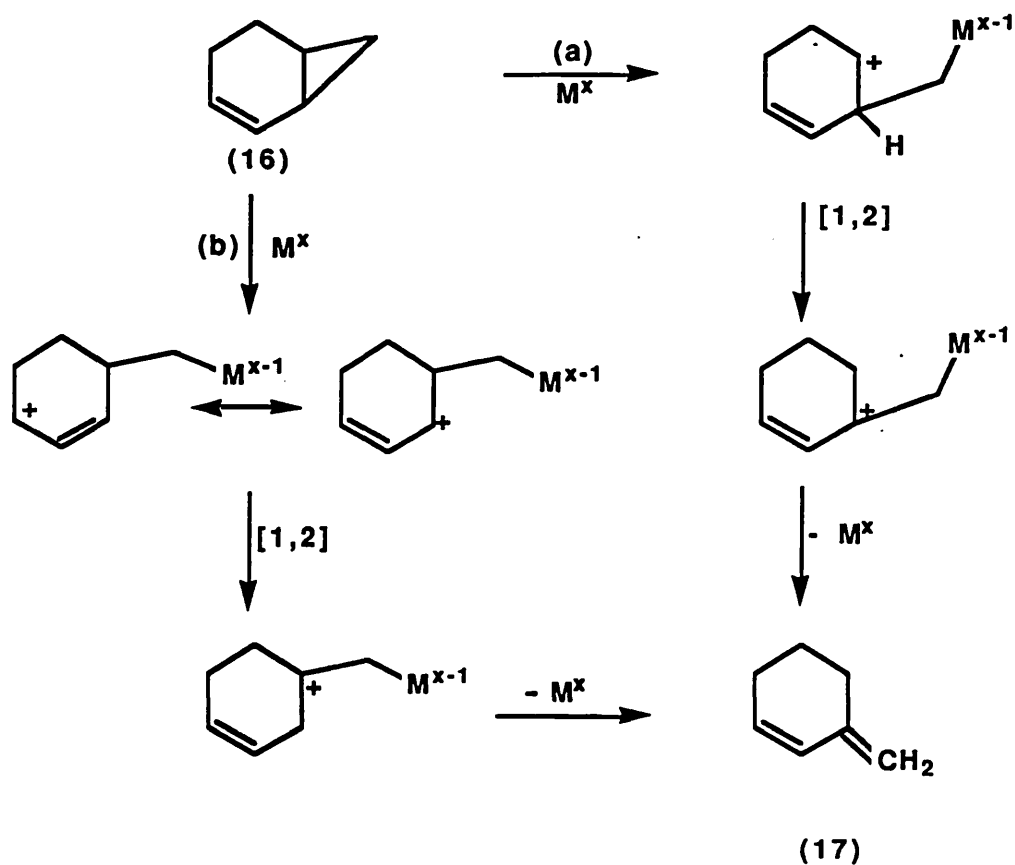
be concluded, by the results of the Rh(I) promoted rearrangements, that the insertion reaction is not very oxidising. The evidence shows that as phosphine ligand electron-donation ability increases in the species (32)-(33) (which is coupled to the ability to stabilise the necessary higher oxidation of (III) at the metal centre) little increase in the catalyst's efficiency is observed; (32) and (33) give almost identical results. The degree to which the insertion reaction may involve an oxidative step must lie somewhere between the oxidation potentials of (31) and (32).

During Gassman's⁽¹⁸⁾ studies on Moore's hydrocarbon, the rearrangement of (10) by the rhodiumdicarbonylchloride dimer (34) in acetonitrile provided (17) specifically (Scheme 27). It was assumed during this study that the isomeric product (17) was in no way derived from the vinyl cyclopropane (16); however for the



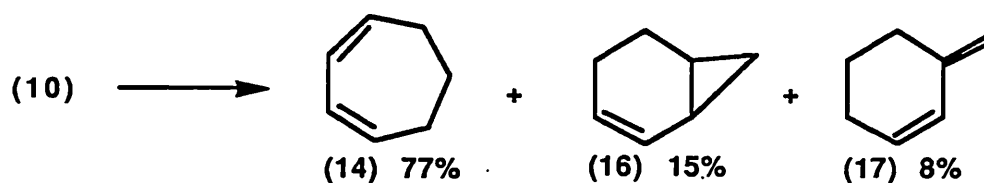
Scheme 27

rhodium(I) species (34) this was never adequately proven by a control experiment on (16). Though their assumption may be true, it must be noted that rhodium(I) catalysts⁽²³⁾ such as (34) are capable of rearranging vinyl cyclopropanes to dienes and hence in the case of rhodium promoters this possibility may not be dismissed. Two possible mechanistic pathways for the conversion of (16) into (17) are given in Scheme 28. Although neither (a) nor (b) take into account any association between the carbon-carbon double bond and the catalyst, both mechanisms are acceptable with respect to those proposed by Gassman⁽¹⁸⁾ (Scheme 17).



Scheme 28

Whilst the catalysts (30)-(33) each provided a degree of specificity for (16) and (17) formation from rearrangement of Moore's hydrocarbon, zinc(II)chloride provided a range of C_7H_{10} isomers including 1,3-cycloheptadiene (14) (Scheme 29). These

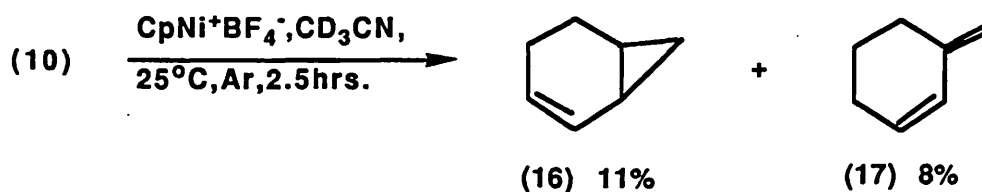


Scheme 29

observations suggest that the Zn^{2+} catalysis is bifunctional. It can behave like Ag^+ providing the simple valence tautomer (14) or duplicate the reactions for the rhodium and rhenium species, though with less efficiency, to give (16) and (17) by the

more complex mechanism. Formation of (14) may be expected as Zn^{2+} and Ag^+ have comparable electronic configurations in which the s electrons have been removed but the lower lying d shell is full. The difference between these 2 cations though, is that Ag^+ may lose its d electrons fairly readily to form complexes in the (II) and (III) oxidation states but this is not possible for Zn^{2+} derivatives. This suggests that formation of (14) involves no direct bonding interaction between the promoter and (10) via an oxidative addition to a strained C-C bond.

The use of the 14 electron species, $\text{CpNi}^+\text{BF}_4^-$ (9), proved to be fairly difficult. The complex was extremely reactive and tended to be deactivated by interaction with the solvent in preference to the Moore's hydrocarbon. Court and Werner(9), had previously discovered that (9) was a 1:1 electrolyte by studies using the solvent nitromethane. However, we found that (9) reacted vigorously and exothermically with rigorously purified nitromethane, even at 0°C , to provide a cream coloured solid of unknown identity. No isomerisation of (10) was observed, the hydrocarbon being reclaimed. Complex formation also occurred with dichloromethane to give a blue/black coloured, unknown solid which again terminated any possible reaction of (9) with (10). Proton nmr spectra of either unknown proved unobtainable, possibly due to the presence of paramagnetic impurities or because the products themselves were paramagnetic. Fortunately, in acetonitrile, where complex formation might in fact be assumed to be stronger, hydrocarbon (10) was rearranged to provide (16) and (17) exclusively (Scheme 30). The reaction was completed in 2.5



Scheme 30

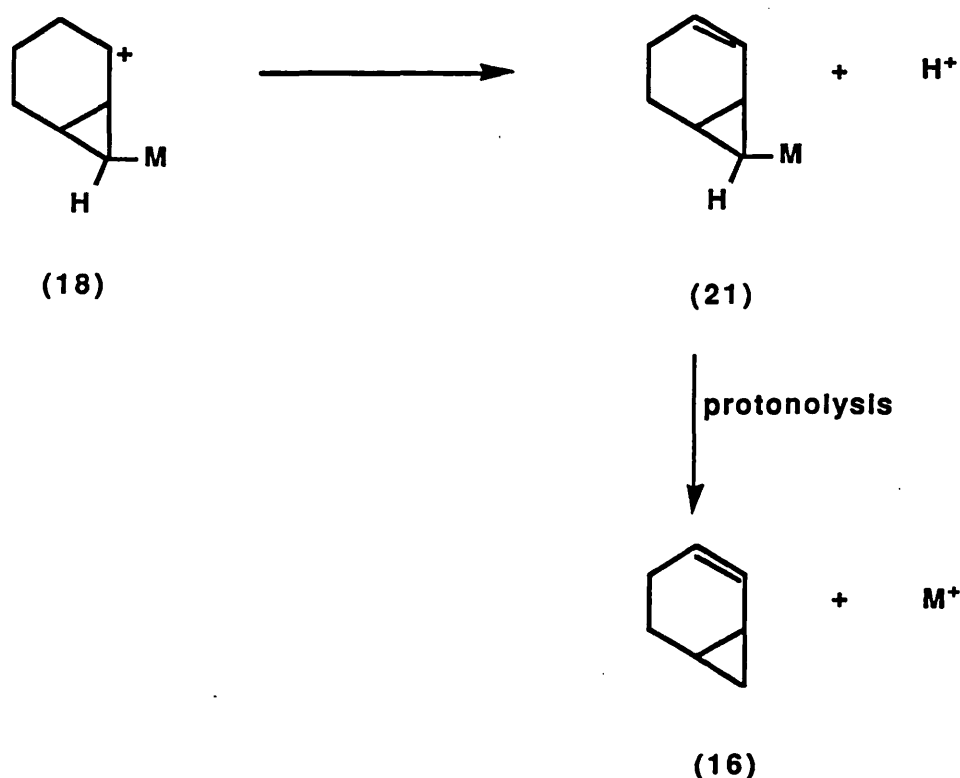
hours aided by sonication, and the species (9) was concluded to be far more efficient than the comparable rhodium and rhenium promoters. Sonication is not the principal

explanation for the faster reaction promoted by (9), as the technique did not enhance reactions promoted by (30) or (33). The results can be explained by the greater Lewis acidity of (9); the complex is not only positively charged but has an overall d configuration of 14. Complexes (30)-(33) are all neutral and d^{16} species. A second virtue of the nickel complex is the greatly decreased steric hindrance around the active metal centre compared to the complexes (31)-(33); this property increases the affinity of the centre to undergo oxidative addition to a strained C-C bond of (10). Facile cleavage of C-C bonds by (9), as noted earlier, could be predicted by Beauchamp's(1) studies on gaseous nickel cations; however, it must be stated that formal oxidative additions to a strained C-C bond may proceed by a quite different mechanism than that predicted for Ni^+ (g) insertion into the C_2-C_3 bond of n-butane.

2.4.2. The Mechanism of Metal Promoted Rearrangement of Moore's Hydrocarbon(10)

From our observations we have, for example, been able to deduce underlying trends in certain groupings such as the rhodium(I) species (31)-(33) and have clarified solvent effects by their individual metal-coordinating ability. During our studies we have determined that there is definite specificity by a given metallic species for certain rearrangement products. While Gassman(18) also observed similar results and consequently provided a possible mechanistic pathway to the products (Scheme 17), his rationale was based on the self evident fact that the strained carbon carbon bond must function as the nucleophile and the metal as an electrophile or Lewis acid. Although the varying products can then be rationalised in terms of carbocationic rearrangements, the essential role of the nature of the metal in determining product ratios is entirely neglected. From the combined results in Table 3, we now wish to suggest a new explanatory mechanism which can predict with a high degree of certainty which products will be formed for a given metallic species.

We dismiss the concept of C_1-C_7 cleavage either by a direct oxidative addition reaction or by outer-sphere electron transfer. Such scission does not provide any likely

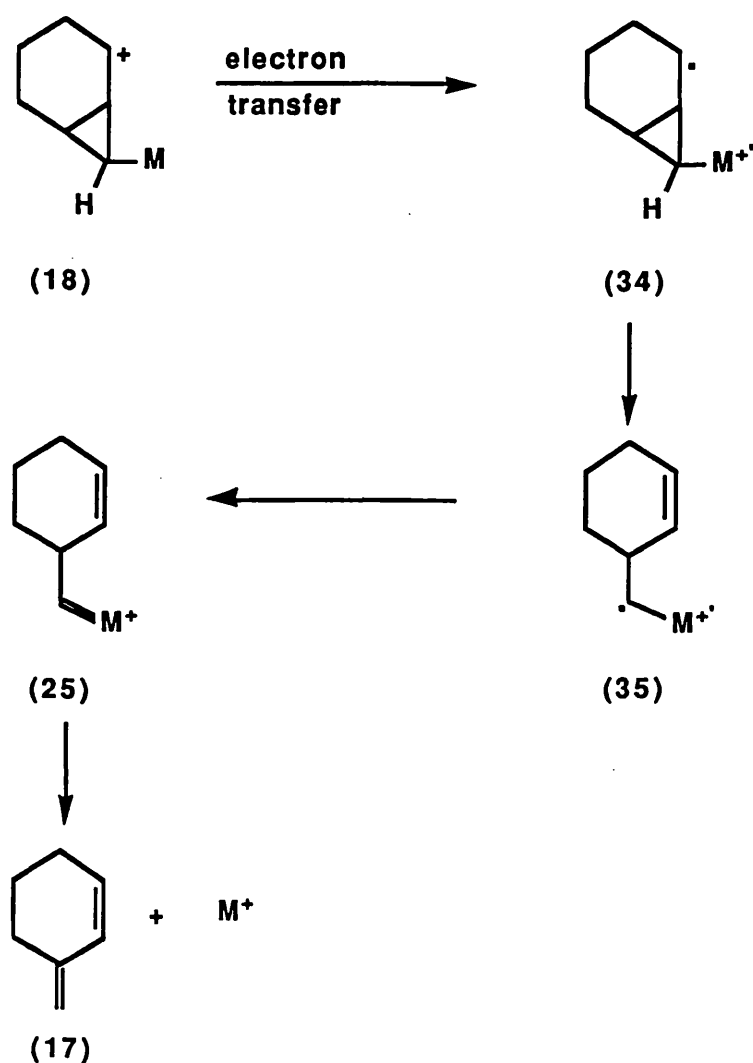


Scheme 31

pathway towards the observed products. Therefore we conclude that isomerisation is initiated by an oxidative addition type reaction into the second HOMO of (10), that is the C₂-C₇ bond, to give a common intermediate of structure (18). Structure (18) may be formally derived from either a concerted insertion *via* the metallocyclobutane and heterolytic cleavage or by an asynchronous addition to the strained carbon carbon bond. The indicated regioselectivity, in which the metal is formally bonded to the cyclopropyl ring and the cyclohexyl carbocation is generated is proposed as the alternative cyclopropyl cation possessing a metallocyclohexane bond is a higher energy species. The products can then be explained by their degree of Lewis acidity. Data in Table 3 show that strong Lewis acids give bicyclo[4.1.0]hept-2-ene (16) either as the major product or sole product. We therefore suggest that the mechanistic route given in Scheme 31 is preferred in these cases. In Scheme 31 the reaction proceeds by traditional carbonium ion chemistry finally yielding (16) by protonolysis of (21). This

mechanism is also predicted by Gassman⁽¹⁸⁾.

However, if we then take note of the metallic promoters which favour formation of exomethylene-cyclohexene, we believe that a carbon centered radical mechanism is operative. In all the respective examples the catalyst is not a strong Lewis acid. We have therefore deduced the mechanistic pathway in Scheme 32 which explains preferred formation of (17) by certain promoters. As the metallic complex involved is not particularly electron deficient, electron transfer from the metal to the secondary carbonium ion in (18) is permitted. Such a transfer then generates intermediate (34), containing a cation-radical at the metal centre and a cyclopropyl carbinyl radical on the hydrocarbon skeleton. Cyclopropyl carbinyls are well known in organic chemistry to undergo very fast, stereoelectronically controlled cyclopropyl ring



Scheme 32

opening⁽²⁴⁾ with exclusive formation of the substituted cyclohexenyl ring. We believe this occurs in the 'weaker' Lewis acid systems to yield species (35), which may also be represented as the metallocarbene (25). Insertion into the neighbouring sp^3 C-H bond then follows to yield (17) and the regenerated metal catalyst.

Thus in conclusion, we wish to propose that the nature of the metal and the ancillary ligands play a dominant role in product evolution. While accepting that the initial oxidative addition step requires electrophilic character at the metal centre, the possibility of subsequent electron transfer to generate a carbon centered radical from the initially generated carbocation provides an alternative mechanistic pathway. Consequently, this latter pathway may be predicted for transition metal complexes with relatively low oxidation potentials.

2.5. Experimental

Melting points were determined on a Kofler hot stage apparatus or in evacuated sealed capillaries on a Mel-Temp apparatus if air sensitive and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 983G grating spectrometer. ^1H nmr spectra were recorded at 60MHz on a Varian EM-360A, at 90 MHz on a Jeol FX 90Z and at 250 MHz on a Bruker WM-250 and are quoted in ppm for stated solutions with tetramethylsilane as an internal standard. ^{13}C spectra, and NOE experiments, were performed at 250 MHz on a Bruker WM-250. Mass spectra were determined with a VG micromass 707B instrument. G.C.-M.S. measurements were carried out using an OV1 gas chromatography column and a Finnigan 4021 Quadrupole mass spectrometer at Quest International, Ashford, Kent. Elemental microanalyses were performed in the Imperial College Chemistry Department microanalytical laboratory.

Analytical thin layer chromatography was performed on precoated glass-backed plates (Merk Kiesegel 60 F₂₅₄) and preparative chromatography was conducted under low pressure using MN Kiesegel 60 (230-400 mesh) silica gel. Preparative plates were made in the laboratory using Rose GF254 silica gel containing 13% gypsum. Ultrasound experiments were carried out in a Semat ultrasound cleaning bath (80W, 55kHz).

Water always refers to distilled water. Petroleum ether (petrol) refers to light petroleum ether with b.p. 40-60°C and was redistilled before use. Diethyl ether, tetrahydrofuran and 1,2-dimethoxyethane were dried by reflux over sodium/benzophenone and distilled before use. Dichloromethane was dried by reflux over phosphorus pentoxide and distilled before use. Benzene was dried over sodium wire and acetonitrile over calcium hydride and both were distilled before use. Pyridine, diisopropylamine, diethylamine and triethylamine were distilled from calcium hydride and stored over potassium hydroxide pellets. Chloro-trimethylsilane was distilled from and stored over calcium hydride. All other solvents and reagents were purified by standard techniques. All solvents were stored under argon.

***Bis*[Tricarbonyldichlororuthenium] (30)**

The title compound (30) was synthesised by the method of Cleare and Griffith(21). $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (0.6g) was refluxed with a mixture of concentrated hydrochloric acid (6 ml) and formic acid (6 ml of 90%) for 24 hours. The reaction mixture was evaporated to dryness over a steam bath and the residue recrystallised from acetone/petroleum ether to provide a very pale yellow crystalline solid which characterised as (30) (3.26g) (Found: C, 14.28; Cl, 27.45%. $\text{C}_6\text{Cl}_4\text{O}_6\text{Ru}_2$ requires C, 14.08; Cl, 27.07%).

***trans*-Chlorocarbonyl *bis*(triphenylphosphine)rhodium (31)**

The procedure according to Wilkinson *et al.*(22) was employed. Rhodium(III) chloride trihydrate (0.50g, 1.90 mmol) dissolved in absolute ethanol (20ml), was added to a refluxing solution of triphenylphosphine (1.80g, 6.90 mmol) in ethanol (75 ml). After 5 minutes, formaldehyde (20 ml of 37% in water) was added and then the system cooled to provide a precipitate of the product (31). Recrystallisation from water and drying *in vacuo* provided a yellow crystalline solid (31) (0.52g, 44%), m.p. 194-196°C (literature value(22) 195-197°C) (Found: C, 64.51; Cl, 5.27; H, 4.02%; $\text{C}_{37}\text{ClH}_{30}\text{OP}_2\text{Rh}$ requires C, 64.32; Cl, 5.13; H, 4.38%).

***Tetrakis* (triethyl phosphite)nickel (3)**

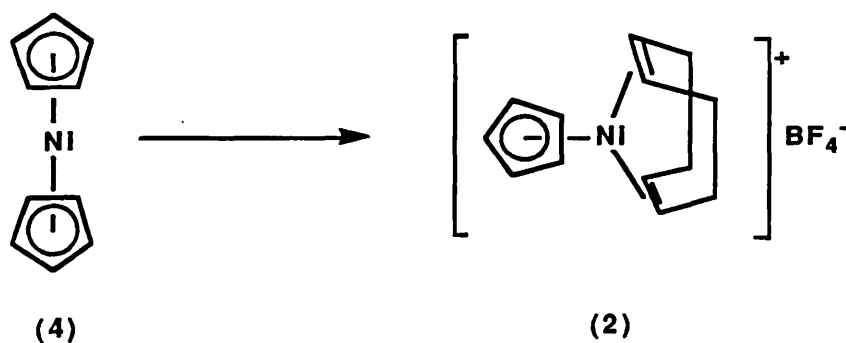
Preparation of (3) was achieved using a modification of the Vinal and Reynolds(4) procedure. Nickel(II) chloride hexahydrate (9.52g, 40 mmol) was dissolved in methanol (150ml), cooled to 0°C and placed under an argon atmosphere. Triethyl phosphite (34.80g, 209 mmol) was added followed by the dropwise addition of diethylamine (5.87g, 80 mmol) over 40 minutes. The white precipitate was filtered under argon, washed with chilled methanol (5 x 10 ml) and dried *in vacuo*. The

compound was stored under argon in sealed ampoules and was characterised as the known species (3) (23.82g, 82%) (Literature yield⁽³⁾, 30-40%), m.p. 108°C (literature value⁽³⁾ 108°C), δ_{H} (60MHz, CDCl_3) 1.25 (12H, t, $J = 7\text{Hz}$, OCH_2CH_3), 3.88 (8H, $J = 7\text{Hz}$, OCH_2CH_3).

Nickelocene (4)

Nickelocene was prepared following the procedure of Jolly and Chazan⁽²⁵⁾. Cyclopentadiene (8.5ml) was added to a mixture of powdered potassium hydroxide (50g, 890 mmol) and 1,2-dimethoxyethane (120 ml) under an argon atmosphere. Addition of a solution of nickel(II) chloride hexahydrate (11.90g, 50 mmol) in dimethylsulphoxide (65ml) followed, over a period of 30 minutes. The system was left with stirring for a further 30 minutes before anaerobic transfer to a mixture of hydrochloric acid (160 ml of 6M) and ice (200g). The precipitate was filtered, washed with water (4 x 20 ml) and dried *in vacuo*. Purification by sublimation at 100°C under reduced pressure, provided (4) (6.83g, 72%) as a green crystalline solid, m.p.(argon atmosphere) 172-174°C (literature value⁽²⁵⁾ 173-174°C).

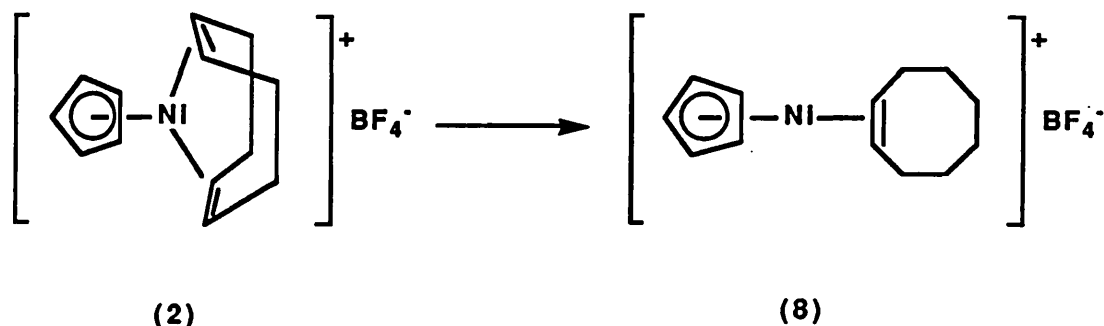
Preparation of π -cyclopentadienylnickel-1,5-cyclooctadiene tetrafluoroborate (2)(6)



1,5-Cyclooctadiene (2.20g, 20 mmol) was added to a solution of nickelocene (4) (1.00g, 5.3 mmol) in propionic anhydride (5ml) under an inert argon atmosphere.

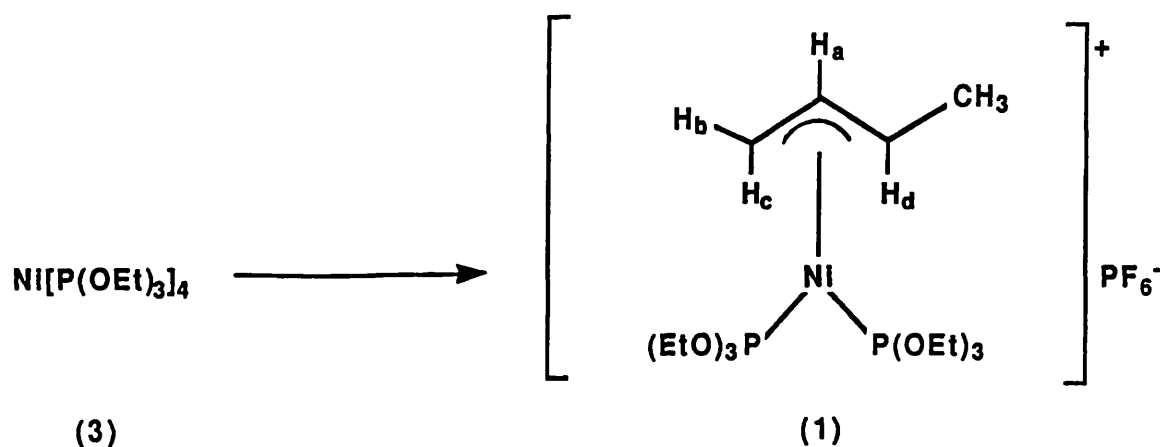
Aqueous hydrofluoroboric acid (1.10 ml of 48% by weight in water) was added dropwise over 25 minutes and then the system allowed to stir for a further 10 minutes. Addition of diethyl ether (75 ml) to precipitate the nickel complex, followed by filtration provided the crude product as the black residue. Two crystallisations from nitromethane/diethyl ether and drying *in vacuo* provided a dark green crystalline solid characterising as (2) (1.43g, 85%); $\nu_{\max}(\text{KBr disc})$ 3 130, 3 020, 2 960, 2 900, 2 850, 1 520, 1 490, 1 470 cm^{-1} ; $\delta_{\text{H}}(90\text{Mz, CD}_3\text{NO}_2)$ 2.60 (8H, m, CH_2), 5.42 (4H, m, cyclo-octadiene *olefinics*), 5.86 (5H, s, cyclopentadienyl-*H*); (Found: C, 49.23; H, 5.44%. $\text{BC}_{13}\text{F}_4\text{H}_{17}\text{Ni}$ requires C, 49.05; H, 5.27%).

Preparation of π -cyclopentadienylnickel-cyclooctene tetrafluoroborate (8)



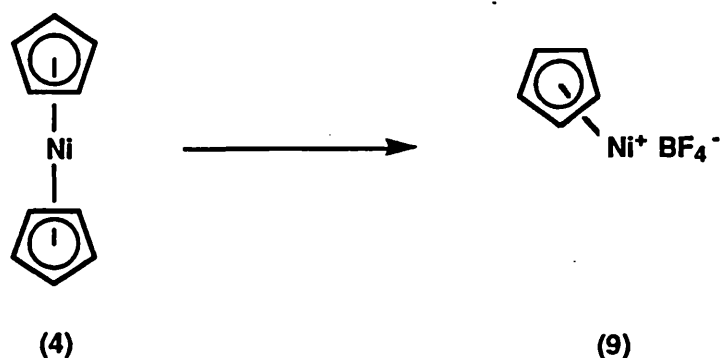
π -Cyclopentadienyl-1,5-cyclooctadiene tetrafluoroborate (2) (430 mg, 1.35 mmol) was dissolved in dichloromethane (30ml). The solution was deoxygenated before anaerobic transfer to a pressure bottle. A hydrogen atmosphere (5.5 atmos.) was applied to the stirred mixture at -78°C . The system was allowed to warm to room temperature over 4 hours and no colour change was apparent. Removal of the solvent *in vacuo* provided a green solid, which was purified by recrystallisation from nitromethane/dichloromethane to yield light green crystals of the title compound (8) (464 mg, 94%), $\delta_{\text{H}}(90\text{MHz, CDCl}_3)$ 2.28-2.75 (12H, m, CH_2), 5.46 (2H, s, cyclooctene-*olefinics*), 5.89 (5H, s, cyclopentadienyl-*H*); (Found: C, 48.20; H, 5.63%. $\text{BC}_{13}\text{F}_4\text{H}_{19}\text{Ni}$ requires C, 48.67; H, 5.96%).

Preparation of *syn*- π -crotylbis(triethyl phosphite)nickel hexafluorophosphate (1)(6)



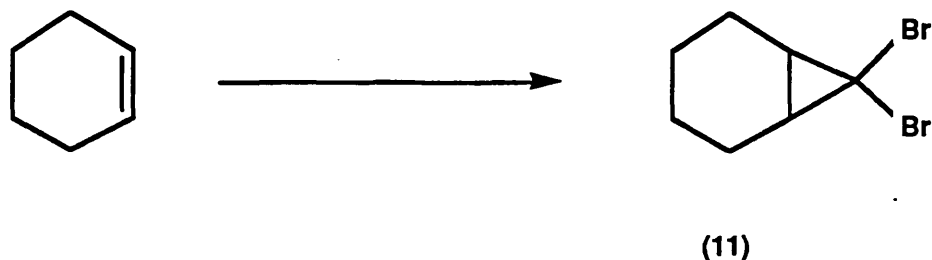
To a slurry of $\text{Ni}[\text{P}(\text{OEt})_3]_4$ (3) (7.32g, 10 mmol) in diethyl ether (10ml) under an argon atmosphere and at -65°C , was added a precooled (-50°C) solution of concentrated sulphuric acid (1.10g, 11 mmol) in diethyl ether (10 ml) by canula under an argon atmosphere. The system was evacuated and excess 1,3-butadiene (*ca* 3 ml) was condensed in from a graduate cold trap. The mixture was allowed to warm to room temperature over 4 hours before setting to reflux for 1.5 hours. The volatiles were removed *in vacuo* and the residue washed with petroleum ether (3 x 5 ml) and then re-dried under reduced pressure. The concentrate was flushed with water (2 x 2.5 ml) into an ice-chilled solution of ammonium hexafluorophosphate (1.63g, 0.010 mole) in water (5 ml) and the precipitate of the crude product filtered, washed with chilled methanol (5 x 3 ml) and dried *in vacuo* to provide (1) (1.24g, 21%) as a yellow crystalline solid, m.p.= $58\text{--}60^\circ\text{C}$ (Literature value (5) $63\text{--}65^\circ\text{C}$), δ_{H} (90 MHz, CDCl_3) . 1.30 (3H, t, $J=7\text{Hz}$, OCH_2CH_3), 1.75 (3H, d, $J_{\text{dCH}_3}=6\text{Hz}$, *syn*- CH_3), 2.64 (1H, d, $J_{\text{bc}}=2\text{Hz}$, H_c), 3.76 (2H, dq, $J_{\text{cb}}=2\text{Hz}$, $J_{\text{ab}}=7.5\text{Hz}$, $J_{\text{ad}}=14\text{Hz}$, H_b and H_d (interchangeable)), 4.04 (2H, q, $J=7.0\text{Hz}$, OCH_2CH_3), 5.29 (1H, dt, $J_{\text{ac}}=J_{\text{ad}}=14\text{Hz}$, $J_{\text{ab}}=7.5\text{Hz}$, H_a).

Preparation of cyclopentadienylnickel tetrafluoroborate (9)



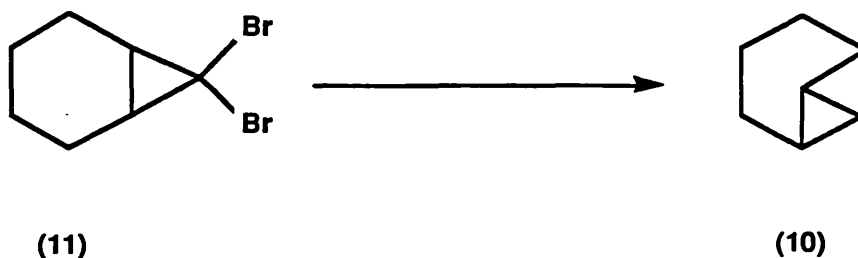
The procedure used was based on that reported by Court and Werner⁽⁹⁾ and all transferences were done under an inert atmosphere using a glove box. Freshly sublimed nickelocene (4) (140mg, 0.741mmol) was placed in a polytetrafluoroethylene reaction vessel. The latter was then attached to a stainless steel vacuum line and evacuated. Gaseous hydrogen fluoride (15ml) was condensed into the vessel by trap to trap distillation, under a static vacuum, from a previously calibrated teflon vessel. Excess boron trifluoride gas was then bubbled through the solution until it became orange. Residual boron trifluoride was evacuated under reduced pressure into a chemical trap and residual hydrogen fluoride was removed by trap to trap transfer under a static vacuum. The solid residue was dried under a high vacuum (10^{-5} mmHg) to yield an orange-brown powder, similar in appearance to that described by Court and Werner⁽⁹⁾, and presumed to be the reactive species (9) (153mg, 98%), δ_{H} (250MHz, CD_3CN) 5.54 (br. s, cyclopentadienyl-*H*).

Preparation of 7,7-dibromobicyclo[4.1.0]heptane (11)



A modification of von E. Doering's procedure (26) was used which resulted in a considerable improvement in yield. Cyclohexene (237g, 2.88 mole) was added to a solution of potassium *t*-butoxide (100g, 891 mmol) in *t*-butanol (550 ml) under an argon atmosphere. Bromoform (75.0g, 297 mmol) was added to the mixture over 2 hours and then the system was left, with stirring, for 12 hours. The crude mixture was poured into water (400 ml), extracted with petroleum ether (5 x 100 ml), the combined extracts were dried (Na_2SO_4 anhydrous) and concentrated, and the residue distilled to provide (11) (74.8g, 99%) as a colourless liquid, b.p. $80^\circ\text{C}/5$ mmHg (Literature value(26) $100^\circ\text{C}/8$ mmHg), ν_{max} . (film) 2 940, 2 856, 1 460, 1 443 cm^{-1} ; δ_{H} (90MHz, CDCl_3) 1.28 (4H, m, 3- CH_2 and 4- CH_2), 1.58 (2H, m, 1- CH and 6- CH), 1.96 (4H, m, 2- CH_2 and 5- CH_2); (Found C, 33.50; H, 3.96%. $\text{C}_7\text{H}_{10}\text{Br}_2$ requires C, 33.11; H, 3.96%).

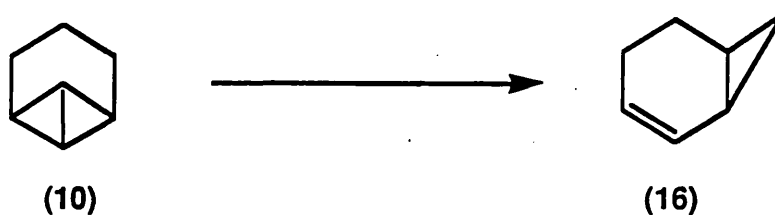
Preparation of tricyclo[4.1.0.0^{2,7}]heptane (10)



The tricyclic hydrocarbon (10) was prepared by a modification of the procedure of Gassman and Richmond(12). It was essential to base-wash (*i*-propyl alcohol and

potassium hydroxide, aqueous ammonia or HMDS) and oven bake all glassware before use to avoid product decomposition. A solution of (11) (66.0g , 260 mmol) in diethylether (500 ml) was placed under an argon atmosphere and cooled to -10°C . Methyllithium (200 ml of 1.3M MeLi:LiBr in hexane) was added by canula over 4 hours and the system allowed to warm to room temperature over 12 hours. The mixture was poured into water (200 ml) and extracted with diethyl ether (4 x 100 ml). The combined ethereal extracts were washed with diethyl ether (3 x 100 ml), brine (3 x 100 ml) and then dried (Na_2SO_4 anhydrous). The ether was removed by distillation through a 14 inch Vigreux column and the residue trap to trap distilled under a static vacuum. Fractional distillation through an 8 inch Vigreux column from anhydrous sodium carbarbonate, under an argon atmosphere, provided the volatile hydrocarbon (10) (6.19g, 25%) as a clear liquid, b.pt. $108-111^{\circ}\text{C}$ (Literature value (12) $111-112^{\circ}\text{C}$), ν_{max} (film) 2 994, 2 927, 2 856, 1 443, 1 412 cm^{-1} ; δ_{H} (250MHz, CDCl_3) 1.34 (6H, m, 3- CH_2 , 4- CH_2 , and 5- CH_2), 1.42 (2H, m, 1- CH and 7- CH), 2.24 (2H, m, 2- CH and 6- CH); $\delta_{13}\text{C}$ (C_6D_6) 5.79 (2C, s, 1- C and 7- C), 20.88 (4C, s, 3- C and 5- C), 21.46 (2C, s, 4- C), 40.16 (2C, s, 2- C and 6- C); $M/Z = 94$ (M^+), 79, 77, 66, 39, 93, 91, 41, 53, 27, 65, 80; (Found: C, 88.97; H, 10.82%. C_7H_{10} requires C, 89.29; H10.63%)

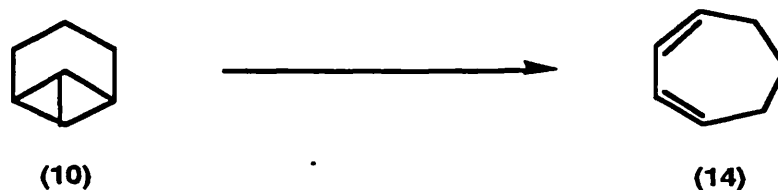
Preparation of bicyclo[4.1.0]hept-2-ene (16)



A deoxygenated solution of Moore's hydrocarbon (10) (300mg, 3.186 mmol) in deuterated chloroform (6.4ml) was added to tin(II) chloride dihydrate (35.94mg, 0.159mmol) under an argon atmosphere. The system was sealed and left with stirring for 24 hours. Trap to trap distillation under a static vacuum then separated the volatiles

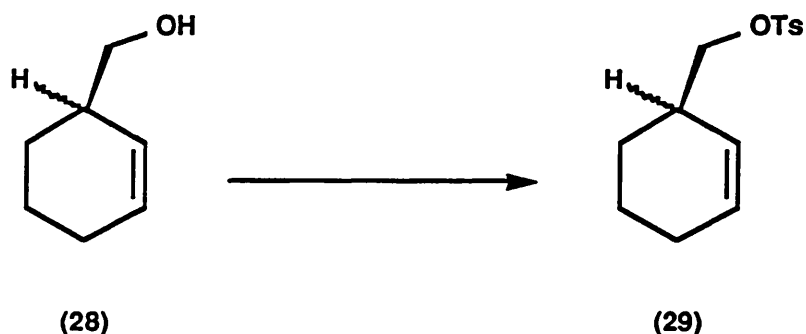
from the metallic catalyst. G.C.-M.S. analysis of the volatiles concluded the presence of two C_7H_{10} isomers, which characterised as the reclaimed starting material (10), and the norcarene (16) (8:7 ratio, respectively); δ_H (250 MHz, CD_3CN) 0.70(2H, m, 7- CH_2), 1.25(2H, m, 1- CH and 6- CH), 1.85(4H, m, 4- CH_2 and 5- CH_2), 5.45(1H, m, 3- CH), 5.90(1H, m, 2- CH); retention time=3.74mins.; $M/Z=94(M^+)$, 79, 77, 39, 91, 93, 66, 65.

Preparation of 1,3-cycloheptadiene (14)



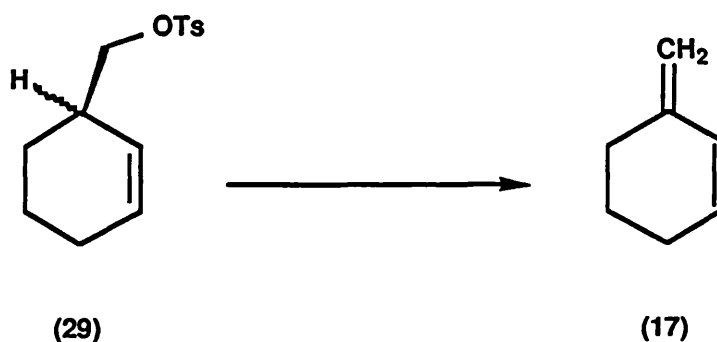
A mixture of silver tetrafluoroborate (30.95mg, 0.159mmol) and deuterated chloroform (6.4ml) were deoxygenated and maintained under an argon atmosphere. A deoxygenated sample of Moore's hydrocarbon (10) (300mg, 3.186mmol) was added *via* catheta and the reaction allowed to proceed for 5 minutes. Isolation of the volatiles by the static vacuum technique yield one C_7H_{10} isomer, identified as the known compound (14), δ_H (250MHz, $CDCl_3$) 1.82 (2H, br.m, 6- CH_2), 2.40 (4H, br.m, 5- CH_2 and 7- CH_2), 5.76 (4H, m, olefinic- H); retention time = 3.89mins.; $M/Z=94(M^+)$, 79, 77, 39, 66, 91, 41, 93.

Preparation of 3-(1'-*p*-toluenesulphonylmethyl)cyclohexene (29).



A modification procedure based on that of Blancou and Casadevall⁽²⁰⁾ was employed. (+)-2-cyclohexene-1-methanol (5.00g, 44.6 mmol) was added to a solution of *p*-toluenesulphonyl chloride (8.50g, 44.6 mmol) in pyridine (15 ml) and the mixture left, with stirring, overnight. The mixture was diluted with water (80 ml) and extracted with diethyl ether (4 x 50 ml). The ethereal extracts were washed with saturated copper(II) sulphate solution (6 x 40 ml) and water (2 x 40 ml) before drying (Na_2SO_4 anhydrous). The volatiles were removed *in vacuo* to yield a tosylate which characterised as (29) (10.98g, 92%), δ_{H} (60MHz, CDCl_3) 1.45-2.30 (7H, m, cyclohexyl-*H*), 2.43 (3H, s, CH_3), 3.85 (2H, d, $J=6\text{Hz}$, OCH_2), 5.57 (2H, br. s, *olefinics*) 7.25 and 7.75 (4H, dd, $J=8\text{Hz}$, *aromatics*).

Preparation of 3-methylenecyclohexene (17).



The Blancou and Casadevall⁽²⁰⁾ procedure was modified and used. The tosylate (29) (7.00g, 26.3 mmol), was dissolved in 2,4,6-trimethylpyridine (18 ml)

and heated to reflux. The volatile product (17) was distilled off and collected. After 3 hours of distillation, the product was dissolved in diethyl ether (80 ml) and the extract washed with saturated copper(II) sulphate solution (4 x 20 ml) followed by water (2 x 20 ml). After drying (Na_2SO_4 anhydrous), the volatiles were removed by distillation through a 10 inch Vigreux column and the residue distilled through a shorter, 4 inch column to yield a clear liquid accurately characterised as (17) (2.06g, 83%), δ_{H} (60MHz, CDCl_3) 2.15 (2H, m, 5- CH_2), 2.75 (4H, m, 4- CH_2 and 6- CH_2), 4.65 (2H, br. s, = CH_2), 5.60 (2H, m, $\text{CH}=\text{CH}$); $M/Z = 94(\text{M}^+)$, 79, 39, 41, 77, 40, 66, 91.

Metal promoted isomerisation of tricyclo[4.1.0.0^{2,7}]heptane (10)

A similar procedure was employed for all rearrangement reactions. All items of glassware were base washed and oven dried prior to use. The base wash most commonly used was a saturated solution of potassium hydroxide in *i*-propyl alcohol, other alternatives included aqueous ammonia and hexamethyldisilane in diethyl ether.

Except for trial experiments to determine the efficiency of several catalysts in the presence of air, all transfers and reactions were performed under a rigorously deoxygenated atmosphere.

5 Molar percent of catalyst with respect to the hydrocarbon (10) was consistently employed. The hydrocarbon (10) was rearranged in a variety of solvents and a concentration of 500mM was used in all experimental runs. Reaction progress was followed by gas chromatography. Consequently, removal of the volatiles from the catalyst was required which necessitated several reaction systems being simultaneously run. Several examples of rearrangement reactions performed are described below:-

Zinc(II) chloride promoted rearrangement of (10)

A solution of Moore's hydrocarbon (10) (102mg, 1.083mmol) in deuterated chloroform (2.3ml) was deoxygenated by bubbling argon gas through the mixture.

Zinc(II) chloride (7.4mg, 0.0054mmol) was placed in a round bottom flask and the system evacuated followed by flushing with argon, this process was repeated several times. The hydrocarbon solution was transferred anaerobically, by catheta, and mixed with the catalyst by stirring. The system was maintained under a closed argon atmosphere and at room temperature (25°C) and analysed at approximately 24 hour intervals. G.C. analysis determined the reaction to be complete after 70 hours. Combined results from G.C.-M.S. and proton nmr showed the presence of three C₇H₁₀ isomers which accurately characterised as the known compounds (14), (16) and (17) in a ratio of 75:15:8, respectively.

***bis* [Tricarbonyldichlororuthenium] (30) promoted rearrangement of (10)**

A deoxygenated solution of (10) (108mg, 1.147mmol) in deuterated chloroform (2.3ml) was combined with the ruthenium dimer (30) (29.4mg, 0.0057mmol) under an argon atmosphere. The system was maintained at 55-60°C in an oil bath and at 12 hour intervals the volatiles removed by trap to trap distillation under a static vacuum and tested for the consumption of substrate (10). After 24 hours the reaction was complete. Combined evidence from G.C.-M.S. and proton nmr spectra (see Table 2 and 3) supported the formation of two isomeric C₇H₁₀ hydrocarbons identifying as (16) and (17) in a ratio of 81:19, respectively.

***trans*-Chlorocarbonyl*bis*(triphenylphosphine)rhodium (31) promoted rearrangement of (10)**

The rhodium species (31) (48.44mg, 0.070mmol) was combined with a solution of (10) (132mg, 1.402mmol) in deuterated acetonitrile (2.4ml) in an ampoule, under an argon atmosphere. The ampoule was sealed and the system heated to 55-60°C in an oil bath. The reaction system was analysed at 24 hour intervals and found to have reached

completion after 48 hours. G.C.-M.S. and proton nmr analysis of the volatiles confirmed the formation of two rearrangement products, which duplicated the characteristics of species (16) and (17) in Table 2. The compounds were formed in a ratio of 19:81, respectively.

Cyclopentadienylnickel tetrafluoroborate (9) promoted rearrangement of (10)

The reactive nickel species (10) (28.2mg, 0.1339mmol) was maintained under rigorously anaerobic conditions and combined with a deoxygenated solution of the hydrocarbon (10) (252.1mg, 2.678mmol) in deuterated acetonitrile (5.4ml). The system was sealed and then subjected to sonication at room temperature. The progress of the reaction was checked at hourly intervals by the usual technique (see above) and the reaction found to be complete after 6 hours. A combination of G.C.-M.S. and proton nmr analysis accurately confirmed the identity of two C_7H_{10} products, (16) and (17) in a proportion of 11:89, respectively.

2.6 References

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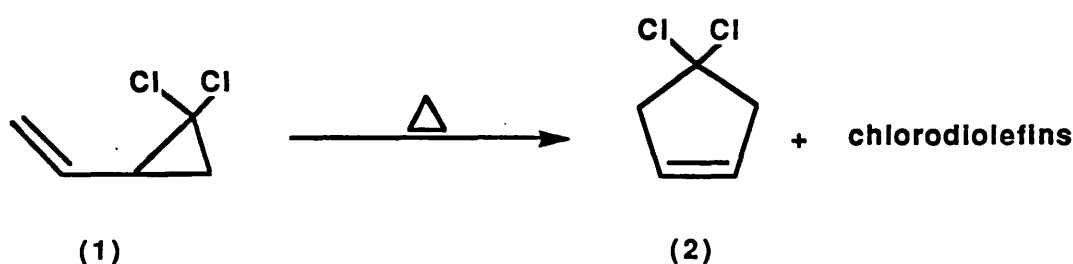
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CHAPTER 3

3. NOVEL REACTIONS OF THE VINYL CYCLOPROPANE ENTITY

3.1. The Vinyl Cyclopropane-Cyclopentene Rearrangement

In 1959, the transformation of 2,2-dichlorovinyl-cyclopropane (1) to 4,4-dichlorocyclopentene (2) (Scheme 1)⁽¹⁾ was discovered.



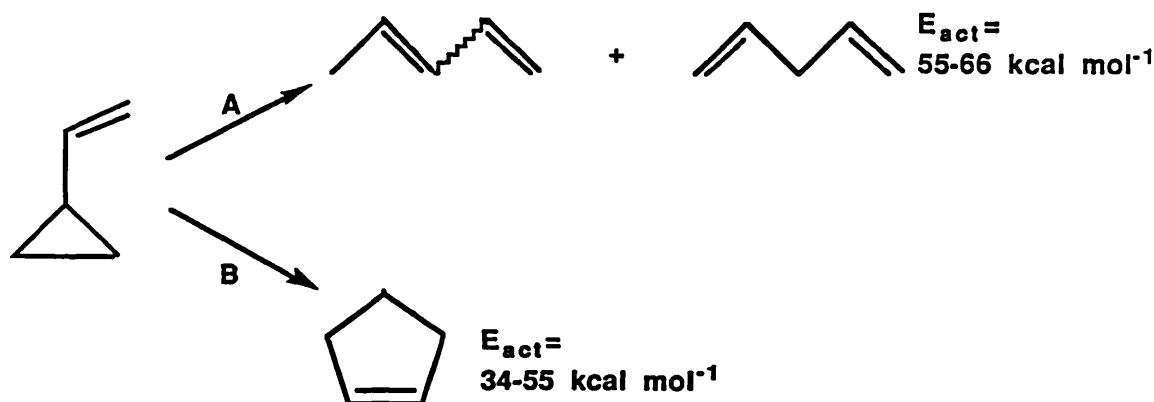
Scheme 1

This reaction type was later extended to the parent vinyl cyclopropane and many other substituted vinyl cyclopropanes⁽²⁾ and is now considered as a major synthetic method for cyclopentane ring construction in organic synthesis.

Several approaches to effecting the vinyl cyclopropane-cyclopentene rearrangement have been reported, including thermal or photolytic inducement, and also transition metal catalysis.

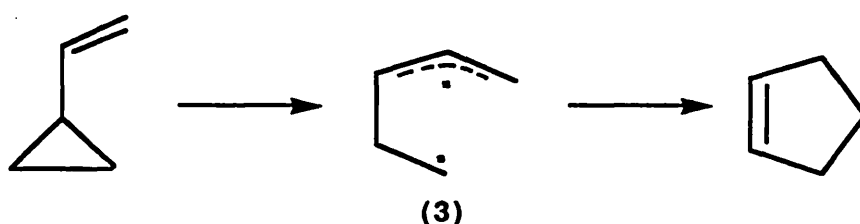
3.1.1. Thermal Rearrangement

Two types of thermally induced rearrangements may occur (Scheme 2) providing either 1,3- and 1,4-dienes (route A) or the cyclopentene moiety (route B). We are concerned with route B only, although it must be stated that under pyrolytic conditions a slight variance in the temperature may sometimes lead to route A products.



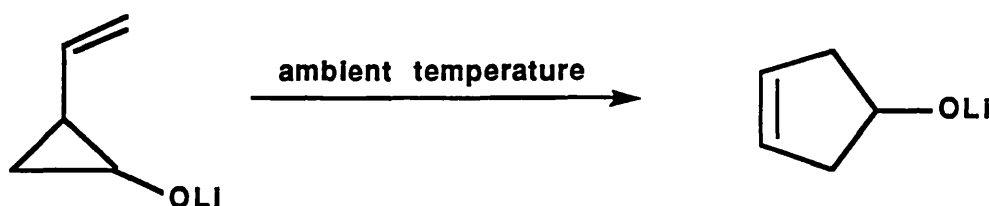
Scheme 2

exclusively. The mechanism is not conclusively known but could be considered as either concerted, or biradical, or a mixture of both. The concerted pathway would proceed by either a symmetry allowed but geometrically impossible 1,3-suprafacial shift with inversion or by a symmetry allowed 1,3-antarafacial shift with retention of configuration. The biradical mechanistic pathway, which is generally favoured would proceed *via* the intermediate (3) (Scheme 3).



Scheme 3

Significant cyclopropyl substituent effects have been found for radical-stabilising functional groups⁽²⁾ (e.g. OR, OSiR₃, SR, Ph). These effects include a decrease in the reaction temperature required and a greater selectivity for route B. The oxy-anion effect⁽³⁾ is a well known feature which decreases the energy barriers needed to furnish the rearrangement reaction (Scheme 4). Substitution at the C=C bond has little significance except in the instance when steric congestion becomes a hindrance, whence more forcing thermal conditions have to be employed.



Scheme 4

Various examples of the thermally induced vinyl cyclopropane-cyclopentene reactions are given in Table 1.

3.1.2. Photochemical Rearrangement

Photochemistry is seldom employed in the vinyl cyclopropane rearrangement reaction. The main reason for this is the involvement of higher energy intermediates leading to a greater number of possible mechanistic pathways with concomitantly decreased selectivity for single product formation. Singlet excited states are required by direct irradiation of the substrate causing $n \rightarrow \pi^*$ transitions; sensitized irradiation leads to triplet species with an energy content far greater than the activation energy needed for cyclopentene formation. The singlet excited state leads to biradical formation (3) (Scheme 3), whilst the triplet state most probably enhances zwitter ion (4) formation.



(4)

To avoid excessively high energy intermediates, tuneable carbon dioxide lasers may be employed to obtain the biradical, singlet state pathway. Examples of some photochemically induced rearrangements can be seen in Table 2.

Table 1: Thermal Rearrangement of Vinylcyclopropanes

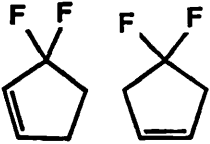
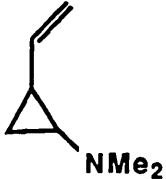
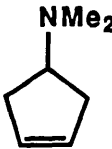
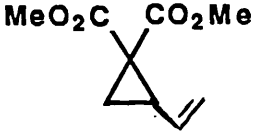
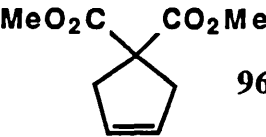
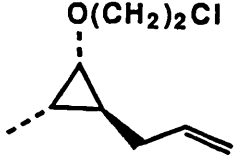
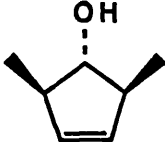
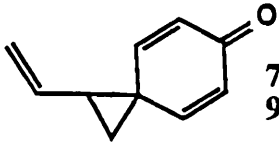
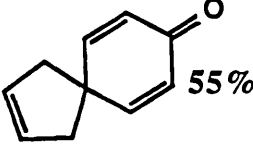
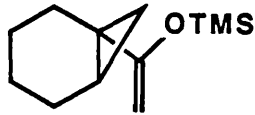
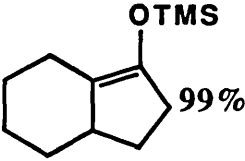
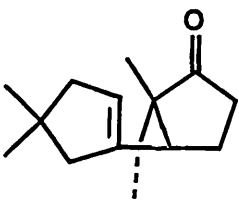
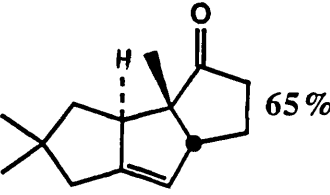
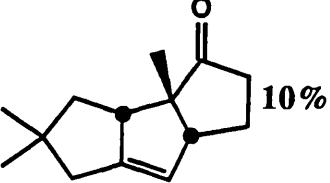
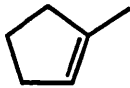
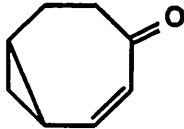
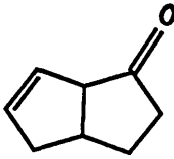
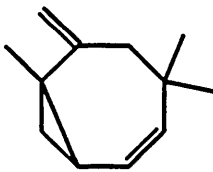
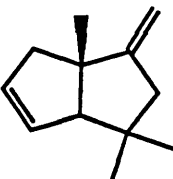
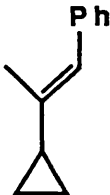
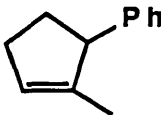
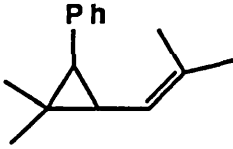
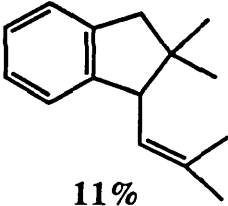
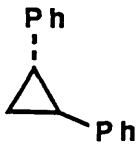
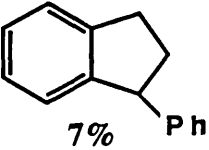
Substrate	Conditions	Cyclopentene Product and yield	Reference
	Sealed tube 258°C, 45 min.	 96 : 4 85%	4
	Gas-phase 178-203°C	 24%	5
	Pyrex chips 400-425°C	 96%	6
	n-BuLi, THF/HMPA, 50°C, 10hr	 74%	7
	70°C, 17 hr; 95°C, 1.5hr	 55%	8
	Sealed tube, 360-450°C C ₆ H ₆ , 2hr	 99%	9
	Pyrex, PbCO ₃ coated, 580°C	 65%  10%	10

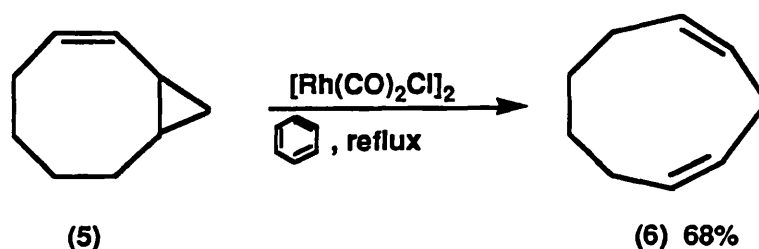
Table2: Photochemical Rearrangements of Vinylcyclopropanes

Substrates	Conditions	Cyclopentene product and Yield	Reference
	450W Hanovia, quartz	 55%	11
	Pentane, N ₂ , 200W Hanovia, pyrex, 2.5 hr.	 39%	12
	MeOH, 450W Hanovia, 10hr	 56%	12
	Hexane, <i>hν</i>	 31%	13
	253.7 nm	 11%	14
	C ₆ H ₆ , 253.7 nm, 8.5 hr.	 7%	15

3.1.3. Transition Metal Catalysed Rearrangements

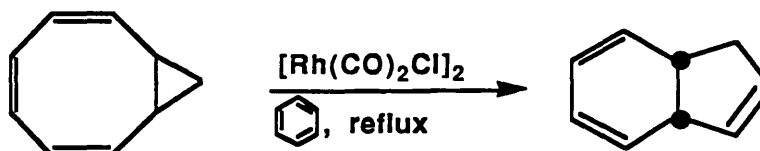
Many transition metal species have been employed in attempts to bring about the vinyl cyclopropane-cyclopentene conversion (Table 3). However, insertion of the starting-metal complex ligand, or rearrangement to dienes, is often observed in a significant proportion of the reactions. The olefinic component is often present as an α,β -unsaturated ketone or as a diene, in order to enhance initial coordination of the metal complex.

Thus, Rh(I) catalysed rearrangement of bicyclo[6.1.0]non-2-ene (5)(Scheme5)



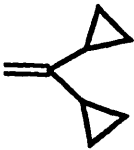
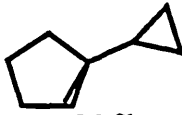
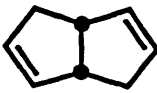
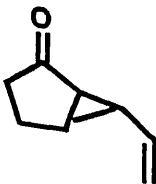
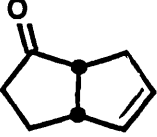
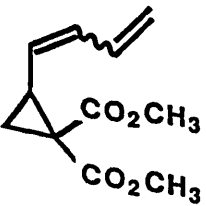
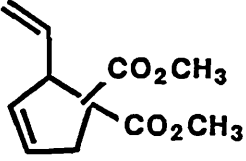
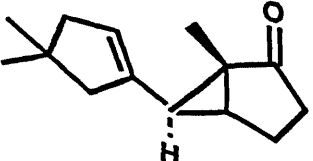
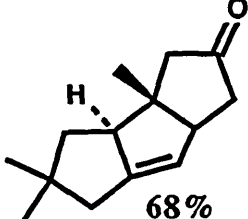
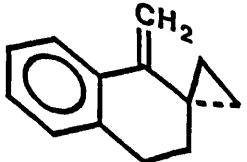
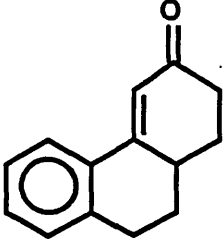
Scheme 5

provides cyclonona-1,4-diene (6) whilst catalysed isomerisation of the more unsaturated substrate (7) (Scheme 6) yields the cyclopentene derivative (8) exclusively(16).

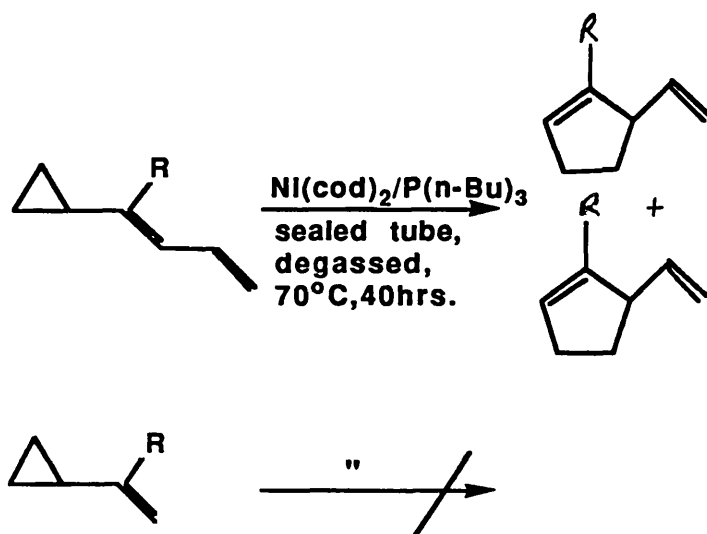


Scheme 6

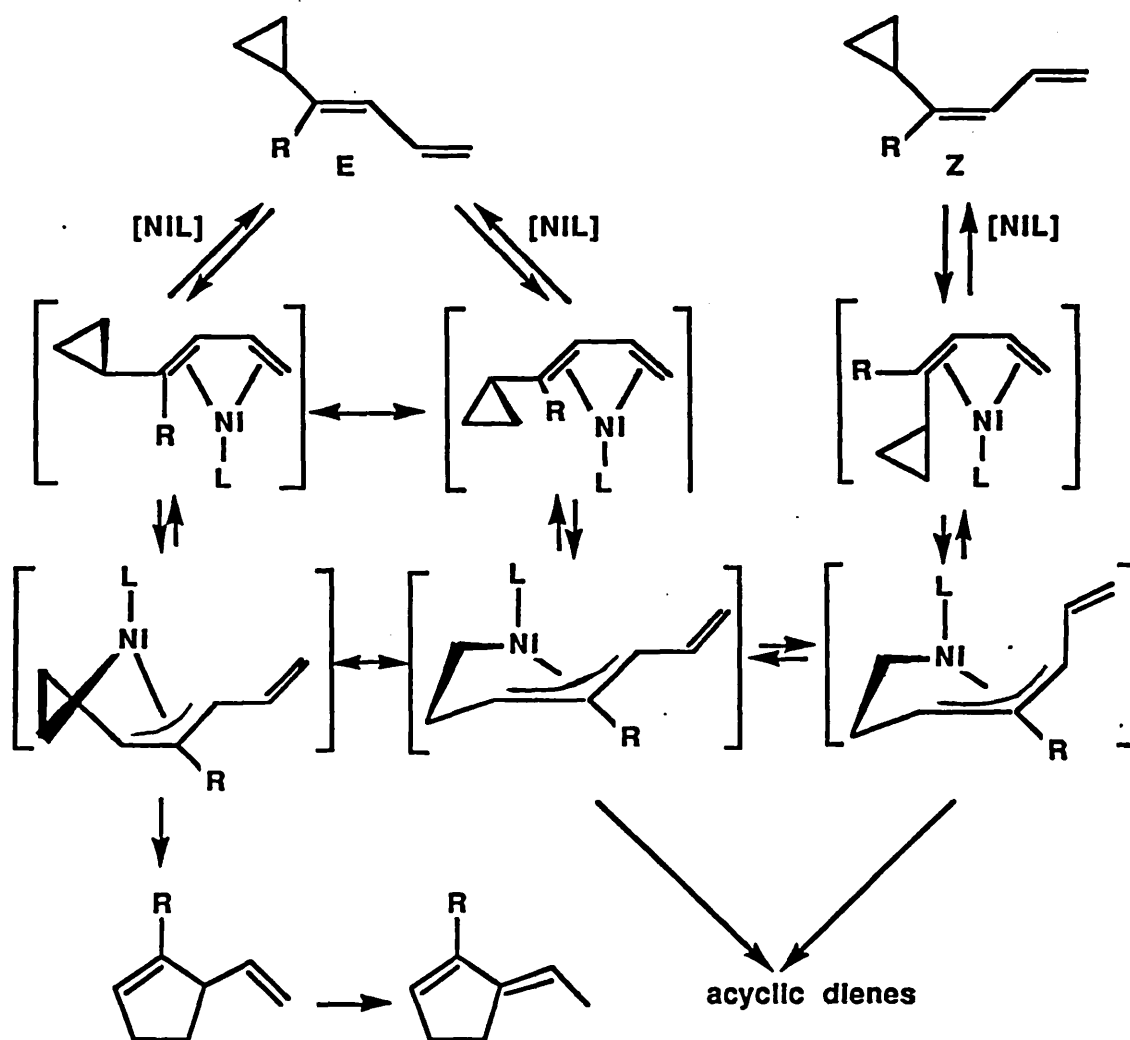
TABLE 3: Transition Metal Catalysed Rearrangements of Vinylcyclopropanes

Substrate	Conditions	Cyclopentene Product and Yield	Reference
	Ni(cod)_2 $\text{P(n-Bu)}_3, \text{C}_6\text{H}_6$	 99%	17
	$\text{Rh(C}_2\text{H}_4)_2\text{-(acac)}$, 80°C , 36hrs	 31%	18
	$\text{Rh(C}_2\text{H}_4)_2\text{-(acac)}$, C_6H_6 48hrs	 70%	19
	$\text{Pd[PPh}_3\text{]}_4$ DMSO, 50°C	 87%	20
	$\text{Rh(C}_2\text{H}_4)_2\text{-(acac)}$, C_6H_6 48hrs	 68%	19
	5 fold excess Fe(CO)_5 , $h\nu$	 80%	21

Nurakami and Nishida⁽¹⁷⁾, also found that nickel(0)-promoted vinylcyclopropane-cyclopentene rearrangement would not proceed in the absence of further conjugation of the vinyl portion of the substrate (Scheme 7). The extra unit of unsaturation is required for initial complexation of the catalyst (Scheme 8). After this, cleavage of the cyclopropyl C-C bond may prevail to yield the cyclopentene products by reductive elimination. The use of iron pentacarbonyls under photolytic conditions does not provide the desired cyclopentene products but yields cyclohexeneone derivatives by carbon monoxide ligand insertion⁽²¹⁾. Although this is unacceptable for the rearrangement reaction in question, the technique has been extended to provide an excellent method for lactone synthesis *via* the reaction of excess iron pentacarbonyl with vinyl epoxides using ultrasonication as a stimulant (ferrilactonisation)⁽²²⁾.

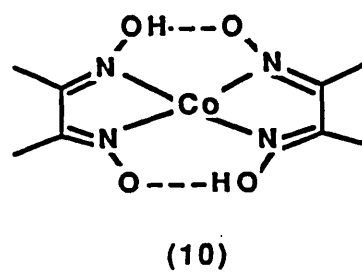
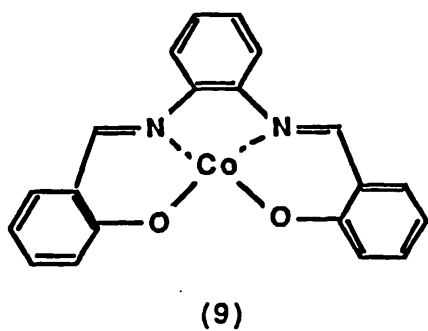


Scheme 7



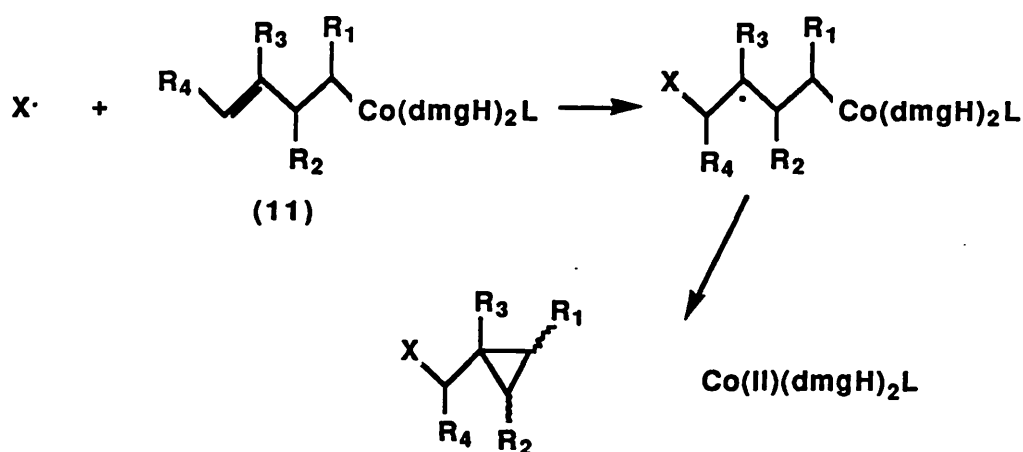
Scheme 8

We have looked into the area of cobalt(II) catalysis as a possible system for vinyl cyclopropane-cyclopentene rearrangement. Pattenden⁽²³⁾ and Johnson⁽²⁴⁾ have both successfully employed cobalt salen (9) and dimethylglyoximate (dmg) (10) complexes in organic synthesis.



Johnson⁽²⁴⁾ has provided a route to functionalised cyclopropane derivatives (Scheme

9) by attack of organic radicals at the terminal unsaturated carbon of cobalt(III) but-3-enyl derivatives (11) followed by homolytic displacement at the α -carbon. This system can be applied to a wide range of cobalt(III) species offering the respective wide variety of substituted cyclopropyl sulphones and (trichloroethyl)cyclopropanes by thermal and photolytic reactions with *p*-toluenesulphonyl halides, trichloromethylsulphonyl chloride and other radical precursors.



$\text{R}_1 = \text{H Me H H H H CN CN CN CN etc}$

$\text{R}_2 = \text{H H Me H H Ph H Me H H}$

$\text{R}_3 = \text{H H H Me H H H H Me Ph}$

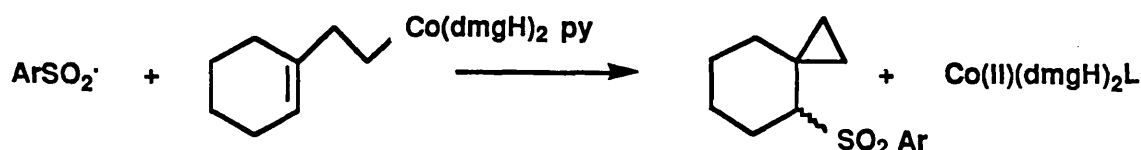
$\text{R}_4 = \text{H H H H Et H H H H H}$

$\text{X} = \text{Cl}_3\text{C}, \text{ArSO}_2, \text{NCCHBr}, \text{etc.}$

$\text{L} = \text{base ligand e.g. py}$

Scheme 9

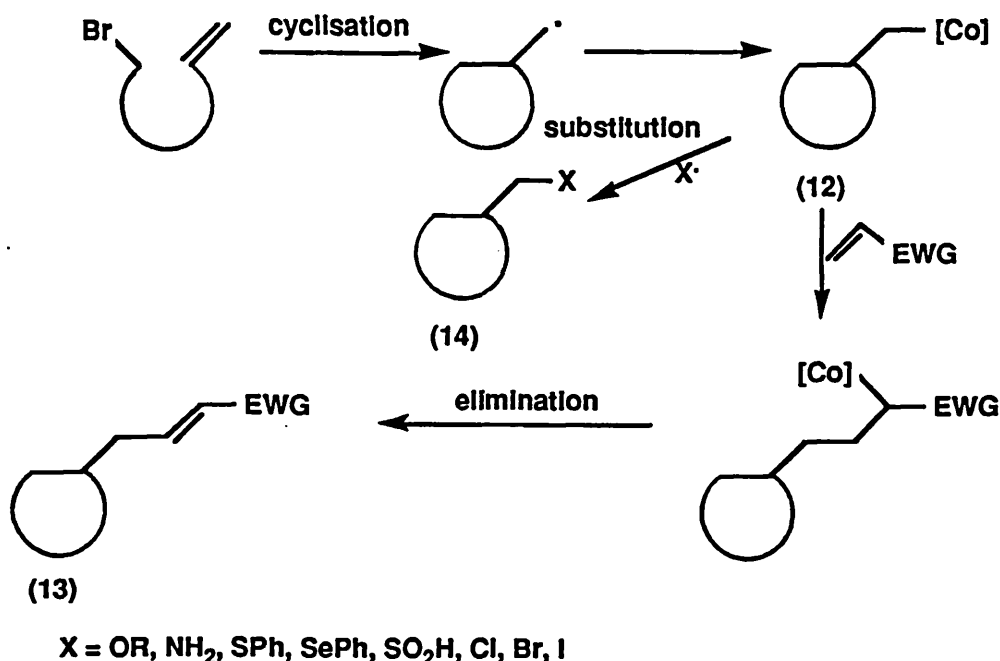
Similarly the reaction can encompass spiro- and fused cyclopropane ring systems (Scheme 10).



Scheme 10

Pattenden⁽²³⁾ has employed cobalt salophen reagents (12) to generate alkyl

radicals which in the presence of activated C=C bonds undergo radical Michael addition to yield new alkene products (13). The reaction is generalised in Scheme 11.



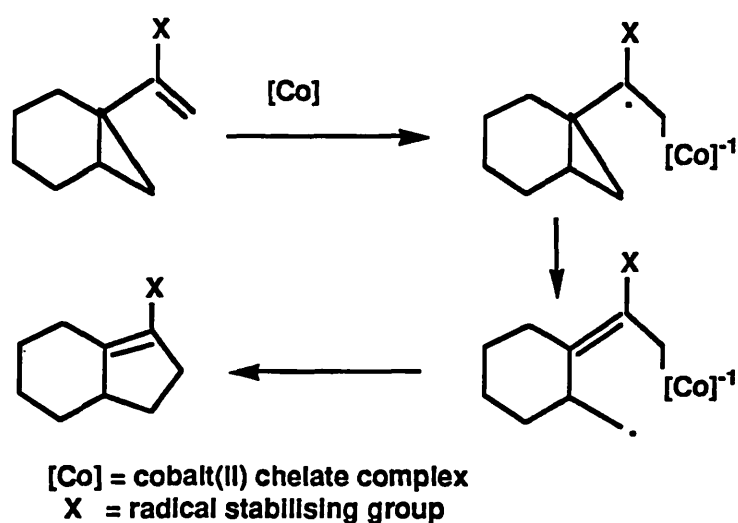
Scheme 11

Alternatively the cobalt(II) complex can undergo free radical substitution providing (14).

Cobalt dimethylglyoximate and salen type complexes have proven versatility for radical type reactions^(23,24). The key feature is the strength of the carbon-cobalt bond and the suitability of the cobalt chelate as a homofugal group; the cobalt entity may be displaced by an incoming radical species thus providing substitution at the sp³ carbon centre, but the carbon may not be displaced by free radical attack at the cobalt centre due to steric congestion around the metal making it inaccessible. Many cobalt (III) and cobalt (II) chelates can be synthesised⁽²⁵⁾, and the latter, although of high spin d⁷ type, that is to say inorganic radicals, can be stored under anaerobic conditions without dimerisation or disproportionation occurring. This advantage rarely occurs in the case of organic species.

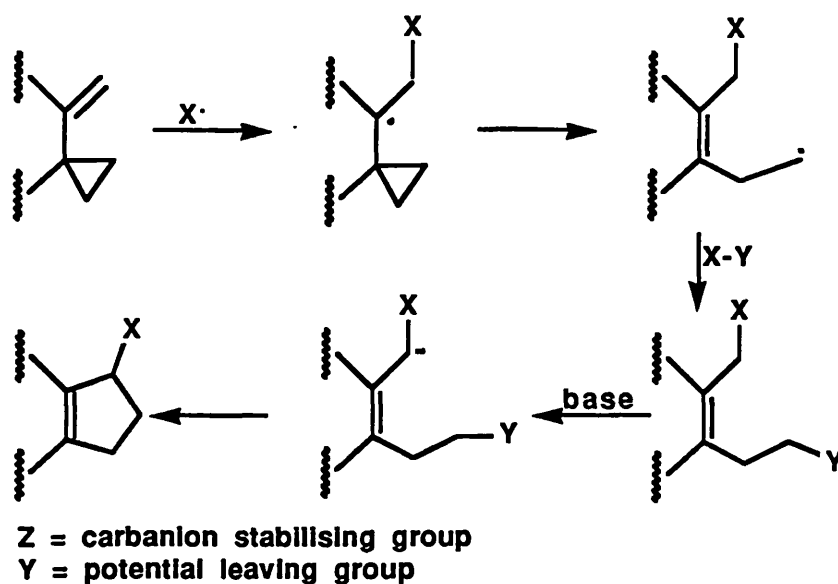
3.2. A Free Radical Approach to the Vinyl Cyclopropane Rearrangement.

With knowledge of the radical nature of cobalt(II) chelate complexes we envisaged they may be possible reagents for the vinyl cyclopropane-cyclopentene rearrangement given in Scheme 12. Indeed the cobalt complexes could be sufficiently more electrophilic than the other metal complexes (Table 3) previously employed and hence would not necessitate an enone type system for initial coordination of the vinyl cyclopropane system. The process, shown in Scheme 12, was part of our



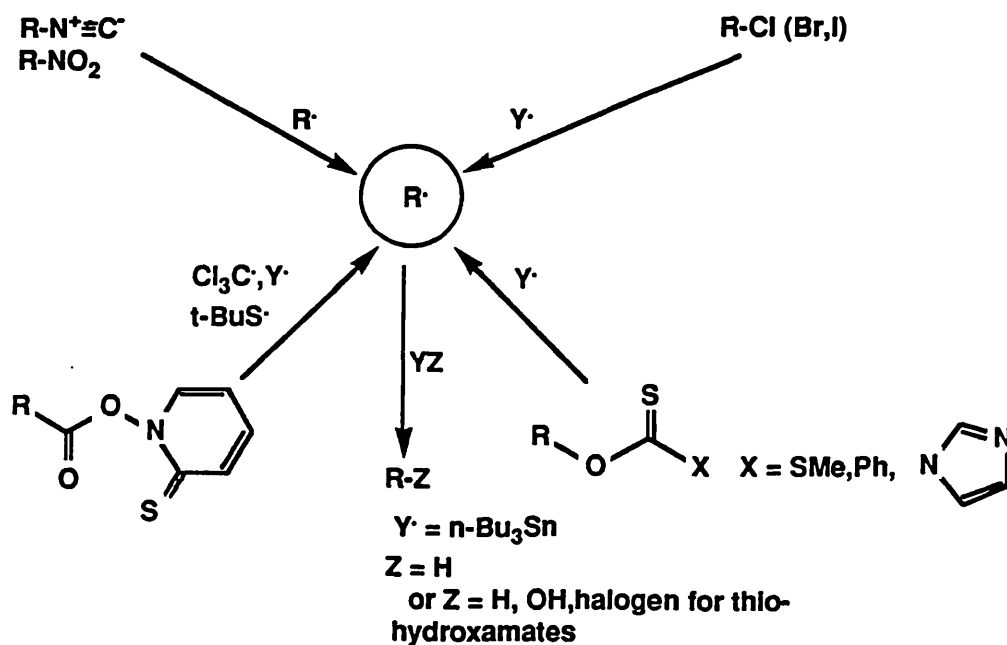
Scheme 12

research program to discover a radical alternative for the vinyl cyclopropane rearrangement reaction. As purely organic radical sources may also be considered the approach is generalised as shown in Scheme 13, whereby a radical ring opening sequence (*vide infra*) is followed by ionic ring closure.



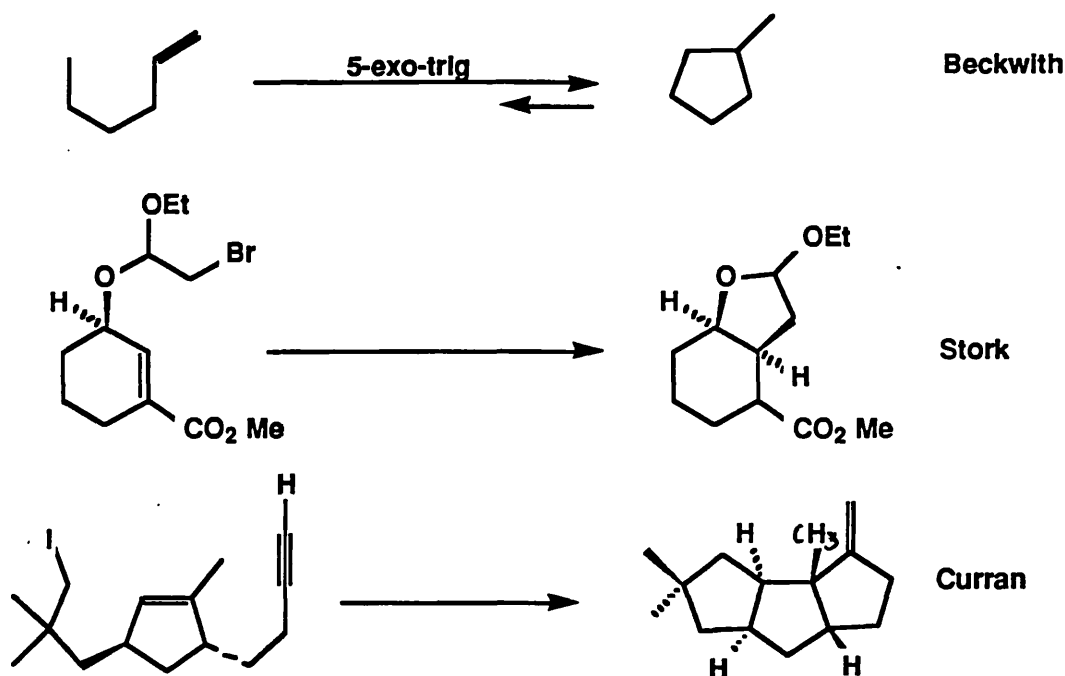
Scheme 13

Although free radical chemistry has not been extensively exploited within the last decade⁽²⁶⁾, it has several advantages over the more traditional carbonium ion and carbanion chemistry. Radicals are neutral and therefore require less solvation. Accordingly they are less prone to steric hindrance or polar effects. Some homolytic radicals substitution reactions are given in Scheme 14⁽²⁷⁾.



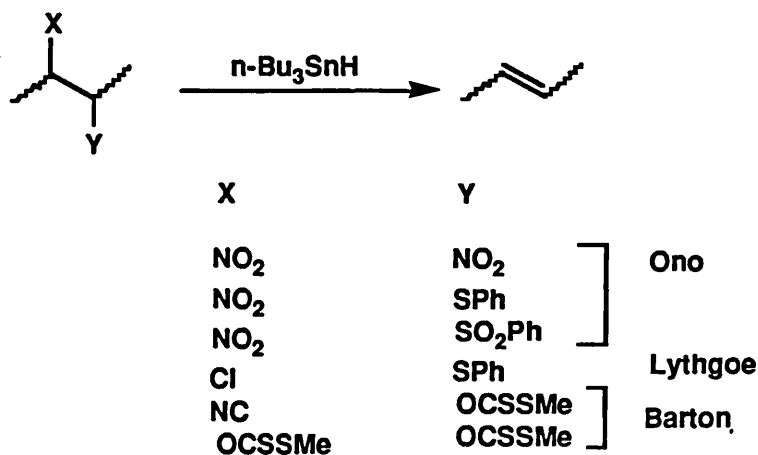
Scheme 14

Radical addition reactions have been notably exploited in cyclisation reactions to form five membered rings. The favoured 5-exo-trig reaction⁽²⁸⁾ was initially studied by Beckwith⁽²⁹⁾ and later used by Stork⁽³⁰⁾ and Curran⁽³¹⁾ in natural product synthesis (Scheme 15). Curran's⁽³¹⁾ system involved a tandem cyclisation, the second cyclisation involving a 5-exo-dig reaction⁽²⁸⁾.



Scheme 15

Tri-*n*-butyl stannane initiated elimination reactions have been studied by Ono⁽³²⁾, Lythgoe⁽³³⁾ and Barton⁽³⁴⁾, Scheme 16.

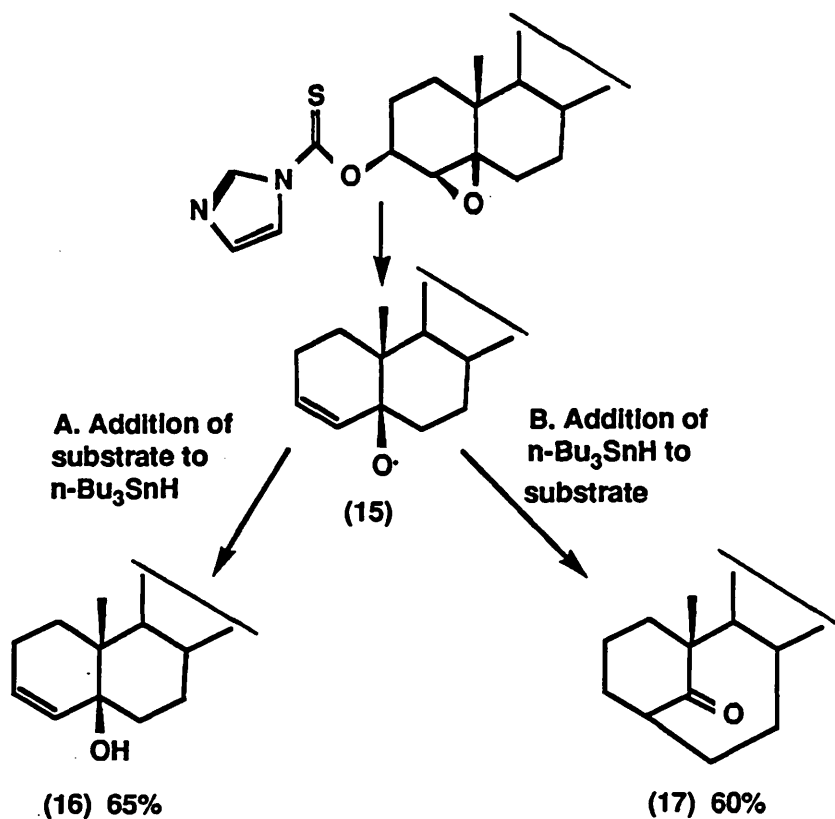


Scheme 16

Homolytic fission of the C-X bond by the tri-*n*-butyl tin radical subsequently results in

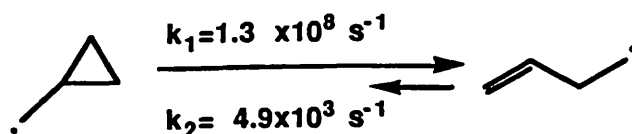
elimination of the relatively stable $Y\cdot$ radical and formation of an alkene.

However, one fundamental class of reaction in free radical chemistry is relatively unexplored, that of rearrangement reactions. Barton, Hay-Motherwell and Motherwell⁽³⁵⁾ have provided an example using tri-*n*-butyl stannane to initiate opening of the epoxide unit in (15) which is then either quenched by *n*-Bu₃SnH, by route A providing compound (16), or many undergo a rearrangement reaction, by route B, to yield (17), Scheme 17. Route B can be reasoned by the selective cleavage of a C-C bond to provide the ketone and a primary radical followed by a favoured 7-exo-trig cyclisation and secondary radical quenching by *n*-Bu₃SnH.



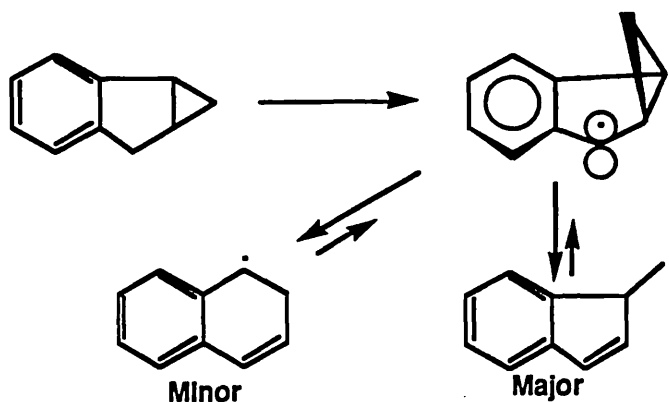
Scheme 17

In a similar fashion we wished to induce radical ring opening of the cyclopropane entity of vinyl cyclopropane substrates (see Scheme 13). The cyclopropyl carbinyl radical rearrangement, shown in its simplest form in Scheme 18,



Scheme 18

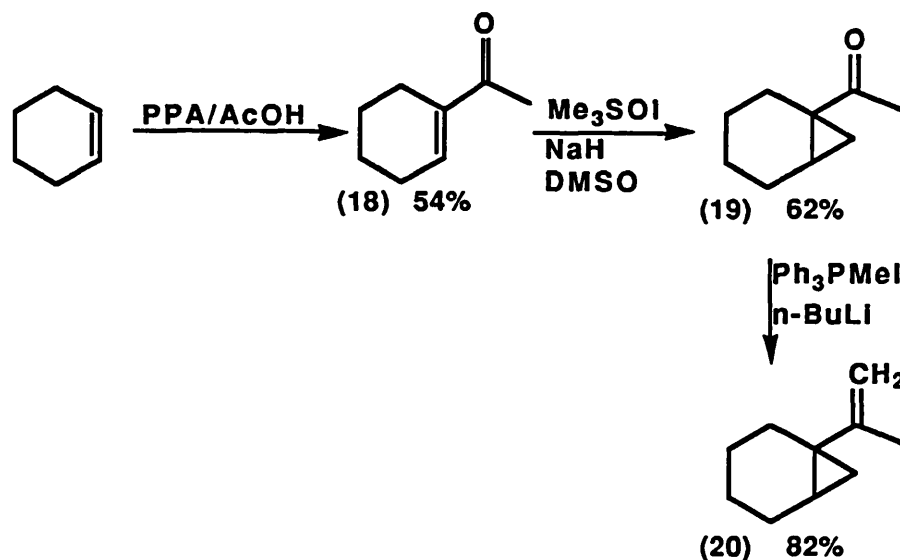
was studied by Ingold⁽³⁶⁾ and accurate rate data were established. This "radical clock"⁽³⁷⁾ has subsequently served as a very useful mechanistic probe⁽³⁸⁾ and a "rate of reaction guide" to other competing radical reactions⁽³⁹⁾. The cyclopropane ring opening is also regioselective by virtue of stereoelectronic overlap control (Scheme 19)⁽³⁸⁾.



Scheme 19

3.2.1. Diphenyl Disulphide, Diphenyl Diselenide and Dibenzyl Disulphide.

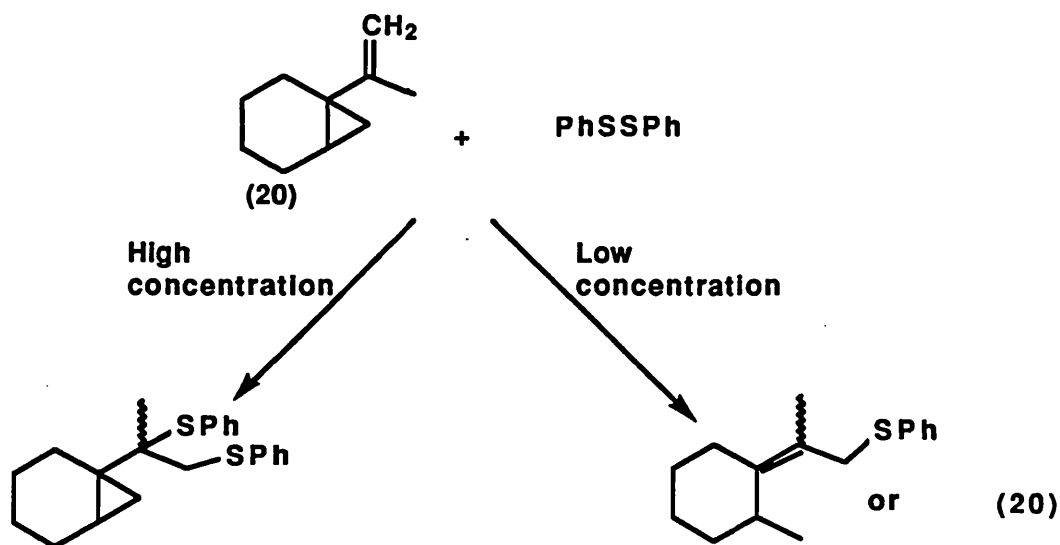
Our initial studies on the vinyl cyclopropane rearrangement reaction used the substrate (20). This was conveniently synthesised from cyclohexene by the three step procedure shown in Scheme 20.



Scheme 20

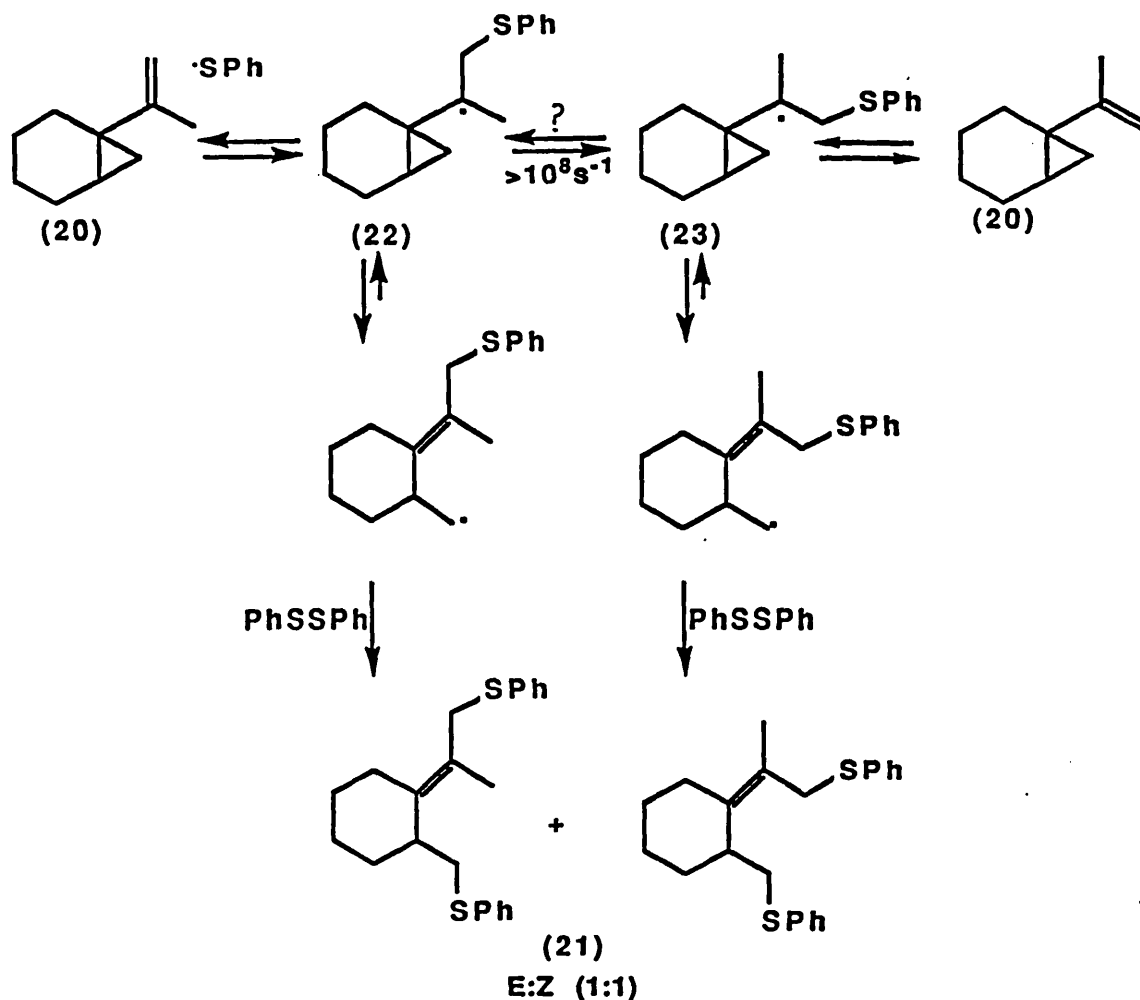
Cyclopropanation of 1-acetyl-1-cyclohexene (18) to provide 1-acetyl-bicyclo[4.1.0]heptane (19) was achieved in reasonable yield using the Corey and Chaykovsky⁽⁴⁰⁾ method. This involved generation of dimethyloxosulphonium methylide by sodium hydride which undergoes methylene transfer to the electrophilic C=C unit of the α - β -unsaturated ketone. The compound (19) could then provide 1-(2-propenyl)bicyclo[4.1.0]heptane (20) by a standard Wittig reaction⁽⁴¹⁾.

Initially we chose to explore some classical systems. Diphenyl disulphide is known to undergo radical additions to carbon carbon double bonds giving 1,2-*bis*-monosulphides in good yield⁽⁴²⁾. Under very dilute conditions, diphenyl disulphide can also be used for *cis*, *trans* isomerisation of non-conjugated olefins without double bond migration⁽⁴³⁾. Hence before we commenced our studies we knew diphenyl disulphide would add to a C=C bond but we did not know the conditions required for cyclopropyl-carbinyl-radical cyclopropane ring opening. The relative concentrations of reagent and substrate in reaction mixture is an important factor. A high concentration led to quenching of the cyclopropyl carbinyl radical before ring opening, whilst low concentration could lead to competitive hydrogen abstraction from the solvent. This is depicted in Scheme 21.



Scheme 21

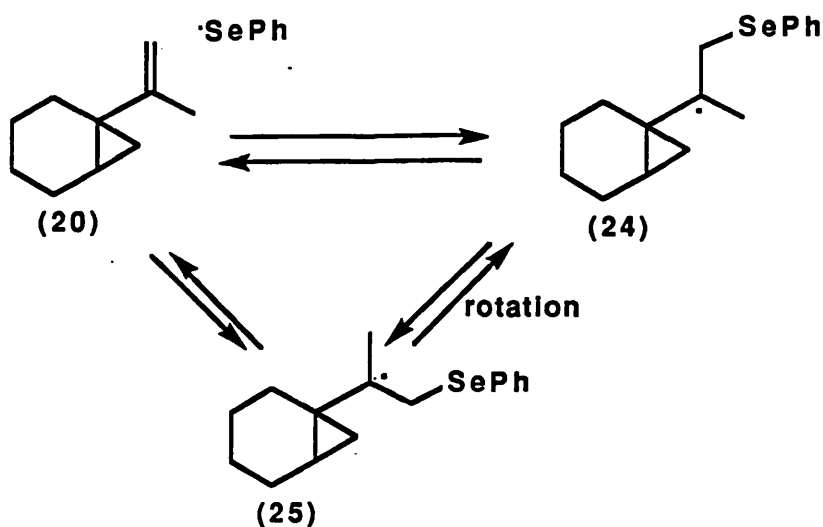
Use of one equivalent of diphenyl disulphide with the substrate (20) in dry benzene ($5 \times 10^{-3}\text{M}$) under photolytic conditions provided no isolated phenylthio ethers, and the substrate was quantitatively reclaimed. However, increasing the concentration to 370 mM provided the diphenyl disulphide adduct (21) exclusively. The yield was low (18%), and the product had to be isolated using preparative plates to remove contaminating unreacted diphenyl disulphide. A reaction mechanism is given in Scheme 22, and as indicated led to a mixture of the E and Z double bond isomers of (21) in equal ratio.



Scheme 22

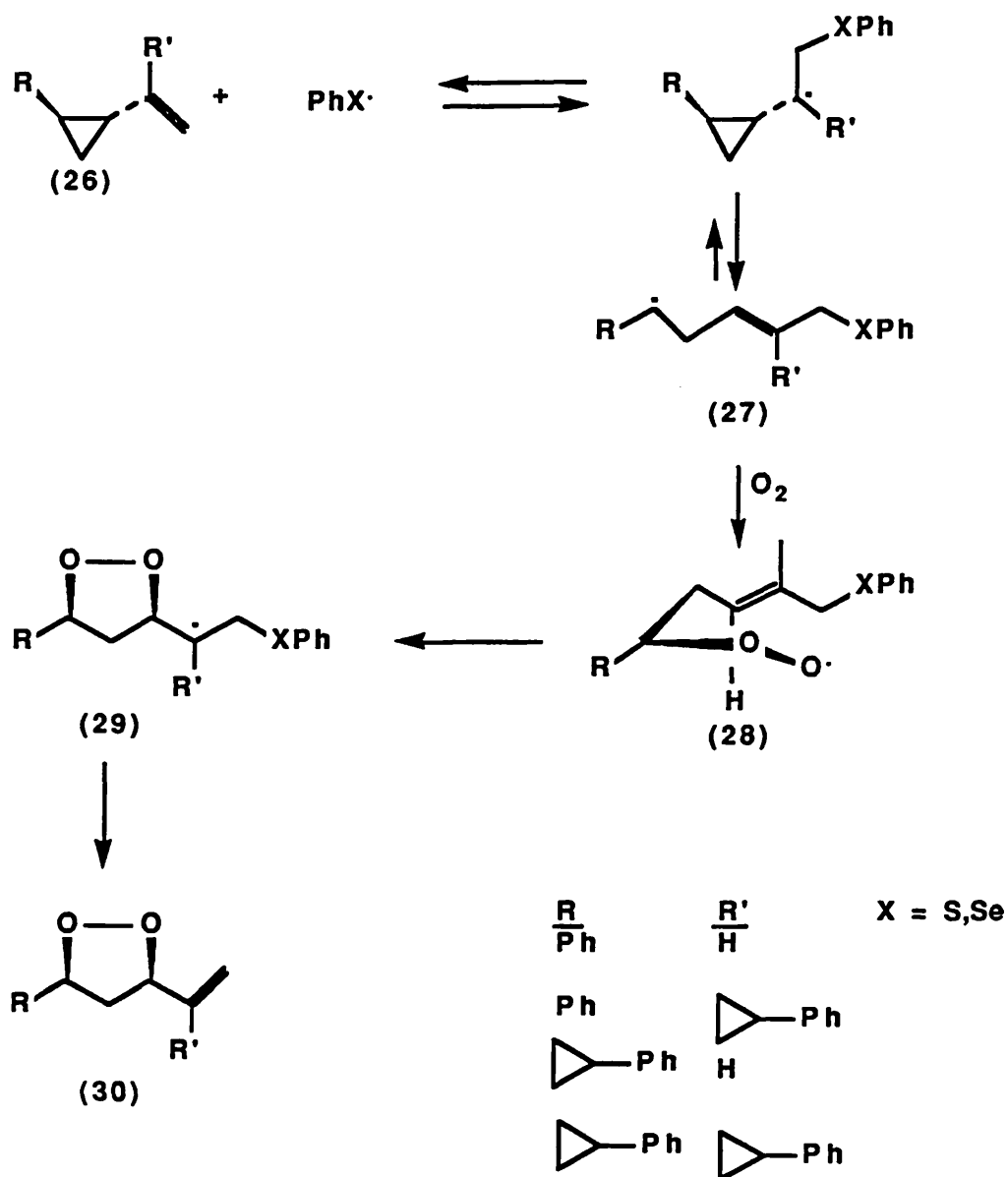
The isomers were detected by proton nmr which gives two singlets for the methyl group, both of equal intensity at $\delta 1.68$. From the above reaction, it therefore follows, that diphenyl disulphide, when homolytically cleaved by photolysis can provide cyclopropyl carbinyl radical ring opened products if a favourable dilution factor was used. Ultrasonication of the same reaction system provided no products; indicating that the sulphur sulphur bond of the reagent will remain intact under sonication.

Unlike diphenyl disulphide, diphenyl diselenide could not be persuaded to undergo addition to the C=C bond of (20) to yield a cyclopropyl ring opened product. Several dilution factors were tested under photolytic and sonication conditions, and all provided reclaimed starting material. Since phenyl seleno radicals, formed by irradiation, are known to promote double bond isomerisation⁽²⁶⁾ we are forced to conclude that the reversible expulsion of PhSe $\cdot$ from the intermediates (24) and (25) in Scheme 23 occurs at a faster rate than the competing ring opening reaction.



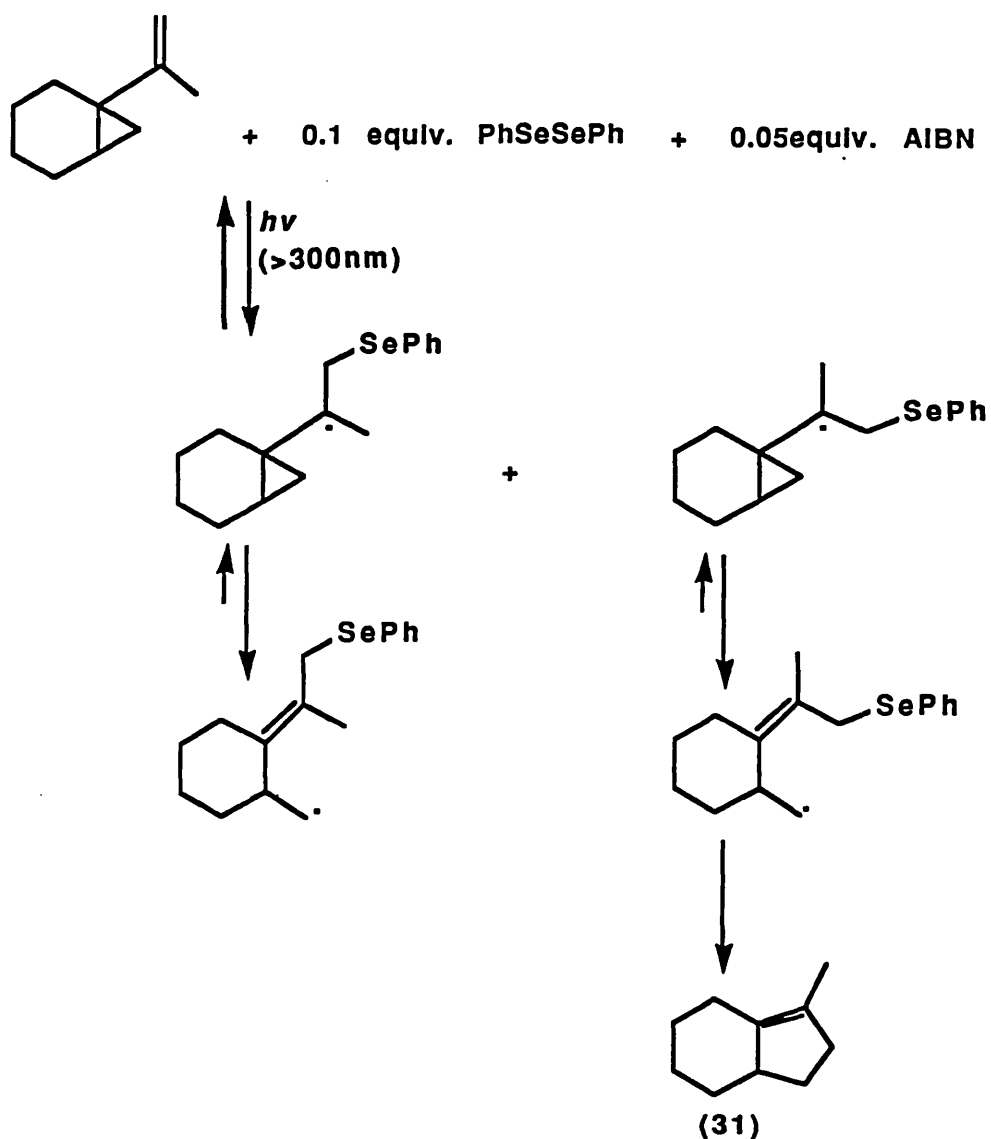
Scheme 23

While our work was in progress, Feldman and coworkers⁽⁴⁴⁾ used diphenyl diselenide and diphenyl disulphide in the presence of 0.5 equivalents of the radical initiator AIBN to open the cyclopropane ring of vinyl cyclopropanes (26). The secondary carbon radical of the intermediates⁽²⁷⁾ was then quenched by dioxygen to yield a peroxy radical (intermediate (28) which *via* a 5-exo-trig cyclisation yielded (29). Expulsion of the sulphur or selenide radical then gave the dioxolane species (30) (Scheme 24).



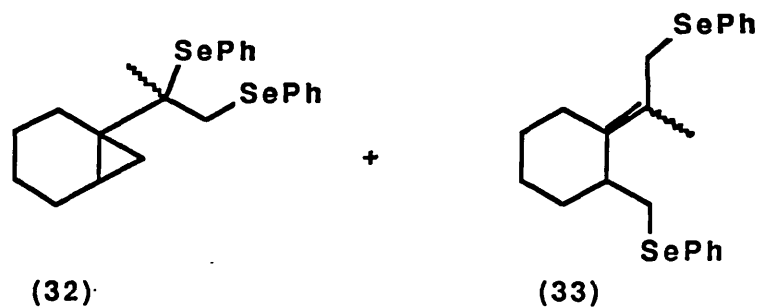
Scheme 24

We decided to reproduce the above reaction conditions in the hope that under anaerobic conditions and in the presence of a catalytic amount of diphenyl diselenide the vinyl cyclopropane-cyclopentene rearrangement might be achieved yielding compound (31) (Scheme 25).

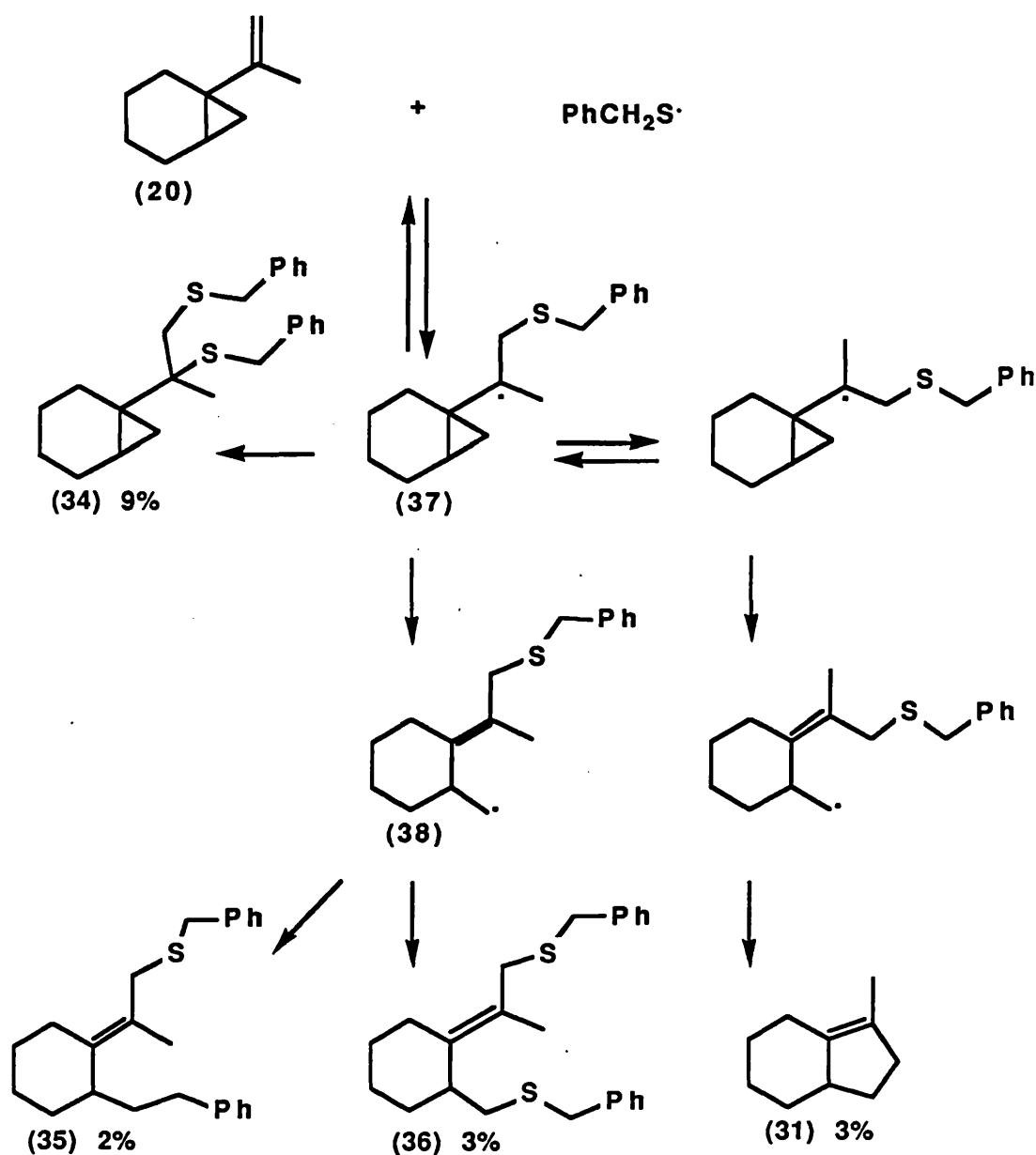


Scheme 25

We found however, that the formation of (31) did not occur but that the presence of AIBN did promote the formation of phenyl selenide adducts to the substrate vinyl cyclopropane (20). The products were characterised by proton nmr which suggested structures (32) and (33) as the selenide containing species formed as by products in the catalytic system.



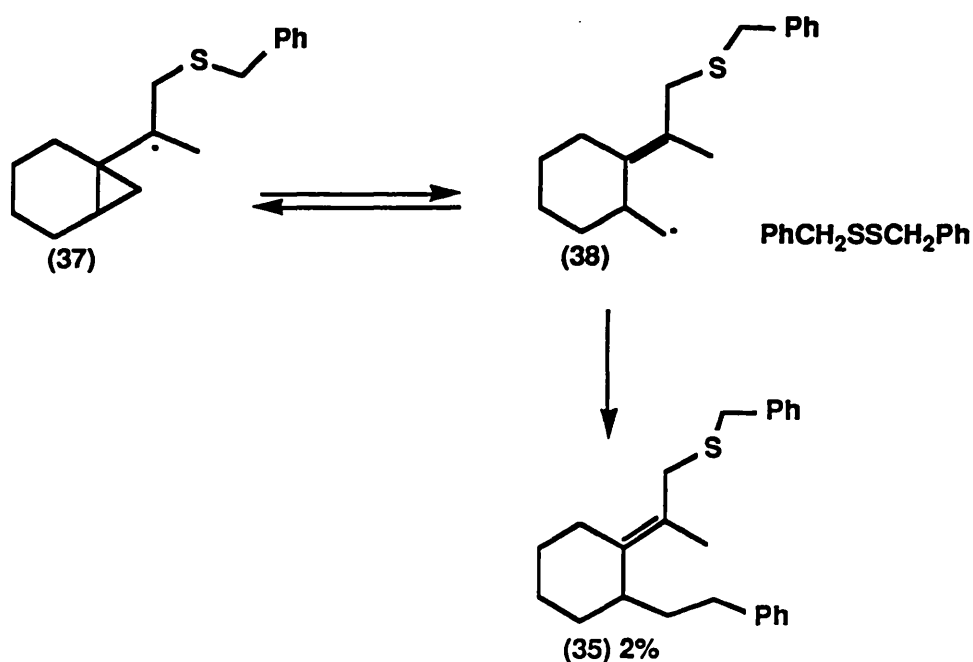
Surprisingly, in contrast to the use of diphenyl disulphide, one equivalent of dibenzyl disulphide under photolytic conditions provided four products characterising as compounds (34)-(37) (Scheme 26).



Scheme 26

Dibenzyl sulphide and 1,2-diphenyl ethane were also identified as by-products. The yields of the reaction are extremely low; however, no vinyl cyclopropane substrate could be reclaimed and most of the product mixture was base line material which could not be identified. The products were isolated by preparative plates to exclude

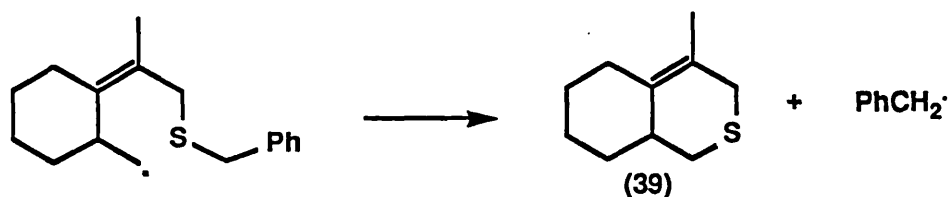
contamination by the by-products, and also by dibenzyl disulphide. Product (36) is similar to that observed in the diphenyl disulphide reaction system (see Scheme 22). However, in the dibenzyl disulphide case only one double bond isomer was observed and was designated as the E isomer (36) by consideration of the steric bulk of the benzyl sulphide group. Even though a lower concentration was used in this reaction system (0.18M) compared to the diphenyl disulphide system (0.37M), less than 50% of the observed products resulted from cyclopropyl carbinyl radical ring opening. The major product (34) is obtained from dibenzyl disulphide quenching of the species (37) before ring opening. Decomposition of the disulphide is also evident by the formation of dibenzyl sulphide, 1,2-diphenyl ethane and product (35). Compound (35) is probably derived according to Scheme 27, although cleavage of a C-S bond appears unlikely compared to the available disulphide bond.



Scheme 27

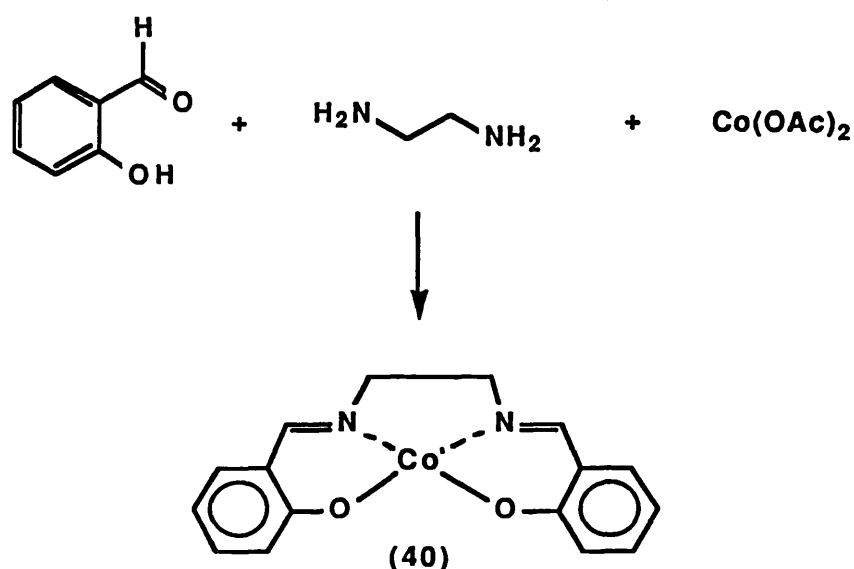
By proton nmr, compound (35) was formed as one stereoisomer, which was presumed to be the E isomer by consideration of the steric factors involved. Formation of the cyclopentene (31) provided the first case of a free radical initiated vinyl cyclopropane-cyclopentene reaction. However, the yield could not be increased either by higher dilution factors or by making the reaction system catalytic with respect to dibenzyl disulphide. From our results with the diphenyl disulphide system we could not predict

the formation of (31). A route to the species (39) was considered to be more likely, but results showed that this reaction (Scheme 28) did not occur.



Scheme 28

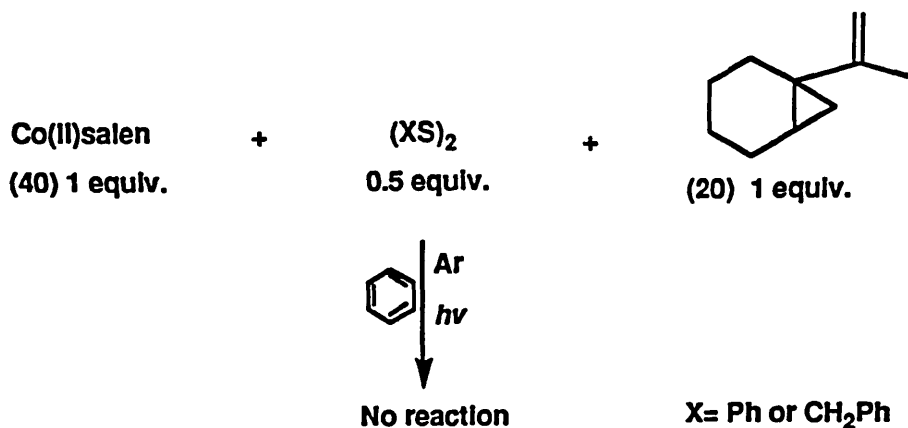
With a knowledge of the above reaction systems in hand we then attempted to modify them by incorporating cobalt(II) chemistry. Synthesis of the cobalt(II) salen complex (40) was achieved using the method shown in Scheme 29⁽⁴⁵⁾ and the complex (40) was obtained analytically pure.



Scheme 29

The species (40) is of high spin and paramagnetic and required storage under an argon atmosphere to prevent decomposition. Subjecting a mixture of the Co(II) chelate complex (40) and one equivalent of the vinyl cyclopropane (20), in a deoxygenated benzene solution, to irradiation provided only reclaimed starting material. Hence the species (40) was not sufficiently electrophilic to allow the vinyl cyclopropane-cyclopentene rearrangement reaction as suggested in Scheme 12. Using one equivalent of (40) and (20) to half an equivalent of diphenyl disulphide or dibenzyl disulphide as

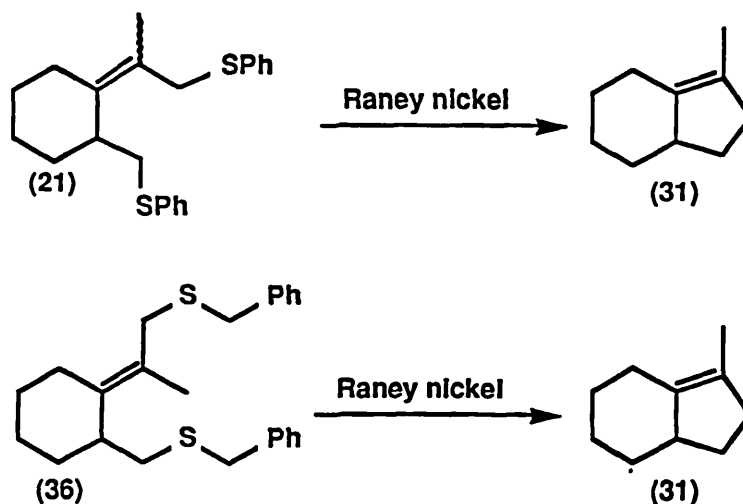
shown in Scheme 30, also provided the reclaimed vinyl cyclopropane (20). *A priori* we knew that the disulphide reagents would react with the substrate (20) under photolytic conditions.



Scheme 30

Thus the Co(II) salen complex (40) must be inhibiting the reaction. To explain this we suggest that inhibition results from addition of the intermediate sulphide radicals to the chelate complex (40). The cobalt-sulphur bonds thus formed are stronger than the alternative cobalt-carbon bonds, consequentially less prone to homolytic cleavage, and thus the reaction system is hindered.

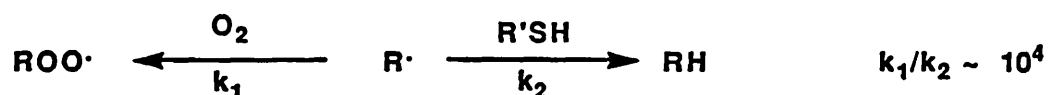
Although we did not take the studies any further due to the low yields generally observed the next step was to test use of Raney nickel to desulphurise the compounds (21) and (36) thus forming the cyclopentene (31) (Scheme 31).



Scheme 31

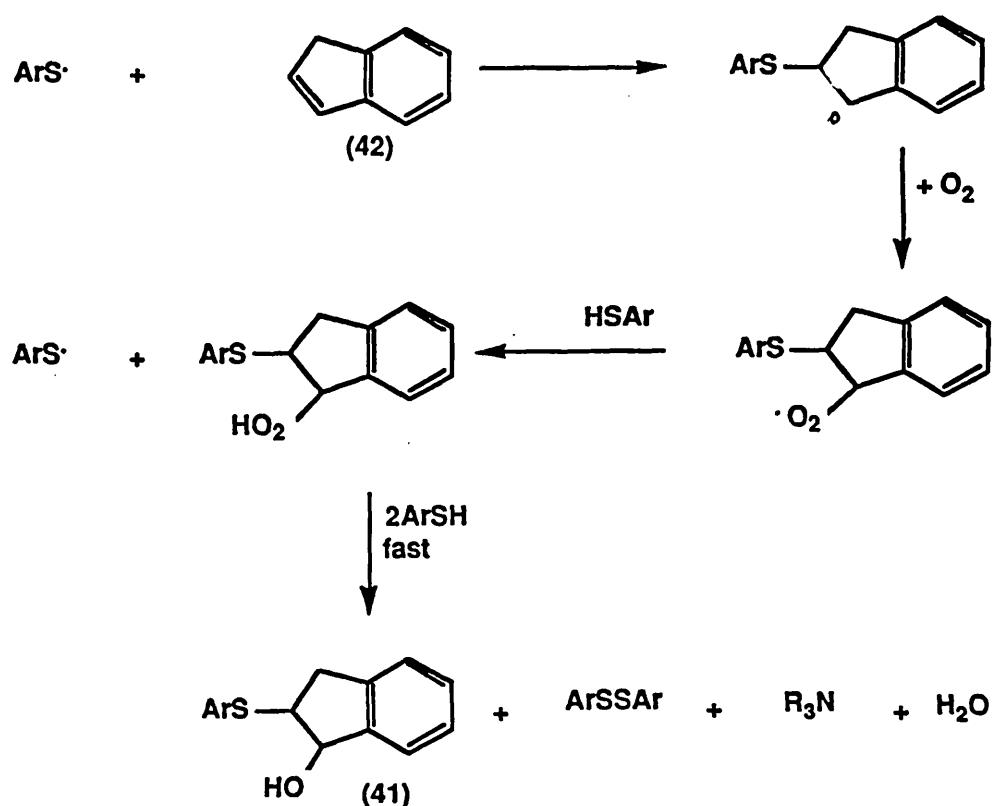
3.2.2. Thiophenol and Oxygen

The rate of trapping of an organic free radical by oxygen has been measured to be approximately 10^4 times faster than the comparable trapping reaction with thiols (Scheme 32)(46).



Scheme 32

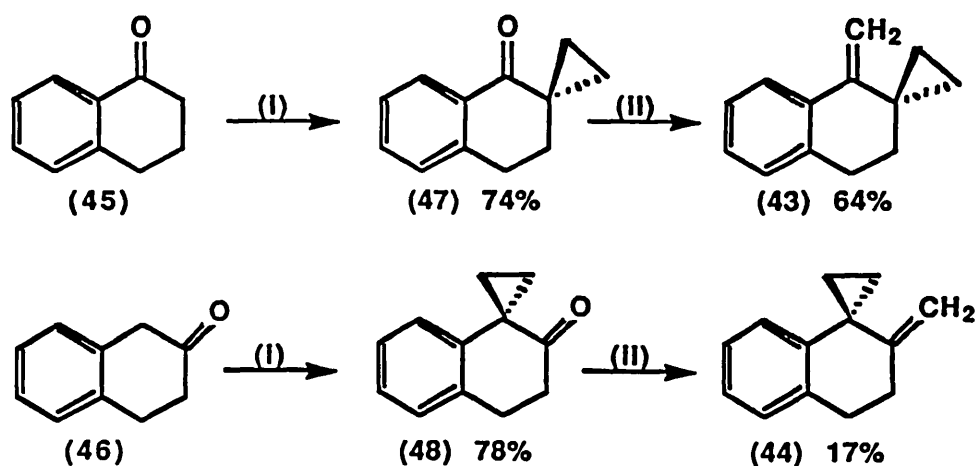
Oswald and coworkers(47) used this principle to devise a mild cooxidation technique for the formation of the 1-hydroxy-2-thiol derivative (41) from the substrate (42). The mechanistic pathway is given in Scheme 33.



Scheme 33

The reaction includes the use of three equivalents of thiol, a catalytic amount of aliphatic amine, an oxygen atmosphere and an n-heptane solvent system at room temperature. Photolysis is not required.

We wished to examine this reaction to achieve ring-opening functionalisation of vinyl cyclopropanes. It was important in devising reaction conditions to provide the necessary oxygen concentration to permit cyclopropane ring opening prior to trapping of the resultant alkyl radical to form a peroxy radical intermediate. In practice the rate of trapping of an alkyl radical by molecular oxygen is comparable to that of cyclopropyl carbinyl radical ring opening and thus a finely balanced system ensues which depends not only on the oxygen concentration but also on the nature of the vinyl cyclopropane employed. The substrates tested in this free radical approach included (20), (43) and (44). The vinyl cyclopropanes (43) and (44) were synthesised by a two step procedure (Scheme 34) from α -tetralone (45) and β -tetralone (46), respectively.

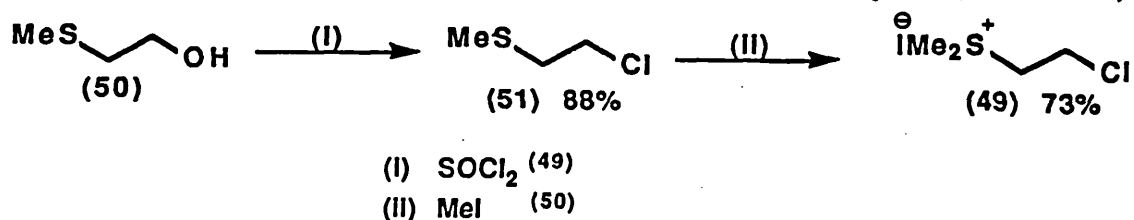


(I) $\text{KO}^t\text{Bu}^t/\text{Bu}^t\text{OH}/\text{ClCH}_2\text{CH}_2\text{SMe}_2\text{I}$

(II) $\text{Ph}_3\text{PMel}/n\text{-BuLi}$

Scheme 34

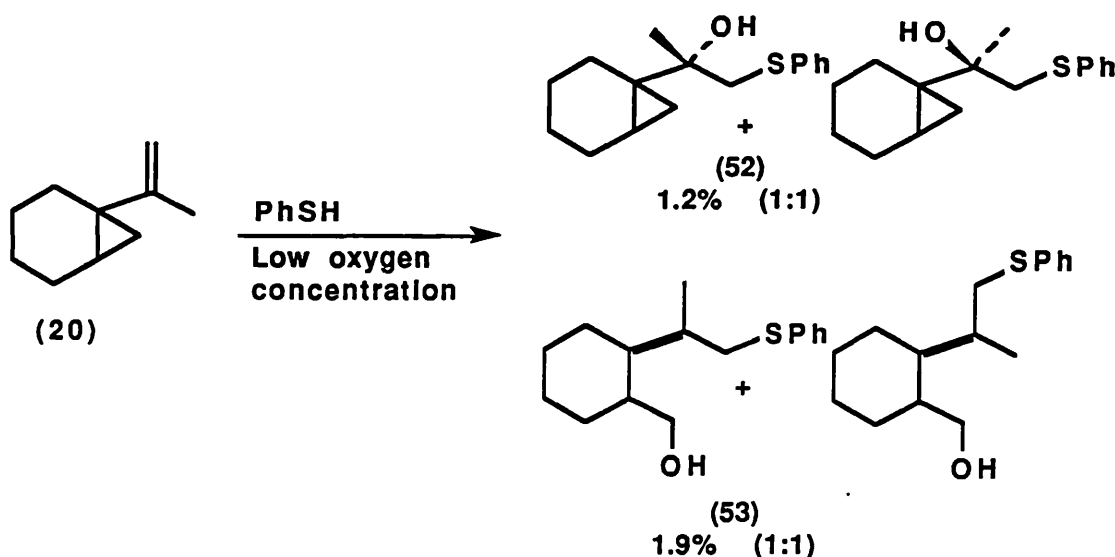
The method of Ruder and Ronald⁽⁴⁸⁾ was used for the spiro-cyclopropanation step and the requisite reagent, 2-chloroethyl dimethyl sulphonium iodide (49), was conveniently prepared by a two step synthesis from 2-(methylthio)ethanol (50) by halogenation and subsequent methyl iodide addition to 2-chloroethyl methyl sulphide (51) providing the unstable sulphonium salt (49) in reasonable yield (Scheme 35).



Scheme 35

The spirocyclopropanated, crystalline compounds (47) and (48) were obtained in a good yield. Although the Wittig reaction (41) was successful when applied to the conjugated ketone substrate (47), its application to compound (48) was low yielding. Attempts to increase the yield by increasing the amount of Wittig salt used by up to three fold, failed to enhance the yield of (44). The latter, (44), is an air stable colourless liquid, however, (43) is extremely air sensitive, a fact which may be predicted by considering its styrene type structure. Consequently, (43) must be stored in the absence of oxygen to prevent polymerisation which provides a white, crystalline solid.

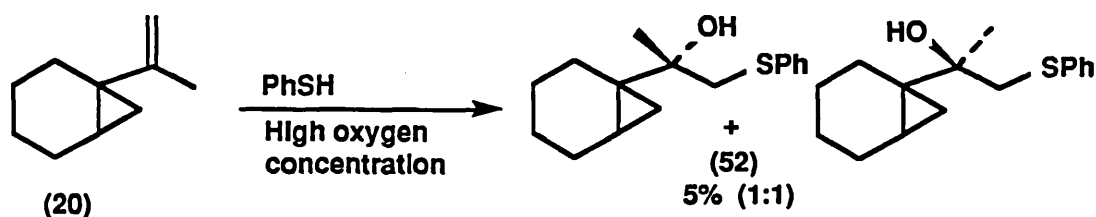
Initial attempts using the PhSH/O₂ method employed the substrate (20). A solution of thiophenol in n-heptane was added very slowly to a mixture of (20) and *t*-butylamine in the same solvent. The oxygen atmosphere was provided by a balloon of oxygen only, and the reaction solvent, and the system was left for several days until tlc analysis confirmed the absence of the substrate (20). Two products were isolated by means of preparation plates and were characterised as the species (52) and (53) (Scheme 36).



Scheme 36

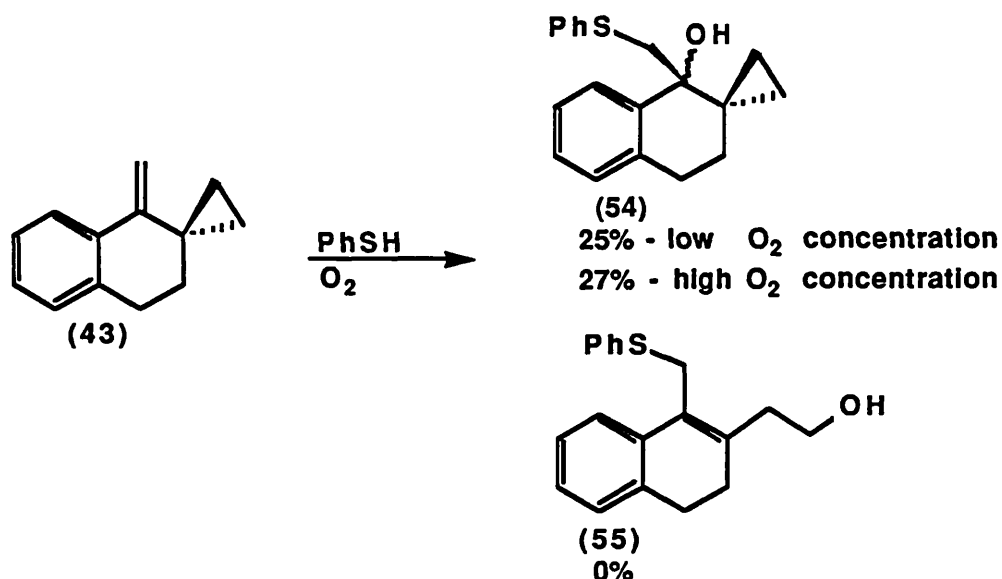
Both compounds were obtained in extremely low yields, the major part of the reaction concentrate being polar base-line material. Proton nmr analysis concluded that both (52) and (53) existed as a 1:1 mixture of their two stereoisomers, respectively. This was concluded by the presence of two singlets for the appropriate methyl group resonance in each case. Proton nmr also recorded the CH_2SPh entity of (52) as two sets of double doublets.

If a high oxygen concentration is used, formation of compound (52) (Scheme 37) occurs exclusively but again in very low yield. The technique involves bubbling oxygen through the solvent system during the reaction so the system is always saturated. To achieve specific formation of compound (53), very low oxygen concentrations must be required.



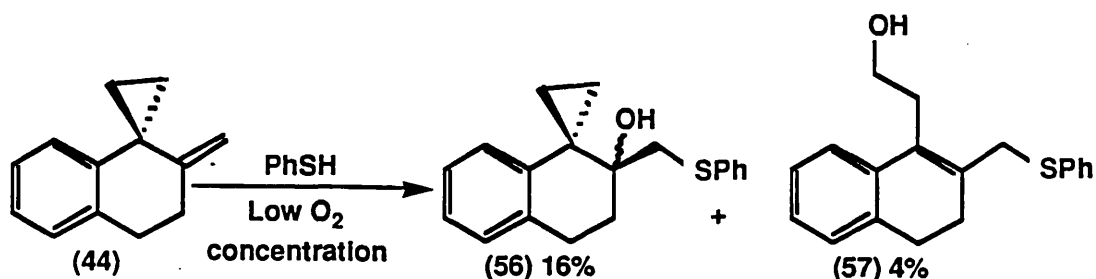
Scheme 37

Use of the tetralone derivatives (43) and (44) produced higher yields for the thiophenol reaction system. The styrene type species (43) gave only the product of direct addition to the double bond, compound (54) and the formation of the rearranged product (55) could not be detected even at very low oxygen concentrations (Scheme 38).



Scheme 38

In this example, the rate of cyclopropyl carbanyl radical initiated ring opening of the cyclopropane ring is almost decreased because of stabilisation of the radical by delocalisation into the benzene ring. Hence radical capture is dominated by oxygen (radical capture by oxygen is approximately 10^2 times faster than α -cyclopropane ring opening in the basic system (see Scheme 18)). Use of the air sensitive compound (43) required a change of reaction conditions to prevent polymerisation; the thiophenol was added to a solution of (43) in *n*-heptane at a faster rate concomitant with the introduction of oxygen gas. Formation of α -tetralone (45) also prevailed in this reaction. Substrate (44), in the presence of thiophenol, *t*-butylamine and a low concentration of oxygen, gave a mixture of products (56) and (57) in overall 20% yield (Scheme 39).

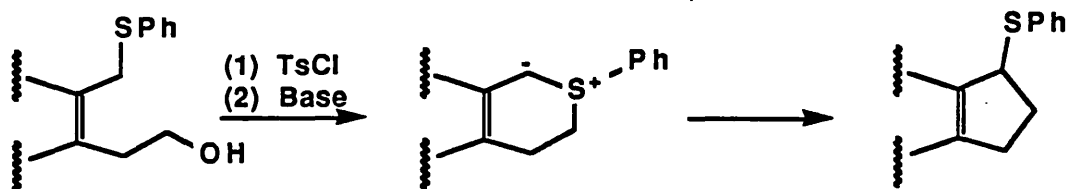


Scheme 39

Once again, however formation of the spiro-cyclopropanated derivative (56)

predominated.

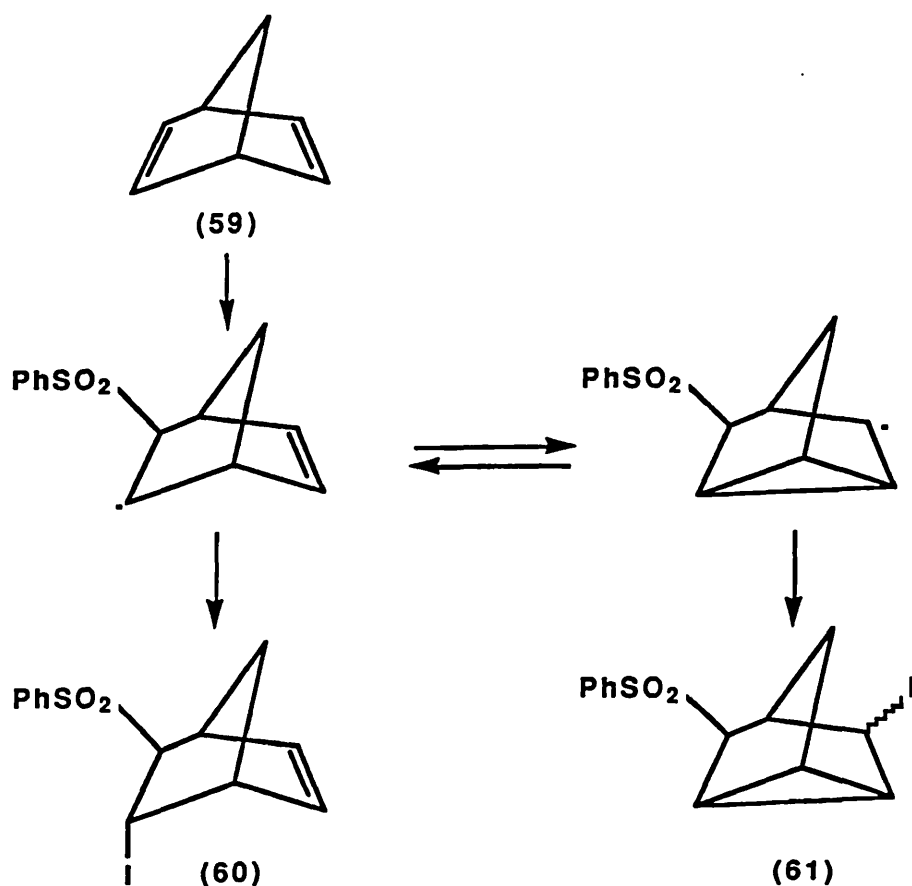
Although the foregoing reactions have demonstrated that the thiophenol/oxygen system can lead to ring opening of vinyl cyclopropanes, the technique is too low yielding for the required products and too dependent on controlled oxygen concentration, to allow a useful synthetic tool to be developed. With this knowledge, the second stage of our procedure (Scheme 40) to yield the substituted cyclopentene (58) was not performed.



Scheme 40

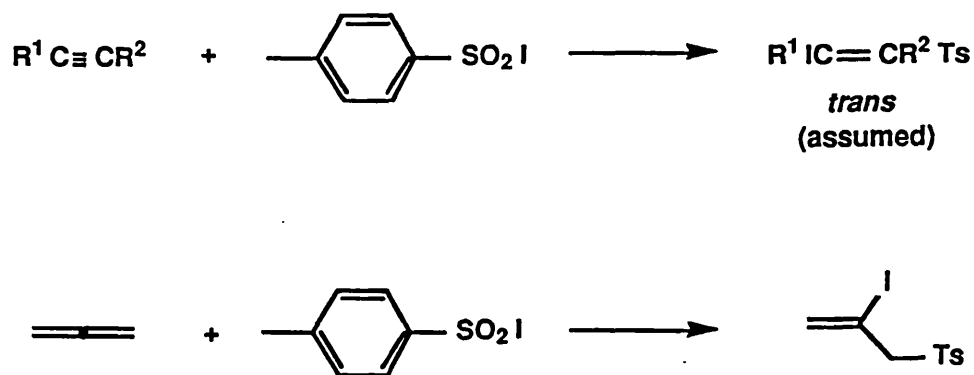
3.2.3. Tosyl Iodide

An alternative reagent which fulfills the necessary criteria outlined in Scheme 13, whereby X is a carbanion stabilising group and Y is a leaving group, was then selected through use of tosyl iodide. In the early 1960's Cristol *et al.*⁽⁵¹⁾ studied the free radical mediated addition of phenyl sulphonyl iodide to norbornadiene (59) (Scheme 41).



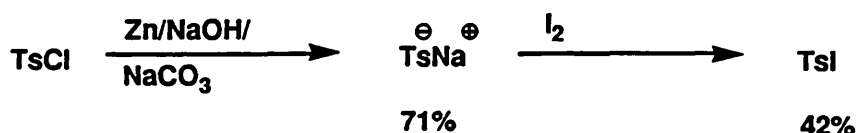
Scheme 41

The experiment was performed in the solvent, chlorobenzene, and did not require irradiation to homolytically cleave the S-I bond; mild thermal inducement was sufficient. A mixture of the compounds (60) and (61) was formed, the latter predominating. Truce and Wolf⁽⁵²⁾ later employed tosyl iodide to yield derivatives of acetylenes and allenes (Scheme 42); in this instance illumination was used to accelerate homolytic scission of the S-I bond.



Scheme 42

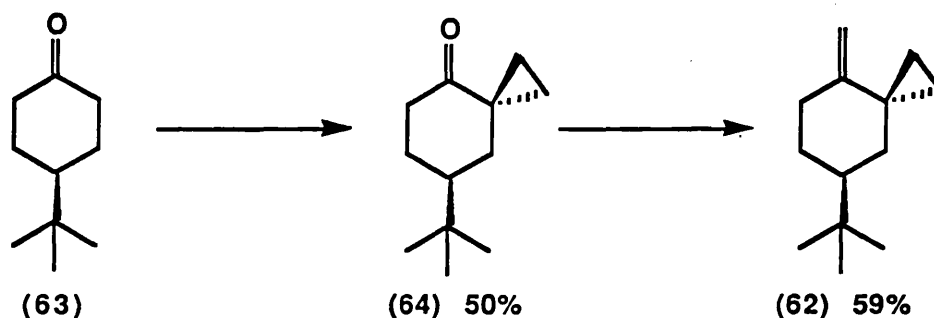
Studies by Waters (53) on the addition of tosyl halides to olefins, determined that tosyl iodide was reactive enough to combine directly with many olefins in daylight, without the addition of a catalyst and at room temperature. In our experiments we decided to use a temperature of 40°C to produce the radical intermediates and to shield the reaction system from light to prevent product decomposition by hydrogen iodide loss. The reagent, tosyl iodide, was synthesised in two steps from tosyl chloride according to Scheme 43.



Scheme 43

Before the tosyl iodide was employed with vinyl cyclopropane substrates, we tested its authenticity on 1-methylcyclohexene. *Trans* addition of tosyl iodide to the double bond system prevailed, in good yield. The *trans* adduct was confirmed by applying the nuclear Overhauser effect. The results are demonstrated in Figure 1, where the irradiated nuclei are depicted in a box.

Our initial work in this area used the substrate 2-methylidene-4-*t*-butylspiro[2.5]octane (62), synthesised by the same route as compounds (43) and (44) (see Scheme 34) (Scheme 44).



Scheme 44

Spirocyclopropanation of the starting ketone (63) proved impossible to achieve in greater than 50% yield for this particular reaction system. Phosphonium ylid treatment of (64) was more successful giving the vinyl cyclopropane (62) in a more acceptable yield.

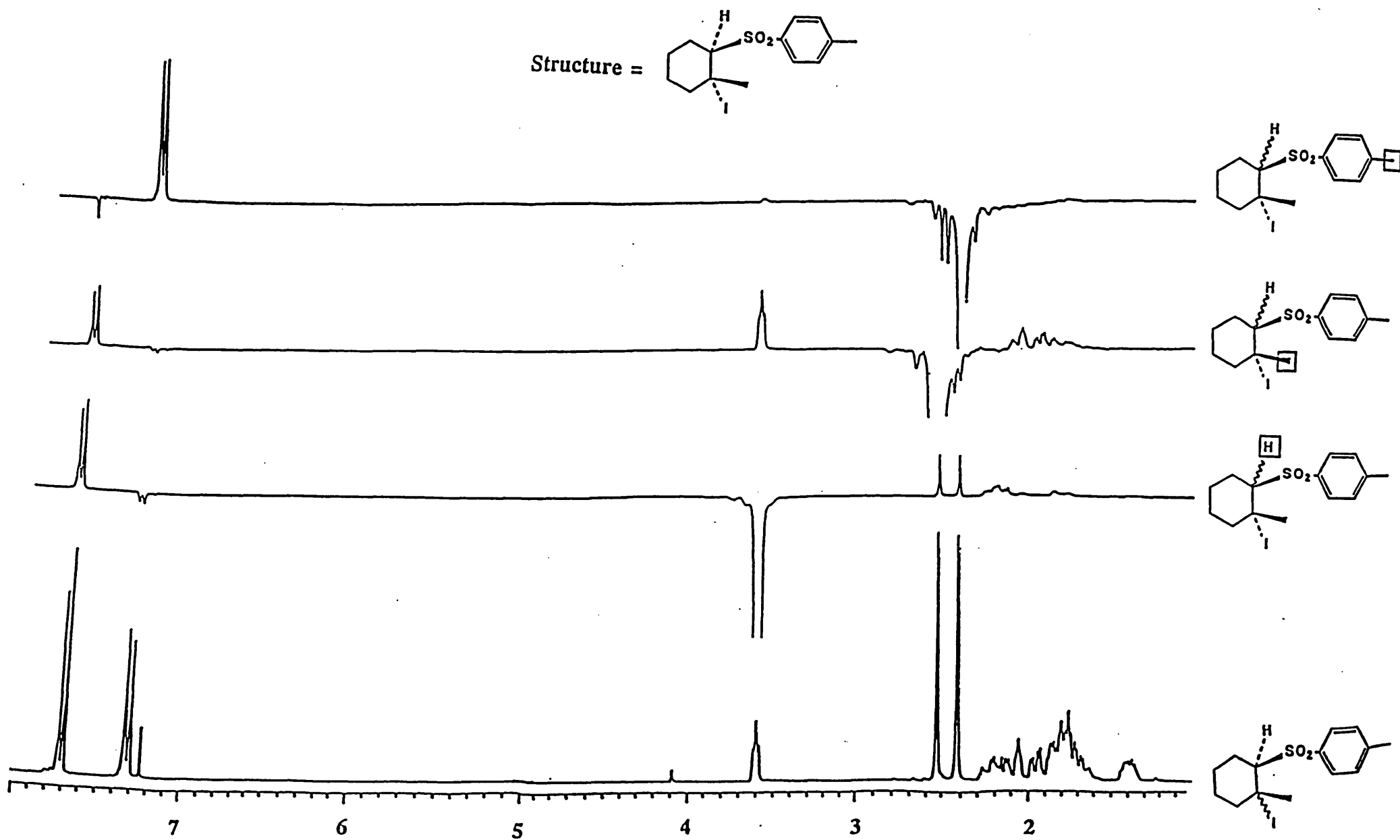
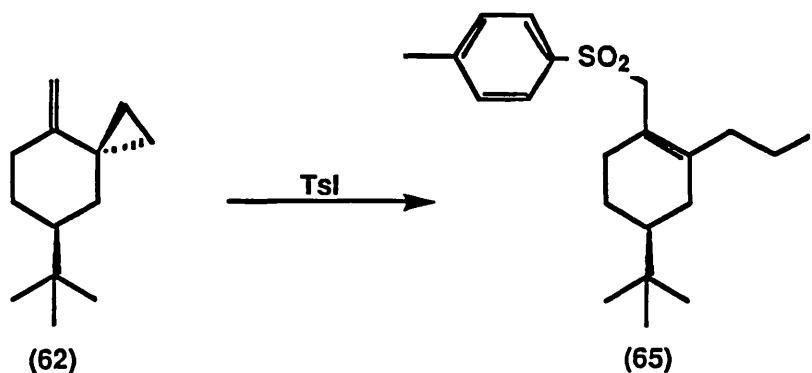


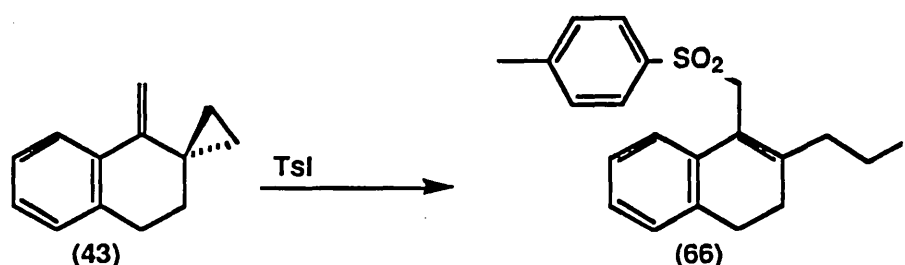
Figure 1

When a solution of one equivalent of tosyl iodide in dichloromethane was added slowly to a solution of the substrate (62) in the same solvent, at 40°C and maintaining rigorously deoxygenated conditions, formation of the tosyl iodide adduct (65) occurred in 47% yield (Scheme 45).



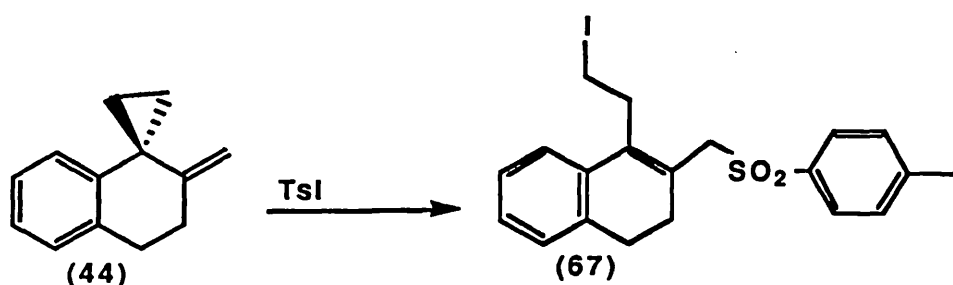
Scheme 45

By modifying the reaction system by reversing the addition procedure and by adding propylene oxide to scavenge protons in the reaction medium, the yield of (65) was increased to 52%. This was not a particularly dramatic effect, but when the modified procedure was applied to the vinyl cyclopropane (43), the yield of (66) was increased from a moderate 42% to effectively quantitative (Scheme 46). This is particularly noteworthy since the intermediate cyclopropyl carbinyl radical is benzylic in this case.



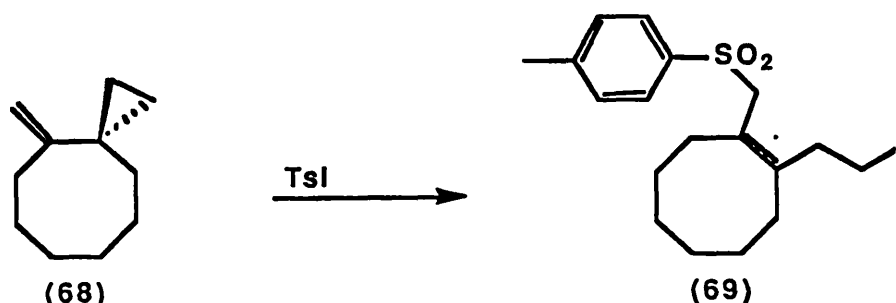
Scheme 46

Tosyl iodide initiated opening of the spirocyclopropane of (44) gave (67) 78% yield (Scheme 47).



Scheme 47

The tosyl iodide method was also successful on the substrate (68) selectively giving the rearranged adduct (69) (Scheme 48)(54).

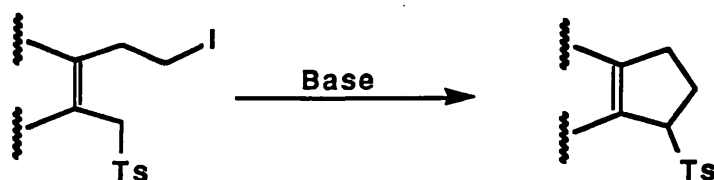


Scheme 48

Undoubtedly, the tosyl iodide procedure for the rearrangement of vinyl cyclopropanes *via* cyclopropane carbonyl free radicals in the most efficient method discovered during this work. We are now confident that similar reaction systems will also mediate the same rearrangement reaction, and they are discussed in section 3.5.

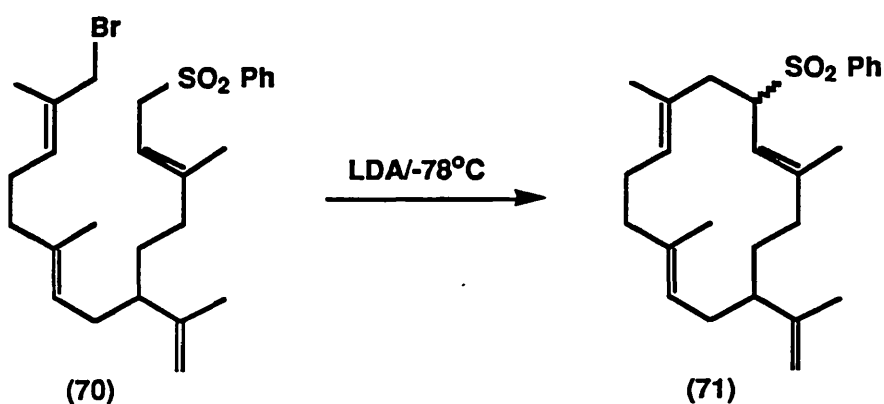
3.3. Anion Reactions of Tosyl Iodide Adducts

Our attention was then focused on the second part of the sequence, *via* ionic ring closure to produce the functionalised cyclopentene skeleton (Scheme 49). In this respect, we were optimistic that ring closure of the allylic sulphone anion would occur exclusively on the heavily inductively stabilised α position, as is well preceded for intermolecular alkylation reactions (55).



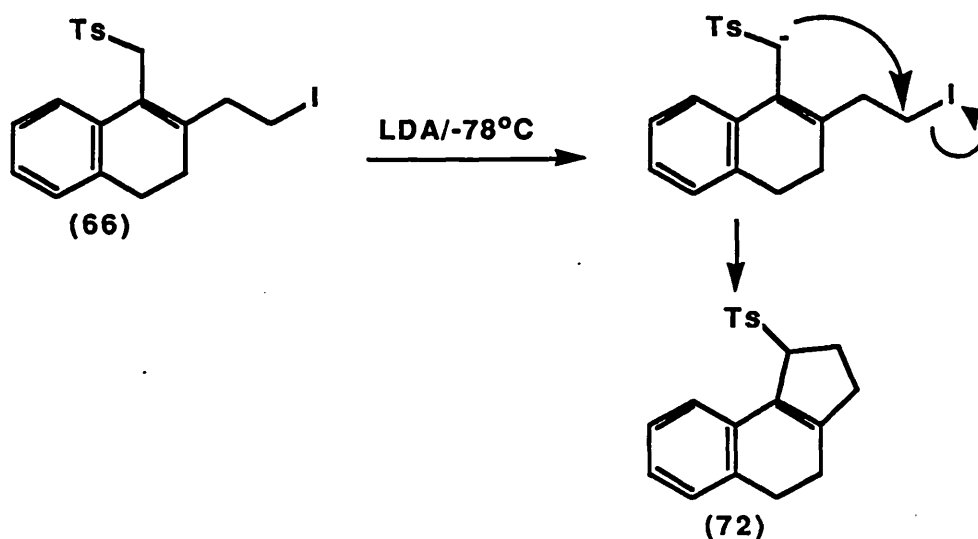
Scheme 49

A particularly striking example of this reaction type is to be found in the work of Kato *et al.* (56) who used lithium diisopropylamide to effect ring closure of the β , γ -sulphone (70) to give species (71) in their synthesis of the cembrene skeleton (Scheme 50). The yield of this transformation was not given.



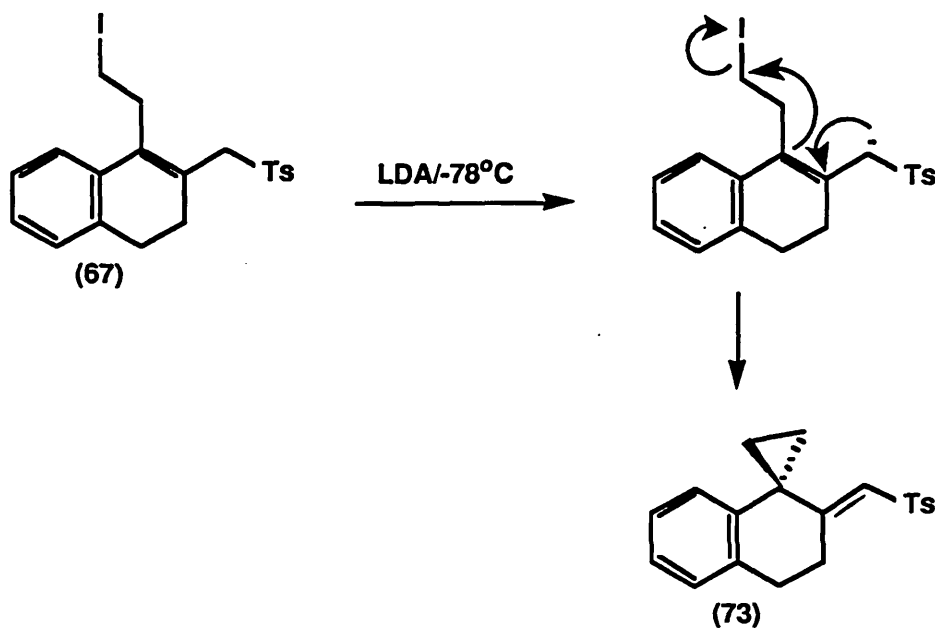
Scheme 50

In the event, however, ionic cyclisation proved to give surprising results. When lithium diisopropylamide was applied to the compounds (65), (66) and (67) efficient ring closure was achieved in only one case. Base induced cyclisation of (66) provided (72) in 92% yield (Scheme 51).



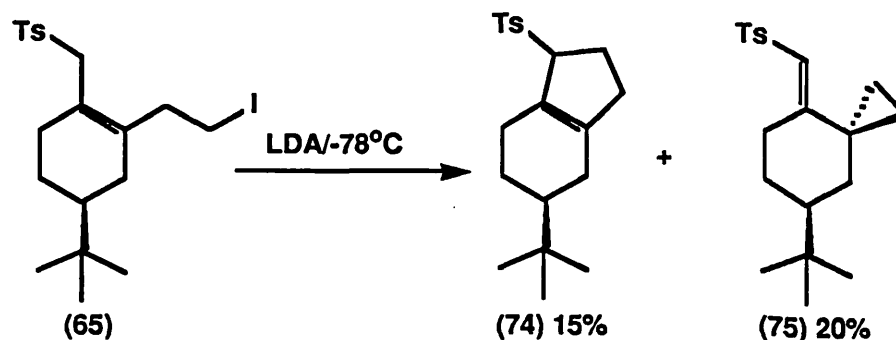
Scheme 51

However, duplication of the reaction conditions for the substrate (67) gave the novel γ alkylation reaction sequence yielding the new vinyl cyclopropane derivative (73) exclusively, plus reclaimed starting material (67) (Scheme 52).



Scheme 52

The tosyl iodide adduct (65) gave a mixture of the two species (74) and (75) in low overall yield (35%) (Scheme 53).

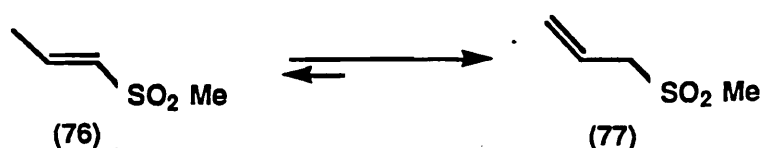


Scheme 53

Changing the base to potassium *t*-butoxide provided the same products in similar yield⁽⁵⁴⁾, hence the nature of the reaction is not dependent on certain bases.

In an effort to explain the anomalous cyclisation behavior our attention was drawn to the proton nmr spectra of the tosyl iodide adducts (66) and (67). In (67) the methyl resonance of the tosyl group lies at δ 2.45, however the tosyl methyl resonance of (66) lies up field at δ 1.84. This implies a positive π -stacking interaction of the tosyl group of (66) with the tetralin benzenoid ring. It is therefore possible that the anion of (66) is held in position, thus allowing the pendant alkyl iodide chain to adopt the required conformation for ring closure to a five membered ring. In structures (65) and (67) where the anionic intermediates have a larger degree of rotational freedom, the bulky tosyl and iodine residues must therefore be oriented in a conformation which allows reaction trajectory to proceed through the normally less favoured γ position.

Formation of α , β -unsaturated sulphones from β , γ -unsaturated sulphones is unprecedented; if we consider the equilibrium study between species (76) and (77) (Scheme 54), it was established that at least 99% of the equilibrium mixture existed in the β , γ -unsaturated form (77)⁽⁵⁷⁾.

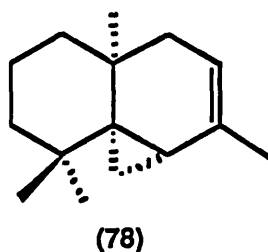


Scheme 54

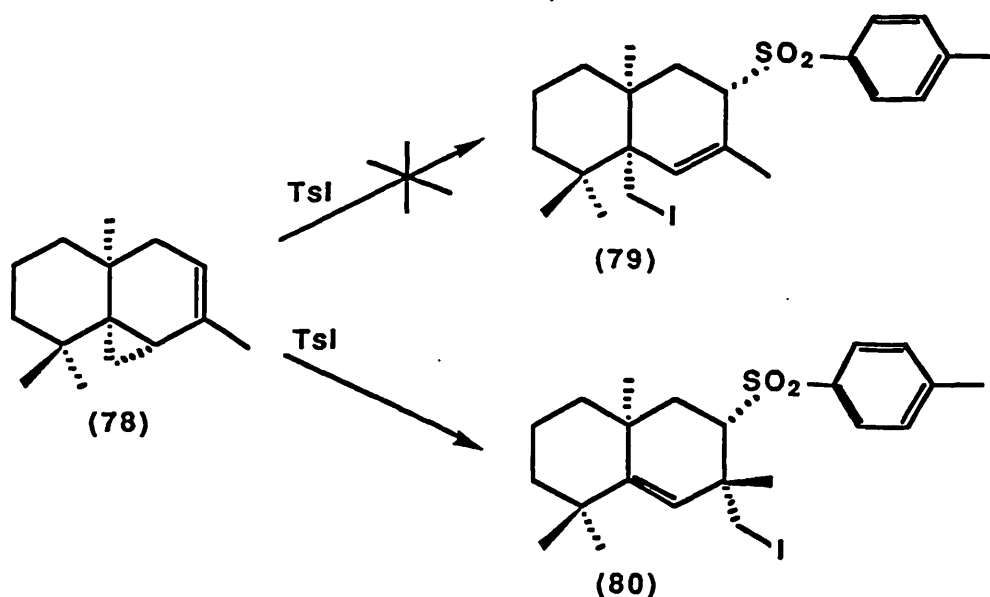
3.4 Tosyl iodide and Thujopsene (78)

As in every research investigation, the reaction of tosyl iodide with thujopsene proved to be an exception to the trend observed in these rearrangement reactions.

The natural product, thujopsene (78), is a tricyclic sesquiterpene. It is mainly found as a constituent of the Japanese Hiba tree, *Thujopsis dolabrata*, *Widdrington spp.* and belongs to the Natural Order Cupressales (58).



The compound (78) was suitable to determine the steric and electronic pathway favoured by the SH_2' reaction. However the expected product (79) did not form. The rearranged species (80) was the only identifiable product, and was obtained in diminished yields (8-11%) (Scheme 55). The structure was determined by x-ray diffraction and is given in Figure 2.



Scheme 55

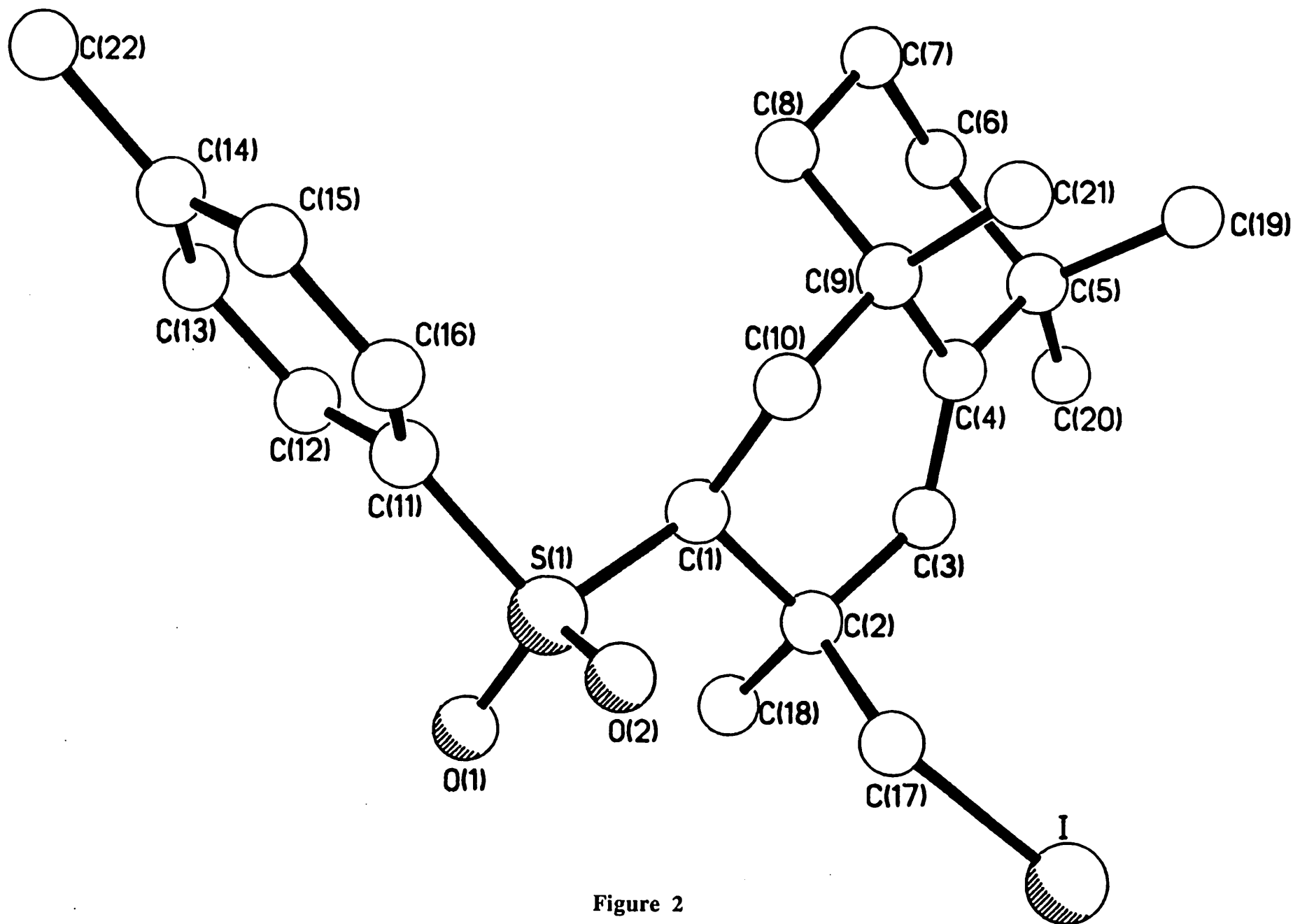
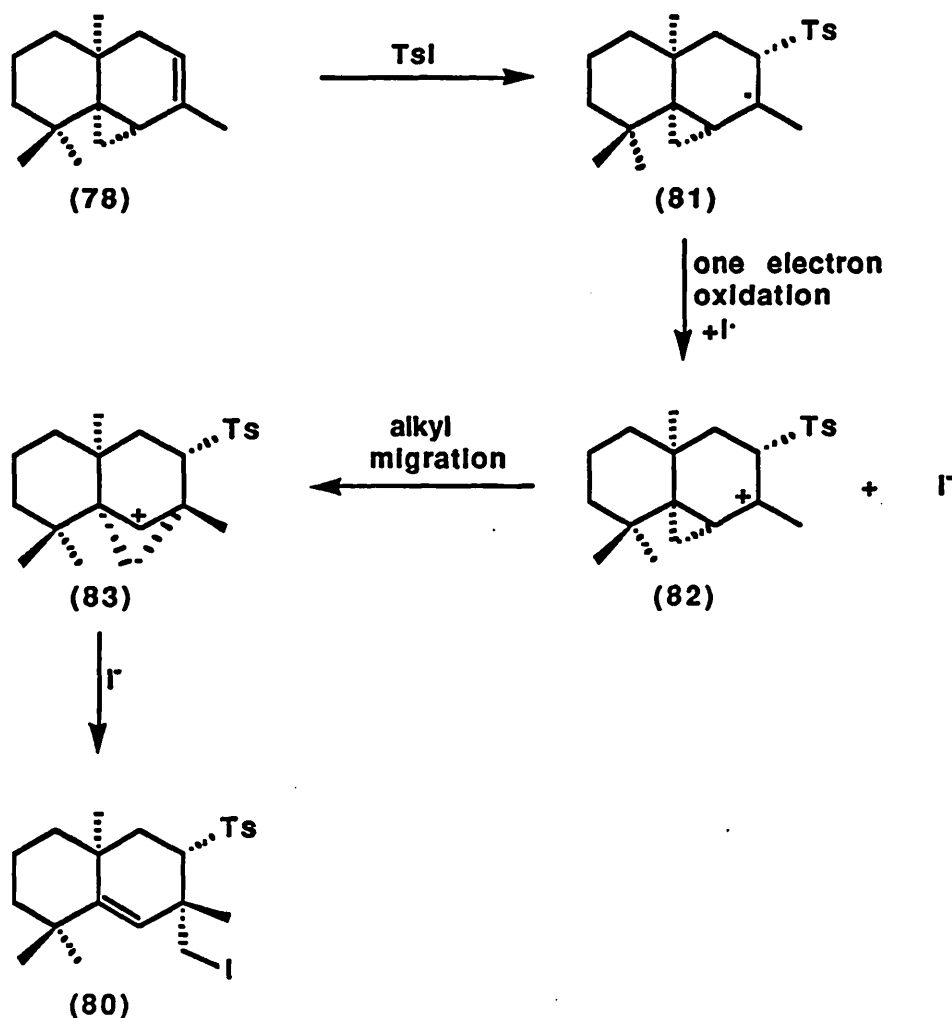


Figure 2

Figure 2**Crystal Data**

$\text{C}_{22}\text{H}_{31}\text{O}_2\text{SI}$, $M = 486.5$, orthorhombic, $a = 8.546(2)$, $b = 13.109(2)$, $c = 19.933(6)\text{\AA}$, $U = 2233\text{\AA}^3$, space group $P2_12_12_1$, $Z = 4$, $D_c = 1.45\text{ gcm}^{-3}$, $\mu(\text{Cu-K}\alpha) = 123\text{cm}^{-1}$, $F(000) = 992$. 1750 independent reflections ($\Theta \leq 58^\circ$) were measured on a Nicolet R3m diffractometer with $\text{Cu-K}\alpha$ radiation (graphite monochromator) using ω -scans. Of these 1690 had $(F_o) > 3\sigma(F_o)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors; a face absorption correction was applied. The structure was solved by heavy atom method and the non-hydrogen atoms refined anisotropically. The absolute configuration was determined by refinement of a free variable η which multiplies all F'' . The positions of the hydrogen atoms were idealised, $\text{C-H} = 0.96\text{\AA}$, assigned isotropic thermal parameters, $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, and allowed to ride on their parent carbon atoms. The methyl groups were refined as rigid bodies. Refinement was by block-cascade full-matrix least-squares and converged to give $R = 0.050$, $R_w = 0.052$ [$w^{-1} = \sigma^2(F) + 0.00342F^2$]. The maximum residual electron density in the final ΔF map was $0.81\text{e}\text{\AA}^{-3}$ and mean and maximum shift/error in the final refinement were 0.004 and 0.033 respectively.

The mechanism of this rearrangement reaction can not be free radical. We consider that formation of (80) is best explained by involving carbonium ion intermediates (Scheme 56).



Scheme 56

Initially the tosyl radical adds to substrate (78), from the least hindered side and at the mono-substituted, least hindered end of the tri-substituted carbon carbon double bond, to provide (81). Intermediate (81) then undergoes one electron oxidation yielding the carbonium ion species (82). Rearrangement of (82) then gives (80) via a cyclobutane intermediate (83). Evidence for this type of reaction was later derived from MNDO calculations on tosyl radical addition intermediate (81). Results suggested that the species is very easily oxidised. Calculations also suggested evidence that formation of the species (81) is not favoured thermodynamically. This could account for the low yield.

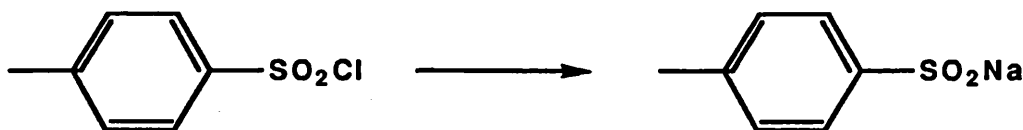
3.5. Conclusions and Future Prospectives

We have elucidated from our studies that free radical mediated, vinyl cyclopropane rearrangements are promising, future synthetic tools. A variety of approaches have been tested, tosyl iodide being the most effective. However a problem is the ring closure which, ironically during our studies, has led to a new route to functionalised substituted vinyl cyclopropanes.

In the future, with the foregoing work as precedent, we hope that a wider range of reagents for the preparative radical mediated vinyl cyclopropane-cyclopentene will be tested.

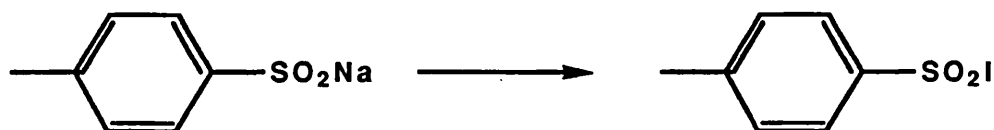
3.6. Experimental

Preparation of sodium *p*-toluenesulphinate



The Vogel⁽⁵⁹⁾ procedure was employed. Zinc powder (10g, 153 mmol) was added, with stirring, to water (75ml) at 70°C. Toluene-*p*-sulphonyl chloride (12.5g, 65 mmol) was added over 10 minutes and, after leaving for a further 15 minutes, the temperature was increased to 90°C. Sodium hydroxide solution (6.5 ml of 12M) was added, followed by sodium carbonate (1g portions) until the mixture was strongly alkaline. The reaction system was filtered and the product, sodium toluene-*p*-sulphinate, was crystallised from the filtrate. A further recrystallisation, from water, yielded the title compound (8.21g, 71%) as a white crystalline solid.

Preparation of *p*-toluenesulphonyl iodide (tosyl iodide)



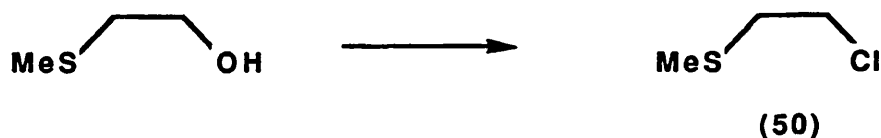
The method of Otto and Trogen⁽⁶⁰⁾ was followed. Iodine (1.67g 13.2 mmol) dissolved in absolute ethanol (25ml) was added drop wise to a solution of sodium toluene-*p*-sulphinate (2.35g, 1.32 mmol) in water (50 ml) until free iodine was visual in the system. The product was filtered off and dried *in vacuo* providing tosyl iodide (1.58g 42%) as a pale yellow solid, m.p. 89-91°C decomp. (Literature value (61) 90-91°C)

Preparation of trimethyloxosulphonium iodide



The procedure of Kuhn and Trischmann⁽⁶¹⁾ was followed. A solution of dimethyl sulphoxide (48g, 0.62 mmol) and methyl iodide (205g, 1.45 mole) was refluxed under an argon atmosphere for 3 days. The solid produced was filtered, washed with chloroform (4 x 50 ml), recrystallised from water and dried *in vacuo* to yield the crystalline adduct (119g, 87%) as colourless prisms, m.p. 192°C decomp. (Literature value⁽⁶¹⁾ *ca* 200°C decomp.).

Preparation of 2-chloroethyl methylsulphide (50)



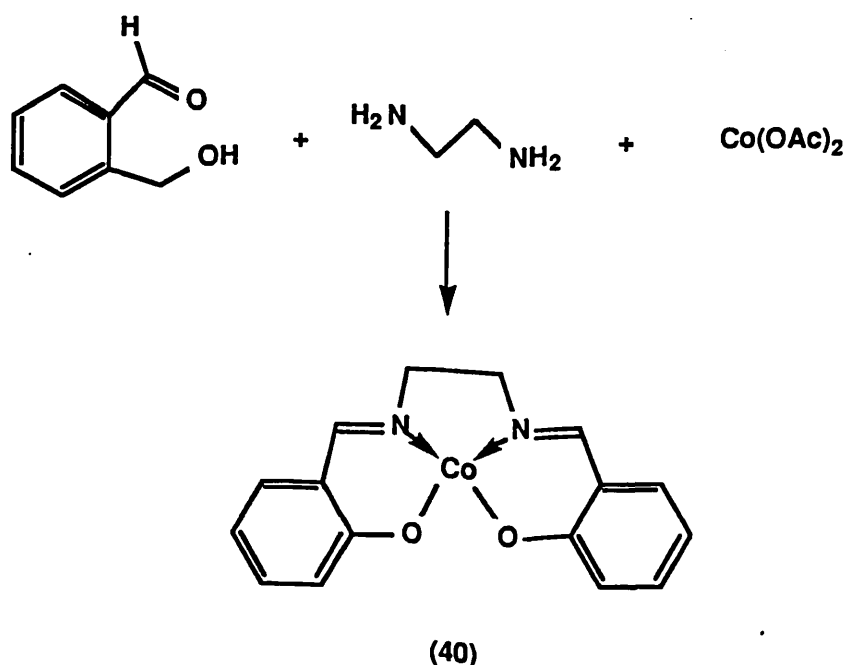
The method of Kirner and Windus⁽⁴⁹⁾ was followed. 2-(Methylthio)ethanol (50g, 0.543 mole) and chloroform (50ml) were placed in a 500 ml 3-necked flask fitted with a pressure-equalising dropping funnel, condenser, and a gas outlet with traps to remove the vapours of hydrogen chloride and sulphur dioxide. Thionyl chloride (68g, 0.567 mole) dissolved in chloroform (45 ml) was added cautiously, dropwise producing a vigorous reaction. After effervescence had completely ceased, the chloroform was removed by distillation at atmospheric pressure, and the residue distilled under reduced pressure to yield (50) (53g, 88%) as a colourless liquid, b.p. 50-55°C/30 mmHg (Literature value⁽⁴⁹⁾ 140°C/760 mmHg).

Preparation of 2-chloroethyl dimethyl sulphonium iodide (49)



A modified procedure of the von E. Doering method⁽⁵⁰⁾ was employed. 2-Chloroethyl methyl sulphide (50) (11.1g, 0.10 mole) was dissolved in acetonitrile (30 ml) and cooled to 0°C. Methyl iodide (14.2g, 0.10 mole) was added and then the system stirred, in the absence of light, for 3 days. Any precipitate which formed was redissolved by the addition of methanol (150 ml) and then precipitated out again by the addition of diethyl ether (200ml). The solid was filtered off, dried *in vacuo* to yield the product (49) (18.4g, 73%) as a white powder, m.p. 80-81°C decomp. (Literature value⁽⁵⁰⁾ 80-81°C decomp.).

Cobalt(II) salen (40)

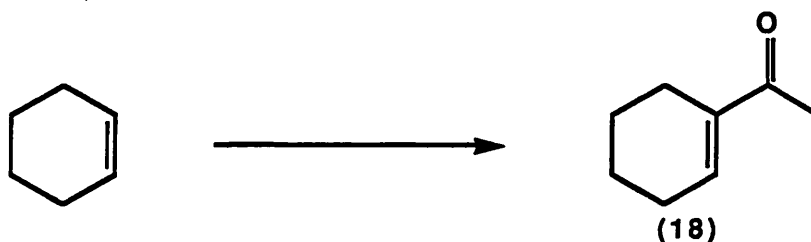


Cobalt(II) salen was made according to the procedure of Pfeiffer *et al.*⁽⁴⁵⁾.

A deoxygenated solution of cobalt (II) acetate tetrahydrate (4.50g, 0.018 mole) in water (20 ml), at 50°C, was added to a deoxygenated solution of ethylenediamine (1.08g, 0.018 mole) in ethanol (50 ml of 96%) also at 50°C and under an argon atmosphere.

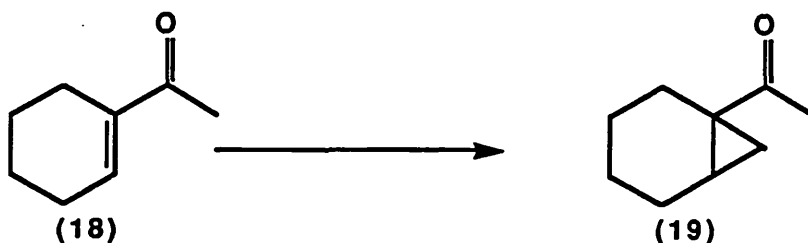
The conditions were maintained and salicylaldehyde (7.50g, 0.061 mole) added dropwise. The red precipitate was filtered under argon, dried under reduced pressure and characterised as the complex (40) (3.82g, 65%) (Found C, 58.89; H, 4.22%. $C_{16}H_{12}N_2O_2Co$ requires C, 59.02; H, 4.34%).

Preparation of 1-acetylcyclohexene (18)



The method devised by Dev (61) was employed. Phosphoric acid (30 ml of 85% in water) was added to phosphorus pentoxide and the exothermic reaction mixture stirred mechanically. Cyclohexene (16.4g, 200 mmol) and glacial acetic acid (12.4g, 220 mmol) were combined and added dropwise to the polyphosphoric acid with rigorous stirring. After 12 hours, the brown mixture was poured onto ice (500g) and allowed to dissolve over 2 hours. Ammonium sulphate (*ca* 40g) was added to the aqueous phase which was then extracted with petroleum ether (5 x 100 ml). The petroleum spirit solution was dried ($MgSO_4$ anhydrous), filtered, and concentrated *in vacuo*. The residue was purified *via* bulb to bulb distillation to afford the product (18) (13.4g, 54%) as a colourless liquid, b.p. 70-72°C/4mm Hg, ν_{max} . (film) 3 031 2 946-2 827, 1 663, 1 636 cm^{-1} ; δ_H (60 MHz, neat) 0.56-2.98 (8H, cyclohexyl-*H*), 2.20 (3H, s, CH_3), 6.68-7.28 (1H, m, C=C-*H*).

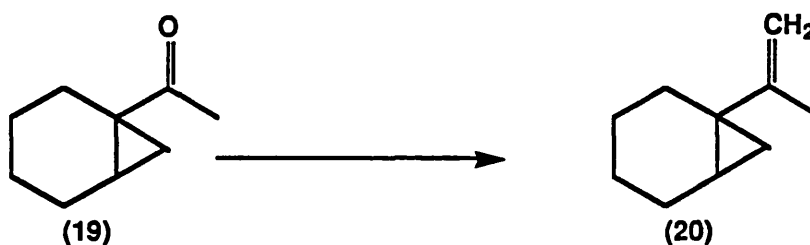
Preparation of 1-acetylbicyclo[4.1.0]heptane (19)



A modified procedure of the Corey and Chaykovsky⁽⁴⁰⁾ method was used with improved yield. Sodium hydride (1.63g, 68 mmol), purified by washing with petroleum ether (4 x 50 ml) and dried *in vacuo*, was combined with trimethyloxosulphonium iodide (14.98g, 68 mmol) and placed under an argon atmosphere. Freshly distilled dimethyl sulphoxide (71.85g, 920 mmol) was added, cautiously, dropwise and with vigorous stirring. After hydrogen evolution had ceased, the mixture was stirred for 1 hour before substrate (18) (8.00g, 64 mmol) addition over 5 minutes. The mixture was maintained under an argon atmosphere and with stirring for 10 hours before pouring into water (150 ml). The aqueous layer was extracted with ether (4 x 100 ml) and the combined extracts dried (Na_2SO_4 anhydrous). The ether was removed by distillation through a 12 inch vigreux column and the residue bulb to bulb distilled to provide the cyclopropanated product (19) (5.49g, 62%) as a colourless liquid, b.p. 66-70°C / 5mmHg (Literature value⁽⁴⁰⁾, 78-85°C / 9mm Hg); ν_{max} . (film) 3 000, 2 931-2 861,

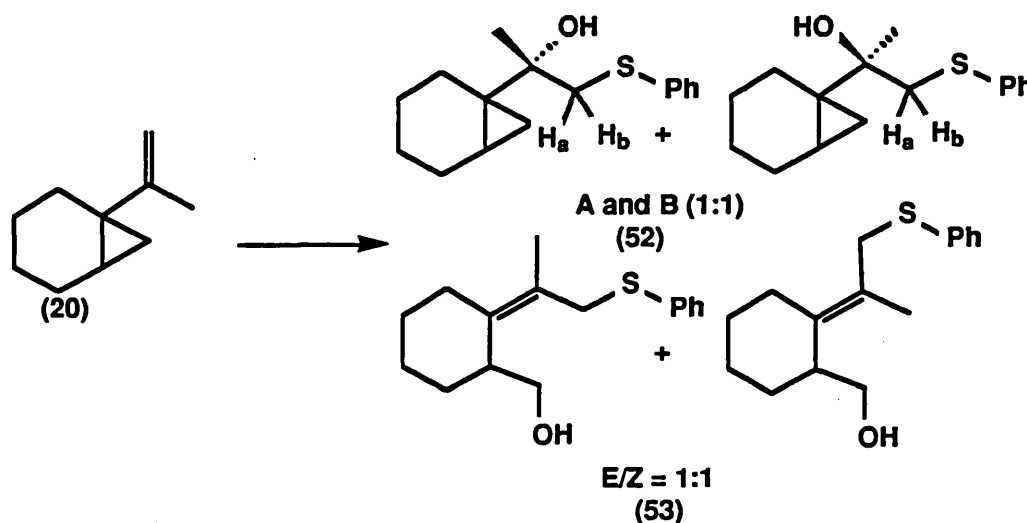
1 683 cm^{-1} ; δ_{H} (CDCl_3) 0.62 (3H, m, cyclopropyl-*H*), 1.08-1.92 (8H, m, cyclohexyl- CH_2), 1.95 (3H, s, CH_3); $M/Z = 138(\text{M}^+)$, 28, 43, 95, 32, 138, 109, 67; (found $\text{M}^+ = 138.1039000$. $\text{C}_9\text{H}_{14}\text{O}$ requires $\text{M}^+ = 138.1044652$)

Preparation of 1-(2-propenyl)bicyclo[4.1.0]heptane (20)



n-Butyl lithium (12.30 ml of 1.47M) was added over 10 minutes to a suspension of triphenylmethylphosphonium bromide (6.470g, 18.1 mmol) in diethyl ether (100 ml), under argon at -30°C. The system was warmed to room temperature over a period over four hours and then ketone (19) (2.500g, 18.1 mmol) was added and the mixture heated under reflux for 18 hours, cooled, diluted with diethyl ether (40 ml) and filtered through a celite/silica pad. The ethereal solution was concentrated *in vacuo* and the residue purified by column chromatography on silica gel eluting with dichloromethane to yield alkene (20) (2.029g, 82%) as colourless liquid; ν_{max} . (film) 3 076, 2 930-2 855, 1 641, 891 cm^{-1} ; δ_{H} (250 MHz, CDCl_3) 0.36, 0.72 and 0.94 (3H, 3m, cyclopropyl-*H*), 1.13-1.98 (8H, m, cyclohexyl-*H*), 1.74 (3H, s, CH_3), 4.68 (2H, ~d, $J = 11$ Hz, = CH_2); $M/Z = 136$ (M^+), 93, 79, 121, 107, 67, 41, 81, 40, 38; (Found: C, 88.10; H, 11.76%. $\text{C}_{10}\text{H}_{16}$ requires C, 88.16; H, 11.84%).

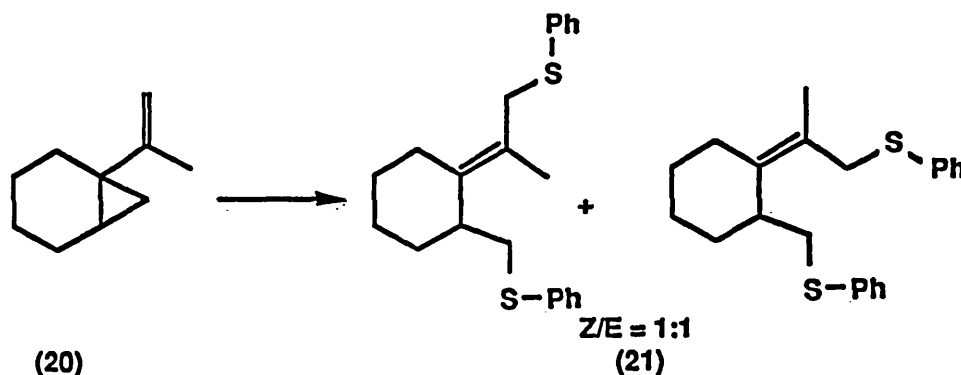
Preparation of 1-(2-hydroxy-1-phenylthioprop-2-yl)bicyclo[4.1.0]-heptane (52) and 1-(hydroxymethyl)-2-(1-phenylthioprop-2-ylidene)cyclohexane (53)



A solution of thiophenol (7.350 g, 6.671 mmol) in *n*-heptane (4 ml) was added to a solution of vinyl cyclopropane (20) (303.0 mg, 2.224 mmol), and *t*-butylamine (16.3 mg, 0.2224 mmol) in *n*-heptane (7.5 ml) under an oxygen atmosphere over a 4h period. The mixture was stirred for 2 days, cooled to -15°C (to allow precipitation of the diphenyldisulphide by-products), and filtered. The precipitate was further extracted with *n*-heptane (3 x 5 ml) and the combined extracts concentrated *in vacuo* and the residue purified on preparative plates to yield (52) (7.0 mg, 1.2%) as a 1:1 mixture of stereoisomers (designated arbitrarily as A and B for nmr purposes) ν_{max} . (CH₂Cl₂) 3 684, 3 040, 2 930-2 856, 1 583 cm⁻¹; δ_{H} (250 MHz, CDCl₃) 0.12 and 0.86 (3H, 2m, cyclopropyl-*H*) 1.02-1.89 (8H, m, cyclohexyl-CH₂) 1.21 (3H, 2s, CH₃) 2.02 (1H, 2s, OH), 3.13 (1/2H, d, *J*=12.9Hz, H_a, isomer A), 3.17 (1/2H, d, *J*=12.4Hz, H_a, isomer B), 3.34 (1/2H, d, *J*=12.9Hz, H_b, isomer A) 3.36 (1/2H, d, *J*=12.4Hz,

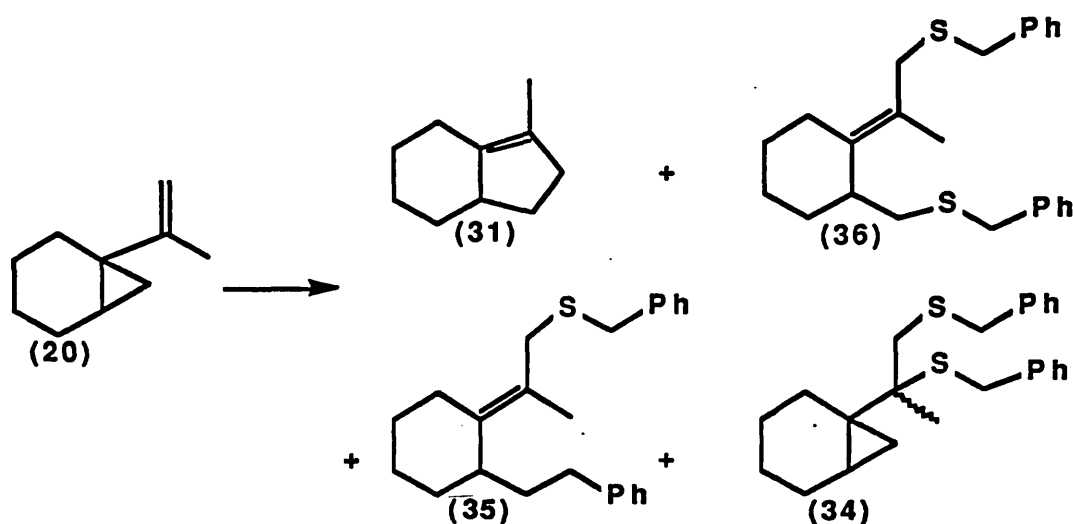
H_b , isomer B), 7.28 (5H, m, *aromatics*); M/Z 262 (M^+), 43, 124, 81, 139, 96, 110, 41, 55, 123, (Found: $M^+ = 262.1377000$. $C_{16}H_{22}OS$ requires $M^+ = 262.1391373$); and (53) (11.1 mg, 1.9%) as a 1:1 mixture of E and Z stereoisomers, ν_{max} . (CH_2Cl_2) 3 061, 3 048, 2 928-2 855, 1 583 cm^{-1} ; δ_H (250 MHz, $CDCl_3$) 1.04-1.73 (6H, m, cyclohexyl-*H*), 1.80(3H, 2s, CH_3), 2.04-2.35 (3H, m, $(CH)(CH_2)C=C$), 2.54 (1H, 2d, $J = 3.3$ Hz, OH), 3.46 and 3.52 (2H, 2d, $J = 12.0$ and 8.6 Hz, CH_2S), 3.56 = 3.81 (2H, m, CH_2O), 7.22 (5H, m, *aromatics*); $M/Z = 262$ (M^+), 124, 43, 125, 110, 81, 67, 230, 231, 123; (Found $M^+ = 262.1277000$. $C_{16}H_{22}OS$ requires $M^+ = 262.1391373$).

Preparation of 1-(phenylthiomethyl)-2-(1-phenylthioprop-2-ylidene)-cyclohexane (21)



Vinyl cyclopropane (20) (0.400g, 2.936 mmol) and diphenyldisulphide (0.6410g, 2.936 mmol) in benzene (8.0 ml) were subjected to photolysis ($\lambda > 300nm$) for 4h, under a stream of argon. The mixture was then concentrated *in vacuo* and the residue purified on preparative plates eluting with 1% ether in petrol to afford (21) (0.1853g, 17.8%) as a yellow oil, ν_{max} . (film) 3 055, 2 925-2 853, 1 583 cm^{-1} ; δ_H (90 MHz, C_6D_6) 1.06-2.35 (9H, m, cyclohexyl-*H*), 1.58 and 1.68 (3H, 2s, CH_3), 2.80-3.48 (2H, m, CH_2S), 6.82-7.46 (10H, m, *aromatics*); $M/Z = 354$ (M^+), 135, 245, 123, 93, 79, 222, 43, 55, 67; (Found: $M^+ = 354.1470000$. $C_{22}H_{26}S_2$ requires $M^+ = 354.1475946$).

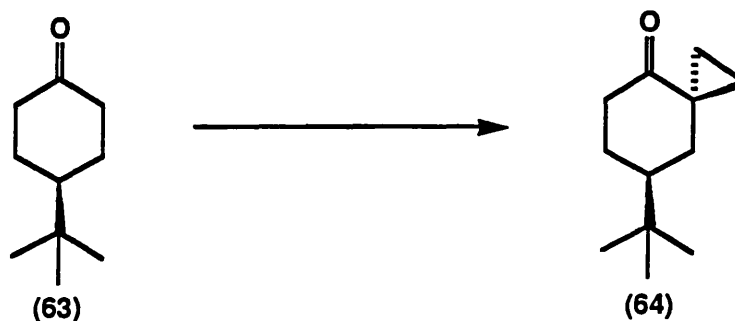
Preparation of 9-methylbicyclo[4.3.0]- $\Delta^{1,9}$ -octene (31), 1-(1,2-bis (phenylmethylthio)prop-2-yl)bicyclo[4.1.0]heptane (34), 1-(1-phenylmethylthio)prop-2-ylidene)-2-(phenylmethylthio)cyclohexane (36), 1-(1-(phenylmethylthio)prop-2-ylidene)-2-(2-phenylethyl)-cyclohexane(35)



The vinyl cyclopropane (20) (243 mg, 1.784mmol) and one equivalent of dibenzyl disulphide (439mg, 1.784mmol) were dissolved in benzene (9.9ml) to provide a 0.18M solution. After rigorous deoxygenation the mixture was subjected to photolysis, under a steady flow of argon using a pyrex filter ($\lambda > 300\text{nm}$). After 6 hours, the solution was concentrated in vacuo and purified on preparative plates eluting with 1% ether in petrol to yield (36) as a pale yellow semi-solid (23.2mg, 3%), ν_{max} . (CHCl_3) 3.054, 2 956-2 859 cm^{-1} ; δ_{H} (90 MHz, CDCl_3) 0.87-1.90 (9H, m, cyclohexyl-*H*), 1.60 (3H, s, CH_3), 2.60 (2H, m, cyclohexyl- $\text{CH}_2\text{-S}$), 3.30 (2H, m, $\text{C}=\text{C-CH}_2\text{S}$), 3.65 (4H, m, SCH_2Ph), 7.22 (10H, m, aromatics), $M/Z = 382$ (M^+), 91 (CH_2Ph^+), 291, 246, 259, 136.(Found $\text{M}^+ = 382.1791000$. $\text{C}_{24}\text{H}_{30}\text{S}_2$ requires $\text{M}^+ =$

382.1788947); **(35)** as a yellow oil (14.4mg, 2%), $\nu_{\max}$. (CHCl_3), 3 055, 2 947-2 852 cm^{-1} ; δ_{H} (90 MHz, CDCl_3) 0.82-1.96(11H, multiplets, cyclohexyl-*H*), 1.61(3H, s, CH_3), 3.02-3.80(6H, m, CH_2SCH_2 and CH_2Ph), 7.27(10H, m, *aromatics*); $M/Z = 350$ (M^+), 91, 213, 259, 167, 28, 83, 85, 121, 32; (Found ($\text{M}-\text{H}$) $^+ = 349.1989000$. $\text{C}_{24}\text{H}_{29}\text{S}$ ($\text{M}-\text{H}$) $^+$ requires $\text{M}^+ = 349.1989980$); **(34)** as a yellow semi-solid (62.8mg 9%), $\nu_{\max}$. (CHCl_3) 3 049, 2 958-2 800 cm^{-1} ; δ_{H} (90MHz, CDCl_3) 0.52-0.98(3H, m, cyclopropyl-*H*), 1.12-1.73(8H, m, cyclohexyl-*H*) 2.13(2H, m, $\text{CCH}_3\text{CH}_2\text{S}$), 3.46(4H, m, SCH_2Ph) 7.15-7.32(10H, m, *aromatics*); $M/Z = 382$ (M^+), 246, 182, 91, 291, 259, 136 (Found $\text{M}^+ = 382.1791000$. $\text{C}_{24}\text{H}_{30}\text{S}_2$ requires $\text{M}^+ = 382.1788947$); and the volatile hydrocarbon **(31)** (7.5mg, 3%), $\nu_{\max}$. (film) 2 988-2 865; δ_{H} (90MHz, CDCl_3) 0.86-2.35 (12H, multiplets, cyclohexyl-*H* and cyclopentyl-*H*), 1.60 (3H, s, $-\text{CH}_3$), $M/Z = 136$ (M^+), 137 (MH^+), 81, 28, 91, 92, 41, 69, 57, 32.

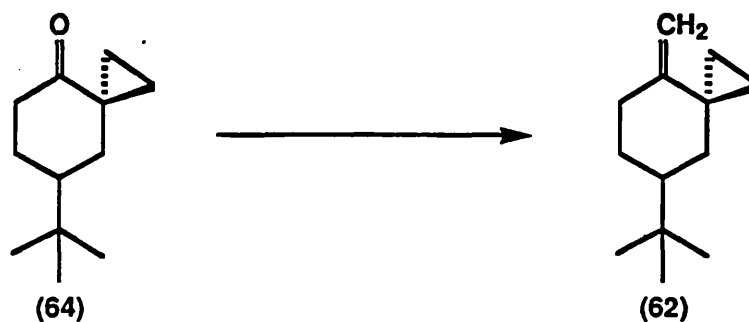
Preparation 7-*t*-butylspiro[2.5.]oct-4-one (**64**)



The synthetic procedure developed by Ruder and Ronald (48) was employed. 4-*t*-Butylcyclohexanone (**63**) (5.00g; 32.0 mmol) was added to a stirred solution of potassium *t*-butoxide (7.24g, 64.5 mmol) in *t*-butanol (65 ml) under argon, after 15 minutes solid 2-chloroethyl dimethyl sulphonium iodide (7.62g; 30.2 mmol) was added slowly *via* a solid addition tube. The mixture was stirred overnight under argon then poured into water (100 ml) and extracted with diethyl ether (3 x 50 ml). The combined ethereal extracts were dried (Na_2SO_4

anhydrous), concentrated *in vacuo* and the residue purified by distillation to afford (64) (2.70g, 50%) as a colourless oil, b.p. 60°C / 0.02mm Hg, ν_{max} . (film) 2 964-2 869, 1 698 cm^{-1} ; δ_{H} (250 MHz, CDCl_3) 0.40-0.64 (4H, m, cyclopropyl-*H*), 0.82 (0.82 (9H, s, *t*-Bu), 1.00-2.06 (5H, m, cyclohexyl-*H*) 2.14-2.67 (2H, m, $\text{CH}_2\text{C}=\text{O}$) ; $M/Z = 180$ (M^+), 96, 57 (C_4H_9^+), 41 (C_3H_5^+), 149, 29, 109, 122, 69, 79; (Found: C, 80.00; H, 11.46%. $\text{C}_{12}\text{H}_{20}\text{O}$ requires C, 79.94; H 11.18%).

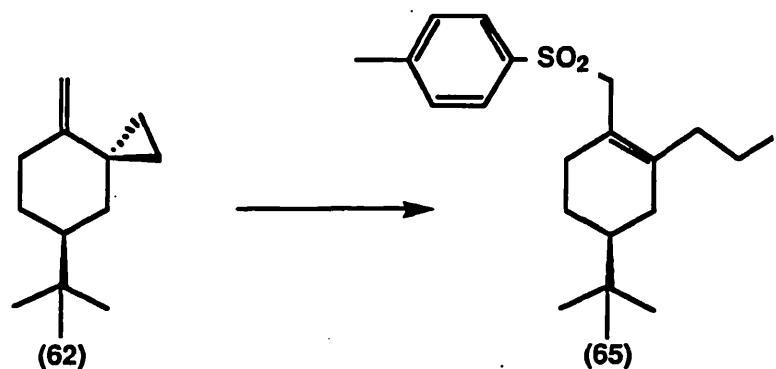
Preparation of 2-methylidene-4-*t*-butylspiro[2.5]octane (62)



n-Butyl lithium (6.94 ml of 1.60M) was added slowly to a suspension of triphenylmethyl phosphonium iodide (4.487g, 11.1 mmol) in diethyl ether (80 ml), under argon at -30°C. The mixture was allowed to warm to room temperature over 4h, then the ketone (64) (2.001g, 11.1 mmol) in diethyl ether (5 ml) was added over 5min. The mixture was heated under reflux overnight, then cooled to room temperature and diluted with diethyl ether (40 ml). The ethereal mixture was concentrated *in vacuo*. The residue was taken up in dichloromethane and filtered through a pad of silica. The filtrate was evaporated *in vacuo* and the residue purified by column chromatography on silica gel, eluting with petrol to yield the vinyl cyclopropane (62) (1.16g 59%) as a colourless oil; ν_{max} . (film) 3 075, 2 937 1 647, 887 cm^{-1} ; δ_{H} (60 MHz, CDCl_3) 0.80-0.60 (4H, m, cyclopropyl-*H*),

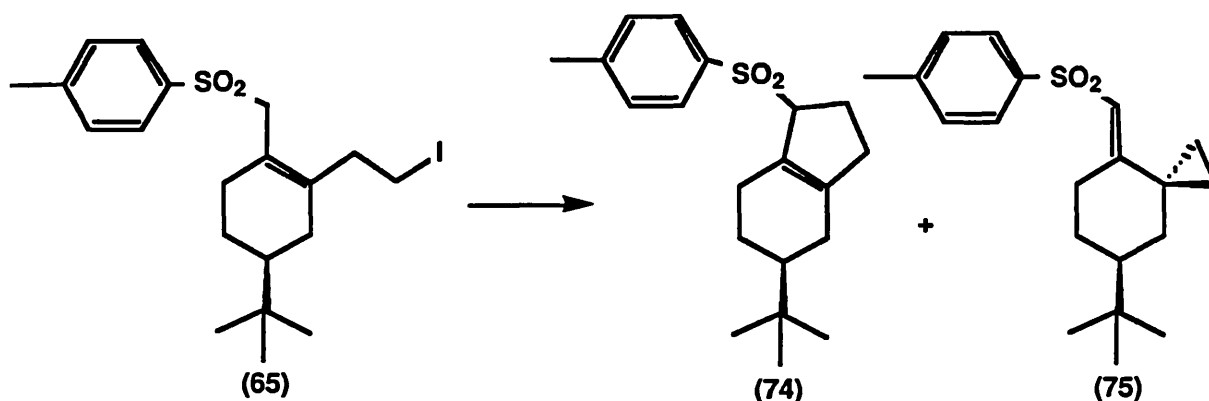
0.82 (9H, s, *t*-butyl), 0.96-2.30 (7H, m, cyclohexyl-*H*), 4.55 (2H, br.s, =CH₂);, M/Z = 178 (M⁺), 57 (C₄H₉⁺), 96, 41, 81, 121 (M⁺-*t*-Bu) 43, 67, 29, 94; (Found M⁺ = 178.1728000. C₁₃H₂₂ requires M⁺ = 178.1722000) (Found: C 87.33; H 12.32%. C₁₃H₂₂ requires C, 87.56; H, 12.44%).

Preparation of 4-*t*-butyl-2-(2-iodoethyl)-1-(*p*-toluenesulphonylmethyl)cyclohexene (65)



Tosyl iodide (633mg, 2.24 mmol) was added to propylene oxide (0.6 ml) in dichloromethane (10 ml) and the solution deoxygenated with argon for 5 min. Vinyl cyclopropane (62) (400mg, 2.24mmol) in dichloromethane (4 ml) under argon, was added to the mixture at 40°C, over 40 min. The reaction was stirred for 12h, concentrated *in vacuo* and the residue purified by column chromatography on silica gel, eluting with dichloromethane to yield the iodide (65) (539mg, 52%), $\nu_{\max}$ (CH₂Cl₂) 3 057, 2 958- 2 868, 1 654 (weak), 1 597, 1 492, 1 147, 1 365 cm⁻¹; δ_{H} (250MHz, CDCl₃) 0.84 (9H, s, *t*-Bu), 1.02-1.32 (3H, m, 4-CH and 5-CH₂), 1.44-2.40 (6H, m, 3-CH₂, 6-CH₂ and CH₂CH₂I), 2.44 (3H, s, CH₃), 3.10 (2H, m, CH₂I), 3.80 (2H, s, CH₂S), 7.33 and 7.74 (4H, 2d, *J*=7.5Hz, aromatics); M/Z = 333(M⁺), 84, 105, 183, 86, 77, 260, 47, 43, 81.

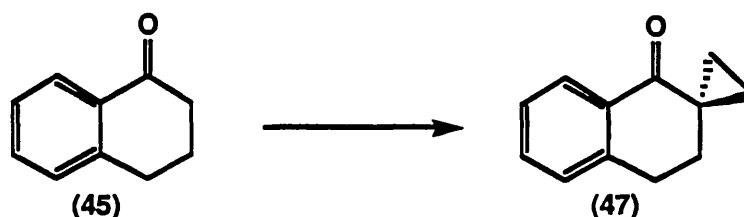
Preparation of 3-*t*-butyl-7-(*p*-toluenesulphonyl)bicyclo- $\Delta^{1,6}$ -nonene (74) and 7-*t*-butyl-4-(*p*-toluenesulphonylmethylidene)-spiro[2,5]octane (75)



A mixture of diisopropylamine (103 mg, 1.015 mmol) and tetrahydrofuran (5 ml) were placed under an argon atmosphere and cooled to -10°C . *n*-Butyllithium (0.39 ml of 2.6M) was added and lithium diisopropylamide formation was allowed over 10 min.. The mixture was cooled to -78°C and the tosyl iodide adduct (65) (467 mg, 1.015 mmol), dissolved in tetrahydrofuran (2 ml) was added slowly over 5 min. and the reaction warmed to r.t. over 3 hrs. The mixture was diluted with diethyl ether (10) and the ethereal extract washed with water (3x4 ml) before drying (Na_2SO_4 anhydrous). After removal of the volatiles *in vacuo*, the residue was purified by column chromatography on silica gel, eluting with dichloromethane, to yield two inseparable species characterising as the semi-solids (74) (15% by nmr) and (75) (20% by nmr); ν_{max} . (CHCl_3) 3 051, 2 960-2 867, 1 598, 1 310, 1 142; δ_{H} (250 MHz, CDCl_3) (74) 0.82-2.20(11H, multiplets, 2- CH_2 , 3- CH , 4- CH_2 , 5- CH_2 , 8- CH_2 and 9- CH_2), 0.78(9H, 2s, *t*-Bu), 1.96(3H, br. s, CH_3), 3.96(1H, 2t, $J = 3\text{Hz}$, 7- CH), 6.85 and 7.82(4H, 2d, $J = 8\text{Hz}$, aromatics); (75) 0.06 and 0.22(4H, 2m, cyclopropyl- H), 0.68(9H, s, *t*-Bu), 0.60-2.20(7H, multiplets, cyclohexyl- H), 1.96(3H, s, CH_3), 6.14(1H, s, olefinic-

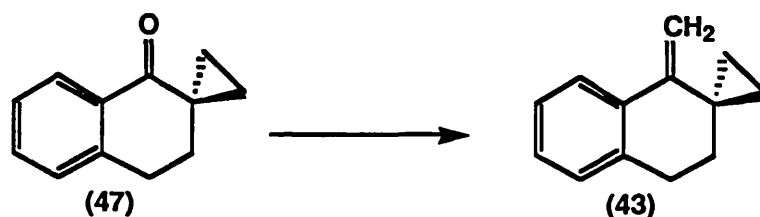
H), 6.85 and 7.82 (4H, 2d, $J = 8\text{ Hz}$, aromatics); $M/Z = 332(M^+)$, 276, 93, 57, 91, 119, 203, 177, 92, 121; (Found $M^+ = 332.1820000$. $C_{20}H_{20}O_2S$ requires 332.1810022).

Preparation of 5,6-benzospiro[2.5]octan-4-one (47)



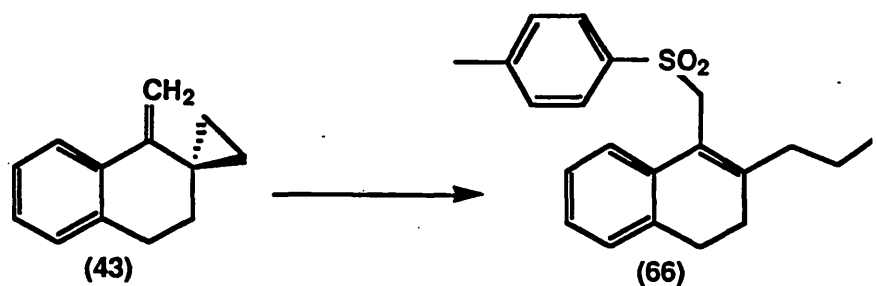
3,4-Dihydro-1(2H)-naphthalenone (45) (4.707g, 34.2 mmol) was added to a solution of potassium *t*-butoxide (7.631g, 68.0 mmol) in *t*-butanol (65 ml) under argon to generate the pink anion. The mixture was stirred for 15 min then 2-chloroethyl dimethyl sulphonium iodide (8.052g, 31.9 mmol) added slowly over 1h *via* a solid addition tube. The reaction was stirred for a further 16h at room temperature then poured into water (150 ml) and extracted with diethyl ether (4 x 50 ml). The ethereal extracts were combined and dried (Na_2SO_4 anhydrous) concentrated *in vacuo* and the residue purified by column chromatography on silica gel, eluting with dichloromethane to yield the spirocyclopropanated compound (47) (4.073g, 74%) as a pale orange crystalline solid, m.p. 50-51°C, ν_{max} (CH_2Cl_2) 3 049-2 940, 1 670, 1 601, 1 365, 1 348 cm^{-1} ; δ_H (250 MHz, $CDCl_3$) 0.78 and 1.34 (4H, 2m, cyclopropyl-*H*), 1.94 (2H, t, $J = 6.5\text{ Hz}$, 4- CH_2), 2.98 (2H, t, $J = 6.5\text{ Hz}$, 5- CH_2), 7.30 and 7.96 (4H, 2 m, aromatics); $M/Z = 172(M^+)$, 171, 188, 115, 26, 144, 128, 90, 131, 129; (Found $M^+ = 172.0891000$. $C_{12}H_{12}O$ requires 172.0888151) (Found: C, 83.49; H, 6.82%. $C_{12}H_{12}O$ requires C, 83.69; H, 7.02%).

Preparation of 4-methyldene-5,6-benzospiro[2.5]octane (43)



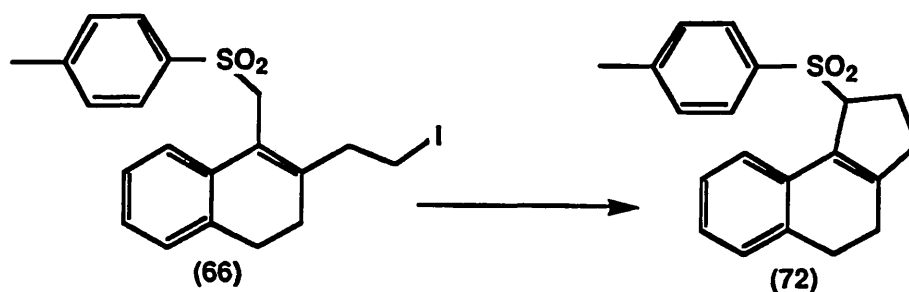
n-Butyl lithium (9.93 ml of 1.45M) was added slowly to a suspension of methyl triphenylmethylphosphonium iodide (5.820g, 14.4 mmol) in diethyl ether (35 ml) at -30°C under argon. After 4h the mixture was warmed to room temperature and ketone (47) (1.645g, 9.56 mmol) in diethyl ether (5 ml) added dropwise. The resultant white mixture was heated under reflux for 16h then cooled and diluted with diethyl ether, filtered and concentrated *in vacuo*. The residue was taken up in dichloromethane and filtered through a pad of silica. The filtrate was evaporated *in vacuo* and the residue purified by column chromatography on silica gel, eluting with petrol to yield the alkene (43) (1.047g, 64%) as a colourless oil which readily polymerises on standing, ν_{max} (film) 3 070-2 928, 1 568 cm^{-1} ; δ_{H} (250MHz, CDCl_3) 0.66 and 0.84 (4H, 2m, cyclopropyl-*H*), 1.64 (2H, t, $J = 6.0\text{Hz}$, 8- CH_2), 2.93 (2H, t, $J = 6.0\text{Hz}$, 7- CH_2) 4.74 and 5.43 (2H, 2s, olefinic-*H*), 7.18 and 7.66 (4H, 2m, aromatics); $M/Z = 170$ (M^+), 141, 142, 129, 155, 115, 128, 169, 171, 143; (Found $\text{M}^+ = 170.1092000$. $\text{C}_{13}\text{H}_{14}$ requires 170.1095506) (Found: C, 91.43; H, 8.32%. $\text{C}_{13}\text{H}_{14}$ requires C, 91.71; H, 8.29%).

Preparation of 2-(2-iodoethyl)-1-(*p*-toluenesulphonyl- methyl)-3,4-dihydronaphthalene (66)



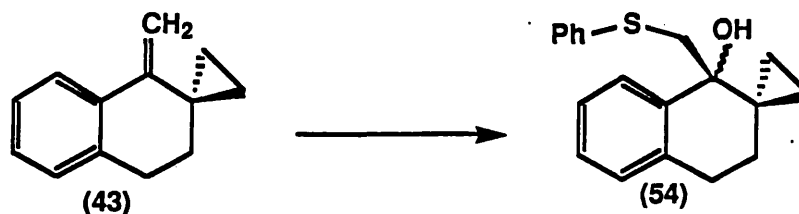
A solution of *p*-Toluenesulphonyl iodide (0.577g, 2.05 mmol) and propylene oxide (0.6 ml) in dichloromethane (9 ml) was degassed with argon for 5 min, then placed in an oil bath at 43-45°C. A solution of vinyl cyclopropane (43) (0.348g, 2.05 mmol) in dichloromethane (4 ml) was added over 30 min and the mixture stirred for a further 10 hours then concentrated *in vacuo* and the residue purified by column chromatography on silica gel, eluting with dichloromethane to yield the iodide (66) (0.874g, 95%) as a pale yellow solid which was then recrystallised from petroleum ether m.p. 125-127°C ν_{max} (CDCl₃) 3 063-2 888, 1 597, 1 316 (SO₂), 1 152 (SO₂) cm⁻¹; δ_{H} (250 MHz, C₆D₆) 1.68 (2H, t, *J* = 7.3Hz, 3-CH₂), 1.84 (3H, s, tosyl-CH₃), 2.34 (2H, t, *J* = 7.3 Hz, CH₂CH₂I), 2.58 (2H, t, *J* = 7.3 Hz, 4-CH₂), 2.83 (2H, t, *J* = 7.3 Hz, CH₂I), 4.14 (2H, s, SO₂CH₂), 6.65 and 7.64 (4H, 2d, *J* = 8.2 Hz, SO₂-aromatics); 6.90 and 7.18 (4H, 2m, aromatics); *M/Z* = 452 (*M*⁺, 169, 141, 170, 325, 129, 148, 157, 91, 128; (Found: *M*⁺ = 452.0306000. C₂₀H₂₁IO₂S requires *M*⁺ = 452.0307039) (Found: C, 53.01; H, 4.63%. C₂₀H₂₁IO₂S requires C, 53.11; H, 4.68%).

Preparation of 4,5-benzo-7-(*p*-toluenesulphonyl)bicyclo[4.4.0]- $\Delta^{1,6}$ -nonene (72)



n-Butyl lithium (0.306 ml of 2.10 M) was added to a solution of diisopropylamine (65.1 mg, 0.6435 mmol) in tetrahydrofuran (5 ml) at 0°C under argon. The solution was stirred for 15 min to allow complete formation of lithium diisopropylamide and then cooled to -78°C. A solution of iodide (66) (264.4 mg, 0.5850 mmol) in tetrahydrofuran (2 ml) was added dropwise over 5 min. The mixture was allowed to warm to room temperature over 1 hour then poured into water (5 ml) and extracted with diethyl ether (5 x 10 ml). The combined ethereal extracts were dried (Na₂SO₄ anhydrous), concentrated *in vacuo* and the residue purified by column chromatography on silica gel, eluting with dichloromethane to yield (72) (174.8 mg, 92%) as a pale yellow solid, m.p. 142-144°C; ν_{max} . (CDCl₃) 3 064-2 886; 1 640, 1 590, 1 311, 1 140 cm⁻¹ δ_{H} (250 MHz, CDCl₃) 2.04-2.80 (8H, complex multiplets, 2-CH₂, 3-CH₂, 8-CH₂ and 9-CH₂) 2.35 (3H, s, tosyl-CH₃), 4.64 (1H, br.t, CH₂CHSO₂) 7.02-7.64 (8H, complex multiplet, aromatics); *M/Z* = 324 (*M*⁺), 169, 167, 168, 170, 141, 91, 165, 153, 41; (Found; *M*⁺ = 324.1193000. C₂₀H₂₀O₂S requires *M*⁺ = 324.1184019) (Found: C, 73.92; H, 6.20%. C₂₀H₂₀O₂S requires C, 74.04; H, 6.21%).

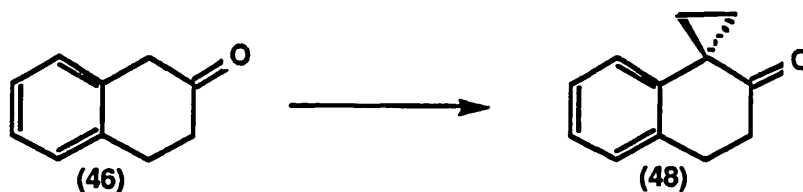
Preparation of 5,6-benzo-4-(phenylthiomethyl)-4-hydroxyspiro[2.5]-heptane (54)



A solution of thiophenol (587.1 mg, 5.329 mmol) in *n*-heptane (1.0 ml) was added over 30min to a mixture of vinyl cyclopropane (43) (302.4 mg, 1.776 mmol) and *t*-butylamine (12.99 mg, 0.1776 mmol) in *n*-heptane (6 ml) under an atmosphere of oxygen. The mixture was stirred for 5 days then cooled to -15°C , and the mother liquor filtered. The residue was washed with *n*-heptane (3 x 5 ml). The combined extracts were concentrated *in vacuo* and the residue purified on preparative plates to yield (54) (128.6 mg, 24.5%) as a pale yellow semi-solid, ν_{max} (CH_2Cl_2) 3 581, 3 049, 3 003-2 934, 1 605, 1 582 cm^{-1} ; δ_{H} (250 MHz, CDCl_3) 0.19, 0.44, 0.76, 1.10 (4H, 4m, cyclopropyl-*H*), 2.53 (2H, m, 8- CH_2), 2.98 (2H, m, 7- CH_2), 3.34 (1H, d, $J = 14\text{Hz}$, CHS), 3.80 (1H, d, $J = 14\text{Hz}$, CHS), 7.24 and 7.68 (9H, 2m, aromatics); $M/Z = 173, 28, 172, 171, 145, 131, 116, 128, 127, 91$; (Found C, 76.92; H, 6.74%. $\text{C}_{19}\text{H}_{26}\text{SO}$ requires C, 76.99; H, 6.80%).

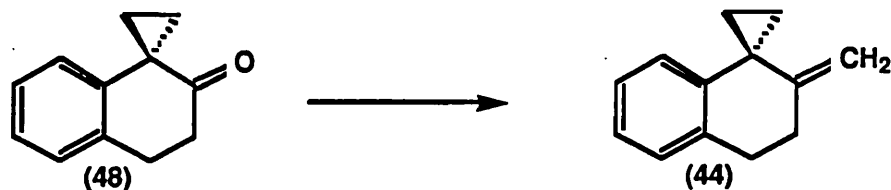
*When the procedure was modified, simply by bubbling oxygen through the reaction mixture, the same product (54) was obtained in 26.4% yield.

Preparation of 7,8-benzospiro[2.5]octan-4-one (48)



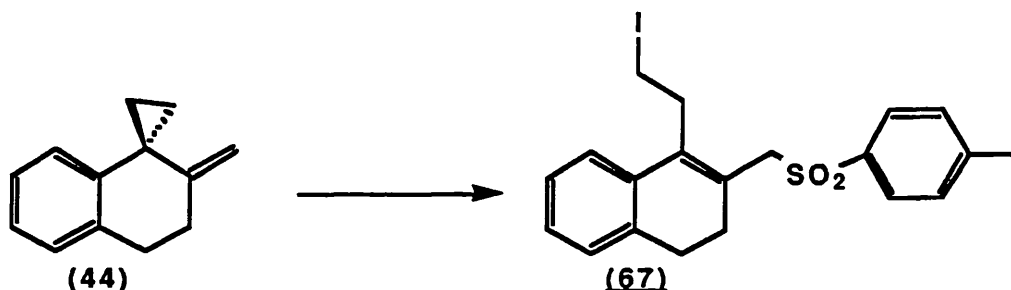
Chloroethyl dimethylsulphonium iodide (8.789g, 34.8 mmol) was added in small portions over 1 hour to a mixture of pre-washed sodium hydride (1.102g, 45.9 mmol), 3,4-dihydro-2(1H)-naphthalenone (46) (5.497g, 37.6 mmol) and *t*-butanol (140 ml) under argon. After 12 hours the system was diluted with petroleum ether (150 ml), washed with water (3 x 50 ml), aqueous sodium hydrogen carbonate (3 x 50 ml), brine (3 x 50 ml) and then dried (Na_2SO_4 anhydrous), concentrated *in vacuo* and the residue purified by column chromatography on silica gel, eluting with 25% ether in petrol to yield (48) (4.687g, 78%) as a pale yellow solid, m.p. 47-49°C; ν_{max} . (CDCl_3) 3 066-2900, 1 698, 1 491 cm^{-1} ; δ_{H} (CDCl_3) 1.23 and 1.72 (4H, 2 q, $J_{\text{gem}} = 4$ Hz, $J_{\text{vic}} = 6$ Hz, cyclopropyl-*H*), 2.63 (2H, t, $J = 6.0$ Hz, 5- CH_2), 3.03 (2H, t, $J = 6.0$ Hz, 6- CH_2), 6.68 and 7.10 (4H, complex multiplet, *aromatics*); $M/Z = 172$ (M^+), 129, 128, 115, 130, 127, 173, 143, 116, 63; (Found: 172.0889000. $\text{C}_{12}\text{H}_{12}\text{O}$ requires $\text{M}^+ = 172.0888151$) (Found: C, 83.94; H, 7.16%. $\text{C}_{12}\text{H}_{12}\text{O}$ requires C, 83.69; H, 7.02%).

Preparation of 7,8-benzo-4-methylenespiro[2.5]octane (44)



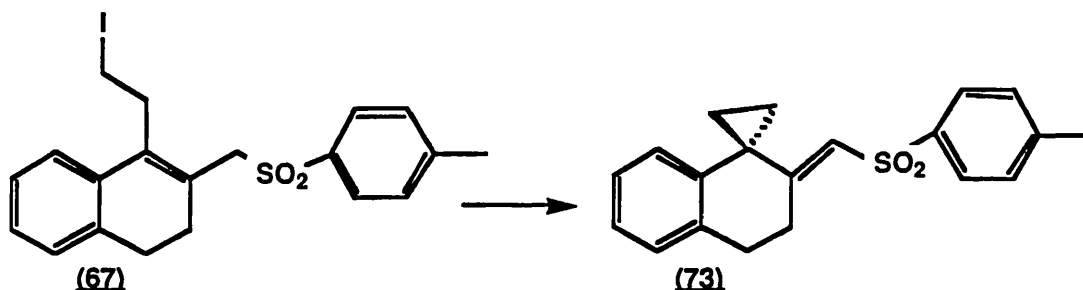
n-Butyl lithium (26.2 ml of 2.10 M) was added dropwise to a suspension of triphenylmethylphosphonium iodide (22.24g, 55.0 mmol) in diethyl ether (100 ml) under argon at -39°C , the mixture was allowed to warm to room temperature over 3h. A solution of ketone (48) (3.164 g, 18.4 mmol) in diethyl ether (10 ml) was added and the mixture was heated under reflux for 24h then cooled and diluted with diethyl ether, filtered, concentrated *in vacuo* and the residue purified by column chromatography on silica gel, eluting with petrol to afford the alkene (44) (0.524g, 17%) as a colourless liquid, ν_{max} . (CDCl_3) 3 020-2 844, 1 642, 1 603 cm^{-1} ; δ_{H} (250MHz, CDCl_3) 1.20 and 1.12 (4H, 2 m, cyclopropyl-*H*), 2.63 (2H, t, $J = 6$ Hz, 5- CH_2), 2.97 (2H, t, $J = 6$ Hz, 6- CH_2), 4.66 (2H, 2s, = CH_2), 6.78 and 7.14 (4H, 2 m, *aromatics*); $M/Z = 170$ (M^+), 169, 141, 142, 155, 128, 115, 129, 167, 153; (Found: M^+ 170.1092000. $\text{C}_{13}\text{H}_{14}$ requires $\text{M}^+ = 170.1095506$) (Found; C 91.71; H, 8.52%. $\text{C}_{13}\text{H}_{14}$ requires C, 91.52; H, 8.52%.

Preparation of 1-(2-iodoethyl)-2(*p*-toluenesulphonyl-methyl)-3,4-dihydronaphthalene (67)



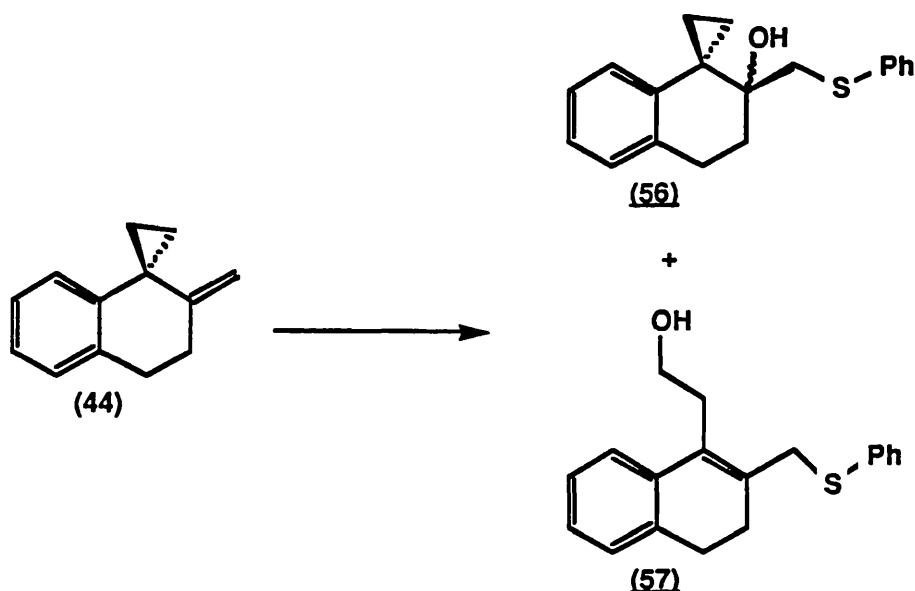
A solution of vinyl cyclopropane (44) (135.3mg, 0.7947 mmol), in dichloromethane (1.60 ml), was added over 30min to propylene oxide (0.24 ml) and *p*-toluenesulphonyl iodide (246.6 mg, 0.8742 mmol) in dichloromethane (3.60 ml) at 40°C under argon. The mixture was stirred for 2h, then concentrated *in vacuo* and the residue purified by column chromatography on silica gel to afford (67) (296.0 mg, 78%) as a white solid, m.p. 35-37°C; ν_{max} . (C_6D_6) 3 061-2 833, 1 624 (weak), 1 596 cm^{-1} ; δ_{H} (250 MHz, CDCl_3) 2.32 (2H, t, $J = 7.5$ Hz, 3- CH_2), 2.45 (3H, s, CH_3), 2.70 (2H, t, $J = 6.8$ Hz, $\text{CH}_2\text{CH}_2\text{I}$), 2.82 (2H, t, $J = 7.5$ Hz, 4- CH_2), 2.94 (2H, t, $J = 6.8$ Hz, CH_2I), 4.10 (2H, s, $\text{CH}_2\text{-SO}_2$), 7.15 (4H, m, *aromatics*), 7.34 and 7.77 (4H, 2d, $J = 8.7$ Hz, $\text{SO}_2\text{-aromatics}$); $M/Z = 452$ (M^+), 297 ($\text{M}^+ - \text{Ts}$), 170, 169, 141, 298, 129, 155, 100, 115; (Found: $\text{M}^+ = 452.0301000$. $\text{C}_{20}\text{H}_{21}\text{IO}_2\text{S}$ requires $\text{M}^+ = 452.0307039$) (Found: C, 53.11; H, 4.68%. $\text{C}_{20}\text{H}_{21}\text{IO}_2\text{S}$ requires C, 53.11, H, 4.76%).

Preparation of 7,8-benzo-4-(*p*-toluenesulphonylmethylidene)-spiro[2.5]octane (73)



A solution of lithium diisopropylamide was prepared *in situ* via addition of *n*-butyllithium (0.149 ml of 2.15M) to diisopropylamine (32.46 mg, 0.3208 mmol) in tetrahydrofuran (2.75 ml) under argon at 0°C. After 15 minutes, the mixture was cooled to -70°C and a solution of (67) (145.1 mg, 0.3208 mmol), in tetrahydrofuran (1.10 ml) added over 8min. The reaction was allowed to warm to room temperature over 3h then diluted with diethyl ether (5 ml) and poured into water (8 ml). The aqueous phase was extracted further with diethyl ether (3 x 5 ml) and the combined ethereal extracts dried (Na₂SO₄ anhydrous), concentrated *in vacuo* and the residue purified by column chromatography on silica gel eluting with dichloromethane to afford (73) (68.9 mgs, 47%) as a white solid, m.p. 90-92°C; ν_{max} . (CDCl₃) 3 026-2 929, 1 600, 1 321, 1 144, cm⁻¹; δ_{H} (250 MHz, DMSO-d₆) 1.24 and 1.36 (4H, 2 m, cyclopropyl-*H*), 2.38 (3H, s, CH₃), 2.74 (2H, t, *J* = 6.8 Hz, 5-CH₂), 2.98 (2H, t, *J* = 6.8 Hz, 6-CH₂), 6.34 (1H, s, SO₂CH), 6.88 and 7.13 (4H, 2 m, aromatics), 7.42 and 7.76 (4H, 2d, *J* = 7.8 Hz, SO₂-aromatics); *M/Z* = 324 (*M*⁺), 169, 141, 56, 170, 167, 153, 43, 115, 91; (Found *M*⁺ = 324.1177000. C₂₀H₂₀O₂S requires *M*⁺ = 324.1184019).

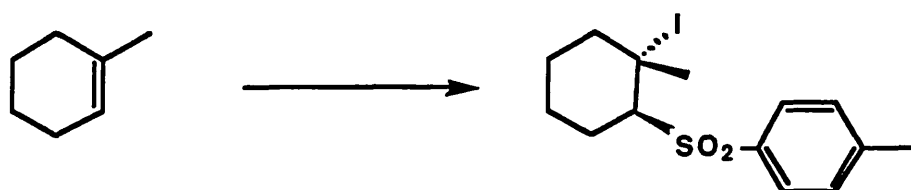
Preparation of 4-hydroxy-4-(phenylthiomethyl)spiro-[2,5]octane (56) and 1-(2-hydroxyethyl)-2(phenylthiomethyl)-3,4-dihydro-naphthalene (57)



A solution of thiophenol (202.0 mg, 1.834 mmol) in *n*-heptane (1 ml) was added to a solution of (44) (103.9 mg, 0.6103 mmol) and *t*-butylamine (4.464 mg, 0.06103 mmol) in *n*-heptane (2.06 ml) over 5h under an oxygen atmosphere. The mixture was stirred for 3 days then cooled to -15°C and filtered. The residue was washed with *n*-heptane (3 x 5 ml) and the combined extracts concentrated *in vacuo* and purified on preparative plates to yield (56) (28.8 mgs, 15.5%) as a pale yellow semi solid, $\nu_{\text{max.}}$ (CH₂Cl₂) 3 578, 3 039-2 890, 1 604, 1 590 cm⁻¹; δ_{H} (250 MHz, CDCl₃) 0.44, 1.20 and 1.38 (4H, 3m (1:2:1), cyclopropyl-*H*), 2.10(2H, m, 5-CH₂), 2.20(1H, s, OH), 2.89(2H,m , 6-CH₂.), 3.09(1H, d, *J* = 14Hz, CHS), 3.31(1H, d, *J* = 14Hz, CHS), 6.72 and 7.26(9H, 2m, aromatics) *M/Z* = 296 (*M*⁺), 124, 131,173, 145, 129, 114, 128, 114, 128, 123, 110; (Found: *M*⁺ = 296.1232000. C₁₉H₂₀OS requires *M*⁺ = 296.1234872); and (57) (8.0 mgs, 4.4%) as a pale yellow semi-solid, $\nu_{\text{max.}}$ (CH₂Cl₂) 3 598, 3 025 - 2 880, 1 602, 1 586 cm⁻¹; δ_{H} (250 MHz, CDCl₃) 2.40 (2H, t, *J* = 8.5 Hz, CH₂CH₂ OH), 2.69 (2H, t, *J* = 7.0 Hz, 3-CH₂), 2.73 (2H, t, *J* = 7.0 Hz, 4-

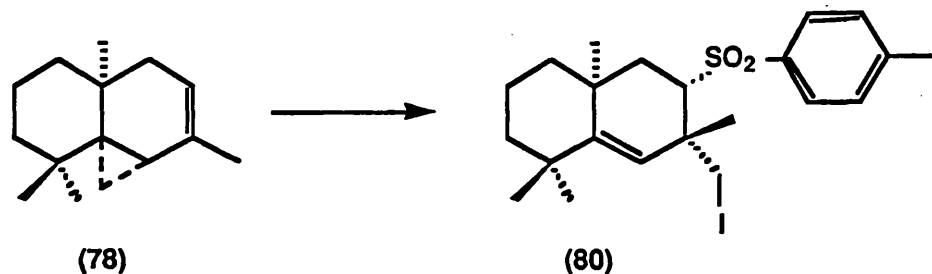
CH_2), 3.62 (2H, t, $J = 8.5$ Hz, CH_2OH), 3.81 (2H, s, CH_2S), 7.12-7.42 (9H, m, *aromatics*); $M/Z = 296$ (M^+), 187, 143, 157, 129, 128, 141, 188, 142, 169; (Found: $M^+ = 296.1232000$. $\text{C}_{19}\text{H}_{20}\text{OS}$ requires $M^+ = 296.1234872$).

The tosyl iodide adduct of 1-methylcyclohexene



1-Methylcyclohexene (250.0 mg, 2.60 mmol) in dichloromethane (7 ml) was added over 30 min to a solution of *p*-toluenesulphonyl iodide (807.1 mg, 2.86 mmol) in dichloromethane (12.5 ml) and propylene oxide (0.87 ml) at 40°C under an argon atmosphere. After 2 hours the mixture was concentrated *in vacuo* and the residue purified by column chromatography on silica gel to yield the adduct (840.2mg, 85%) as a white solid, m.p. 85-87°C (decomp), ν_{max} (CH_2Cl_2) 3 047, 2 942-2 965, 1 347, 1 144 cm^{-1} ; δ_{H} (90MHz, CDCl_3) 1.44-2.40 (8H, ms, *cyclohexyl*), 2.42 (3H, s, ICCH_3), 2.58 (3H, s, aromatic - CH_3), 3.62 (1H, t, $J = 3.0\text{Hz}$, SO_2CH), 7.31 and 7.78 (4H, 2d, $J = 8.0\text{Hz}$, *aromatics*); $M/Z = 95$ ($M^+ - \text{Ts} - \text{HI}$), 94, 156, 91, 67, 55, 81, 127, 77, 251; (Found: C, 44.78; H, 5.00%. $\text{C}_{14}\text{H}_{19}\text{IO}_2\text{S}$ requires C, 44.45; H, 5.06%).

The tosyl iodide adduct of Thujopsene



A solution of tosyl iodide (335mg, 1.188mmol) in dichloromethane (5ml) and propylene oxide (0.36ml) was deoxygenated. The solution was lowered into a preheated oil bath at 40°C, and a solution of cyclopropane (78) (221mg, 1.080mmol) in deoxygenated dichloromethane (3ml) added immediately. The reaction was followed by tlc and the substrate (78) was consumed after 12h. The mixture was concentrated *in vacuo* and the residue purified by column chromatography on silica gel, eluting with dichloromethane to afford the tosyl iodide, rearranged adduct (80) (57.8mg, 11%) as a white crystalline solid (by petroleum ether recrystallisation), m.p. 96-98°C (decomp), $\nu_{\max}$. (CHCl₃) 2930-2845, 1579, 1311, 1145, δ_{H} (250MHz, CDCl₃); 0.88-2.08(8H, m, 2-CH₂, 8-CH₂, 9-CH₂, 10-CH₂), 1.02(3H, s, 1-CCH₃), 1.17(6H, 2s, 7-C(CH₃)₂), 1.54(3H, s, 4-CCH₃), 2.44(3H, s, tosyl-CH₃), 3.20(1H, 2m, 3-CH), 3.69(2H, 2d, $J=9\text{Hz}$, CH₂I), 5.12(1H, s, 5-CH), 7.33 and 7.74(4H, 2d, $J=8\text{Hz}$, aromatics); $M/Z = 157, 203$ (M⁺-HI-Ts), 111, 119, 91, 41, 105, 55, 133, 331, (M⁺-Ts); (Found C, 54.45; H, 6.24%. C₂₂H₃₁IO₂ S requires C, 54.32; H, 6.42%).

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