SOME STUDIES OF SMALL RING SPECIES

A thesis presented by

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Abstract

The literature on olefin metathesis is reviewed and the arguments for excited cyclobutane or tetramethylene complex intermediates presented. A new, convenient catalyst for the reaction is devised. Studies of the effects of functional groups in the olefin on the course of the reaction indicate that its potential as a general method in organic synthesis is severely limited.

The decomposition of α-diazoketones and peracid oxidation of acetylenes are discussed, with particular reference to the question of formation of ketocarbenes and oxirens as intermediates. A simple test is described which provides the first chemical proof for the participation of oxirens in the thermal and photochemical decompositions of α-diazoketones. The use of silver or copper catalysts for the decompositions prevents oxiren formation. In the light of these results, earlier reports in the literature are re-interpreted.

A review of molybdenum-based oxidising reagents is presented, and the use of these reagents for olefin epoxidation explored with particular reference to positional and stereo-selectivity. The peracid oxidation of imino-ethers to hydroxamic acids via oxazirans is developed, and a potential new method for hydroxamic acid synthesis by molybdenum pentoxide oxidation of N-silyl amides discovered. Studies of the molybdenum-catalysed oxidation of acetylenes implicate a ketocarbene-molybdenum complex as intermediate. The application of the newly-discovered test for oxirens rules out the possibility of their formation in the presence of molybdenum or iron.

For Irena.

We see little, presume a great deal, and so jump to a conclusion.

John Locke.

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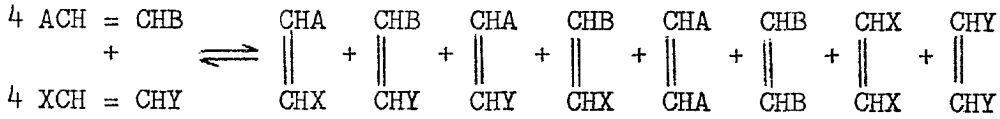
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SECTION 1. OLEFIN METATHESIS

1.1. Introduction.

In 1964, Bailey and Banks reported a new type of olefin transformation,[1] which has been variously termed dismutation,[2] disproportionation[1] and metathesis.[3] The reaction, which is catalysed by a variety of compounds of, principally, the Group VI and VII transition metals and especially those of molybdenum and tungsten, may be represented in general terms by Scheme 1. It is reversible,[2] and leads to equilibrium mixtures of olefins, the equilibrium having been shown[3] to obey the random redistribution theory of Beatty and Calingaert.[4]



Scheme 1.

A wide variety of heterogeneous catalysts has been developed and the reaction is now used industrially on a large scale (e.g. Phillips Triolefin Process). Typically, the vaporised olefins are passed over oxides of Nb, Ta, Mo, W, Re or carbonyls of Mo, W, Re or sulphides of Mo, W on a support of alumina, silica or other refractory material at 0-600°. These catalysts, conditions and applications have been reviewed in detail by Bailey.[5]

Great interest in the metathesis reaction as a potential laboratory-scale procedure was stimulated by the discovery[3] of homogeneous catalysts which would effect disproportionation in solution at room temperature and atmospheric pressure in periods of a few seconds or minutes. The first of these was the system $WCl_6/EtAlCl_2/EtOH$ reported by Calderon and

co-workers.[3,6] A representative list of these catalysts is shown in Table 1. In many cases variations in the oxidation level of the transition metal compound or degree of alkylation of the aluminium also provide active catalysts. In a typical experiment with Calderon's catalyst, ethylaluminium dichloride (.04M) is added to a solution of tungsten hexachloride (.01M) and ethanol (.01M) in dry benzene under nitrogen, followed by the olefin (1.00M) in benzene. The reaction is terminated after 2-3 minutes by addition of a small quantity of alcohol, water or other active-hydrogen compound.

Several basic types of reaction have been distinguished in olefin metathesis. "Homo-metathesis", or disproportionation of a single, unsymmetrically substituted olefin,[3] leads to the formation of an equilibrium mixture containing the starting-material and two new symmetrical olefins in the ratio 2:1:1. When "homo-metathesis" of terminal olefins is carried out under conditions where the ethylene can be swept out of the system as it is formed, a good yield of a single higher- molecular weight alkene can be obtained.[13] This reaction is only possible with a limited range of the homogenous catalysts, however (e.g. those based on $M(NO)_2 Cl_2 L_2$ or the Mo and W carbene complexes), because most of the simple catalysts derived from halides of Mo or W cause rapid polymerisation of 1-alkenes.[20]

Cross metathesis between two different olefins produces a complex mixture of up to eight new products (Scheme 1).

Metathesis of cyclic alkenes results in a ring-opening polymerisation reaction.[21,22] Thus, cyclooctene gave a wide range of products from dimers to high polymers which were unsaturated macrocycles with a single repeating unit.[22,23] The reversibility of metathesis was demonstrated by the production of low-molecular weight oligomers when polyoctenomer from a previous ring-opening polymerisation was re-treated with

Transition Metal Cpd.	Co-catalysts.	References.
WCl_6	$EtAlCl_2$ (+EtOH)	3,6
WCl_6	BuLi	7
WCl_6	$SnBu_4$	8
WCl_4	$AlCl_3$	9
$WOCl_4$	$AlCl_3$ or $EtAlCl_2$	10
$WOCl_2(OEt)_2$	$EtAlCl_2$	11
$W(CO)_5 P.Ph_3$	$AlCl_3$	10
WO_3	$AlCl_3$	10
$MoCl_5$	$EtAlCl_2$	12
$M(NO)_2 Cl_2 I_2$ [a,b]	$Et_3 Al_2 Cl_3$	13
$MoCl_3(OCOPh)_2$	$Me_3 Al_2 Cl_3$	14
$R_4 N^+[(CO)_5 M{:}COR^1]^-$ [a]	RmAlXn	15
$ReCl_5$	$SnBu_4$	16
$ReOBr_3 PPh_3$	$EtAlCl_2$	17
$TaCl_5$	$EtAlCl_2$ + RCl	18
$Rh(NO)_2 Cl$	$Me_3 Al_2 Cl_3$	19
$MnCl_2 py_2$	$EtAlCl_2$	17

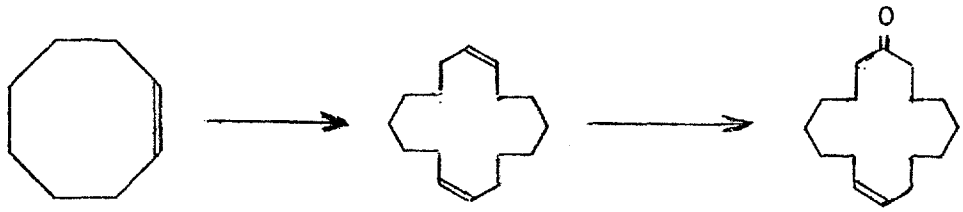
Table 1.

Notes.

a. M = Mo, W.

b. L = pyridine, triphenyl phosphine or pyridine-N-oxide.

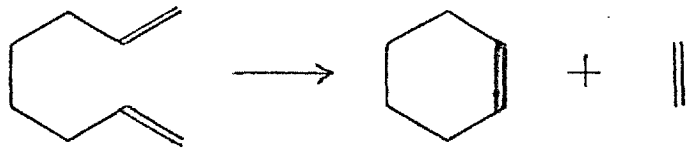
Calderon's catalyst in dilute solution.[22,24] Wideman[25] has reported that by modification of the reaction conditions the $WCl_6/EtAlCl_2$ catalyst can be used to obtain a good yield of dimer (1) from cyclooctene, and has used this as abasis for the synthesis of a musk perfume (2) (Scheme 2). No experimental details of the modification were reported, however.



1 2

Scheme 2.

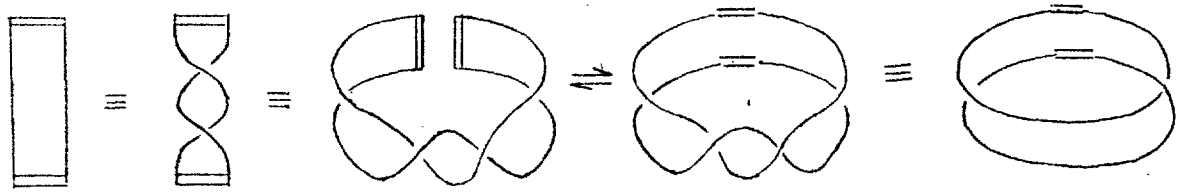
Cross-metathesis between a cyclic and an acyclic olefin produces an acyclic diene. The reaction is generally complicated by further cross-disproportionations of the primary product, but in the specific case of "ethenolysis" a high yield of a single α,ω-diene can be obtained by reacting a cyclic alkene with excess ethylene.[2,26] The reverse of this reaction has been reported in the metathesis of octa-1, 7-diene to cyclohexene and ethylene (scheme 3).[20]



Scheme 3.

A novel and ingeneous method of synthesising catenanes was developed by Wasserman[27] and Wolovsky[28] using the "Mobius twist" approach. The ring-opening polymerisation of cyclooctene produces a polyunsaturated oligomer which is shown in Scheme 4 in a "stretched" form with one double bond at each end (3). The oligomer is then given

two half twists (4) and the ends brought together for metathesis (5), which results in the formation of two linked rings (6). The catenanes were identified in the reaction mixture by mass spectrometry.



3 4 5 6

Scheme 4.

Attention has been turned recently to studies of side-reactions accompanying metathesis. Although the most active catalysts are relatively free of side-reactions and are very specific for disproportionation,[6,20] the use of the slower catalysts may result in oligomerisation.[10] With the molybdenum-nitrosyl complexes, use of $EtAlCl_2$ as co-catalyst or of high temperatures favours isomerisation reactions.[20]

Tungsten hexachloride alone promotes the alkylation of benzene by olefins and addition of $EtAlCl_2$ enhances the reaction.[29] In detailed studies reported by Kothari and Tazuma[30] it was shown that, particularly when the catalyst was preformed in benzene or toluene before addition of the olefin, the alkylation of the solvent could become the primary and even exclusive reaction. However, a careful comparison of their results with those of Calderon[6] shows that the best alkylation conditions (W:Al:olefin = 1:2:500 - No EtOH present) are very different to the optimum metathesis conditions (W:EtOH:Al:olefin

=1:1:4:100), and under the latter conditions Calderon noted very little alkylation of the solvent and generally used a preformed catalyst for the metathesis. Kothari and Tazuma also reported that addition of pyridine or triphenylphosphine (1 or 2 moles per mole of W) greatly slowed down metathesis whilst suppressing alkylation.

It has been reported[31] that acetylenes can be disproportionated over heterogeneous catalysts (WO_3 or MoO_3 on SiO_2). [1-^{14}C]-hex-2-yne gave labelled but-2-yne and unlabelled oct-4-yne. Cyclobutadiene intermediates were proposed, but proof of this is lacking.

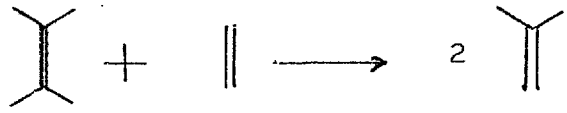
1.2. Mechanism.

^{14}C and deuterium labelling studies have established that, for both homogeneous and heterogeneous catalysts, the metathesis reaction is a transalkylidenation (Scheme 6) and not a transalkylation process. Thus, in the metathesis of d_8-but-2-ene with but-2-ene, the products of which were examined by mass spectrometry,[6] only one new species was observed, of mass 60. This is consistent with a transalkylidenation producing $CD_3CD{=}CHCH_3$. The cross-metathesis of d_8-but-2-ene and hex-3-ene also produced only one new product, of mass 74. [2-^{14}C] propene gave ^{14}C butene, but unlabelled ethylene.[32,33] A transalkylation would be expected to produce radioactive ethylene. Similarly, from [1-^{14}C] propene only radioactive ethylene was obtained.[33,34]

The transalkylidenation suggests a four-centre mechanism in which two olefin molecules become bound to the metal catalyst and a cyclic movement of bonds results in the generation of two new olefins.

Boelhouwer, Mol and Moulijn[35] proposed a mechanism in which two vinylic hydrogen atoms from each double bond were transferred to the metal catalyst and an intermediate cyclobutadiene was generated.

Crain[36] produced strong evidence against this mechanism however, by showing that metathesis of tetramethylethylene with ethylene gave only isobutene (Scheme 5). If Mol's mechanism were in operation, transfer of two methyl groups as well as two hydrogens to the catalyst surface would be required, and furthermore return of each methyl group to the original carbon atom that it was detached from would be necessitated. Crain failed to find any evidence for the formation of propene or n-butenes in the reaction mixture.

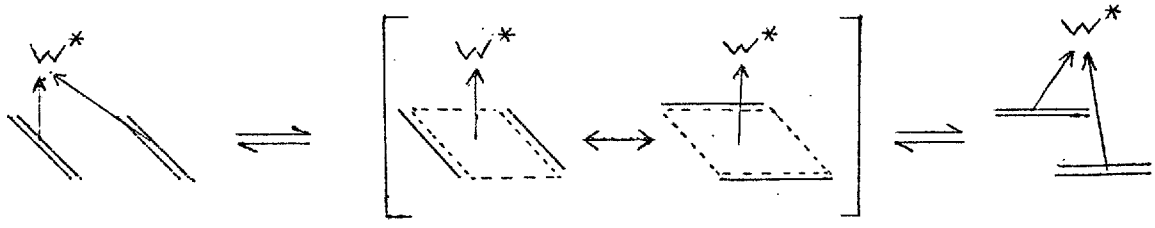


Scheme 5.

Mol and Boelhouwer[37] themselves provided evidence, later, against the cyclobutadiene mechanism, by showing that disproportionation of [2-^{2}H]-propene gave no deuterium in the ethylene produced.

Most other workers have accepted a "pseudocyclobutane", "quasicyclobutane" or excited cyclobutane as the intermediate[5].

Calderon's view of the reaction[6] is depicted in Scheme 6 and involves transalkylidenation (W* represents the active catalyst species).



Scheme 6.

Kinetic studies have not, so far, given a very great insight into the mechanism of olefin metathesis. Begley and Wilson,[38] studying propene disproportionation over a WO_3/SiO_2 catalyst at high temperature and pressure, obtained kinetic results which appeared to support a Rideal model. Lewis and Wills,[39] however, obtained data for a $MoO_3/CoO/Al_2O_3$ catalyst at lower temperature and pressure which appeared to support a Langmuir-Hinshelwood model, a view which was also supported by Clark and Moffat.[33]

Kemball and co-workers were unable to determine the reaction order from their kinetic studies of propene disproportionation over a $Mo(CO)_6/Al_2O_3$ catalyst, although they were able to demonstrate the reversibility of the reaction and supported a Langmuir-Hinshelwood model with reaction between two adsorbed molecules as the rate-determining step.[40] Their infrared[41] and G.L.C.[40] results showed the loss of CO groups during activation, leading to the proposal of $Mo(CO)_x(C_3H_6)_{6-x}$ as the intermediate with a probable value of 3 or 4 for x.

Rather more illuminating were Hughes' results[42] with the homogeneous $Mo(NO)_2Cl_2L_2/R_mAlCl_n$ catalysts. The kinetic data were in good agreement with a model in which two olefin molecules are reversibly complexed to the catalyst and the metathesis reaction itself is the rate-determining step. Neither the exact stoichiometry, oxidation state nor stereochemistry of the active catalyst could be determined, however.

The formation of a "quasicyclobutane" intermediate by a concerted process involves, formally, a 2+2 cycloaddition reaction of the olefin bonds in a manner strictly forbidden by the Hoffmann-Woodward Rules. In this respect the reaction resembles the metal-catalysed formation of norbornadiene from quadricyclene[43] and of tricyclooctadiene from cubane,[44] isomerisations very difficult to

perform in the absence of a catalyst. This entire class of "cyclobutanation" reactions has received theoretical treatment by Mango,[45,46] who has demonstrated that the formation of a cyclobutane from two olefins, or its reverse, is allowed in the presence of suitable orbitals of a transition metal. Mango considered the interaction of olefin SS, SA, AS and AA orbitals (S = Symmetric; A = Antisymmetric) with hybrids derived from the metal s, px, py, pz, dxy, dyz, dxz, dz^2 and dx^2-y^2 orbitals for an octahedral complex and obtained the correlation diagram shown in Figure 1.

This interpretation has been heavily criticised by van der Lugt,[47] who constructed a correlation diagram (Figure 2) using the dxy and dxz orbitals of a square-planar d^8 metal complex to show that the concerted conversion of cyclobutane to 2 molecules of ethylene remains symmetry-forbidden in the presence of the metal, and proposed that the catalytic effect in metathesis is derived from a lowering of the activation energy for the production of a doubly-excited state of the cyclobutane intermediate by making use of the lower energy of the excited metal orbitals.

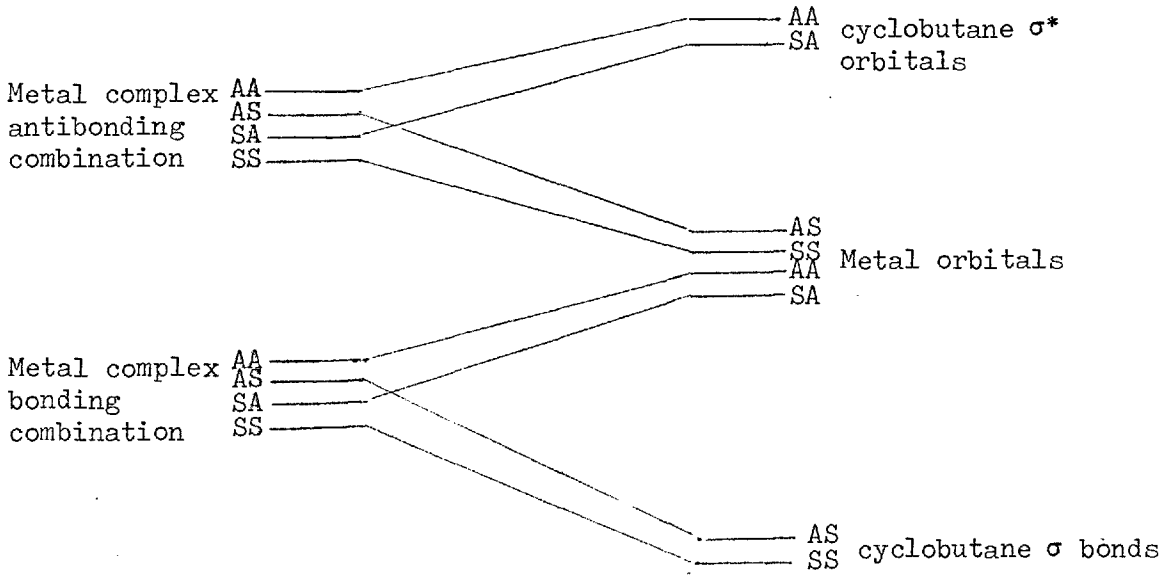


Figure 1.

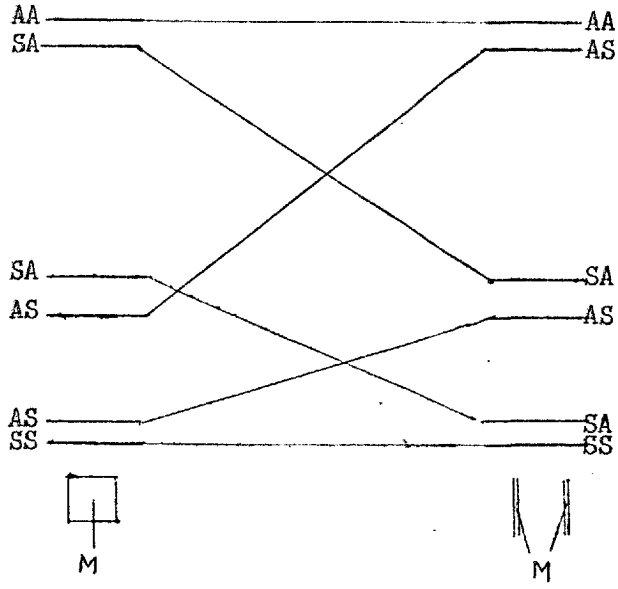


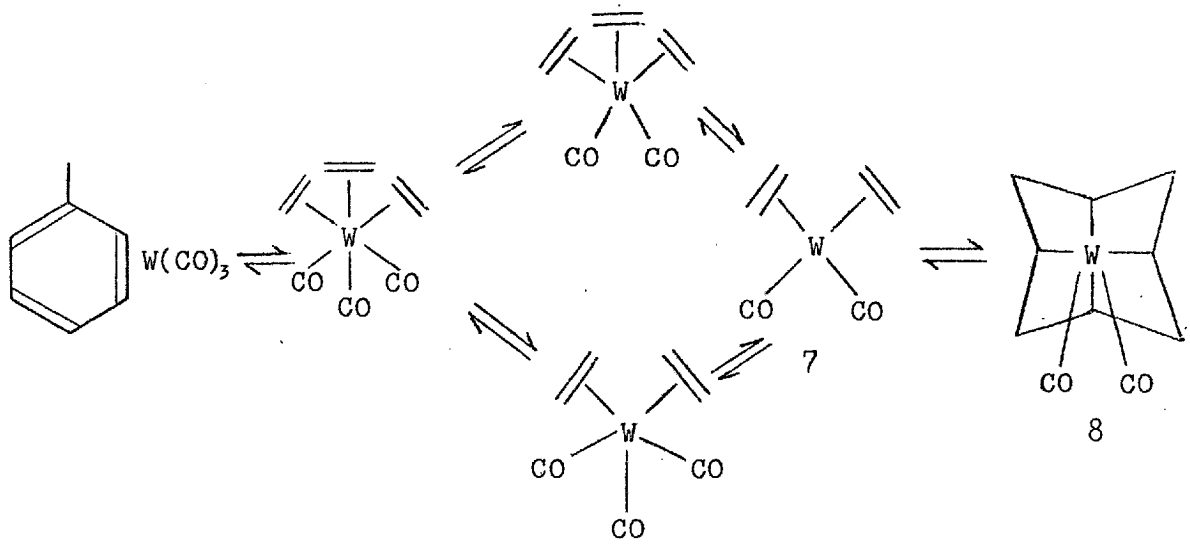
Figure 2.

These mechanistic arguments are open to several criticisms. Firstly, it has been pointed out[37,48] that cyclobutanes are stable to the reaction conditions, and so cannot be intermediates, and moreover since the free energies of formation of cyclobutane and of two molecules of ethylene are very similar one would expect to see cyclobutanes as significant by-products of the metathesis, which is not the case.[48] Furthermore, it is difficult to see how a cyclobutane, as such, could retain any significant degree of bonding to the metal catalyst. However, these arguments neglect the influence that a high degree of excitation of the "quasicyclobutane" might have on the transition state and reaction course.

The complete uncertainty about the precise nature of the active catalyst, typically generated (in homogeneous cases) by addition of excess aluminium alkyl to the transition metal halide, renders any discussion based on square-planar or octahedral arrangements of the intermediate complexes speculative. Moreover, following these discussions by Mango and van der Lugt, it has been shown that the

isomerisations of quadricyclene[49] and cubane[44] proceed in a non-concerted manner via σ-bonded metal-carbon intermediates.

Recent Pettit[48,50] has developed a new point of view on the reaction mechanism. The metathesis intermediate is considered to be a tetramethylene complex of the transition metal. The formation of four carbene ligands from the two starting olefins accounts for the transalkylidenation, explains the nature of the bonding in the transition state, and since a cyclobutane molecule is never realised the experimental observations are accounted for. This mechanism, in which all the bonds are simultaneously ruptured and two electrons are completely withdrawn from the olefin to each vinylic carbon atom, may be regarded formally as an extreme version of the vaguer "excited cyclobutane" discussed by earlier workers. Pettit[50] has also found that (arene)$W(CO)_3$ complexes are active disproportionation catalysts, and the reaction Scheme which he has constructed (Scheme 7) on the basis of competition experiments provides the first clear picture of the oxidation state and geometry of the active catalyst.



Scheme 7.

The intermediate (8) is a tetra-methylene complex whose formation from (7) results in an increase of donor electrons from four to eight on the W atom, giving it an inert gas structure.

Complexed cyclobutadienes were suggested[31] as the intermediates in acetylene disproportionation. However, Mango[51] has shown that the concerted conversion of two acetylene molecules to a cyclobutadiene on a metal atom is not a ground-state process, and concluded that the reaction must involve either a stepwise process or catalytic action of two metal atoms. Pettit's mechanism does not, without modification, circumvent these difficulties. If (toluene)$W(CO)_3$ is a catalyst for the metathesis of alkynes and if, by analogy, the reaction proceeds via four complexed RC: groups, then in order to maintain the inert gas structure of the intermediate it can be predicted that all the CO groups must be lost, a point which should be open to experimental verification.

In a very recent paper, it has been reported[52] that carbonyl complexes containing metal-metal bonds between Mo, W and Re can be reduced by aluminium alkyls to give metathesis catalysts. It has not yet been determined whether the metal-metal bond remains intact during the reaction, but if this is the case then the operation of multi-metal catalysis would render the above theoretical mechanistic discussions redundant.

1.3. Stereochemistry.

An important feature of the metathesis reaction, common to all the catalyst systems employed to date, is that a mixture of cis- and trans-isomers is produced for every olefinic product, and moreover the starting material itself undergoes geometric isomerisation during the course of the reaction. The cis-trans ratios are generally found

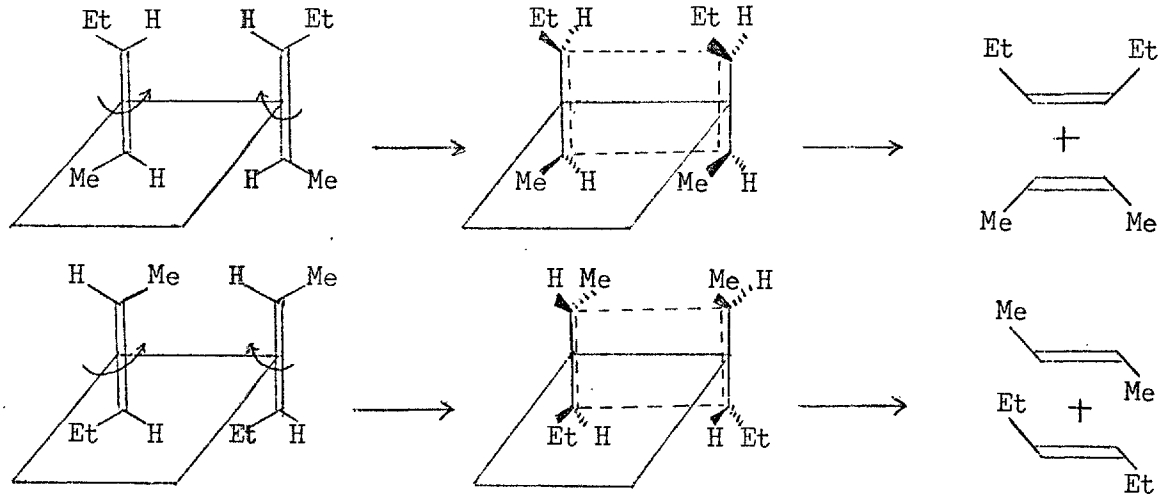
to be in accord with the thermodynamic equilibrium ratios for any given olefin when the most active catalysts are used,[6,53] although Menapace and Wang[7] reported that a slight dependence of the final product ratios on the geometric nature of the starting material was observed with the less active WCl_6/BuLi system.

On the other hand, Hughes[53] has observed with the $M(NO)_2 Cl_2 L_2$ catalysts that cis-pent-2-ene gives largely cis-but-2-ene and cis-hex-3-ene initially, whilst trans-pent-2-ene gives mainly trans-but-2-ene and trans-hex-3-ene initially and that the rate of isomerisation of the starting material and products declines at the same rate as the metathesis itself. Similarly, although Calderon[6] found rather less specificity in the initial stages of the reaction with the $WCl_6/EtAlCl_2$ catalyst, he also concluded from studies of the steric course of the reaction that the metathesis itself is the principle means of geometric isomerisation.

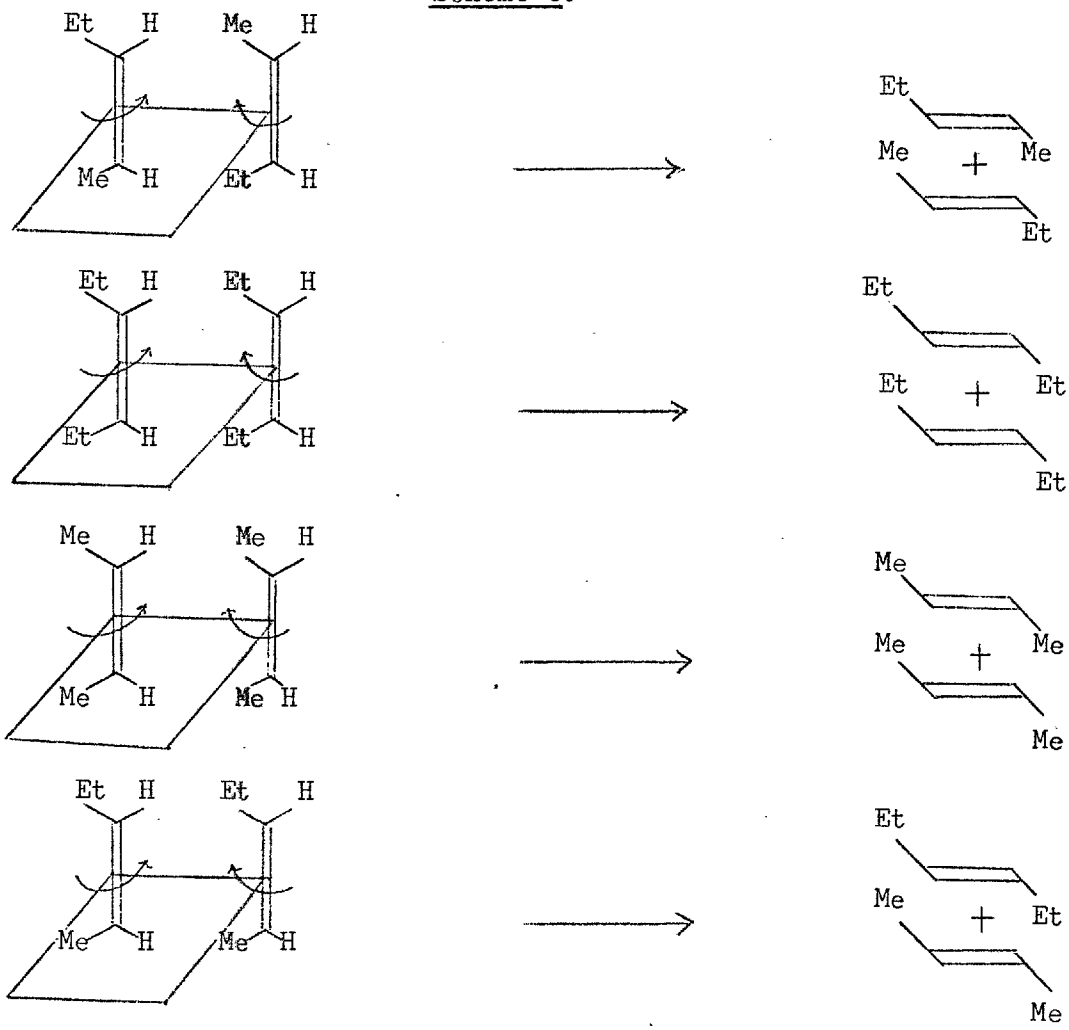
Now, if the metathesis involves a concerted cyclobutanation, which requires disrotation of the two olefin molecules in the reactive complex[53] and if the bis-olefin metal complex always takes up the most stable conformation in which steric interactions are minimised, then no isomerisation will occur on metathesis. The situation for metathesis of cis-pent-2-ene and of trans-pent-2-ene is depicted in Scheme 8.

There are a number of routes by which isomerisation can be achieved through metathesis and all involve less stable arrangements of the complex. The most important of these (for the cis-pent-2-ene metathesis) are illustrated in Scheme 9.

The results of Calderon and Hughes suggest that there is some preference for the most stable configuration of the intermediate complex, which accounts for the stereoselectivity observed in the early stages of the reaction.

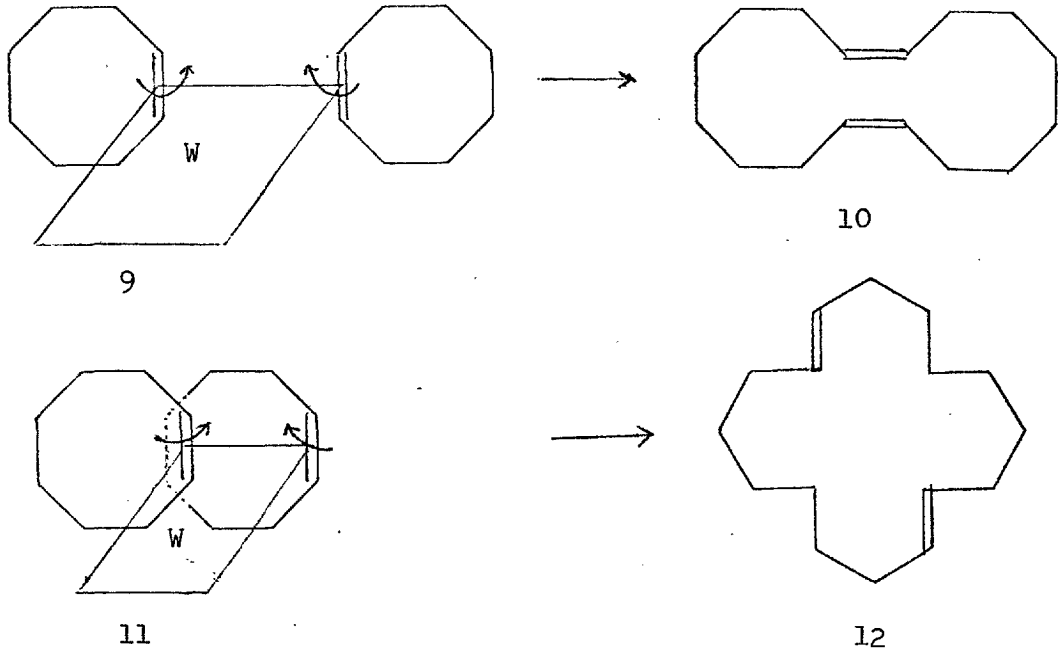


Scheme 8.



Scheme 9.

In the light of this, Wideman's report[25] that the dimerisation of cis-cyclooctene to cyclohexadeca-1,9-diene (Scheme 2) gives a mixture of 35% cis-cis, 53% cis-trans and 12% trans-trans products is interesting. Reaction of the expected conformer (9) would give a cis-cis product (10), whilst an "overlapped" complex such as (11) would give trans-trans diene (12).



9 10

11 12

The major, cis-trans product could be formed by a thermal or metal-catalysed isomerisation subsequent to, and independent of, the metathesis. If, however, it is actually formed by metathesis, this would argue strongly against the concerted, disrotation mechanism. Pettit's tetramethylene complex would not necessarily require retention of configuration since rotations or inversions could conceivably occur in the intermediate carbenoid complex. It appears, therefore, that detailed stereochemical studies of the metathesis of cyclic olefins might provide a method of distinguishing between the two major mechanisms proposed for the olefin disproportionation reaction.

1.4. Discussion.

Disproportionations of pent-2-ene and of hept-3-ene with the $WCl_6/EtAlCl_2/EtOH$ and the $Mo(NO)_2Cl_2I_2$ (L = pyridine, triphenylphosphine)/$Et_3Al_2Cl_3$ catalysts were carried out to verify the literature claims[6,20] and establish suitable, routine working conditions for the reactions. The metathesis was found to be exceedingly sensitive to small traces of impurities, so that rigorous purification and drying of solvents and substrates and complete exclusion of air was essential. For this reason, regular repeats of the model reaction were carried out to check that all operations were being correctly conducted - for example, after each preparation of a fresh batch of solvent, olefin or catalyst component.

In a typical experiment, the tungsten-based catalyst caused metathesis of hept-3-ene to hexene and octene in less than 3 minutes in benzene. An identical result was obtained in chlorobenzene and as the latter had a more convenient G.L.C. retention time, making routine monitoring of the reaction easier, this solvent was used in all subsequent experiments. The molybdenum nitrosyl catalysts disproportionated pent-2-ene to butene and hexene in 1-2 hours in chlorobenzene. Alkylation[30] of the chlorobenzene was not observed.

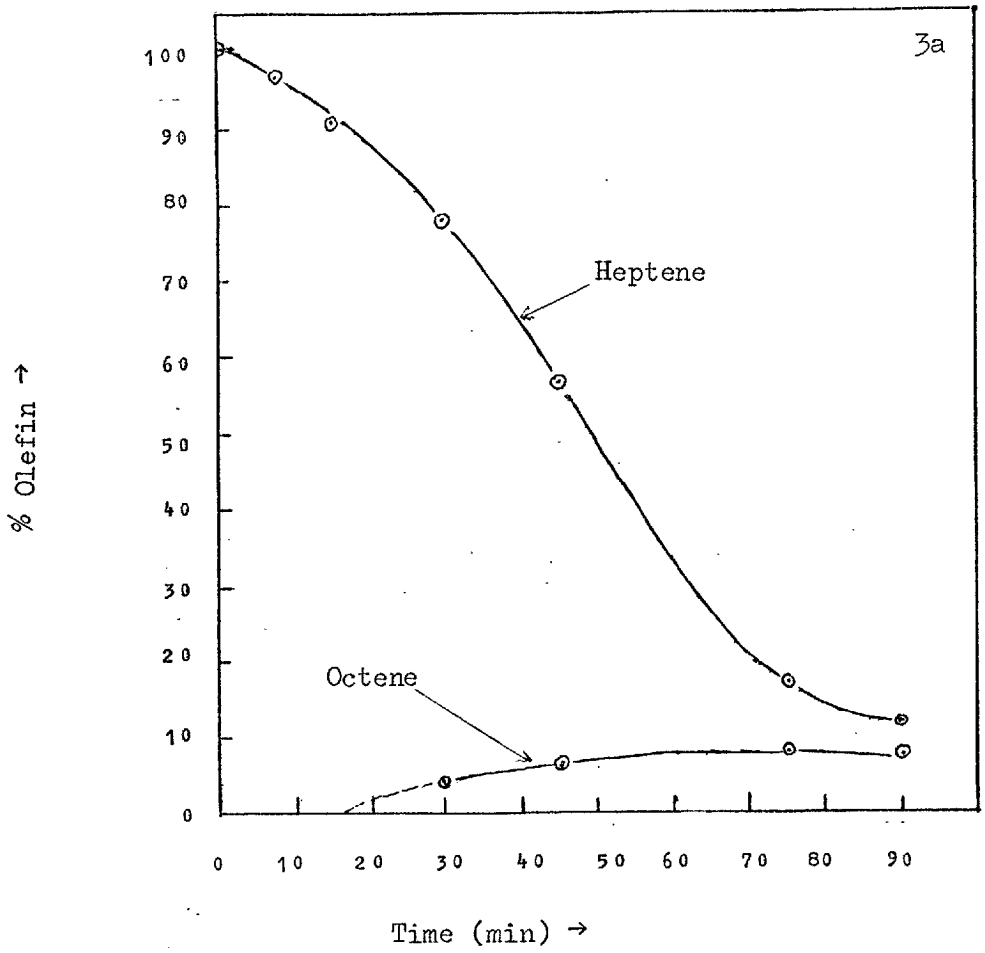
Since pure tungsten hexachloride oxidises readily in air, it was of interest to see whether the initial product of oxidation, namely $WOCl_4$, would act as a metathesis catalyst. It was found that a 1:1:4 mixture of $WOCl_4$, EtOH and $EtAlCl_2$ readily disproportionated hept-3-ene and a similar result was subsequently reported by Hérisson et al.[10] for pent-2-ene. Pure tungsten hexachloride was therefore generally handled for brief periods in air during weighing

procedures, without any noticeable deleterious effects on the reaction.

The most difficult component of the catalyst system to handle experimentally was the aluminium alkyl, which reacts rapidly and violently with air and was generally transfered from one nitrogen-flushed vessel to another by means of a syringe with a fine-bored needle. The reactivity of this component stimulated the search for a more stable and milder co-catalyst, and it was found that lithium aluminium hydride would effectively serve this purpose in combination with tungsten hexachloride. Detailed studies were carried out to determine the optimum reaction conditions for this new metathesis system.

In a series of experiments, a solution of hept-3-ene in chlorobenzene (2 M olefin per litre of solvent) was treated at room temperature with a mixture of WCl_6 and $LiAlH_4$, the W:olefin ratio being maintained at 1:20 and the W:Al ratio varied from 1:1 to 1:6. In each case, small aliquots of solution were removed at intervals and examined by G.L.C. Results are shown graphically in Figures 3 to 7.

It will be observed from these graphs that the concentration of hept-3-ene begins to fall from the moment of mixing of the reagents, whereas oct-4-ene does not begin to appear for some time. Thus, there is an induction period for the reaction and it appears that hept-3-ene is consumed in activating the catalyst. An estimate of the induction period was made by projecting the straight, central portion of the [octene]/[heptene] vs T graph (Figures 3b-7b) back onto the time axis, and using the figures obtained in this way for the whole series it was found that the induction period decreases in a roughly linear manner as the Al/W ratio is increased (Figure 8).



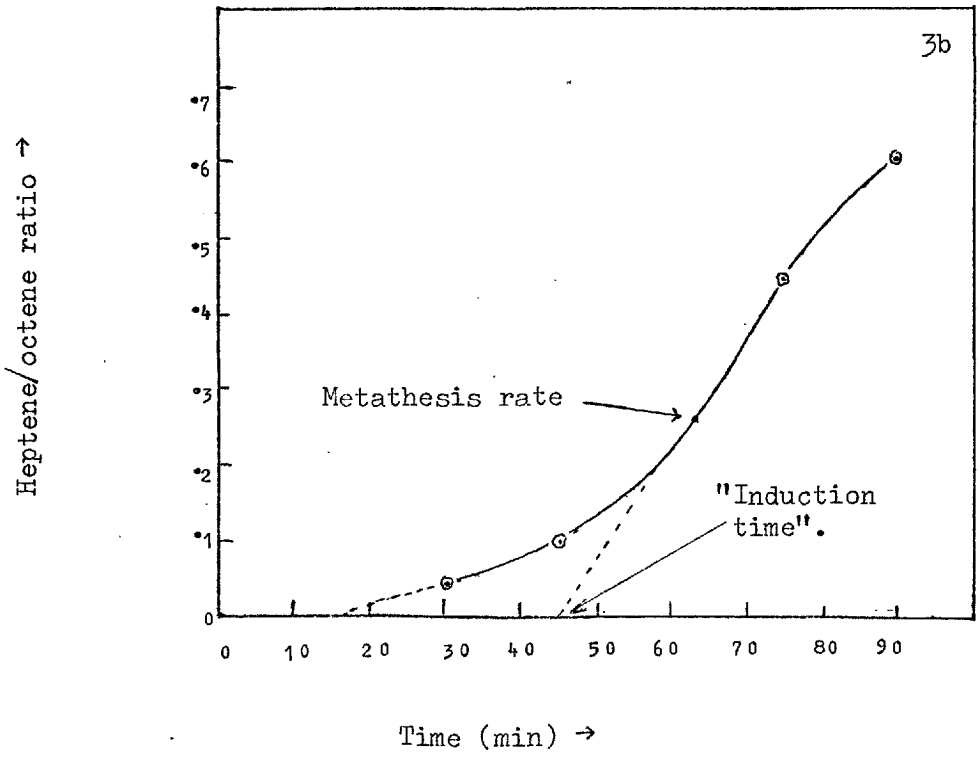


Figure 3. W:Al:Olefin = 1:1:20. Olefin/ClPh = 2M/litre.

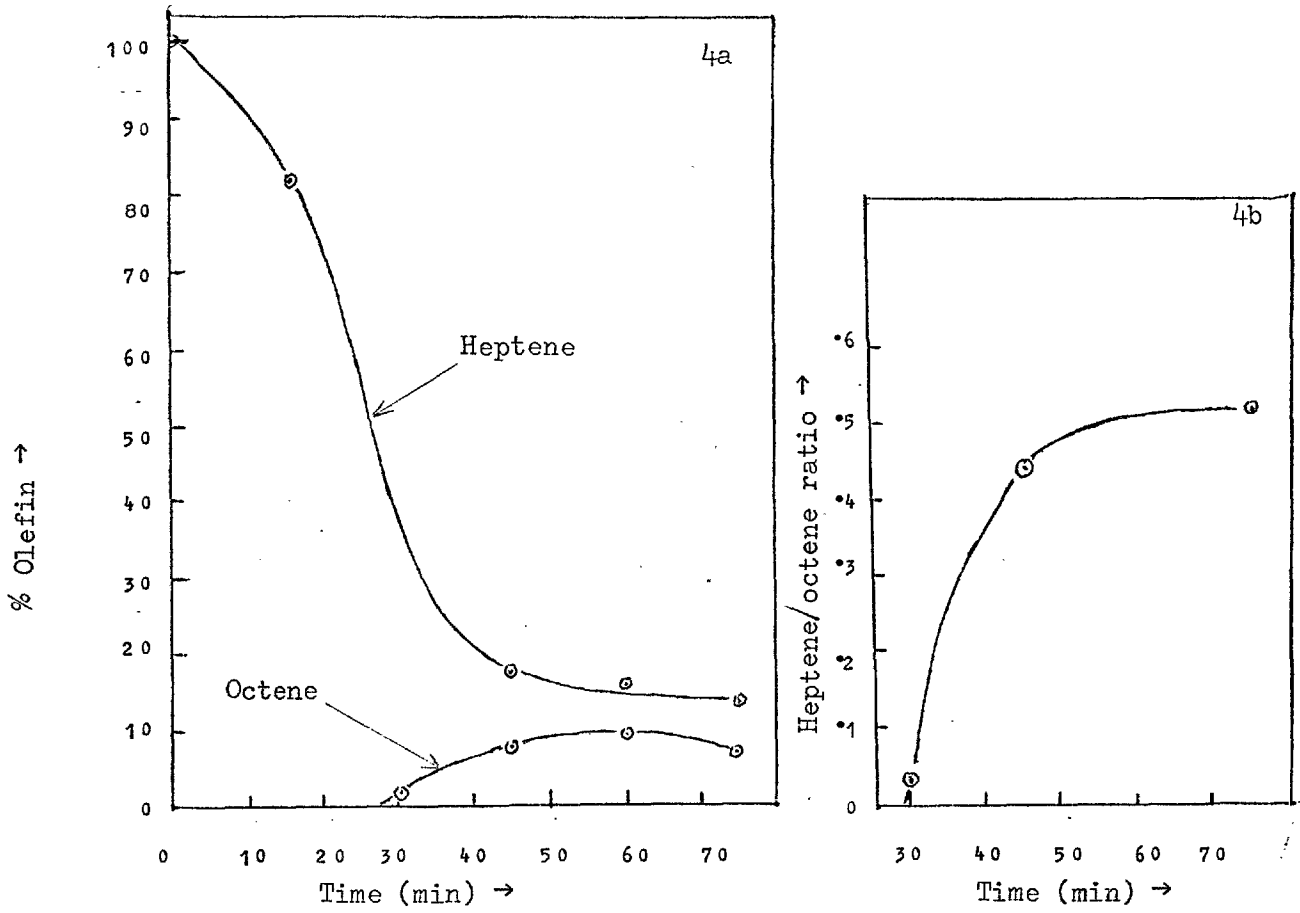


Figure 4. W:Al:Olefin = 1:2:20. Olefin/ClPh = 2M/litre.

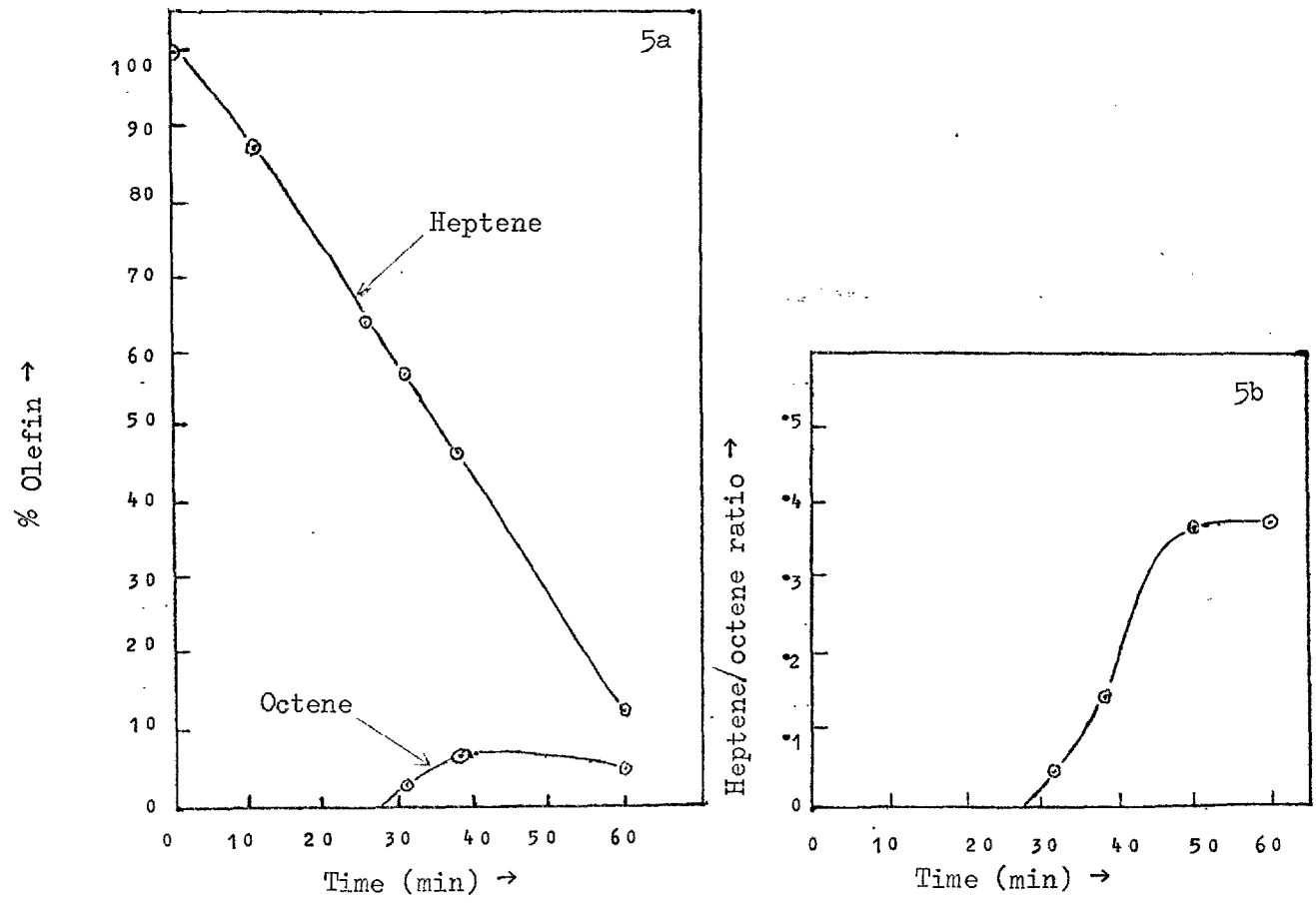


Figure 5. W:Al:Olefin = 1:3:20. Olefin/ClPh = 2M/litre.

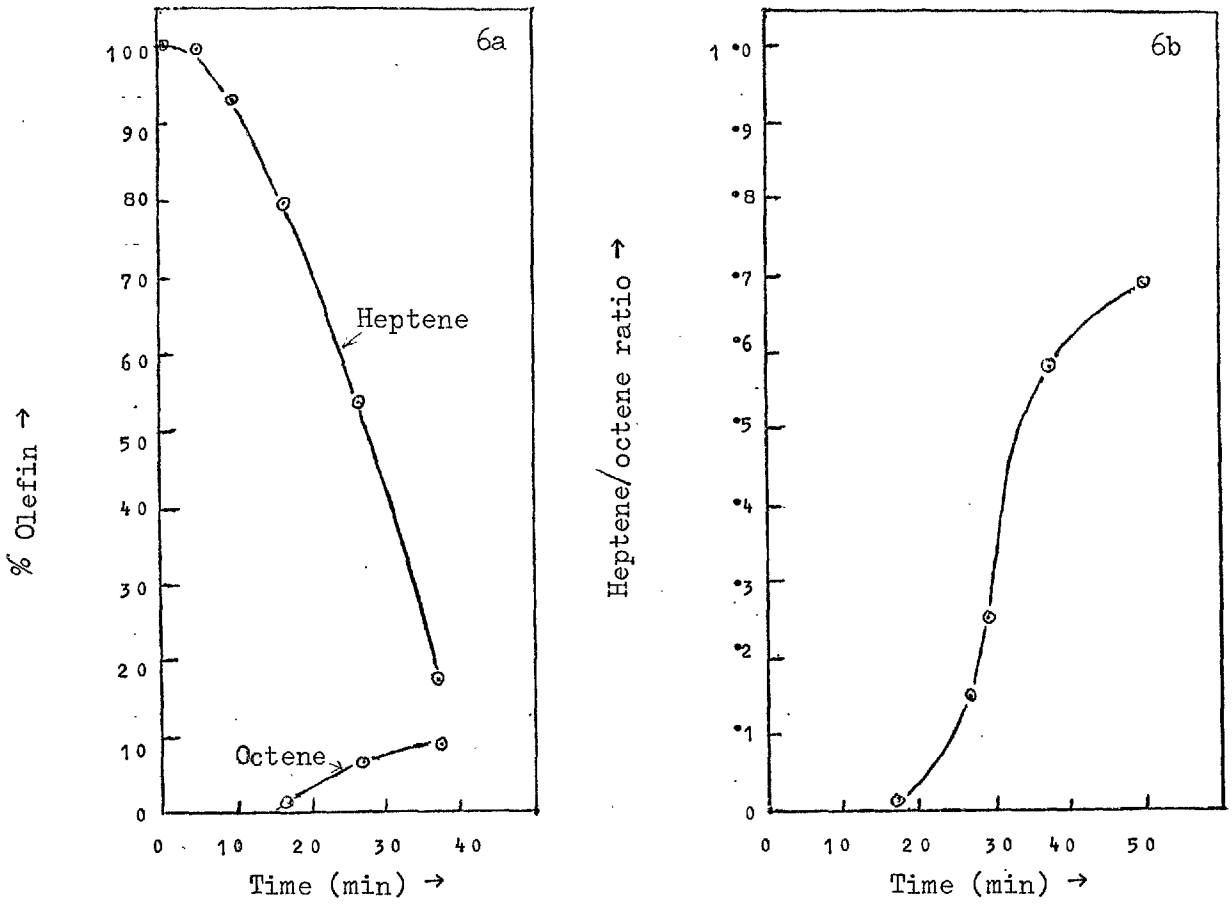


Figure 6. W:Al:Olefin = 1:4:20. Olefin/ClPh = 2M/litre.

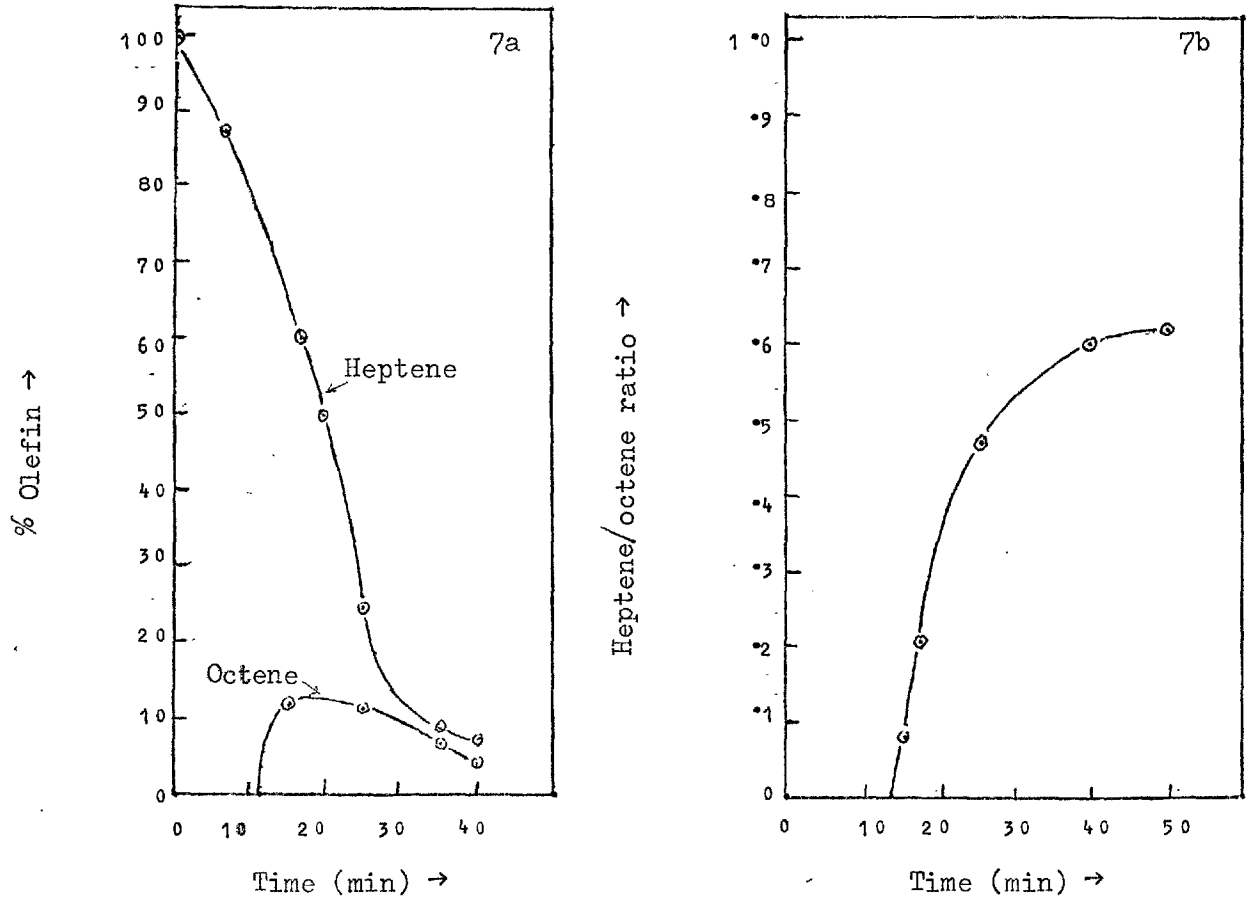


Figure 7. W:Al:Olefin = 1:6:20. Olefin/ClPh = 2M/litre.

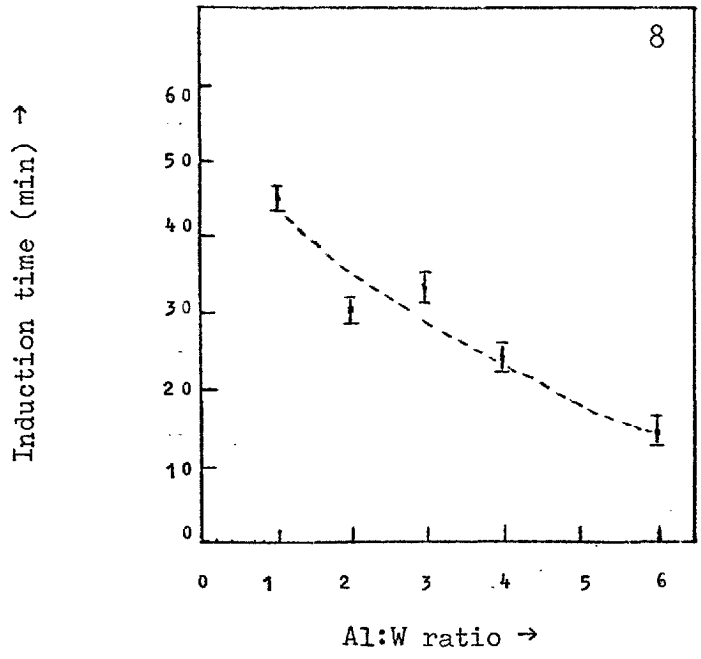


Figure 8. Induction time vs. Al:W ratio.

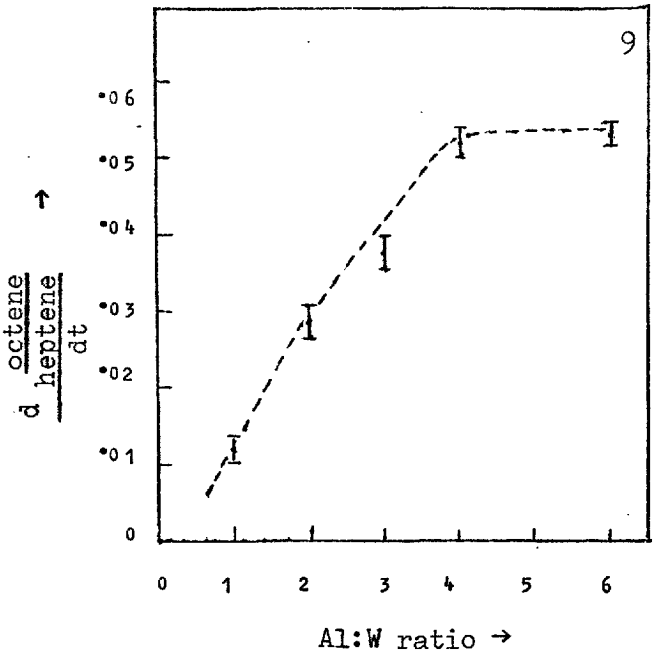
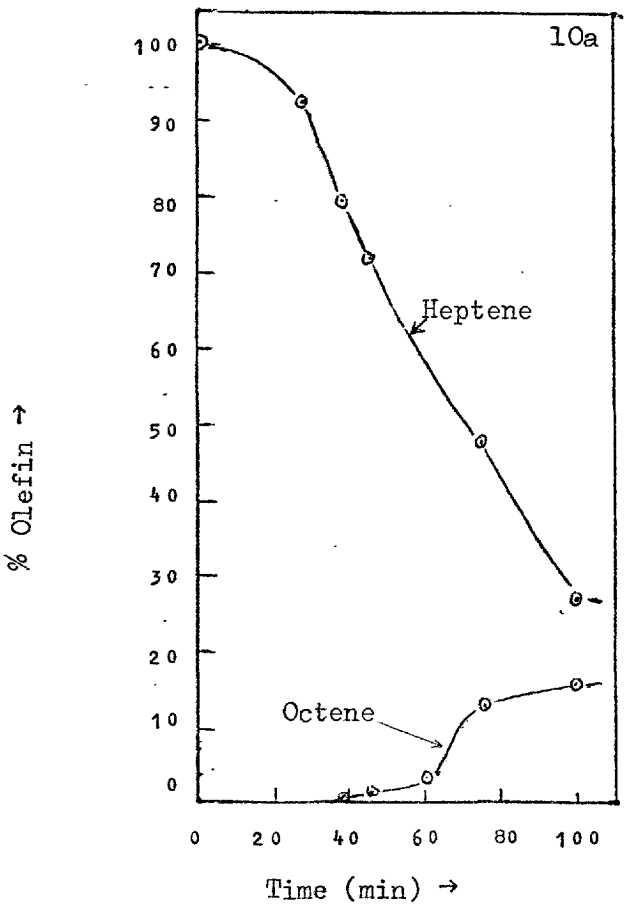


Figure 9. Metathesis rate vs. Al:W ratio.



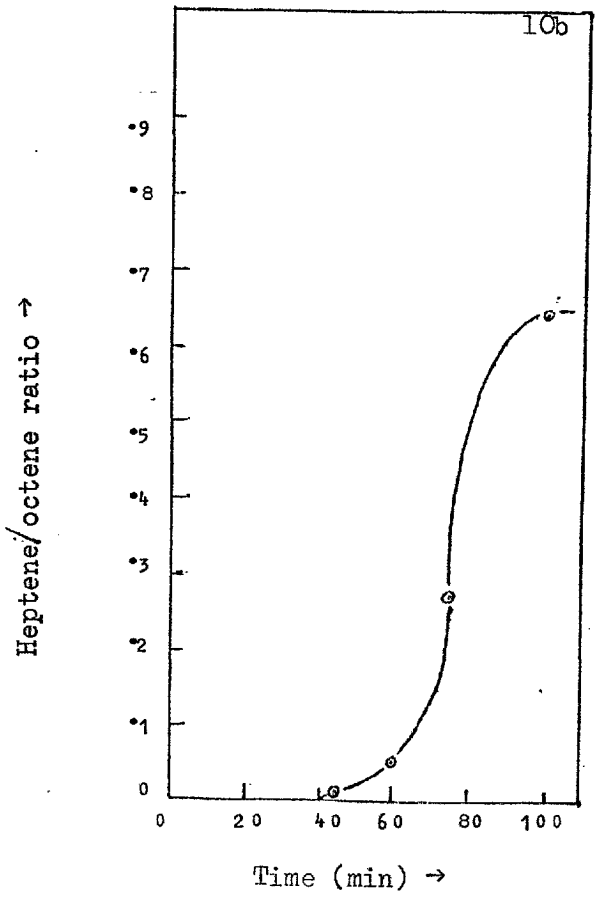
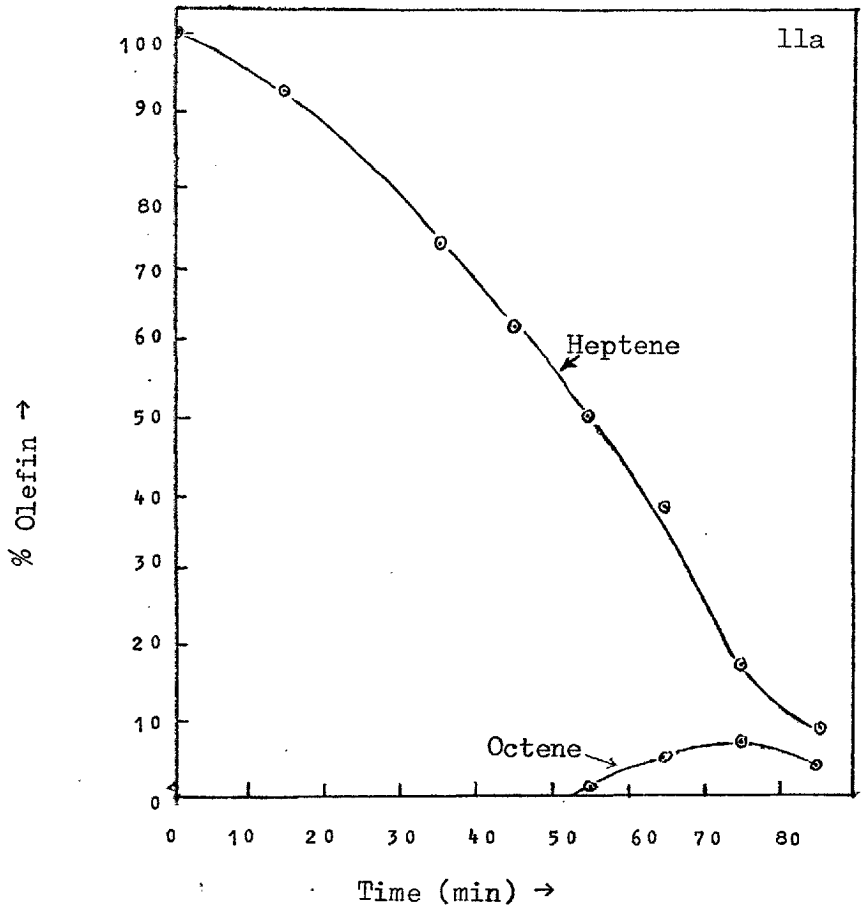


Figure 10. W:Al:Olefin = 1:4:50. Olefin/ClPh = 2M/litre.



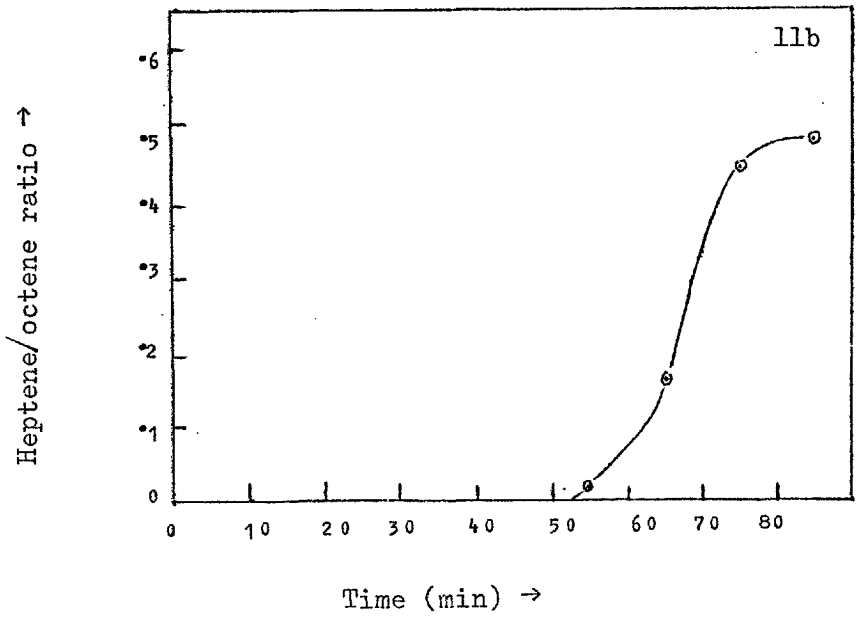
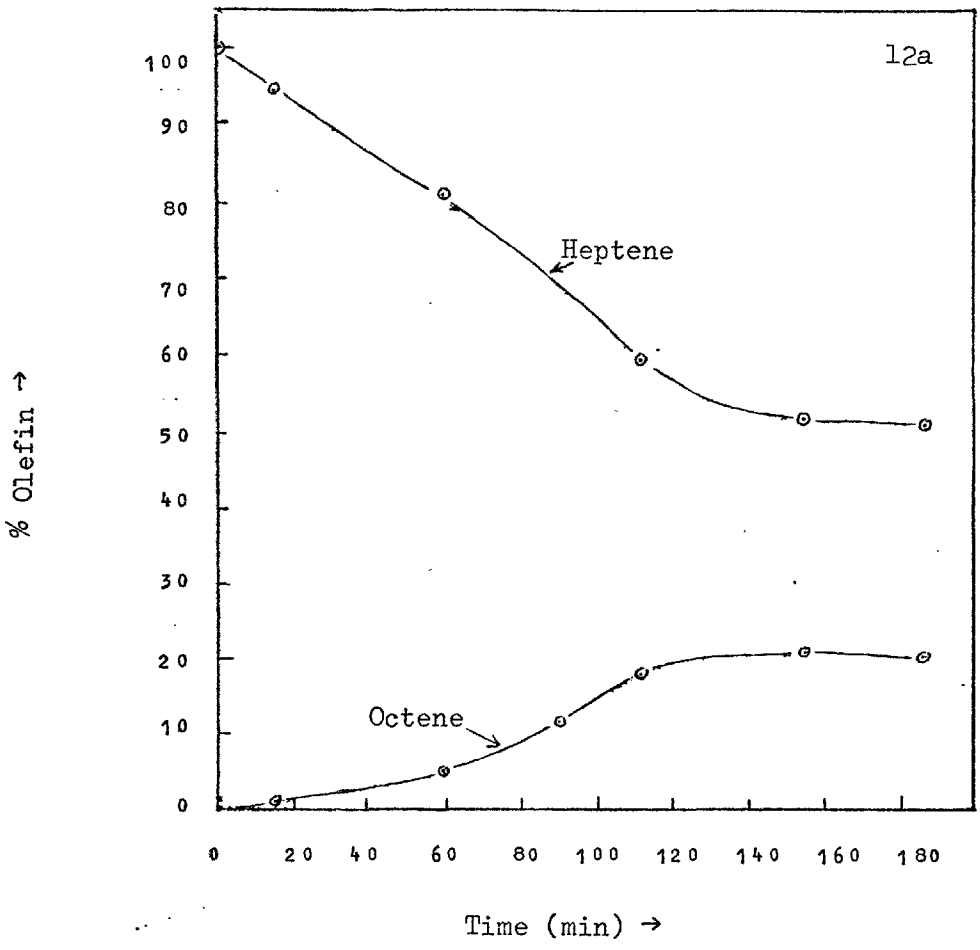


Figure 11. W:Al:Olefin = 1:4:20. Olefin/ClPh = 0.5M/litre.



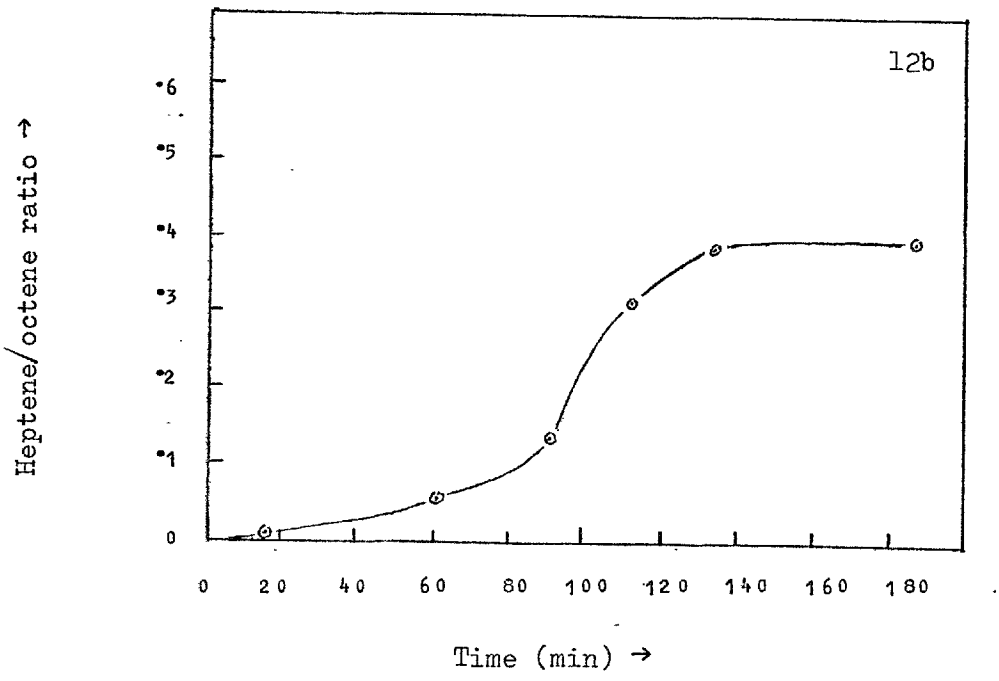
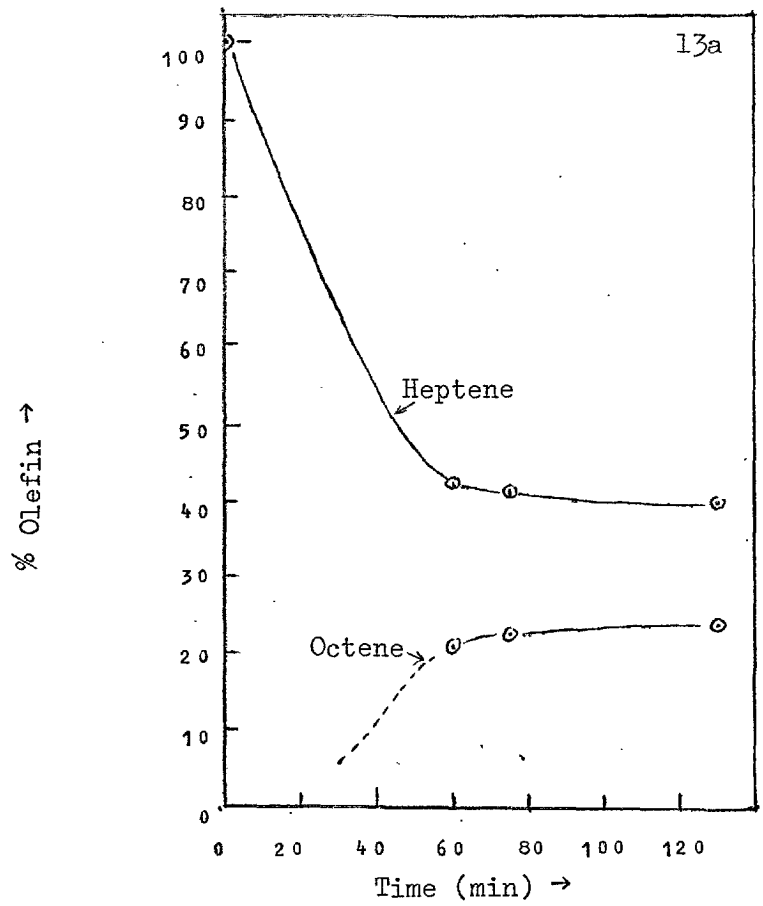


Figure 12. W:Al:Olefin = 1:4:100. Olefin/ClPh = 5M/litre.



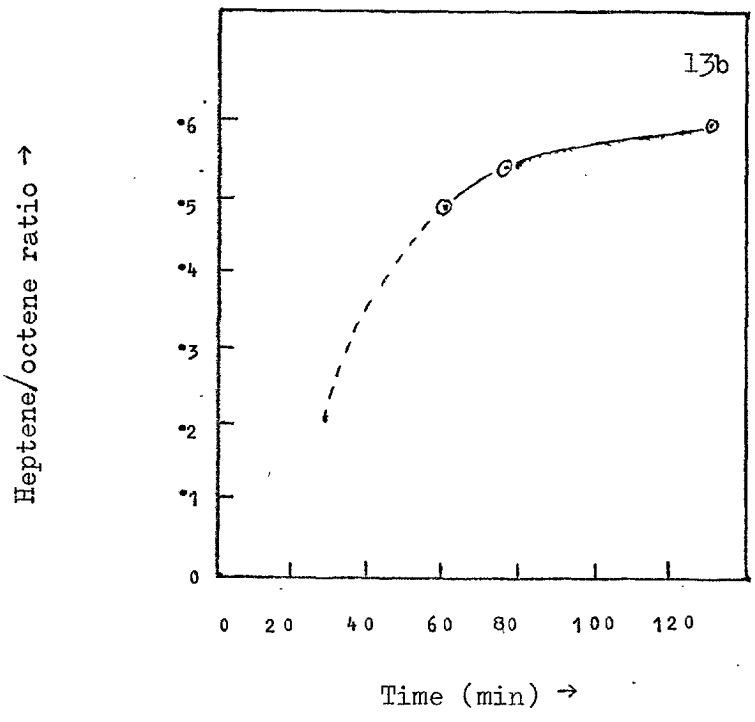
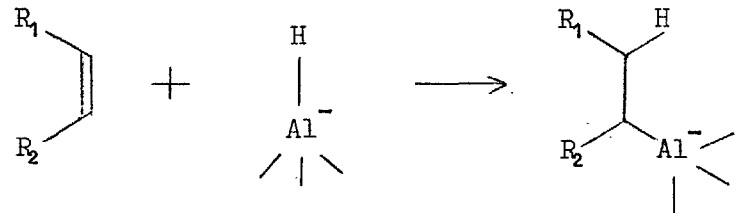


Figure 13. W:Al:Olefin = 1:4:80. Olefin/ClPh = 6M/litre.

Lithium aluminium hydride is known to react with olefins by addition, producing alanes (Scheme 10). The reaction is most favourable for terminal olefins,[54] but is known to be catalysed by the salts of transition metals.[55] Hence it appears that an aluminium alkyl is formed, and the active catalyst is then generated by the same mechanism that operates for the $WCl_6/EtAlCl_2$ system.



Scheme 10.

The absolute concentration of oct-4-ene reaches a maximum value and then declines. The concentration of hept-3-ene similarly continues to decline throughout the reaction, whilst the octene/heptene ratio tends towards a maximum value. Thus, there is at least one secondary reaction occurring in addition to metathesis which gradually removes all olefins from the solution. This reaction could be polymerisation, but with the relatively high catalyst levels used in these experiments, continued alkylation of the metal catalysts could easily account for eventual consumption of all the olefin present. It will be noted that the octene/heptene ratio generally tends to a value greater than 1/2, which suggests that the heptene is being removed faster than the octene as would be expected for such an alkylation process.

In each run (Figures 3b-7b), the gradient of the octene-4/heptene-3 ratio against time at the point when the metathesis had proceeded to

half the theoretical limit ([O-4]/[H-3] = 0.25) was taken as a measure of the rate of the metathesis (see Figure 3b). A plot of this value for each run against the Al/W ratio used shows that the optimum Al/W ratio is 4/1 (Figure 9). Calderon has reported that an Al/W ratio of 4/1 is the most effective with the $WCl_6/EtAlCl_2$ catalyst.[6]

Under the optimum conditions derived above (W:Al:olefin = 1/4/20; concentration of olefin = 2M/litre of solvent) the yield of oct-4-ene was about 35% of the theoretical.

A further series of variations were then carried out to maximise the yield of the reaction. Increasing the olefin:W ratio whilst keeping the olefin concentration constant had the effect of greatly increasing the induction time and increasing the yield of oct-4-ene. For an olefin:W ratio of 50:1 (Figure 10) the yield was 70% of theoretical, but at higher ratios the reaction became increasingly sluggish and failed to go to completion, probably due to decomposition of the catalyst (indicated by formation of a thick grey-green precipitate over 2-3 hours). Keeping the olefin/W/Al ratio constant (20/1/4) and lowering the olefin concentration had the effect of increasing the induction period from 15 minutes for a solution containing 2Mheptene per litre of chlorobenzene to over 50 minutes for a solution of 0.5M/litre of solvent, whilst the yield of oct-4-ene dropped to 30% of theoretical (Figure 11). Thus, increases in both the olefin:W ratio and olefin concentration improved metathesis efficiency up to a W/Al/olefin ratio of 1/4/100 and an olefin concentration of 5M per litre of ClPh, when the yield of oct-4-ene was 75% of theoretical (Figure 12). Further increases in olefin concentration (to 10M/litre ClPh) gave large amounts of by-products some of which appeared to result from metathesis of isomers of the starting material. The

rate of metathesis itself also began to decrease.

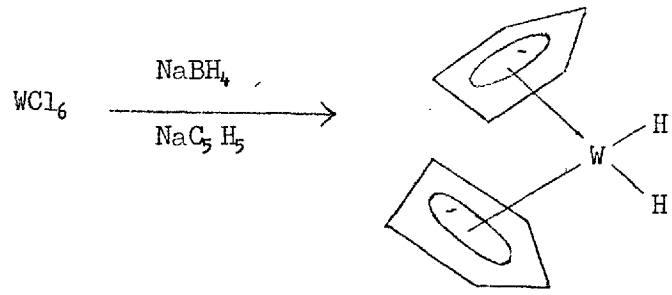
Finally, the best results achieved were those in which a W/Al/olefin ratio of 1/4/80 and olefin concentration of 6M/litreClPh were employed (Figure 13). A mixture of 18.5% hexene (i.e. 74% of theory), 39.8% heptene (79.6% theory) and 23.4% octene (93.6% theory) was produced in 130 minutes, as well as a mixture of three other products (ca.10% total) indicated by their G.L.C. retention times to be butene, pentene and nonene, which would suggest that a small amount of isomerisation occurs. $LiAlH_4$ is known to isomerise internal to terminal olefins in forming alanes.[56] The reaction under these conditions was successful on a preparative scale, with 20g(0.2M) of hept-3-ene.

Experiments with oct-1-ene and 2-methylbut-1-ene showed that the $WCl_6/LiAlH_4$ system will also disproportionate terminal olefins, in contrast to the polymerisation caused by the $WCl_6/EtAlCl_2$ catalyst.[20]

Other potential catalysts were briefly investigated. Sodium borohydride would not serve as a co-catalyst in place of lithium aluminium hydride.

Photolysis of molybdenum or tungsten hexacarbonyl in the presence of alkenes is known to lead to successive replacement of the CO groups by olefinic ligands.[57] Photolysis of $Mo(CO)_6$ in solution containing hept-3-ene or oct-1-ene did not, however, produce any metathesis.

Bis-cyclopentadienyl tungsten dihydride[58] (13) was synthesised (Scheme 11). Reaction with hept-3-ene in chlorobenzene led to a slow decomposition of the metal complex, but no metathesis.



13

Scheme 11.

Only a very limited range of olefins have ever been reported to undergo disproportionation, namely simple acyclic monoenes and dienes, and cyclic olefins with rings of eight carbon atoms or more, in no case containing any other functional groups. Investigations were therefore carried out to determine what the effects of functional groups on the course of the reaction would be.

In order to simplify and standardise these studies, the experiments were carried out by pre-mixing pent-2-ene, hept-3-ene or oct-2-ene with simple compounds containing the desired functional group, e.g. esters, ethers etc., and adding the mixture to the standard $WCl_6/EtAlCl_2$ catalyst in chlorobenzene, monitoring the results by G.L.C. Alternatively, the compound under study was added to the catalyst mixture first, followed immediately by one of the olefins. This procedure had the advantages of avoiding the necessity of developing a new G.L.C. analysis system for each new compound, of giving a direct comparison of the relative effects of different functional groups and of obviating the need for synthesising a large number of compounds. Furthermore, since all compounds examined had to be vigorously purified to avoid poisoning of the catalyst by extraneous material, purity controls were easier to

conduct in a system where only one new compound was being introduced in each successive experiment.

The initial results of this survey of functional-group effects are shown in Table 2.

It will be seen immediately that in all cases interference with the disproportionation reaction occurred. With simple esters the inhibition was complete, whilst in more hindered cases traces of metathesis products were observed. The same results were obtained with the molybdenum nitrosyl catalyst: thus, ethyl acetate completely stopped metathesis of hept-3-ene, and n-hexylbenzoate of pent-2-ene.

Diethyl ether completely prevented metathesis of hept-3-ene (Table 2) and this point was further illustrated by an experiment in which metathesis of a solution of hept-3-ene was commenced and after 100 seconds one equivalent of diethyl ether was added, whereupon the reaction immediately ceased. Again, the more hindered ethers (MeOPh and PhOPh) permitted a slow, incomplete reaction, which was also observed when the molybdenum nitrosyl catalyst was used. For example, traces of disporportionation products were formed from pent-2-ene after 4 days stirring with $Mo(NO)_2Cl_2(PPh_3)_2$ and $Et_3Al_2Cl_3$ in the presence of MeOPh.

Nitriles, amides, tosylates and sulphones caused immediate precipitation of the catalysts from solution, and no metathesis could be achieved in their presence.

Alkylhalides reacted violently with the catalysts and the resulting solutions were effective only for olefin polymerisation. Although chlorobenzene is a very effective solvent for metathesis, the presence of bromobenzene largely inhibited the reaction, and the eventual disappearance of all the olefin signified polymerisation to

Functional Compound	Olefin	Functional Compound: olefin ratio	Extent of metathesis %	Time (Min)	Comments
EtOAc	hept-3-ene	0.9	0	5	a
"	"	1.0	0	35	a
MeOBz	"	0.5	0	145	
n-hexylOBz	pent-2-ene	1.0	0	155	
PhOBz	hept-3-ene	0.5	trace	15	ca. twice as much metathesis after 120 min.
2,4,6-trimethyl phenyl butyrate	"	1.0	"	215	Soln. wine-red
"	"	0.5	"	95	Soln. wine-red
Et_2O	"	0.3	0	75	a
"	"	1.0	0	5	a
"	"	1.0	0	10	a
MeOPh	"	1.0	10	240	
PhOPh	"	1.0	50	400	All olefin disappeared overnight
"	oct-2-ene	1.0	trace	6	Nearly all olefin disappeared in 6 min.
Ph_3COPr	hept-3-ene	1.0	0	250	a
"	oct-2-ene	0.3	0	120	
MeCN	hept-3-ene	0.3	0	5	a
PhCN	"	1.0	0	280	
$MeCONMe_2$	"	0.5	0	2	a. Soln. became rapidly clear
$PhNO_2$	"	1.0	5	70	No increase in metathesis after 170 min.
"	"	1.0	5	28	No more after 20 hours
cyclohexyl OTs	"	1.0	0	170	a
Sulpholane	"	1.0	0	210	a
n-BuBr	"	1.0	0	30	b
PhBr	"	1.0	trace	60	All olefin disappeared in 180 min.
CCl_4	"	1.0	0	60	b
CH_2Cl_2	oct-2-ene	1.0	0	7	b. All olefin gone in 7 min.

Table 2.

Notes.

a. Thick precipitate developed.

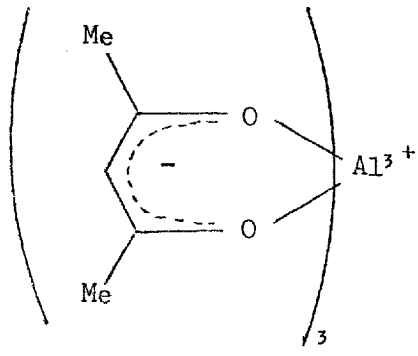
b. Effervescence and heat on mixing.

have occurred.

The conclusion drawn from all these results is that electron lone-pairs on oxygen and nitrogen complex more strongly than olefins with the active catalyst and thereby block the coordination sites. Thus the scope of the olefin metathesis reaction is severely limited, although the results suggest that vinylic molecules containing an OH or CO_2H group can be disproportionated providing that the group is well protected by formation of a highly hindered ether or ester. The practical difficulties of removing such protecting groups lowers the potential utility of this method, however.

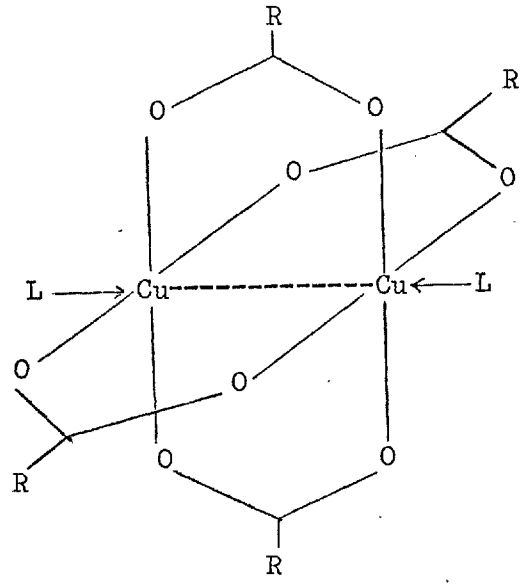
The strong complex formation observed between oxygen and metals suggested a possible way of circumventing the inhibition. It was argued that binding of substituent oxygen atoms to an alternative metal would reduce their ability to coordinate to the metathesis catalyst. Under these circumstances disproportionation of the vinylic complex should proceed.

The first test of this hypothesis was made with aluminium acetylacetonate (14), in which both oxygen atoms of the β-diketone are strongly bound to aluminium. No disproportionation of hept-3-ene could be achieved in its presence, however.



14

Copper salts of carboxylic acids have a dimeric structure[59] in which each CO_2^- group bridges two copper atoms. Two solvent molecules are generally associated with the complex though relatively weak coordination bonds (15 ; L = Solvent molecule).

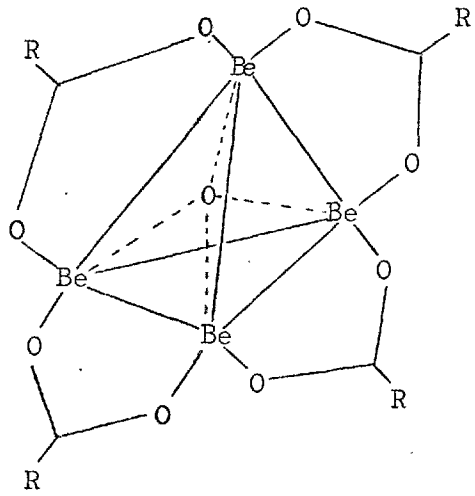


15

Hydrated copper butyrate[60] (15 ; R = Pr, L = H_2O) was prepared, and the water molecules exchanged for pyridine.[61] Very slight disproportionation of pent-2-ene was achieved in the presence of bis-pyridine complex using the $WCl_6/EtAlCl_2$ catalyst.

The lack of success with this copper-complex was attributed to the fact that the side-ligands L are fairly weakly bound, and dissociation in solution would produce a concentration of free ligand easily sufficient to poison the metathesis catalyst. Better results were therefore hoped for with the beryllium salts of carboxylic acids, and basic beryllium acetate[62] (16 R = Me) and butyrate[63] (16 R = Pr) were synthesised. A trace of disproportionation occurred when the acetate and oct-1-ene were added to $Mo(NO)_2Cl_2.Py_2$ and $Et_3Al_2Cl_3$. Slow and incomplete metathesis of hept-3-ene by $WCl_6/EtAlCl_2$ over 6 hours was observed in the presence of the butyrate salt. The method shows

slight promise as a means of reversibly protecting unsaturated acids for the metathesis reaction.



16

Each Be-Be bond is bridged by a CO_2^- group. Only 4 of the 6 bridging groups are shown.

1.5. Experimental.

Infrared spectra were taken on a Unicam SP200 Spectrometer. All IR bands quoted are in reciprocal wavenumbers.

Melting-points were taken on a Kofler Hot-Stage apparatus. All melting-points and boiling-points are uncorrected.

G.L.C. analyses were performed on a Perkin-Elmer F11 Dual-Column Flame Ionisation Chromatograph fitted with two glass columns (6' x ¼" o.d. 15% Squalane on Chromosorb P. 80/100 mesh).

Nitrogen was purified generally by passage through a train containing Dreschel bottles of Fieser's solution, concentrated sulphuric acid and KOH pellets. Nitrogen for dry-box procedures was purified by passage through a column of activated BTS catalyst[64] (Badische Anilin-und-Soda-Fabrik; copper oxide reduced for 2 hours at 140°

in a stream of hydrogen) followed by two columns of Drierite[65] ($CaSO_4$ impregnated with cobalt chloride and activated at 250° for 2 hours). Nitrogen for metathesis reactions was passed through both purifying trains. All connecting tubes were polythene or glass.

Tungsten Hexachloride

Commercial material (Koch Light or Alpha Inorganics) was purified[6] by heating for 1 hour at 200-220° in a stream of pure nitrogen, when orange vapours of $WOCl_4$ and yellow vapours of WO_2Cl_2 sublimed off, leaving pure, blue WCl_6, which was stored under nitrogen over P_2O_5.

Benzene

Distilled off P_2O_5 and stored over sodium-lead alloy under nitrogen.

Chlorobenzene

Distilled off P_2O_5 or sodium-lead alloy and stored over sodium-lead alloy under nitrogen. b.p. 131°/772 mm.

Pyridine

Refluxed 1.5 hours over BaO and distilled off BaO. Stored over KOH pellets. b.p. 117.5°/762 mm.

Olefins

Commercial material was fractionally distilled off P_2O_5 through a 9" Vigreux Column, stored over P_2O_5 and filtered through Grade I Alumina immediately before use.

pent-2-ene b.p. 36°/760 mm.

hept-3-ene b.p. 96°/772 mm.

oct-1-ene b.p.120°/773 mm.

oct-2-ene b.p.122-4°/772 mm.

Ethylaluminium dichloride[66]

Triethylaluminium (20.0 ml; 16.8g of commercial product, 90% pure; .133M) was placed in a 250 ml 3-necked flask under nitrogen and $AlCl_3$ (36.4g; .271M) added at once. Effervescence occurred, and during 10 minutes considerable heat was evolved and a grey precipitate formed. The flask was cooled in ice and the pressure inside slowly lowered to 60 mm. The flask was very gradually warmed and the product distilled, using a nitrogen bleed.

Ethylaluminium dichloride distilled at 112-113°/60 mm. as a water-white liquid. Yield 35.86g 67% based on $AlCl_3$. Stored under nitrogen in a flask fitted with a rubber septum.

Commercial $EtAlCl_2$ was also bought (Fluka),and distilled under reduced pressure before use.

Ethylaluminium sesquichloride[66]

To triethylaluminium (.5692g; .0050M) under nitrogen was added by injection ethylaluminium dichloride (2.0109g; .0158M), giving ethylaluminium sesquichloride by disproportionation.

$Mo(NO)_2Cl_2$ [67]

$Mo(CO)_6$ (10.00g; .0372M) was suspended in dry dichloromethane (95 ml) in a 3-necked flask which was flushed with nitrogen. NOCl was passed into the suspension, giving a red-brown colour to the solvent. After 5 minutes the stream of NOCl was stopped and there was a sudden, rapid effervescence and a green precipitate formed. After standing for 1 hour, the dichloromethane was removed under reduced pressure, using finally oil-pump suction via a cold-trap at -196°. A small quantity of $Mo(CO)_6$ (.115g) was recovered from the cold-trap. Yield of dichlorodinitrosyl molybdenum 8.08g; 95% based on the hexacarbonyl consumed. The product was stored under nitrogen

νmax (Nujol): 1800(S), 1685(S), 1600(W)cm-1. Lit: 1805(S), 1690(S), 1600(W)cm-1.

$Mo(NO)_2Cl_2(P\phi_3)_2$ [67]

Triphenylphosphine (12.17g; .0464M) in dry benzene (50 ml.) was added to $Mo(NO)_2Cl_2$ (3.56g; .0157M) under nitrogen and the mixture refluxed for 20 minutes, then cooled and filtered. The bis-triphenylphosphinedichlorodinitrosylmolybdenum was recrystallised from benzene/pet.ether as a green solid. Yield 10.61g; 90%.
νmax (Nujol): 1780(S), 1665(S)cm-1. Lit: 1790(S), 1670(S)cm-1.

$Mo(NO)_2Cl_2Py_2$ [67]

Dry pyridine (28.5 ml.) was added to $Mo(NO)_2Cl_2$ (2.21g; .0097M) under nitrogen. A green precipitate formed rapidly and was collected, washed with a little pyridine, then pet.ether (30-40°) and recrystallised from pyridine/pet.ether. Yield 2.05g; 55%.
νmax (Nujol): 1770(S), 1670(S), 1650(Sh),cm-1. Lit: 1790(S), 1680(S), 1675(Sh)cm-1.

Compounds Used In Studies Of Functional Group Effects.

Ethyl acetate

Fractionally distilled off K_2CO_3 76°/743 mm. Passed down a column of Grade I alumina immediately before use.

Methyl benzoate

Dried over sodium-lead alloy and filtered through Grade I alumina.

n-hexyl benzoate [68]

To n-hexanol (10.25g; .1M) in dry benzene (30 ml.) and pyridine (15.90g; 0.2M) was added dropwise benzoylchloride (14.25g; .1M) with cooling and stirring. After 2 hours the pyridine hydrochloride was filtered off and the solution passed down a column of Grade III alumina. The benzene was removed under reduced pressure, toluene

(5 ml.) added and the product distilled under reduced pressure. Yield, 15.80g, b.p. 152-4°/20 mm., n_D^{15}= 1.4963, νmax (film) 1720(S)cm-1.

The product was dried over P_2O_5 immediately before use.

Phenyl benzoate

Benzoyl chloride (14.1g; .1M) in dry benzene (25 ml.) was added dropwise with stirring and cooling to a mixture of phenol (9.41g; .1M) and pyridine (8.0g; .1M) in dry benzene (25 ml.). After 45 minutes stirring the pyridine hydrochloride was filtered off, the solution passed through Grade III alumina, the benzene removed and toluene (25 ml.) added to the residue. The toluene was removed on an oil-pump to give crude phenyl benzoate (15.6g; 79%), Mpt 66.5-67.5°. Two recrystallisations from absolute ethanol and vacuum drying gave pure product, m.p. 70° (Lit 71°) νmax (Nujol) 1720(S)cm-1. Immediately before use, the phenyl benzoate was dissolved in warm chlorobenzene and stood over sodium-lead alloy.

2,4,6-Trimethylphenylbutyrate

n-Butyrylchloride (5.33g; .05M) in dry benzene (25 ml.) was added dropwise with cooling and stirring to a solution of 2,4,6-trimethylphenol (6.80g; .05M) and pyridine (4.0g; .05M) in dry benzene (30 ml.). After stirring 45 minutes, the mixture was filtered, passed through Grade III alumina and evaporated under reduced pressure. Toluene (5 ml.) was added and the mixture distilled in vacuo. Pure 2,4,6-trimethylphenylbutyrate was collected at 140-142°/14 mm. Yield 4.9g; 47.5%. n_D^{18}=1.4941. νmax (film) 1740(S)cm-1.

The product was dried over sodium-lead alloy before use.

Diethylether

Distilled off P_2O_5 and stored over sodium-lead alloy.

Anisole, Diphenylether

Filtered through Grade I alumina and stored over sodium-lead alloy.

Trityl-n-propylether[69]

To n-propanol (3.75g; .063M) in dry pyridine (15 ml.) was added triphenyl chloromethane (5.00g; .018M) and the mixture stirred overnight, poured into water (50 ml.), filtered and dried at the pump. The crude product (5.3g) was recrystallised from absolute ethanol, giving white crystals of trityl-n-propylether. m.p. 53-4° (Lit:55°). Yield 4.22g. 77.8%.

The product was dissolved in chlorobenzene and dried over sodium-lead alloy before use.

Acetonitrile, benzonitrile

Filtered through Grade I alumina and dried over sodium-lead alloy.

N,N-dimethylacetamide

Freshly distilled and dried over sodium-lead alloy.

Nitrobenzene

Dried over sodium-lead alloy.

Cyclohexyl Tosylate

To cyclohexanol (5.0g; .05M) in dry pyridine (60 ml.) at 0° was added tosyl chloride (19.0g; .10M) and the mixture stood in a refrigerator for 3 days, then poured into ice-water (300g) and extracted with ether (100 ml.). The ethereal phase was dried over calcium sulphate and evaporated. The residue was recrystallised from pet.ether at -78°, giving pure cyclohexyl tosylate, 11.30g, 90%. m.p. 42.5-43°. Lit: Mpt 45-6°. νmax (Nujol): 1385(S), 1360(S), 1190(S), 1180(S), cm^{-1}.

The product was stored in a refrigerator in a sealed bottle.

Sulpholane

Distilled off NaOH pellets under vacuum. b.p. 143-4°/8 mm. $n_D^{18} = 1.4835$. (Lit b.p. 149.5-150°/15 mm. $n_D^{18\cdot2} = 1.4833$). Stood over sodium-lead alloy before use.

Carbon Tetrachloride, Dichloromethane

Dried over sodium-lead alloy and filtered through Grade I alumina.

Aluminium Acetylacetonate[70]

Recrystallised from chloroform m.p. 190° (Subl) Lit. 191-3°. Vacuum Dried.

Cu(butyrate)$_2$. H_2O[60]

n-Butyric acid (17.8g; .20M) was dissolved in water (25 ml.) containing sodium hydroxide (8.0g; .20M), and the solution added to copper sulphate (26g; .104M) in water (50 ml.). The turquoise precipitate of copper butyrate was filtered off and vacuum dried over calcium chloride. Yield 22g; 81%. νmax (Nujol): 3,400(S), 1610(b,S) 1385(S), 1355(W), 1325(S)cm^{-1}.

Cu(butyrate)$_2$. pyridine[61]

To Cu(butyrate)$_2$ H_2O (6.38g; .025M) in boiling benzene (100 ml.) was added pyridine (2.00g; .025M). The mixture was stirred, cooled, filtered and the filtrate evaporated to give a dark green solid which was washed with a little cold ether and recrystallised from ether and vacuum dried. Yield 6.2g. 78.5%. νmax (Nujol): 1620(S), 1385(S), 1355(W), 1340(W), 1320(M)cm^{-1}.

Basic Beryllium Acetate[62]

Beryllium carbonate (2.0g; .03M) was dissolved in hot glacial acetic acid (5 ml.). After evolution of CO_2 had ceased the solution was cooled and filtered. The product was dissolved in hot chloroform (5 ml.), filtered and recrystallised from dry benzene. Yield 1.35g.

52%. m.p. sublimed above 270° (Lit: 283-4° sublimes). νmax (Nujol): 1640(b,S)cm-1.

Basic Beryllium Butyrate[63]

Beryllium carbonate (3.0g; .044M) was dissolved in hot butyric acid (15.84g; .180M) and the solution allowed to cool overnight. The unreacted butyric acid was distilled out under reduced pressure (89-90°/45 mm.) and the residue recrystallised 5 times at -78° from pet.ether (40-60°) to give white crystals. Yield 3.4g. 79%. m.p. 24.5-5° (Lit: 25-7°). νmax (Nujol): 1630(b,S)cm-1.

Metatheses

Reactions were conducted in a 25 ml. cylindrical, flat-bottomed flask fitted with nitrogen inlet and outlet tubes and a rubber septum. After introduction of any solid, air-stable catalyst components and a magnetic stirrer-bar, the flask was flushed for at least 15 minutes with nitrogen before injection of liquid reagents. Small aliquots (0.1-0.2 ml.) were removed at intervals as desired, using a syringe, and immediately injected into sealed 5 ml. flasks containing methanol (0.2 ml.), the sample flasks generally being cooled in an acetone-cardice bath immediately before a G.L.C. sample was taken with a microsyringe. The bulk reaction was terminated at the desired time by injection of methanol (0.25 ml.).

The following metatheses are representative of conditions employed:

a). To $Mo(NO)_2Cl_2(PPh_3)_2$ (.0167g; 2.2×10^{-5} M) under nitrogen was added chlorobenzene (1.0 ml.) followed by $Et_3Al_2Cl_3$ (.05 ml.) and then pent-2-ene (1.0 ml.; .01M) giving a brown solution. G.L.C. after 2 hours showed disproportionation to butene and hexene. Two small peaks of longer retention time than the hexene indicated a

slight amount of isomerisation.

b). To WCl_6 (.0389g; 0.98 x 10^{-4} M) under nitrogen was added benzene (3.0 ml.) followed by a solution of ethanol in benzene (.20 ml. containing 0.98 x 10^{-4} M EtOH), then $EtAlCl_2$ (8 drops), then hept-3- ene (1.50 ml; 0.01M). The reaction was terminated with methanol (0.2 ml.) after 2.0 minutes. G.L.C. showed an equilibrium mixture (1:2:1) of hexene, heptene and octene.

c). WCl_6 (.1964g; 4.91 x 10^{-4} M) and $LiAlH_4$ (.0760g; 2.00 x 10^{-3} M) were weighed into the metathesis flask, which was flushed with nitrogen and chlorobenzene (5.0 ml.) added, followed immediately by hept-3-ene (1.50 ml; 0.01M), giving a W:Al:olefin ratio of 1:4:20. The mixture was stirred rapidly and samples removed at 5-10 minute intervals for G.L.C. analysis.

d). To WCl_6 (.9910g; .0025M) and $LiAlH_4$ (.3820g; .0101M) under nitrogen in a 100 ml. flask was added hept-3-ene (20.00g) in chlorobenzene (33.4 ml.). The mixture was stirred for 130 minutes, and terminated by addition of methanol (1.5 ml.). G.L.C. analysis showed hexene (14.1%), heptene (38.2%) and octene (19.7%).

e). To WCl_6 (.0391g; .99 x 10^{-4} M) under nitrogen were added chlorobenzene (3.0 ml.), a solution of ethanol in chlorobenzene (0.20 ml. containing 1.01 x 10^{-4} M EtOH), ethylaluminium dichloride (5 drops) and then a mixture of hept-3-ene (1.50 ml; .01M) and benzonitrile (1.0g; .01M). GL.C. analysis after 4 hours 40 minutes showed no trace of reaction.

f). To WCl_6 (.0104g; 0.26 x 10^{-4} M) under nitrogen was added chlorobenzene (1.5 ml.), $EtAlCl_2$ (8 drops), diphenylether (0.425 g; .25 x 10^{-2} M) and hept-3-ene (.375 ml; .25 x 10^{-2} M). G.L.C. analysis showed a tiny amount of metathesis after 15 minutes, the amount

increasing steadily over 6.5 hours to half the equilibrium amount. After stirring overnight, however, G.L.C. showed complete disappearance of all olefins from the solution; only the solvent peak remained.

Bis-(cyclopentadienyl) tungsten dihydride.[58]

a). Cyclopentadiene

Dicyclopentadiene (20 ml.) was placed in a flask which was immersed in a heating bath at 250° and the cyclopentadiene formed was distilled out through a 9" Vigreux column, adjusting the heating rate by altering the depth of immersion of the flask so that the temperature at the still-head was maintained at 48-50°. The cyclopentadiene was collected in a flask cooled in an acetone-cardice bath to -78°, and was stored at that temperature until used.

b). Cyclopentadienyl sodium

Sodium sand (2.4g; .1M) was placed in a 3-necked flask fitted with a reflux condenser, nitrogen inlet and a rubber septum. After flushing with nitrogen, anhydrous, degassed THF (50 ml.) was added and the mixture stirred as cyclopentadiene (7g) was added portionately by injection until all the sodium had dissolved, giving a rose-coloured solution of cyclpentadienyl sodium (0.1M).

c). Bis-(cyclopentadienyl) tungsten dihydride[58]

Sodium Borohydride (.50g; .013M) was placed in the bottom of a large test-tube containing a magnetic stirrer, having a side-arm near the top, and fitted with a reflux condenser. Nitrogen was flushed through the tube via the side-arm, and a solution of cyclopentadienyl sodium (.03M) in THF (15.0 ml.) was added. The mixture was cooled in an ice-bath and rapidly stirred as tungsten hexachloride (2.0g; .005M) was added portionately. An exothermic reaction occurred,

and the mixture turned dark brown. After completion of addition, the mixture was refluxed for 4 hours, then the THF was distilled out under vacuum, the reflux condenser replaced by a cold-finger condenser and the residue sublimed at 100°/0.1 mm. for 24 hours. The sublimate, bright yellow crystals of bis-(cyclopentadienyl) tungsten dihydride (0.05g; 3%) was stored under high vacuum.

Reaction of bis-(cyclopentadienyl) tungsten dihydride with hept-3-ene

The tungsten complex (.0158g; .0005M) was dissolved under nitrogen in chlorobenzene (2.0 ml.) giving a pale yellow solution to which hept-3-ene (.75 ml; .05M) was added. The solution was stirred for 24 hours, during which time it darkened to brown-black. No conversion of the hept-3-ene was detected by G.L.C.

Photolyses of $Mo(CO)_6$ with olefins

a). $Mo(CO)_6$ (.0301g; 1.14×10^{-4} M) and hept-3-ene (1.30 ml; 8.7×10^{-3} M) were dissolved in chlorobenzene (15.0 ml.) in a quartz vessel under nitrogen and irradiated with a medium-pressure mercury lamp. The solution quickly turned yellow, but after 4 hours there was no metathesis observable.

b). $Mo(CO)_6$ (.0527g; .0002M) and oct-1-ene (1.60ml; .01M) in cyclohexane (30 ml. "spectrosolv" dried over P_2O_5) were photolysed in a quartz vessel under nitrogen with a medium-pressure mercury lamp for 5 hours. No reaction of any kind could be detected by G.L.C.

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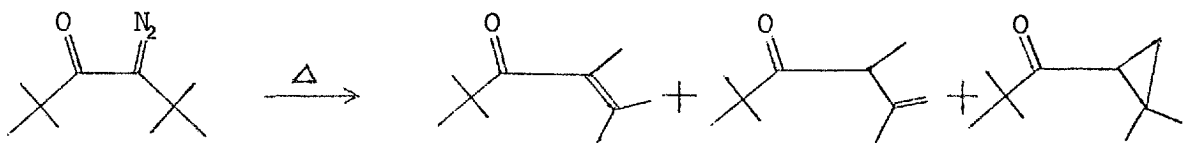
SECTION 2. OXYGEN TRANSFER REACTIONS

2.1. Review of ketocarbenes and oxirens.

Following the discovery of the Wolff rearrangement,[1] and the development by Arndt and Eistert[2] of a simple method of synthesising diazomethyl ketones from acid chlorides and diazomethane, which was later extended to higher homologues of diazomethane,[3] the decomposition of α-diazoketones has become an important method of organic synthesis.[4,5] Recent, alternative methods of preparing diazoketones have added to their usefulness as synthetic intermediates.[6-11]

Apart from the acid-catalysed decomposition of diazoketones, which proceeds via reversible protonation of the diazo carbon[12] and subsequent decomposition of the intermediate diazonium (or carbonium) ion (for some typical examples see references 13-18), four principal methods of catalysis of diazoketone decomposition leading to nitrogen loss may be distinguished, namely thermal, photochemical, silver-catalysed and copper catalysed reactions.

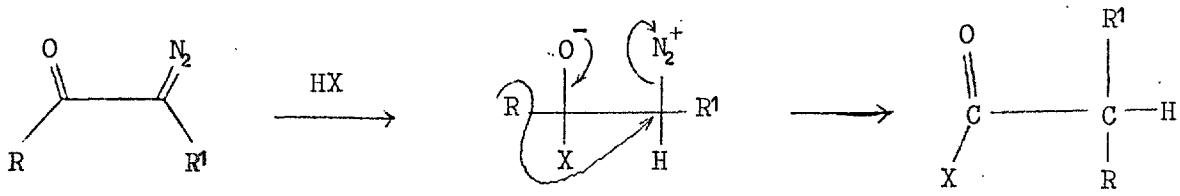
The thermal decomposition of α-diazoketones, either neat or in inert solvents, generally leads to keten formation.[19] These ketens can sometimes be isolated, for example, azibenzil gives diphenylketene.[20] In contrast ketens from diazomethylketones can rarely be isolated, however; generally the keten attacks a molecule of starting material, with formation of a butenolide.[21] Thermolysis of di-t-butyl diazoketone (1) gives a very low yield of di-t-butyl keten: the principle product (2) arises from a 1,2 methyl migration (Scheme 1).[22,23]



1 2

Scheme 1.

In the presence of compounds such as alcohols or amines an acid derivative is usually isolated.[3] Eistert[24] suggested that under these conditions a keten is not actually formed, but that the reaction proceeds via attack on the diazoketone (Scheme 2).



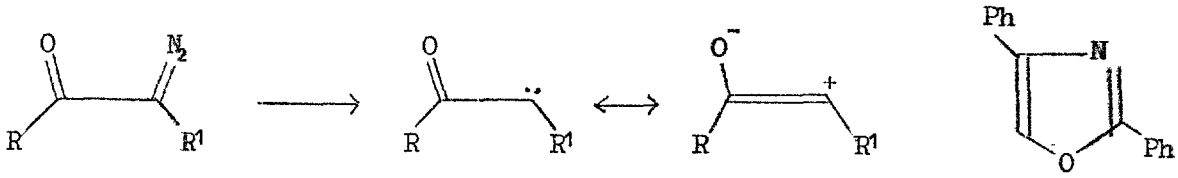
Scheme 2.

Only recently have kinetic studies by Jugelt and Schmidt[25] been able to rule out this mechanism, by showing that the rate-determining step (nitrogen loss) of the diazoketone decomposition is independent of the concentration and basicity of any amines present, and that the kinetic isotope effect for N,N-dideutero-aniline, k_D/k_H, is approximately 1.

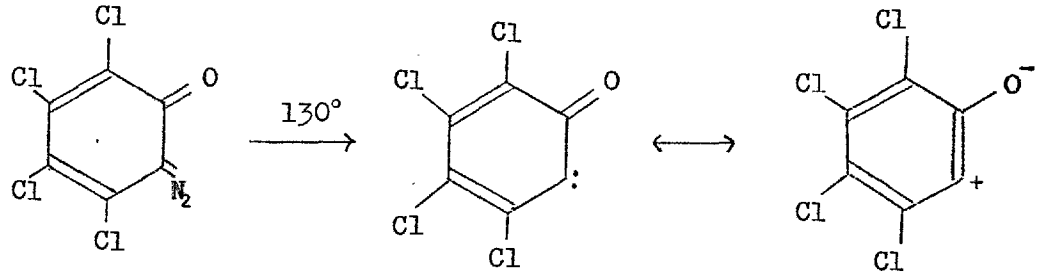
A subject of much dispute in the literature has been the question of whether migration and nitrogen loss are concerted or non-concerted. Fry[26] argued in favour of a concerted pathway on the basis of studies of the decomposition of α-naphthyl-CH_2COCHN_2 in boiling aniline, in which he claimed to have observed a significant isotope effect, $k_{14C}/k_{12C} = 1.5\% \pm 0.5\%$, for the CH_2 group, which implies participation of the migrating group in the rate-determining step of the reaction.

Huisgen[27,28] attempted to trap any intermediate ketocarbene in the Wolff rearrangement by making use of its potential 1,3 dipolar character (Scheme 3). These attempts met with very little success (e.g. decomposition of diazoacetophenone in benzonitrile gave only 0.4% of the oxazole (3)) except in cases such as the diazooxide (4)

where special stabilising factors are involved and the mechanism is not necessarily the same as for simple diazoketones.



3

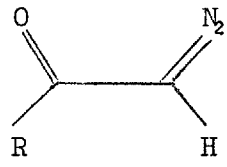


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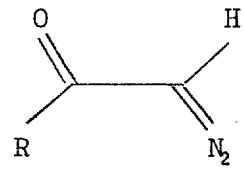
Scheme 3.

Kaplan and Melloy[29a] have reported detailed NMR studies of the conformations of diazomethylketones in solution. The cis conformation (5) was found to predominate (> 90%) over the trans conformation (6). On the basis of these results, it was argued that the Wolff rearrangement proceeds solely from this cis form via a smooth concerted process, with migration and nitrogen loss occurring simultaneously. On the other hand, disubstituted diazoketones should have an almost exclusively trans conformation (7) which is unfavourable for a concerted Wolff rearrangement, and it was proposed that this accounted for the results observed with di-t-butyldiazoketone (1) and with α-methylenediazoketones (see below).

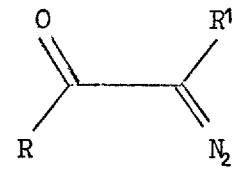
The recent report[29b] that Wolff rearrangement of α-diazo-homoadamantanone proceeds without oxiren participation is also in agreement with this theory, since this diazoketone is rigidly fixed in a cis-conformation and should not, therefore, give a free ketocarbene (see Section 2.2).



5



6



7

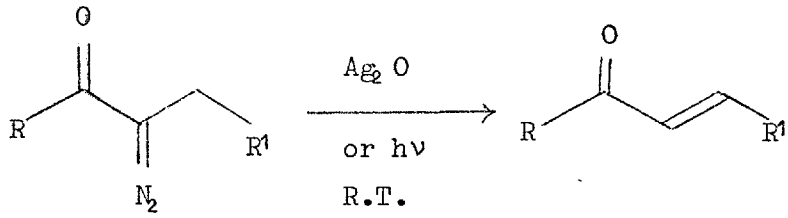
The first real evidence for the intermediacy of ketocarbenes in the thermal Wolff rearrangement was provided by Jugelt and Schmidt[25] in 1969, when kinetic studies with para-substituted azibenzils in di-n-butylether in the presence of amines were interpreted in terms of a two-step ketocarbene-keten mechanism.

The situation is very similar for the photochemical Wolff rearrangement. Thus, in inert solvents the photolysis of azibenzil gives diphenylketen; in aqueous media diphenyl acetic acid is formed.[30] The intermediate keten has also been trapped with amines,[31] alcohols[32,33] and thiols.[31] Again, 1,3-dipolar trapping experiments[27,28] were successful only in cases where special stabilising factors could significantly increase the lifetime of a ketocarbene intermediate. However, Ando and Jones[33] found that the photochemical Wolff rearrangement of 2-diazocyclohexanone is suppressed in the presence

of benzophenone and that the triplet intermediate produced will add non-stereospecifically to olefins giving cyclopropanes. Padwa and Leyton[32] showed that in the photolysis of diazoacetophenone in alcohols, H-abstraction from the solvent, producing acetophenone, competes with Wolff rearrangement to the phenylacetic ester, and that the amount of H-abstraction is very greatly increased by benzophenone sensitisation. These results have all been interpreted in terms of a common ketocarbene intermediate which Wolff-rearranges in its singlet state but undergoes H-abstraction or addition to olefins in its triplet state.

Silver catalysts are commonly used for the Wolff rearrangement,[4,5] although they are often more successful with diazomethylketones than with higher homologues.[3] Newman and Beal[34] developed a homogeneous catalyst comprising of silver benzoate and triethylamine in methanol and proposed a chain-radical mechanism leading to keten formation. Later, however, more detailed studies with this system argued in favour of the rearrangement of a silver-triethylamine complex of an intermediate ketocarbene to give the keten.[35]

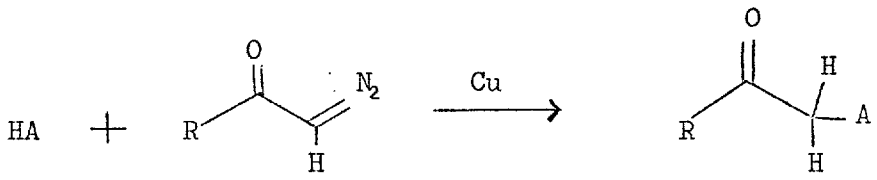
In 1957, Franzen[36] reported that diazoketones bearing an adjacent methylene group (8) are decomposed by silver oxide at room temperature to give α,β-unsaturated ketones (9) by a 1,2-hydrogen migration (Scheme 4), whilst at higher temperatures the Wolff rearrangement predominates. The temperature dependence of the reactions suggests that they diverge from a common intermediate, and lends support to the idea that this is a ketocarbene-silver complex, with a greater activation energy for Wolff rearrangement than for H-migration. Photochemical decomposition of α-methylene diazo ketones also produces α,β-unsaturated ketones.



8 9

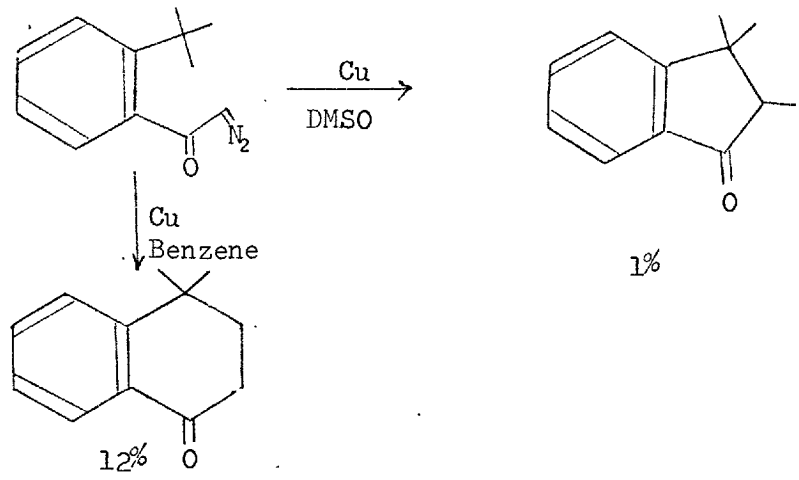
Scheme 4.

By contrast, the use of copper catalysts, with few exceptions,[37] completely inhibits Wolff rearrangement.[38] In inert solvents with copper, diazomethylketones lose nitrogen and dimerise to diacylethylenes.[39,40] In the presence of protic compounds HA (e.g. alcohols, amines, phenols) the groups H and A usually replace the diazo group (Scheme 5).[38]



Scheme 5.

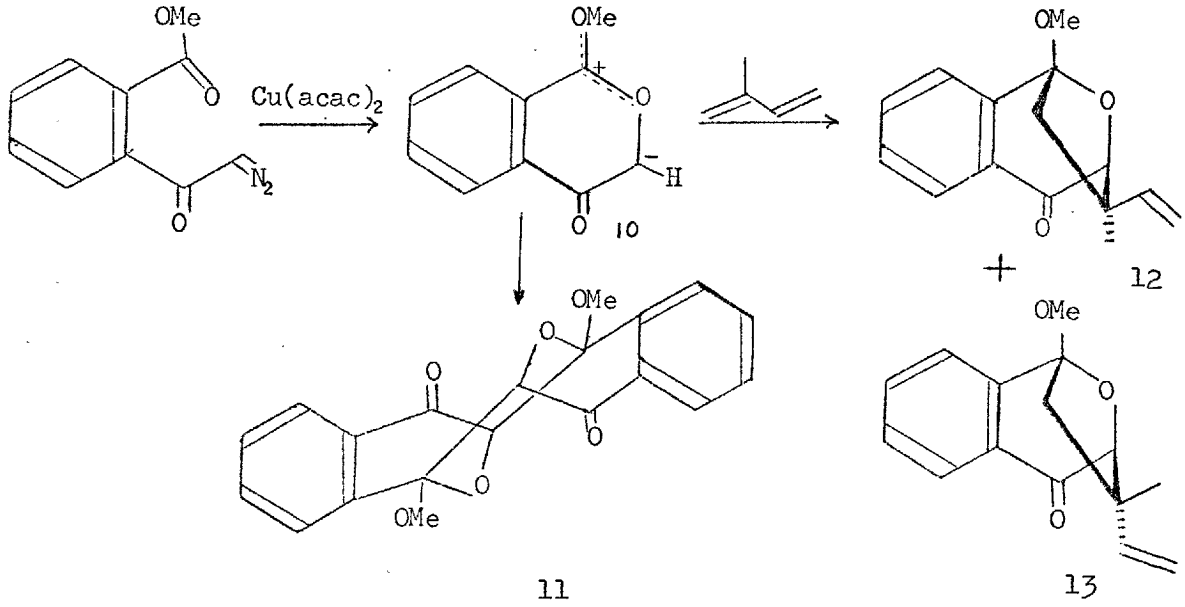
Intramolecular insertion into suitably-juxtaposed C-H groups is sometimes observed, and there is one report of insertion into a C-C bond occurring in very low yield in a very polar solvent (Scheme 6).[41]



Scheme 6.

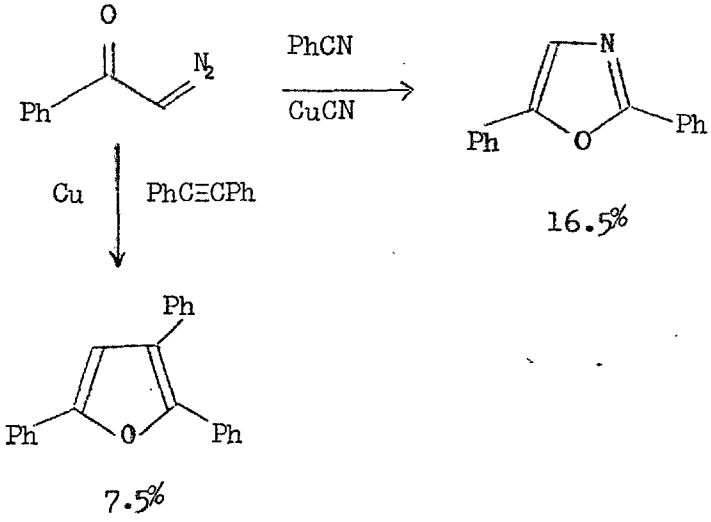
Another characteristic reaction of diazoketones in the presence of copper is the addition of the acylmethylene to double bonds to give cyclopropanes, which is particularly favourable in intramolecular cases.[42-45]

Copper-catalysed decomposition of diazoketones in the presence of ketones or esters leads to attack of the acylmethylene group on the oxygen of the carbonyl group, with subsequent formation of enol ethers,[46] dioxolanes[47] or tetrahydrofurans.[47] In a very interesting example reported by Japanese workers,[48] the 1,3-dipolar intermediate (10) generated by intramolecular attack underwent dimerisation (11), and adducts (12) and (13) could be isolated by trapping with isoprene (Scheme 7).



Scheme 7.

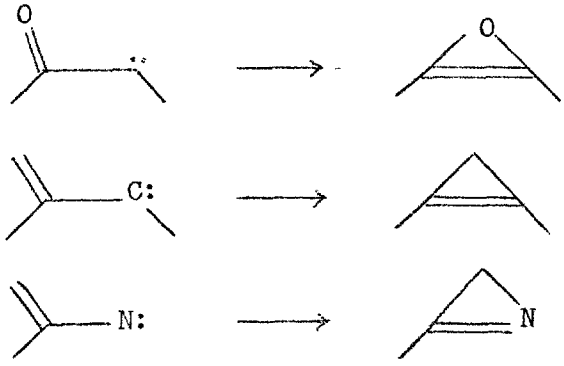
The results obtained with copper catalysts are best interpreted in terms of an intermediate copper-ketocarbene complex.[47,49] Huisgen[50] has successfully trapped the ketocarbene intermediate as a 1,3 dipole with benzonitrile and tolane (Scheme 8).



Scheme 8.

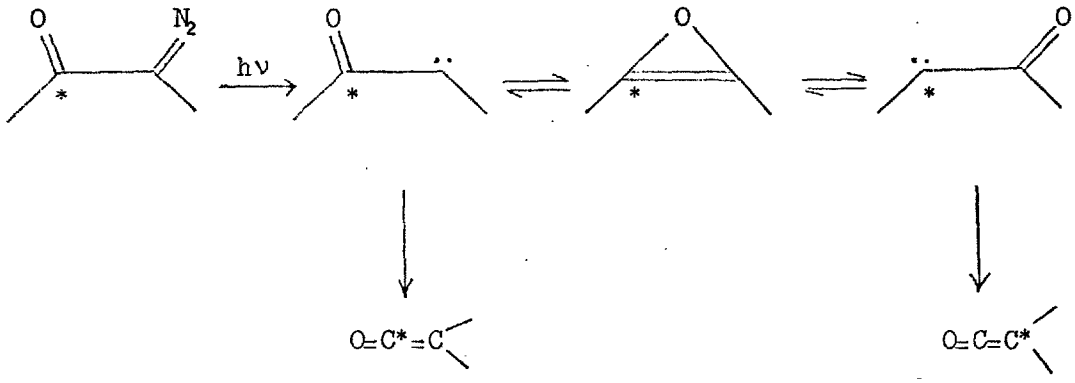
The possibility of oxiren formation during diazoketone decompositions has also received attention in the literature. Oxirens are members of a general class of 3-membered, unsaturated heterocycles, the other known members of which, either as stable compounds or reactive intermediates, are azirens,[51] thiirens,[52] thiiren-1-oxides,[53] thiiren-1,1-dioxides,[54] silirens[55] and germirens.[55] An analysis of the structure of oxiren leads to three distinct synthetic possibilities:

a). Ketocarbene-oxiren equilibrium



Scheme 9.

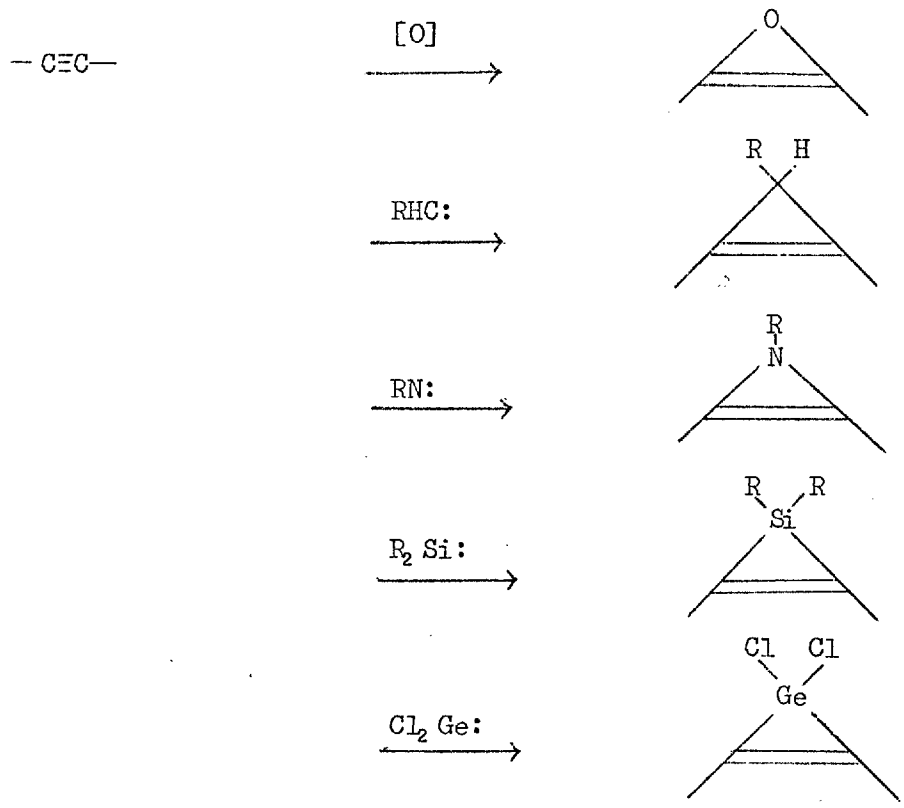
To investigate this possibility, which finds analogy in the formation of cyclopropenes from vinylcarbenes[56] and of azirens from vinyl nitrenes[57] (Scheme 9), Huggett[58] studied the Wolff rearrangement of carbonyl-^{13}C labelled diazoacetophenonone. He found that all the label was retained in the carbonyl group of the product (phenylacetic acid), indicating the absence of oxiren formation. Franzen[59] studied the photolysis of carbonyl-^{14}C labelled azibenzil, and also found no scambling of the label in the diphenylacetic acid obtained. Later, Strausz[60] repeated Franzen's work and reported 54-61% scrambling of the label in carbonyl-^{13}C azibenzil, also finding oxiren participation in the photochemical rearrangements of [2-^{13}C]-3-diazobutan-2-one (14) in the gas phase and in solution (Scheme 10).



Scheme 10.

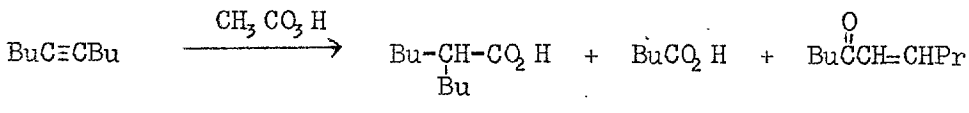
b). Oxidation of acetylenes

The addition of oxygen to a triple bond finds analogy in the addition of carbenes[61] and possibly of nitrenes,[62] silenes[55] and germenes[55] to acetylenes (Scheme 11).

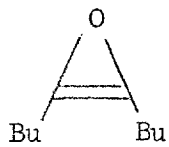


Scheme 11.

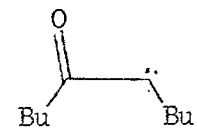
Schlubach[63,64] reported that the peracid oxidation of dipropyl and dibutyl acetylenes gave, in addition to the cleavage products butyric and valeric acids, compounds whose structures were assigned as dipropyl and dibutyl (15) oxirens. It was later shown by Franzen[65] that these compounds, whose IRs showed bands at 1630 and 1685-95 cm^{-1}, were in fact α,β-unsaturated ketones (16) and that a rearranged acid (17) is also formed, the mechanism being interpreted in terms of a ketocarbene intermediate (18).



17 16

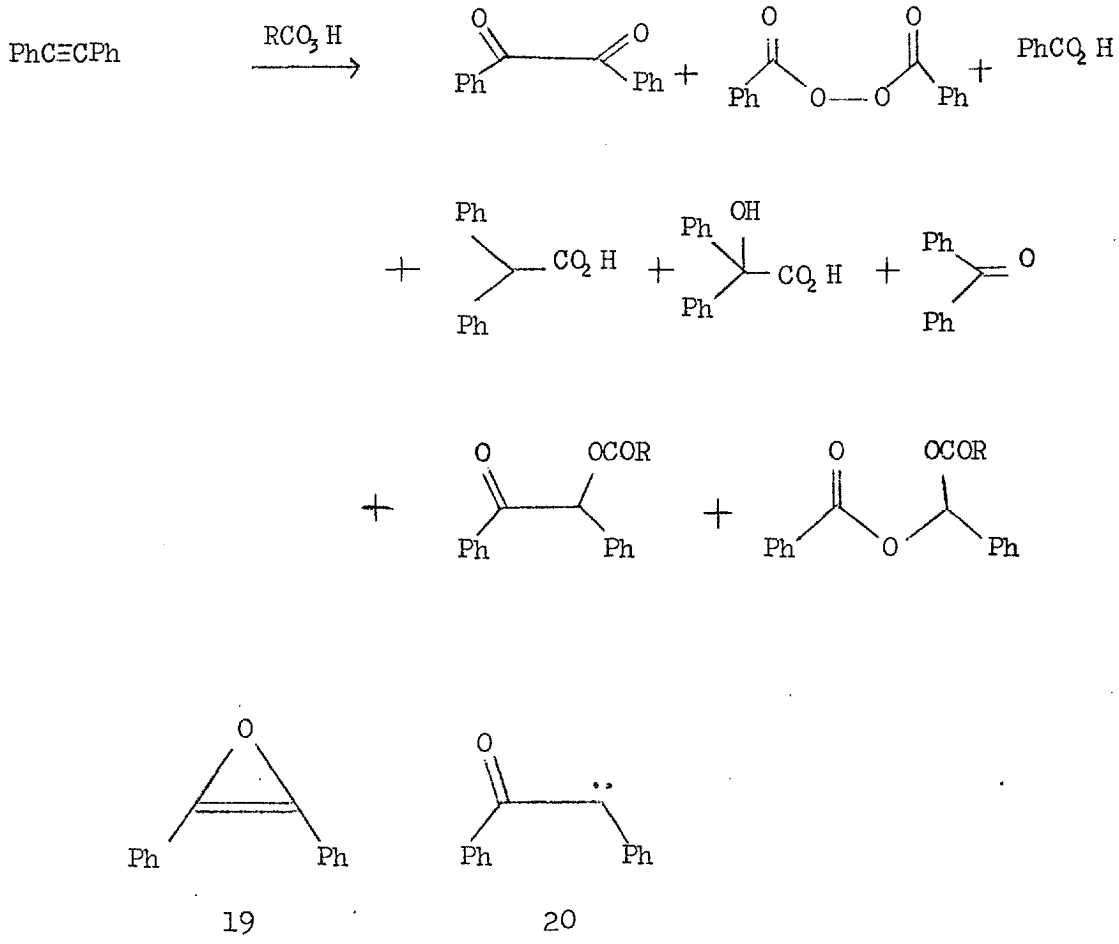


15



18

McDonald and Schwab[66] and Stille and Whitehurst[67] have reported the oxidation of phenyl and diphenylacetylenes with peracids. The results (Scheme 12) were interpreted in terms of an intermediate oxiren (19), but the products could clearly all arise from the corresponding ketocarbene (20).

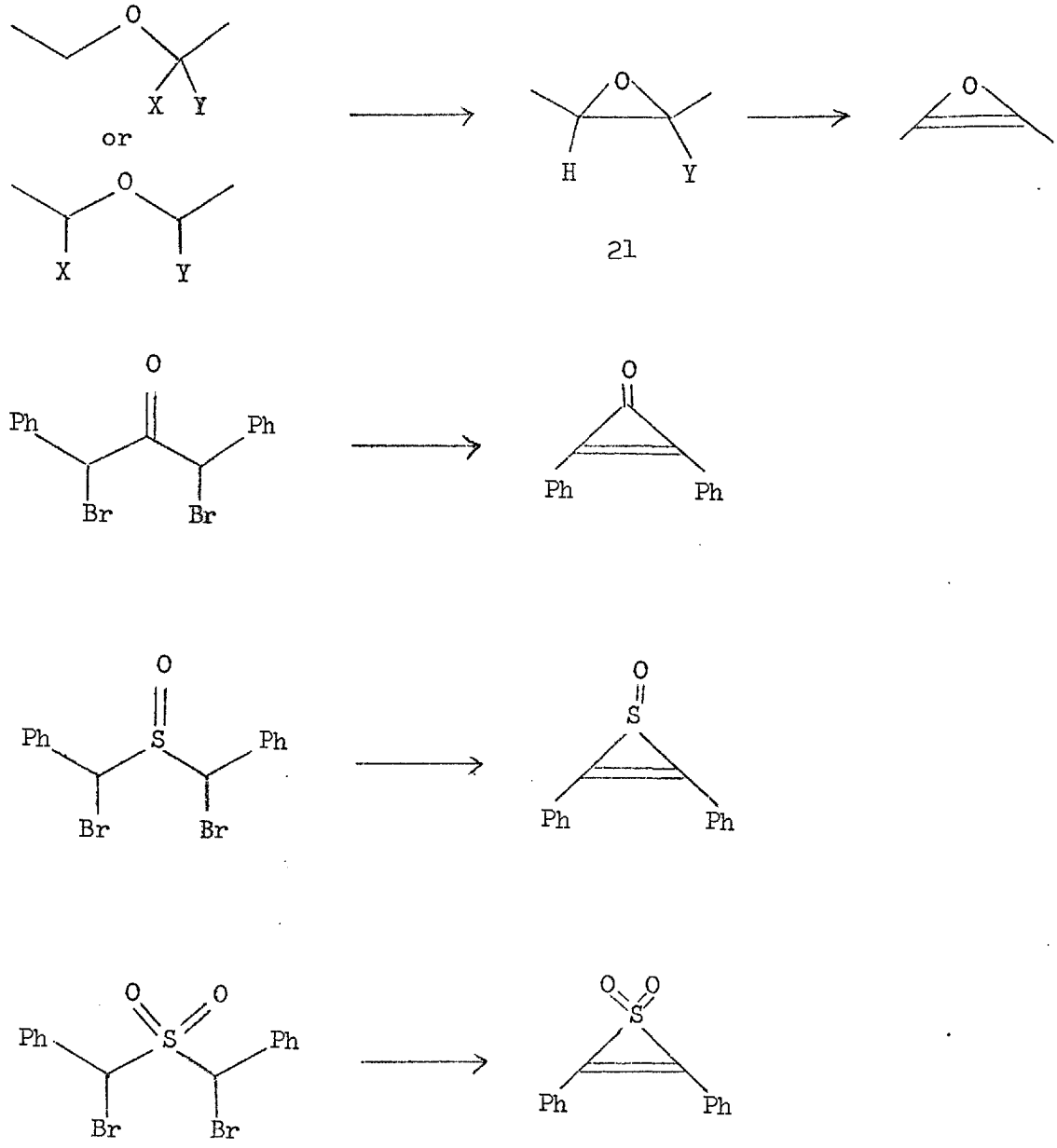


19 20

Scheme 12.

c). 1,3 elimination in α,α' disubstituted ethers

This reaction finds analogy in the synthesis of the stable cyclopropenones,[68] thiiren-1-oxides[53] and thiiren-1,1-dioxides[54] (Scheme 13).



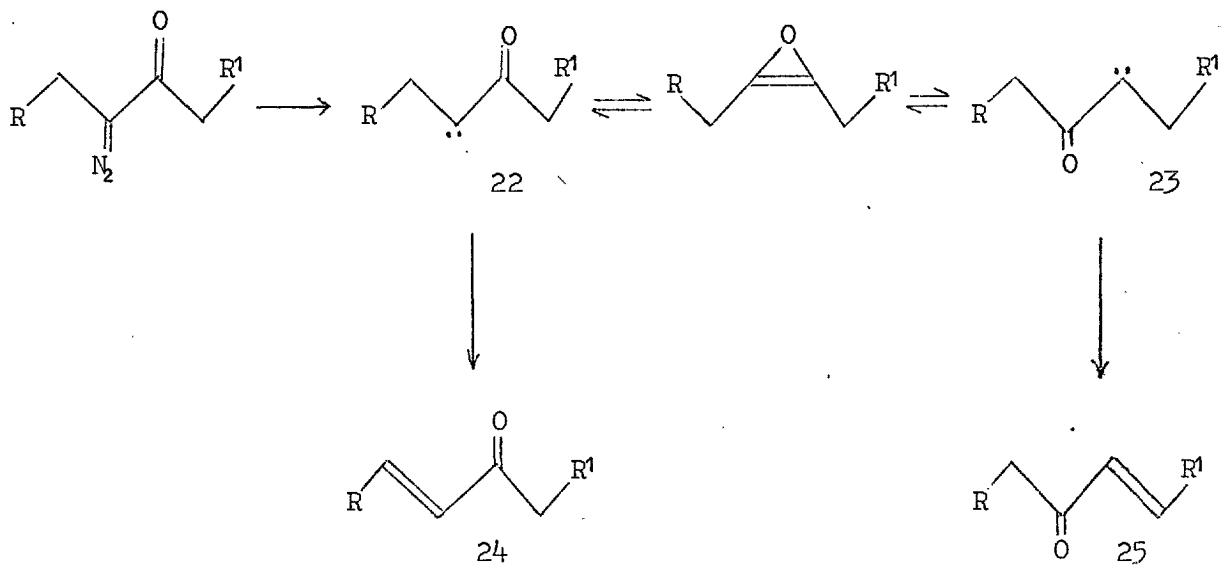
Scheme 13.

However, although some studies of this type of reaction appear to have been carried out,[69] reports of the results have not yet appeared in the literature. The base-catalysed rearrangement of chloroepoxides (21; Y=Cl) to ketones is well known,[70] but concrete evidence for the intermediacy of oxirens is lacking.

2.2. The decomposition of α-diazoketones: discussion and results.

The discrepancies in the literature[58-60] stimulated us to search for an unambiguous chemical method of determining whether or not oxirens are formed during the decomposition of α-diazoketones.

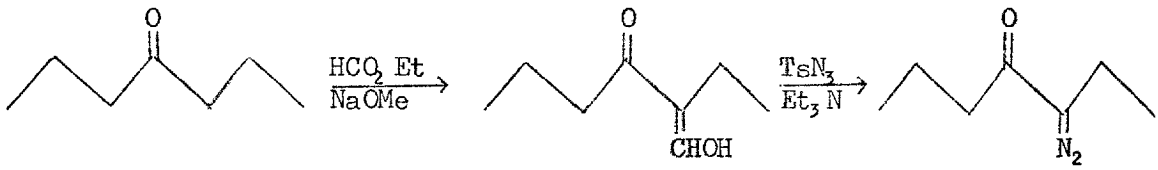
It was reasoned that when a diazoketone was decomposed under Franzen's conditions,[36] leading to α,β-unsaturated ketone, if an oxiren was involved in the reaction then the isomeric ketocarbenes (22) and (23) should be generated, so that for unsymmetrically-substituted diazoketones two isomeric α,β-unsaturated ketones (24) and (25) should result (Scheme 14).



Scheme 14.

3-diazoheptan-4-one (26) was chosen for the initial studies, since it was anticipated that differences in the behaviour of the derived ketocarbenes would be minimal.

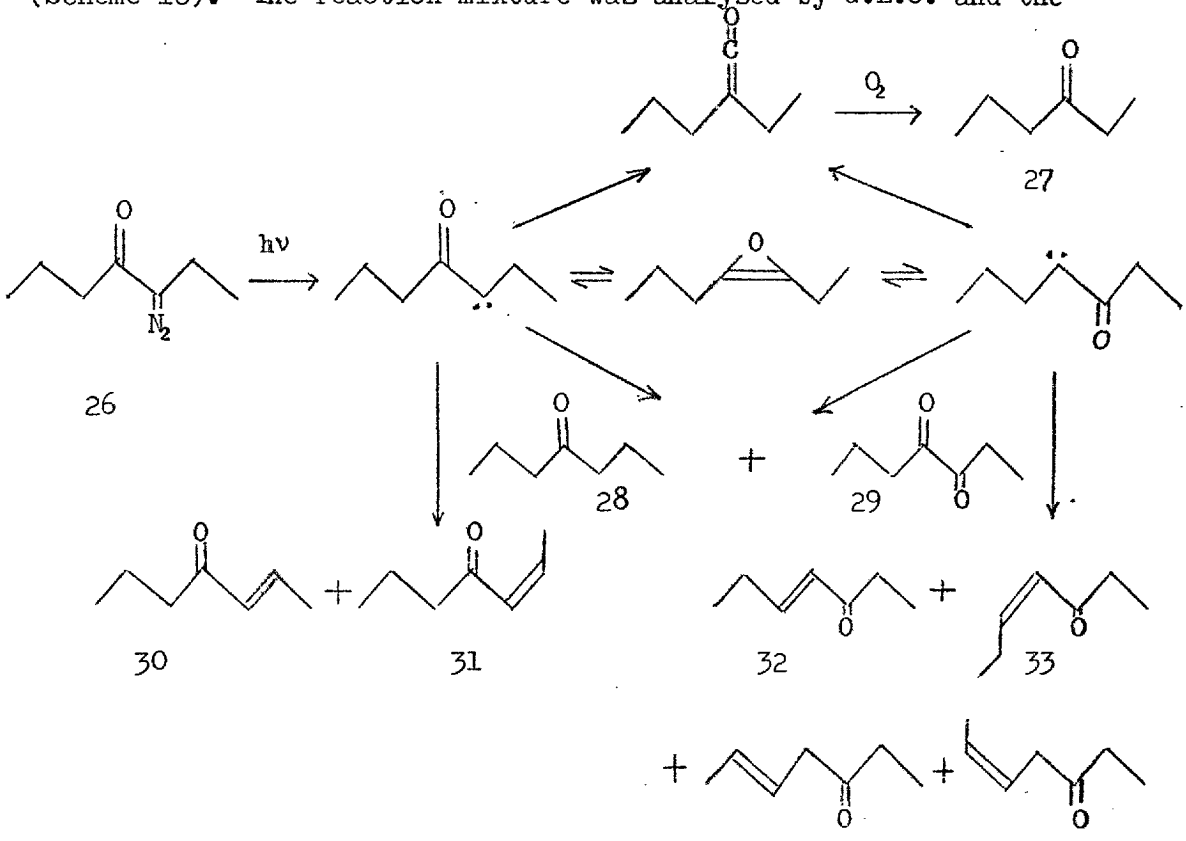
It was synthesised from di-n-propylketone by the method of Menz and Regitz[11] (Scheme 15) and was pure by tlc and IR, and had precisely the expected NMR spectrum. G.L.C. analysis showed that it contained none of the products to be described below in any detectable quantities.



26

Scheme 15.

Photolysis of 3-diazoheptan-4-one (26) in anhydrous ether led to its rapid decomposition, with formation of a number of products (Scheme 16). The reaction mixture was analysed by G.L.C. and the

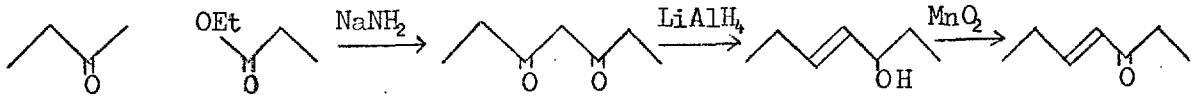


Scheme 16.

products identified by a combination of G.L.C./mass spec., isolation, preparation of derivatives, and comparison with authentic samples.

The traces of hexan-3-one (27) must be formed by aerial oxidation, during work-up, of the keten produced in the competing Wolff rearrangement. This type of oxidation is well known.[71] Traces of heptan-3,4-dione (29) formed by oxidation and of heptan-4-one (28) formed by hydrogen abstraction from the solvent were also detected. When the photolysis was conducted in aqueous dioxan, no homogeneous acid fraction could be isolated by extraction with sodium carbonate. Franzen[36] has reported a similar result in the photolysis of dialkyldiazoketones.

The structure of trans-hept-4-en-3-one[72] (32) was proved from its mass spectrum, and by comparison with an authentic sample synthesised by the method shown in Scheme 17, which makes use of the "anomolous" reduction of β-diketones to α,β-unsaturated alcohols[73] with $LiAlH_4$.



32

Scheme 17.

The deconjugated enones arise by a secondary photochemical process from the conjugated enones. Thus, photolysis in ether of pure trans-hept-4-en-3-one (32) mainly produced the corresponding cis-isomer (33) together with some of the β,γ-isomers (34 and (35) formed by photoenolisation.[74,75] An analogous deconjugation of hept-2-en-4-one (30) would give hept-1-en-4-one, but no trace of this latter material could be detected amongst the reaction products of the diazoketone (26). It has been reported[76] that this β,γ-isomer

is very unstable with respect to the conjugated enone. Suitable control experiments established that there was no overall loss of unsaturated ketones under the conditions of the photolysis.

The decomposition of the diazoketone (26) was also carried out thermally and using silver and copper catalysts. The results of all these studies are presented in Table 1. The percentage ratio of oxygen-migrated products (hepten-3-ones) to the total amount of enones (hepten-3-ones plus hepten-4-ones) produced is included as a measure of oxiren-participation. For complete equilibrium, assuming no substituent effects, a figure of 50% would be expected.

Vapour-phase photolyses of the diazoketone (26) were carried out by injecting pure samples into the G.L.C. instrument and varying the inlet temperature for different injections. The results are presented graphically in Figure 1.

Expt. No.	m.Mole.	Conditions.	Solvent.	Temp. °C.	Time Hr.	Hepten-3-ones % / All Heptenones	Absolute Yield enones %.
1	2.15	hν	Ether	20	1.5	44	30
2	12.5	hν	Ether	20	3.5	43	a
3	1.09	hν+Ph_2 CO	Ether	20	1.5	Trace	a
4	1.57	Reflux	Cyclo-hexane	80	24	18	a
5	2.18	Ag_2 O	15:85 aqueous dioxan	20	5	0	65
6	2.15	CuO	Cyclo-hexane	80	1.0	0	60
7	Vpc pyrolysis			465		36	a

a. Not estimated.

Table 1. Decompositions of 3-diazoheptan-4-one (26).

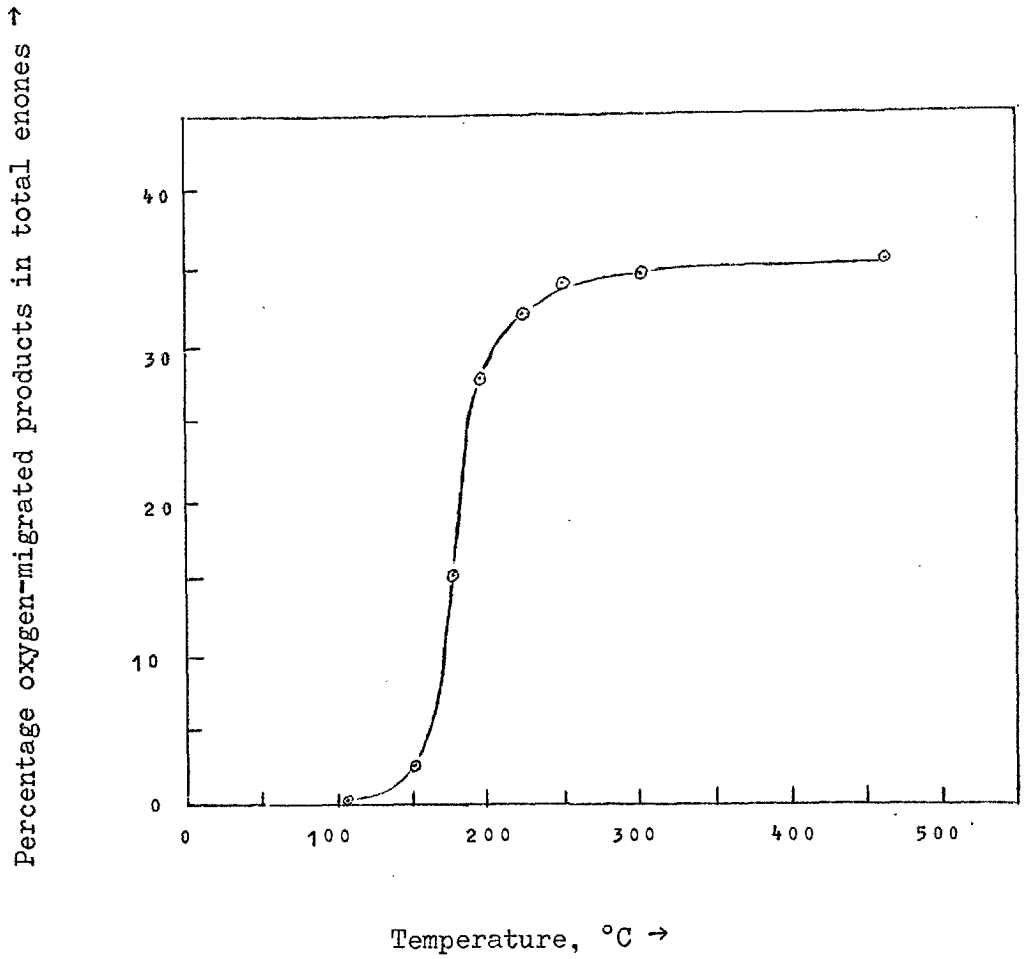


Figure 1. Vapour-phase pyrolysis of 3-diazoheptan-4-one (26).

The results categorically show oxygen migration and hence oxiren participation during the photochemical and thermal decompositions of the diazoketone (26). They provide the first chemical proof that oxirens are formed in such reactions and show that the degree of participation increases with temperature (Figure 1) and, in this case, is even more favoured in the photochemical reaction. By contrast, the silver and copper catalysed decompositions gave no trace of products derived from oxirens. In a further experiment, decomposition of 3-diazoheptan-4-one with copper oxide in refluxing methanol afforded 3-methoxyheptan-4-one[77] in high yield as the sole product of the reaction.

Oxygen migration via oxiren requires the intermediacy of a free

ketocarbene, and the complete lack of oxygen migration noted in the metal-catalysed decompositions implies that no free ketocarbene is formed. As outlined above (Section 2.1.), there is good evidence that copper forms complexes with carbenes and that silver is also involved in some kind of interaction with the reacting diazoketone molecule. The intermediacy of such complexes would inhibit oxiren formation.

The results[78] on the photochemical and thermal decompositions of 3-diazoheptan-4-one completely support those of Strausz,[60] in contrast to earlier studies,[58,59] and a possible explanation for the discrepancies in the literature is suggested. Huggett and co-workers[58] searched for oxiren participation in the Wolff rearrangement under "conditions of the Arndt-Eistert synthesis", which implies use of silver oxide as catalyst and which has now been shown not to involve oxiren participation. Franzen[59] carried out his reactions with a long-wavelength light source (a "Sunlamp", 24 hour photolysis) whereas Strausz[60] used a higher energy medium pressure mercury lamp similar to that used in the present studies. It is quite possible, therefore, that the Wolff rearrangement observed by Franzen was proceeding by a low-energy reaction profile, or by a concerted migration-nitrogen loss thus by-passing oxiren intermediates.

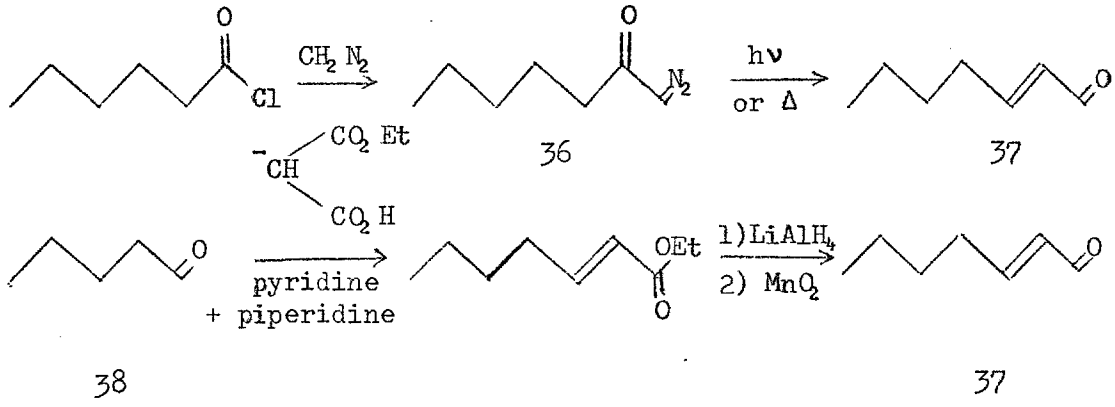
Several alternatives to the oxiren explanation for oxygen migration may be dismissed. Thus, the enones produced are stable, with respect to oxygen migration, under the photochemical conditions used. Intermolecular oxygen exchange is ruled out by the dilution studies (Table 1; Expts. 1 and 2) which showed no significant change in the amount of 1,2 oxygen migration with concentration. Reversal of the Wolff rearrangement can also be discarded as a possible explanation since this cannot explain the label-scrambling results obtained by Strausz.[60] Moreover, studies by Rowland and Russell[79] indicate that

this process, at best, is a very minor reaction pathway in keten-photolysis.

The possible intervention of triplet state intermediates was also considered. Photolysis of the diazoketone (26) in the presence of benzophenone, such that the photosensitiser absorbed >95% of the light present, yielded only traces of the enones obtained by direct excitation. Control experiments showed that the enones were essentially unreactive under these conditions. Thus, it can be assumed that triplet species do not rearrange via oxiren intermediates. It has similarly been demonstrated that the Wolff rearrangement requires a singlet state ketocarbene and is prevented by photo-sensitisation.[33]

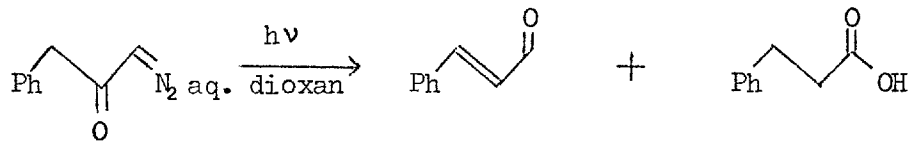
In order to test the generality of oxiren participation in diazoketone decompositions, several different substrates were studied.

1-diazoheptan-2-one (36)[80] was synthesised by the standard method for diazomethylketones (Scheme 18). Photolysis in ether gave a mixture containing a 4% yield of the expected oxygen-migration product hept-2-enal (37), which was identified by comparison with an authentic sample synthesised[81] by a known route (Scheme 18) from pentanal (38). The thermal decomposition of 1-diazoheptan-2-one in refluxing cyclohexane also afforded hept-2-enal (ca. 3%).



Scheme 18.

Similarly, photolysis of 1-diazo-3-phenylpropan-2-one (39)[82] gave traces of cinnamaldehyde (< 5%). The major product, in aqueous dioxan, was 3-phenylpropionic acid derived by Wolff rearrangement (Scheme 19). Heating the diazoketone (39) in refluxing cyclohexane similarly gave only trace quantities of cinnamaldehyde.

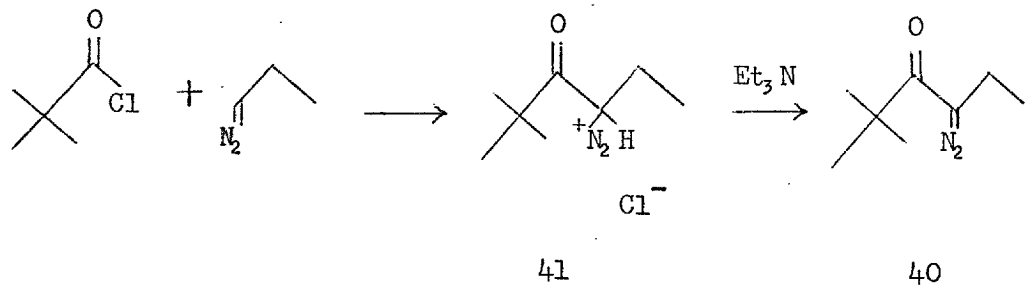


39

Scheme 19.

The low yields of α,β-unsaturated aldehydes from the diazomethylketones (36) and (39) reflects the preponderance of Wolff rearrangement in such terminal diazoketones. This result is in agreement with the suggestion of Kaplan and Melloy[29a] that in these cases the overwhelming preponderance of the cis-conformation (5) of the 1-diazoketone leads to its smooth transformation to keten, and finds analogy in the recent report[29b] that a diazoketone rigidly fixed in the cis-conformation forms only traces of the oxiren during Wolff rearrangement.

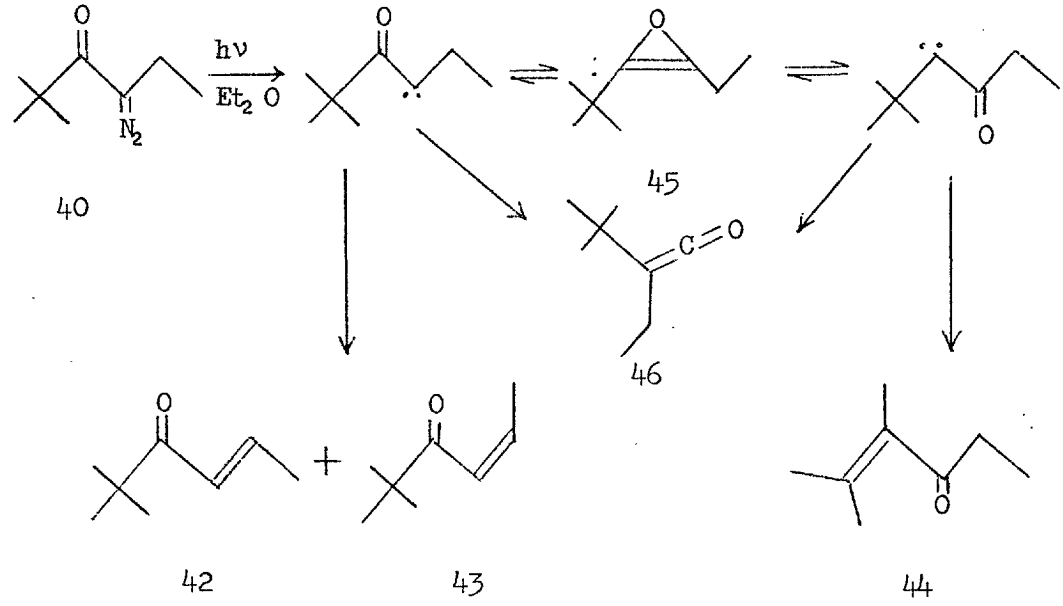
It was of interest to see whether groups other than hydrogen could be induced to migrate following oxiren rearrangement. Since there is good precedent in the literature[22,23] for methyl migration to a carbenoid centre, 2,2-dimethyl-4-diazohexan-3-one (40) was prepared by condensation of pivaloyl chloride with diazopropane in the presence of triethylamine (Scheme 20). In the absence of the amine only decomposition products characteristic of the diazonium ion (41) were obtained.



41 40

Scheme 20.

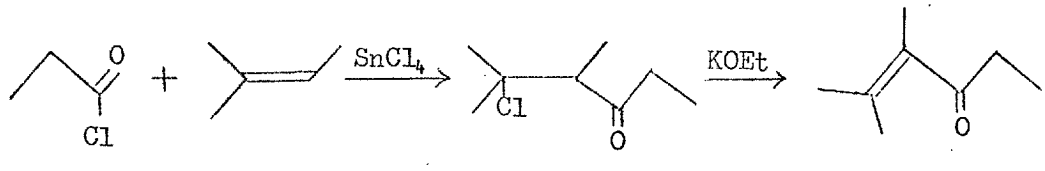
Photolysis of the diazoketone (40) in anhydrous ether produced a mixture containing the unsaturated ketones (42) to (44). The trans- and cis-enones (42) and (43) are produced by a hydrogen migration without an oxygen shift. The 2,3-dimethylhex-2-en-4-one (44), however, can only arise via the oxiren intermediate (45), (Scheme 21).



40 45 46 42 43 44

Scheme 21.

Authentic 2,3-dimethylhex-2-en-4-one (44)[83] was synthesised for comparison by a known route (Scheme 22).



44

Scheme 22.

Traces of a keten, assigned as (46), were observed in the crude reaction product of the diazoketone photolysis, as shown by a weak absorption bond at 2120 cm^{-1} in the i.r. spectrum, but this was not isolated. The results of a series of photochemical and thermal decompositions of the diazoketone (40) are given in Table 2 and the results of its vapour-phase pyrolysis are shown in Figure 2. The enone product (44) was shown to be completely stable to the conditions of the photolysis both in the presence and absence of benzophenone. Whilst only 14% of the rearranged enone (44) was formed by the photolysis of the diazoketone (40) in ether, an interesting effect was noted with increasing solvent polarity (Table 2). As the dielectric constant of the reaction medium increased so did the amount of oxiren participation, so that with 2:3 aqueous dioxan over 40% of the enone fraction consisted of the rearranged isomer (44).

From the above results, oxiren participation is generally favoured in the photochemical reactions compared with the analogous thermal reactions. The degree of oxiren involvement increases with the polarity of the solvent in the photolyses, and increases with temperature in the thermolyses. There are two principle explanations for these observations. Firstly, two competing processes could exist, one involving hydrogen migration concerted with nitrogen loss, which by-passes oxiren formation, and the other involving a non-concerted nitrogen loss to give a free ketocarbene intermediate which is in rapid equilibrium with the corresponding oxiren. Alternatively, in all cases a free ketocarbene is produced in which there is a significant activation energy difference between hydrogen migration and oxiren formation such that the higher energy conditions favour the latter process. The results above do not distinguish between these two possibilities although it is interesting to note that Jugelt

Expt. No.	m.Mole.	Conditions	Solvent	Volume ml.	Temp. °C.	Time Hr.	$\frac{(44)\ (\%)}{(42)+(43)+(44)}$	Absolute Yield enones%.
8	2.27	hν	Ether	40	25	1.0	14	35
9	1.36	hν	Ether	40	25	1.0	14	a
10	1.03	hν	1:9 aq. dioxan	40	25	1.0	18	a
11	0.84	hν	1:4 aq. dioxan	40	25	1.0	33	35
12	1.00	hν	1:4 aq. dioxan	40	25	2.0	38	a
13	1.06	hν	2:3 aq. dioxan	40	25	1.0	41	a
14	0.96	hν+Ph_2CO	Ether	40	25	1.0	Trace	a
15	1.46	Reflux	Cyclo-hexane	2.50	80	24	9	45
16	0.99	Reflux	Cyclo-hexane	2.50	80	24	12	41
17	1.00	Ag_2O	Ether	10	25	24	0	61
18	Vpc pyrolysis			-	465	-	21	a

a. Not estimated.

Table 2. Decompositions of 2,2-dimethyl-4-diazohexan-3-one (40).

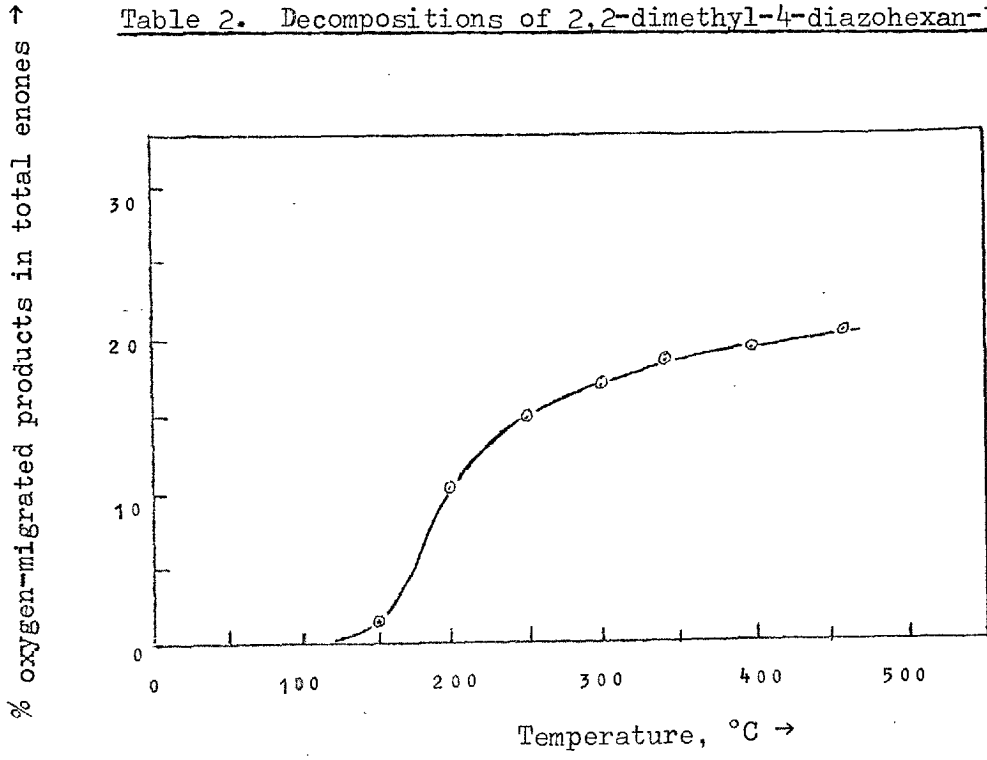
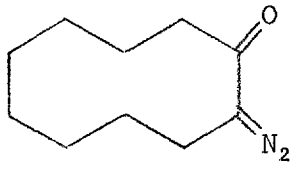


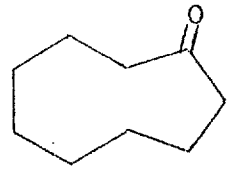
Figure 2. Vpc pyrolyses of 2,2-dimethyl-4-diazohexan-3-one (40).

and Schmidt[25] reported a very big increase in the rate of nitrogen loss from diazoketones as the dielectric constant of the medium was increased. The fact that an increase in dielectric constant also favours oxiren formation tends to give support to the theory that there are two competing processes, one via a concerted H-migration-nitrogen loss.

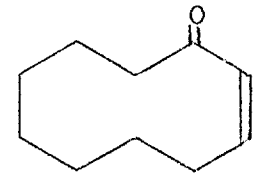
Recently Ciabattoni et al.[23] have compared the thermal decomposition of 2-diazocyclodecanone (47) with the peracid oxidation of cyclodecyne (48). Both reactions gave the same products (49) to (52), but in very different ratios such that the oxidation gave mainly bicyclic ketones (51) and (52) with little enone (ratio 67:33 in refluxing benzene) and the thermolysis of the diazoketone (47) gave principally enone (50) with very little bicyclic ketones (ratio 14:86 in refluxing benzene). Ciabattoni proposed that the enone (50) arose from H-migration in a ketocarbene intermediate formed by the diazoketone decomposition, whilst the bicyclic ketones were formed by intramolecular addition of a C-H group to an oxiren formed in the acetylene oxidation.



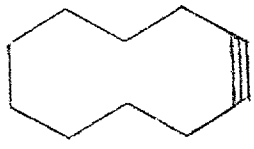
47



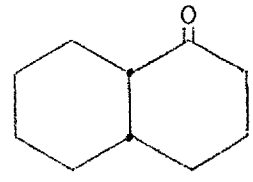
49



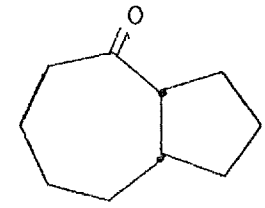
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48



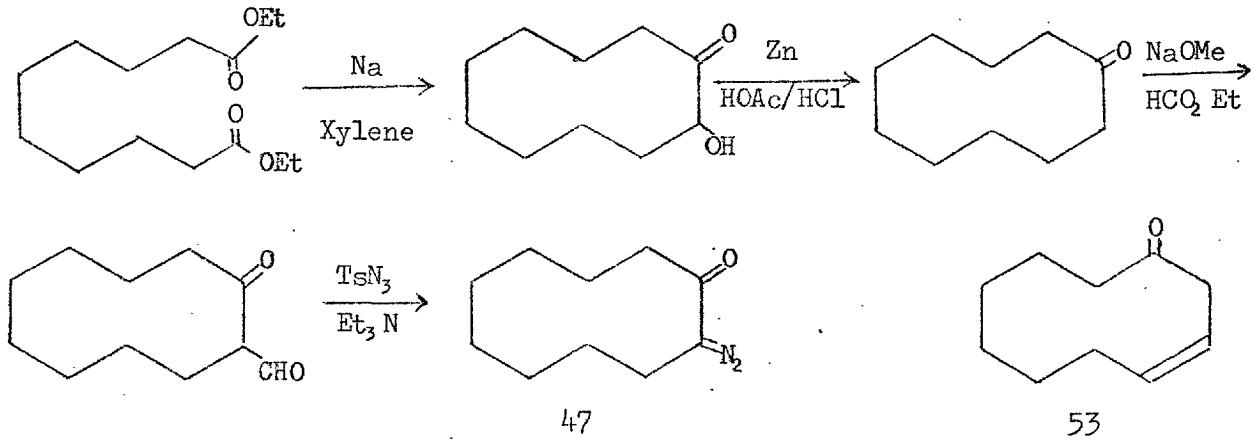
51



52

In the light of the results now obtained, however, a different explanation of Ciabattoni's observations was suggested. It could be reasoned that the thermal decomposition of the diazoketone (47) should give a considerable amount of concerted nitrogen-loss-hydrogen migration leading to the enone (50), whereas in the oxidation of the acetylene (48) a ketocarbene (or oxiren) is formed which principally reacts by transannular C-H insertion reactions to give the bicyclic ketones (51) and 52). From the trends noted with the acyclic diazoketones (26) and (40) above, it can then be predicted that photolysis of 2-diazocyclodecanone (47) should result in a greatly increased amount of the insertion products (51) and (52) compared with the thermal decomposition of the diazoketone (47).

2-Diazocyclodecanone (47)[84,85] was synthesised by the literature method (Scheme 23) and its decomposition carried out under a variety of conditions (Table 3), the products being identified by G.L.C./mass spec. initially. In refluxing benzene (Experiment 19) a result identical to Ciabattoni's was obtained. Silver-catalysed decomposition gave almost exclusively cis-cyclodec-2-enone (50),[86] a result also reported by Regitz.[85] The enone (50) was isolated by thin-layer chromatography and on photolysis was found to undergo considerable (86%) deconjugation to cyclodec-3-enone (53), as reported by Carlson and Bateman.[87]



47 53

Scheme 23.

Table 3. Decompositions of 2-diazocyclodecanone (47).

Expt. No.	Conditions	Solvent	Temp. °C.	Time Hr.	Ratio % [a] (49)	(50)+(53)	(51)+(52)	Ratio % [b] (51)+(52)	(50)+(52)	Cyclodecanone products.
19	Reflux	Benzene	80	15	38	53	9	14	86	(50) only
20	Ag_2O	Ether	25	24	1	93	6	6	94	"
21	Ag_2O	Ether	25	24	Trace	95	5	5	95	"
22	CuO	Cyclo-hexane	80	1	57	26	17	39	61	"
23	hν	Cyclo-hexane	25	1	40	39	21	36	64	(50):(53)=19:81
24	hν	Ether	25	1	60	27	13	33	67	Mainly (53)
25	hν	1:4 aq. dioxan	25	1	3	70	26	27	73	Mainly (53)
26	Vpc pyrolysis		500	-	0	62	38	38	62	-

a. (49) + (50) + (51) + (52) + (53) = 100%.

b. (50) + (51) + (52) + (53) = 100%.

It can be seen that photolysis of 2-diazocyclodecanone produces a considerable increase in the ratio of bicyclic ketones (51) and (52) to cyclodecenones (50) and (53) compared with the thermal decomposition, although the ratio is still below that obtained in the peracid oxidation of cyclodecyne. Comparison of the results of the photolyses in different solvents indicates a strong dependence on the polarity of the medium and that the trend is opposite to that observed in the photolysis of the acyclic diazoketone (40) (see Table 2). This difference probably reflects the importance of conformational effects in determining the reaction course, a possibility which Ciabattoni also recognised.[23]

A comparison of the direct photolysis with the sensitised decomposition of the diazoketone (47) was also interesting. Padwa and Leyton[32] have pointed out that triplet-state ketocarbenes are very good hydrogen abstractors, and since 1,2-migrations are inhibited in the triplet state (see above) the sensitised photolysis of the diazoketone should give mainly the bicyclic ketones (51) and (52). This was found to be the case when 2-diazocyclodecanone was photolysed in the presence of benzophenone: the ratio of bicyclic ketones to cyclodecenones increased to 73:27. No trace of cyclononanone (49), produced from the keten as a result of Wolff rearrangement, could be observed, indicating inhibition of this reaction under the photo-sensitised conditions.

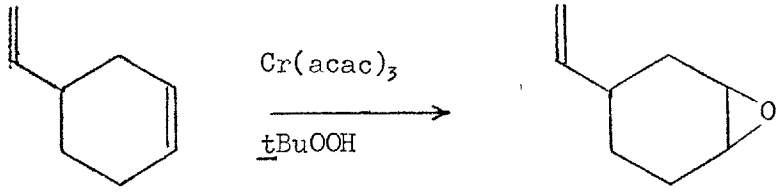
2.3. Review of molybdenum-catalysed oxidations.

Brill and Indictor[88] have shown that the decomposition of organic hydroperoxides is catalysed by olefins : Ea for the decomposition of t-butyl hydroperoxide is 39 Kcal/mole in octane at 150-180°, and 21 Kcal/mole in neat olefins at 60-100°. The structure of the olefin was found to have little effect on Ea or the

rate of decomposition, the latter being greatly increased in polar solvents such as methanol, pyridine and DMF but lowered in non-polar solvents such as benzene.

The epoxide yields from the decompositions showed the opposite effects: they depended greatly on the structure of the olefin, varying from 5-10% for the least substituted olefins up to 50% for the most substituted. Epoxide yields in all solvents except benzene were lower than in the neat olefins.

Brill and Indictor concluded from this work that the reaction had little synthetic value for epoxide formation, but they later carried out systematic studies of the effects of metal salts on the reaction[89] and found that epoxide formation was catalysed by many transition metal acetylacetonates. In particular, when small amounts of chromium, molybdenum and vanadium complexes were used the yields of epoxides were 100%, and the activation energy for the uncatalysed reaction (21 Kcal/mole) was lowered considerably for $V(acac)_3$ (9 Kcal/mole), $MoO_2(acac)_2$ (12 Kcal/mole), and $VO(acac)_2$ (15 Kcal/mole), although increased for $Cr(acac)_3$ (23 Kcal/mole). All these figures apply to decompositions in neat olefins. There were indications of a remarkable degree of specificity in the epoxidations. For example, 4-vinylcyclohexene gave only 1,2-epoxy-4-vinylcyclohexane (54).



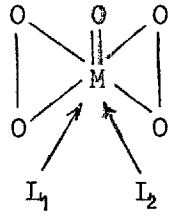
54

Sheng and Zajacek[90] later reported more detailed studies of the epoxidation reactions in which it was found that a wide range of compounds of molybdenum and vanadium, such as the carbonyls, halides, oxides, sulphides and oxosalts are effective catalysts. The highest yields of epoxides were obtained with MoO_2 , $MoCl_5$ $Mo(CO)_6$ and $MoO(acac)_2$, the optimum temperature being 90-100° and non-polar solvents the most efficient. Addition of t-butanol decreased the rate of hydroperoxide decomposition but there was no corresponding decrease in the epoxide yield at given hydroperoxide conversion up to a t-butanol concentration of 80 weight %. The rate of epoxidation increased with the number of alkyl substituents on the double bond. With cumene hydroperoxide and its substituted derivatives the presence of electron-withdrawing groups such as para-nitro markedly increased the rate of reaction. Studies with pure cis- and trans-but-2-enes showed 100% specificity: the cis olefin gave exclusively cis-epoxide and the trans-olefin, trans-epoxide.

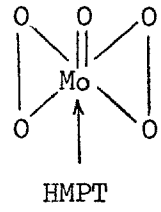
Conjugated dienes[91] were found to be less reactive than simple olefins, but good yields of mono and di-epoxides could be isolated. With isoprene, there was considerable preference for epoxidation of the more substituted double bond. A similar preference was noted with non-conjugated dienes. Allylic substituents generally made the reaction slower and gave reduced yields of epoxides, except in the case of allylic alcohols, when vanadium catalysts generally gave very rapid reactions and high epoxide yields.[91]

Mimoun and co-workers[92,93] discovered that diperoxy complexes of molybdenum and tungsten (55; M=Mo,W .L_1 ,L_2 =tertiary amides, phosphoramides, aromatic amines and their oxides, phosphines) will epoxidise olefins very efficiently in dichloromethane at room

temperature. Studies with the yellow hexamethylphosphorictriamide (HMPT) complex (56) established that the olefin complexes at the vacant site on the metal, giving a hepta-coordinate molybdenum species. Epoxidation follows with complete stereospecificity and is severely inhibited by conjugation of the double bond with electron-withdrawing groups such as -CN and $-CO_2H$.

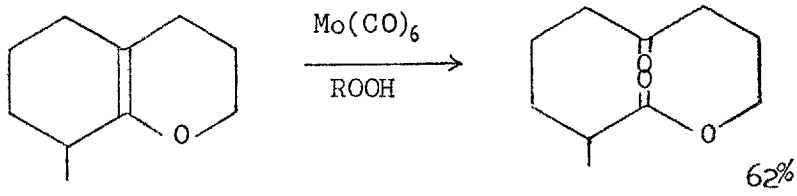


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56

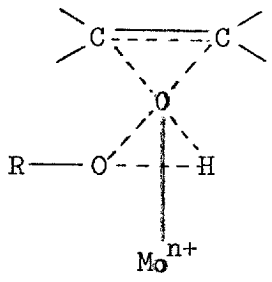
The molybdenum or vanadium catalysed oxidations of tertiary amines to amine oxides[94] and of triphenyl phosphine to triphenyl phosphine oxide[95] have been reported. Rapp and Borowitz[96] found that the oxidation of cyclic enol ethers proceeds beyond the epoxide stage and affords dicarbonyl compounds by cleavage of the double bond. The reaction was used for the synthesis of model macrolides (Scheme 24).



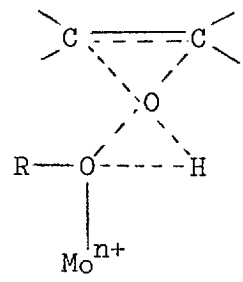
Scheme 24.

The mechanism of hydroperoxide oxidations has been studied by kinetic methods. The first-order dependence of the reaction rate on hydroperoxide, olefin and catalyst concentrations and the dependence on the nucleophilicity of the olefin and electrophilicity of the hydroperoxide led to the proposal by Sheng and Zajacek[90]

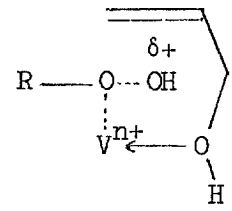
of fast complexation of the hydroperoxide to the metal and transfer of oxygen as the rate-determining step, via a transition state such as (57) or (58). The possibility of π-complex formation between the olefin and the metal was dismissed, but without any real evidence for doing so. However, in order to account for the very facile epoxidation of allyl alcohols by vanadium, the intermediacy of a complex with the alcohol (59) was proposed.[91]



57

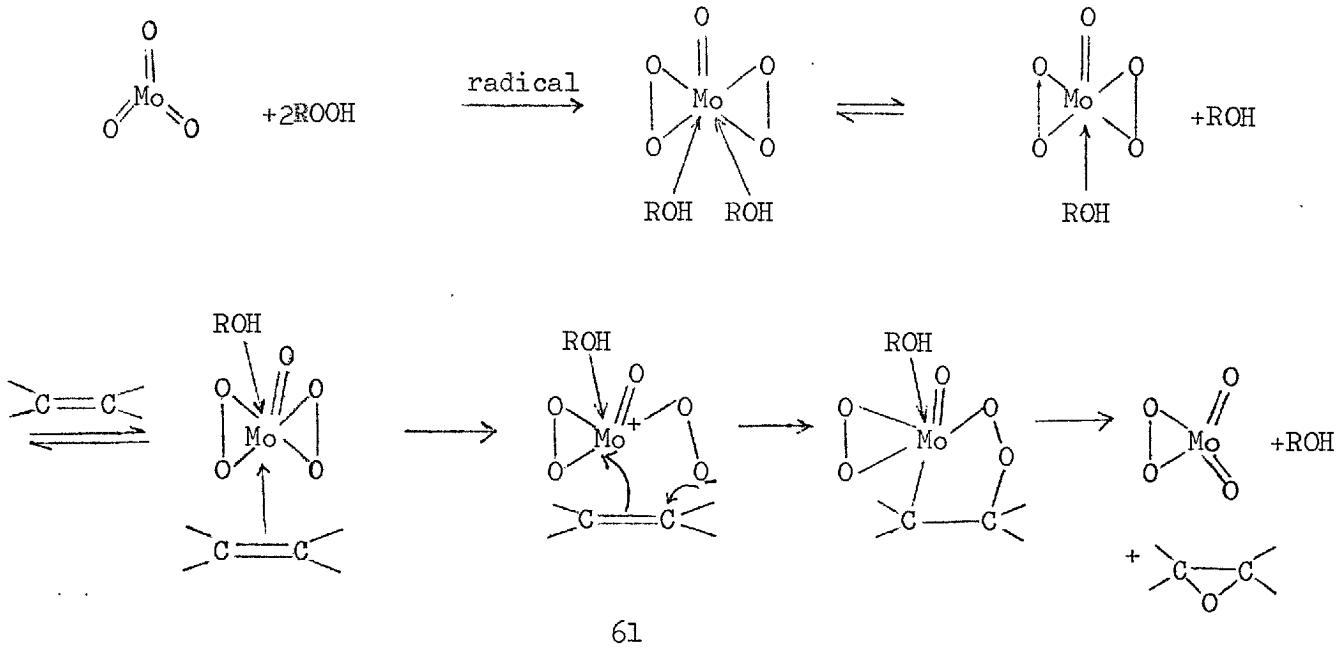


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59

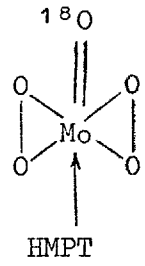
This overall picture of the mechanism was later supported by kinetic studies by Hiatt and Howe[97] with substituted styrenes. However, in recent studies by a group of French workers[98] it was observed that the initial black catalyst solution formed when molybdenum naphthenate was used acquired a pale yellow colour after addition of hydroperoxide, and permolybdic acid could be isolated from the reaction mixture. On this basis a mechanism (Scheme 25) similar to that proposed by Mimoun for the diperoxy-molybdenum complex (56) was suggested.



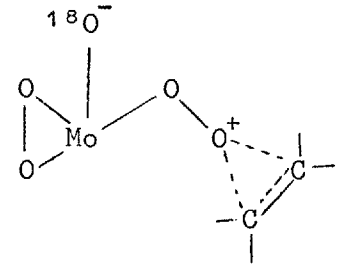
61

Scheme 25.

Sharpless[95] established that when the peroxy-molybdenum complex (56) was labelled with ^{18}O at the oxo-oxygen (60), no ^{18}O labelled epoxycyclododecanone was formed from trans-cyclododecene, and only unlabelled triphenyl phosphine oxide was formed from triphenyl phosphine, which supports the mechanism above. However, he criticised the proposal of a five-membered transition state (61) by showing that in competitive experiments between norbornene and cyclohexene and between cis and trans cyclododecene, the reactivity ratios were very similar to those for other epoxidation reagents (e.g. Cr^{VI}, peracids) which are known to react via 3-membered transition states, and very different to those for reagents (e.g. OsO_4, benzonitrile oxide) which are known to react via 5-membered transition states. It was argued, therefore, that the epoxidation of olefins with peroxy-molybdenum complexes proceeds through a 3-membered transition state, e.g. (62).



60

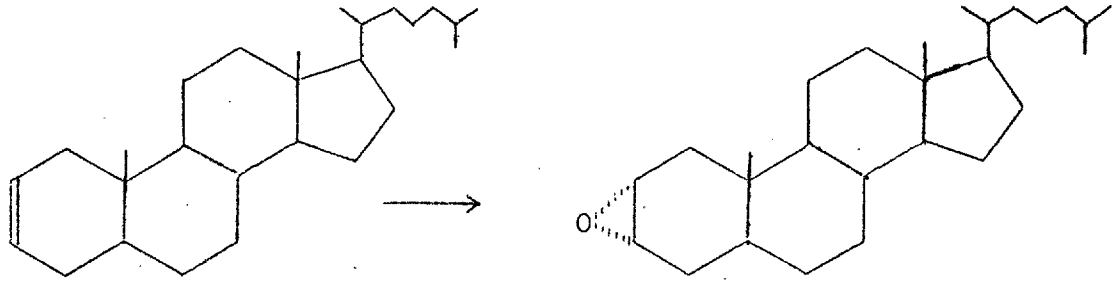


62

2.4. Epoxidation of olefins.

On heating a mixture of cis- and trans-oct-2-ene in chlorobenzene with tBuOOH and a catalytic amount of $Mo(CO)_6$ at 90° for one hour, the hydroperoxide decomposed completely to t-butanol and two new products were formed in a total of 85-90% yield, identified as 2,3-epoxyoctanes by G.L.C./mass spec. This is entirely in accord with the reports by Sheng and Zajacek.[90]

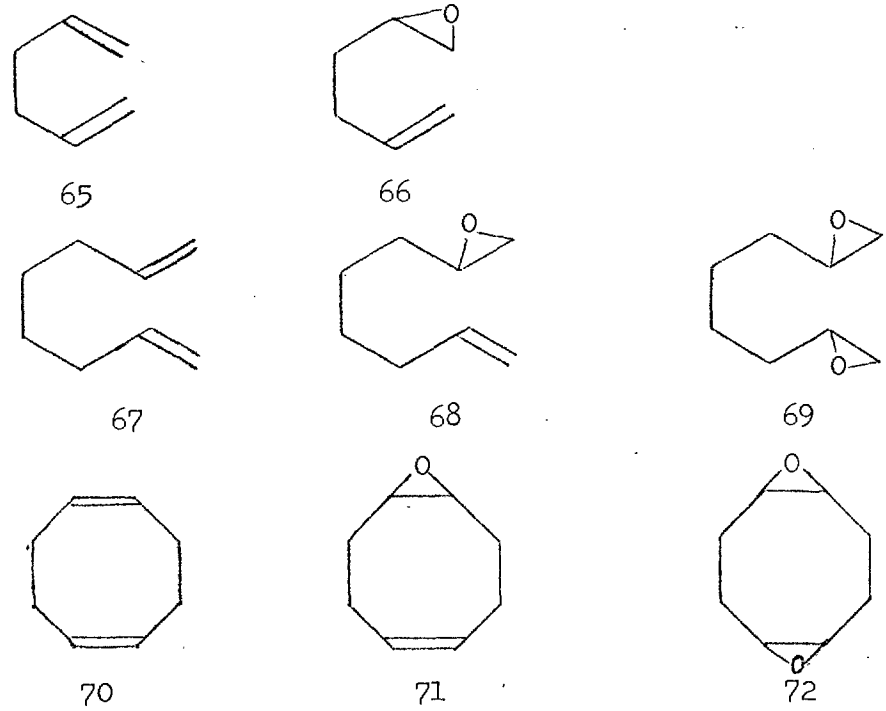
In order to examine the stereospecificity of the reaction with a hindered olefin, the epoxidation of cholest-2-ene (63) was carried out. The 2α,3α-epoxide (64) was formed as the only product (54% yield). No 2β,3β-epoxide could be detected in the reaction mixture by tlc, and attack of the reagent hence occurs exclusively from the less hindered side of the steroid molecule.



63

64

Several non-conjugated dienes were treated with one equivalent of tBuOOH to examine the selectivity for mono-epoxidation (Scheme 26). Hexa-1,5-diene (65) gave almost exclusively the mono-epoxide (66). Octa-1,7-diene (67) gave a mixture of mono- and di-epoxides (68) and (69) in the ratio 6:1. Cycloocta-1,5-diene (70) gave an 8.4:1 ratio of mono- and di- epoxides (71) and (72). Soon after these studies were carried out, Sheng and Zajacek[91] reported the oxidation of non-conjugated dienes to monoxides. The only cases they studied in which the two double bonds were in identical environments were octa-1,7-diene and cycloocta-1,5-diene, when good yields of monoxides were obtained using an olefin:hydroperoxide ratio of 2:1, but the proportions of di-epoxides were not reported.

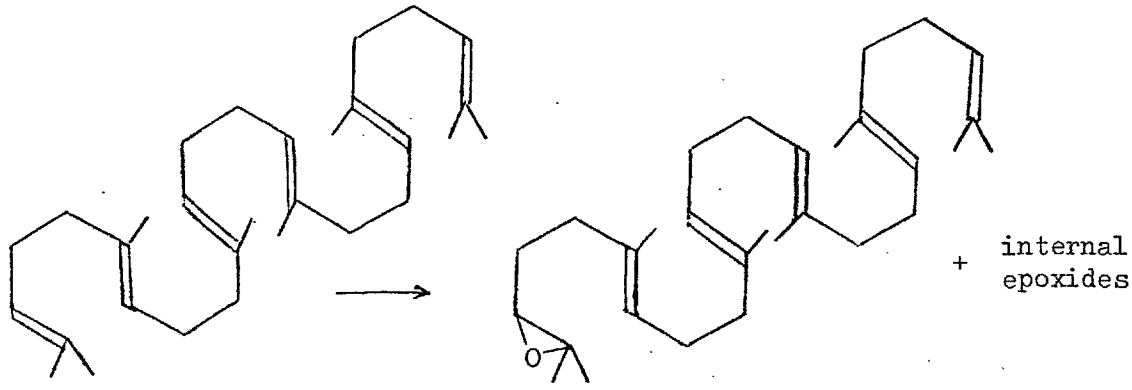


Scheme 26.

Van Tamelen[99] has shown that in polar media such a glyme-water, squalene (73) is oxidised with 81% selectivity at the "terminal" (2,3) double bond by N-bromosuccinimide. Selectivity with this substrate, in which all the double bonds are trisubstituted, must be due to differences in the availability to attack of the

various double bonds as a result of positional and conformational effects.

Squalene was heated with one equivalent of tBuOOH in benzene in the presence of $Mo(CO)_6$. A mixture of two predominant products was isolated by preparative tlc (68.5% conversion of squalene) and these were identified as the terminal (74) (22% based on squalene converted) and internal (75; mixture of 6,7 and 10,11) (27% based on converted squalene) epoxides.



73 74 75

Distinction between the terminal and internal epoxides was made on the basis of their NMR spectra. The internal epoxides showed a singlet at τ8.7 for the trans-methyl group on the epoxide ring, and a sharp peak at 8.3 for the two cis-methyl groups on the terminal double bonds. The terminal epoxide exhibited a doublet at 8.7, the cis-methyl on the epoxide ring being slightly downfield from the trans-methyl, and a much weaker signal at 8.3, since there is now only one cis-methyl group attached to a double bond.

A series of further oxidations of squalene were carried out in an attempt to improve the selectivity of the reaction. The results are reported in Table 4. It will be seen that the best yields of epoxides were obtained in non-polar solvents (benzene, cyclohexane), but that the degree of selectivity for terminal epoxidation is not

very high under these conditions. A 1:2 mixture of terminal and internal epoxides would be expected on the basis of random attack: the actual 1:1.23 ratio found indicates about 17% selectivity for the terminal position. The use of polar solvents greatly reduced the yield of epoxides, as found by Sheng and Zajacek. Two equivalents of hydroperoxide gave a much higher conversion of squalene, but the overall yield of mono-epoxides was lowered because of further oxidation. A control experiment established that no reaction occurred when squalene-2,3-oxide was heated with t-butanol and $Mo(CO)_6$ in benzene.

Squalene Mx10³	tBuOOH Equiv.	Conversion[a] %	Terminal Epoxide[b] %	Internal Epoxide[b] %	Solvent
1.26	1	68.5	22.0	27.2	Benzene
2.43	1	0	0	0	tBuOH
1.32	1	68.5	combined yield 47.6%		cyclo-hexane
1.15	2	90.8	11.7	13.2	Benzene
1.11	1	C	C	C	PhH/MeOH
0.17	1	C	C	C	DMF

a. Reaction times 2-2.5 hours. 90°C.

b. Based on squalene converted.

c. Reaction mixtures not worked up. Tlc indicated very low conversion and epoxide yields.

Table 4. Squalene Oxidations.

Since the peroxy-molybdenum complex (56) is effective in more polar solvents such as dichloromethane,[43] it was hoped that a much higher degree of selectivity could be achieved with this reagent.

In the event, however, treatment of squalene with the complex (56) in CH_2Cl_2 gave a mixture which tlc indicated to contain roughly equal amounts of terminal and internal epoxides and the reaction was not investigated further.

The effects of substituents on the course of epoxidation were briefly investigated. Crotonaldehyde completely failed to react when heated with tBuOOH and $Mo(CO)_6$ in benzene. When methyl sorbate (76) was treated with one equivalent of hydroperoxide for two hours, a 41.4% yield of the 4,5-epoxide (77) was isolated by plc. No 2,3-epoxide was found. Earlier studies have established that the 4,5-epoxide is the sole product when methyl sorbate is oxidised with peracids and that the 2,3-double bond is very resistant to attack.[100,101]

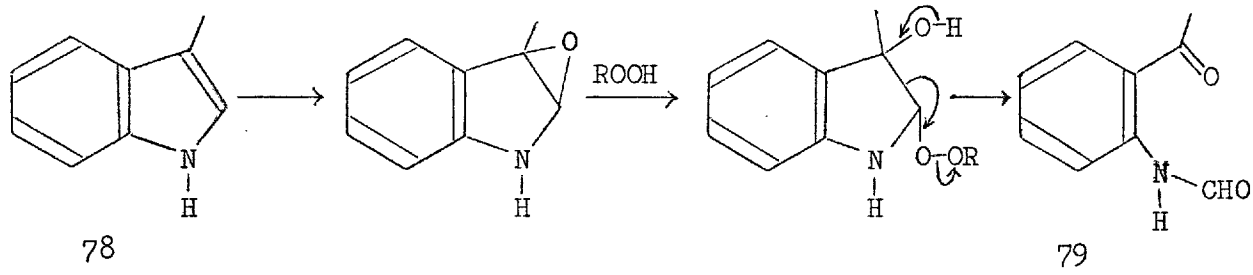
When methyl sorbate was gradually treated over 5 hours with an excess of tBuOOH (3 equivalents), G.L.C. showed that the yield of 4,5-epoxide reached a maximum (≥55%) and then rapidly declined due to secondary oxidations, and eventually all the epoxide was consumed. No significant quantities of the further oxidation products could be isolated by thin-layer chromatography.



76 77

When sorbic acid was treated with an excess of hydroperoxide the acid was recovered unchanged after two hours, which is in accord with the report by Mimoun et.al.[93] that epoxidations effected by molybdenum-peroxy complexes are greatly inhibited by the presence of conjugated-CN and $-CO_2H$ groups within the substrate.

Skatole (78), with an electron-donating group attached to the double bond, was very rapidly oxidised by hydroperoxide, and there was a considerable amount of decomposition - at least a dozen products were indicated by tlc. A dicarbonyl compound (79) was isolated in 13% yield and is clearly formed by a mechanism (Scheme 27) similar to that which results in double-bond cleavage in the enol-ether oxidations.[96]



78 79

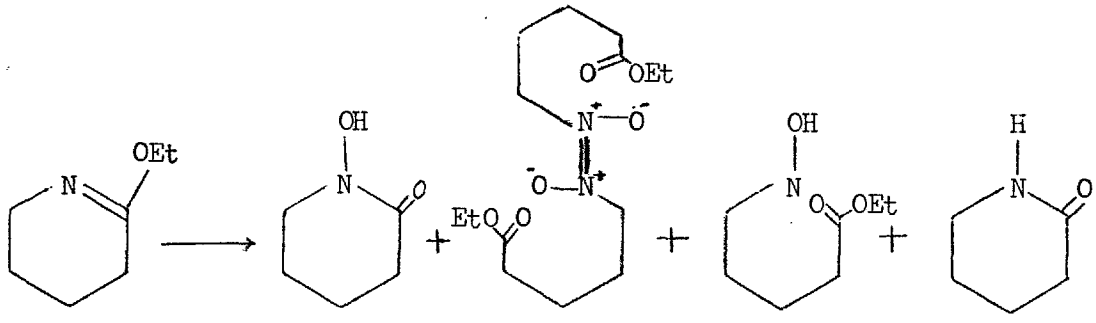
Scheme 27.

2.5. Synthesis of hydroxamic acids.

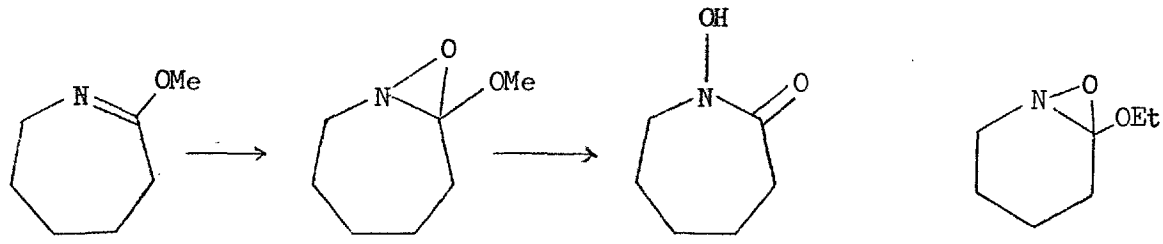
Whilst the oxidation of amides to hydroxamic acids is a very important process for the synthesis of many natural products, very few methods of carrying out this reaction are known and none involve a direct, one-step conversion.[102]

A preliminary investigation of the oxidation of imino-ethers to hydroxamic acids was carried out by Blake,[103] who found that 2-ethoxy-3,4,5,6-tetrahydropyridine (80) is converted by m-chloroperbenzoic acid in methanol to a mixture of products (Scheme 28). Under the best conditions found by Blake (very slow addition of peracid to the imino-ether, followed by a long period of stirring before work-up) a 50% yield of the hydroxamic acid (81) was claimed, together with 20% of the trans-nitroso ester dimer (82) and small amounts of the oximino ester (83) and 2-piperidone (84). The

Oxidation of O-alkyl imino esters of 2-piperidone and hexanolactam in methylene chloride at -60° has also been reported to occur, giving the corresponding N-hydroxylactams in 3% and 10% yields respectively. In the case of O-methyl hexanolactim (85), when the reaction was carried out in the presence of excess anhydrous potassium carbonate the oxaziran (86) was isolated in 17% yield.[102]



80 81 82 83 84



85 86 87

Scheme 28.

It was decided to attempt the development of a method of oxidising imino-ethers to hydroxamic acids using the molybdenum catalysts, but prior to this the report by Blake was checked.

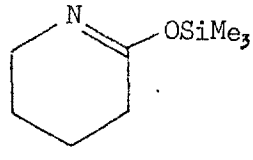
2-ethoxy-3,4,5,6-tetrahydropyridine (80) was synthesised and oxidised under Blake's conditions, giving a very poor yield of N-hydroxy-2-piperidone (3%). A series of experiments in which

the reaction-time and work-up procedure were varied established that the best yield of hydroxamic acid is obtained when the reaction is carried out very rapidly. Under these conditions a 54% yield of N-hydroxy-2-piperidone was isolated.

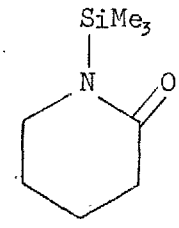
Although the oxidation reaction is obviously very fast, it was observed that the reaction mixture gave a positive starch-iodide test for a considerable time after mixing of the reagents was complete. This suggests that the oxaziran (87) is an intermediate in the oxidation, since oxazirans are known to possess oxidising properties.[103] The nitroso ester dimer (82) arises from a further oxidation reaction: when two equivalents of peracid were used, no hydroxamic acid was isolated, but a 78% yield of the dimer (82) was obtained.

Reaction of the imino-ether (80) with hydroperoxide and $Mo(CO)_6$ in benzene gave a complex mixture of products, of which the only one isolated in significant yield was 2-piperidone (18%). A control experiment established that N-hydroxy-2-piperidone was stable to the reaction conditions. Similarly, no hydroxamic acid could be isolated when the imino-ether (80) was treated with MoO_5.HMPT in dichloromethane.

It was hoped that the trimethylsilyl derivatives of amides might be more susceptible to N-hydroxylation. Treatment of 2-piperidone with trimethylsilyl chloride and triethylamine gives, not the O-silyl amide (88), but the N-silyl amide (89).[104]



88



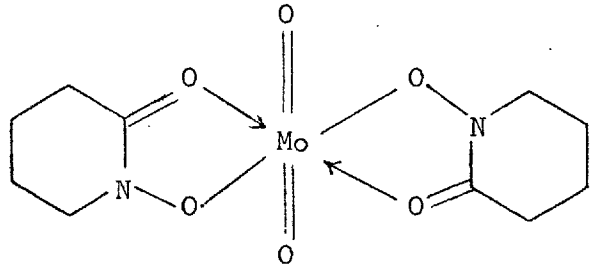
89

The synthesis of N-trimethylsilyl-2-piperidone (89) was

effected in 56% yield by the literature procedure.[105] The product, after distillation, was indicated by IR and NMR to be contaminated with 2-piperidone (20%). Re-treatment with Me_3SiCl reduced the proportion of 2-piperidone to 10%, but it could not be entirely eliminated.

When the silyl amide (89) was stirred with MoO_5 HMPT in dichloromethane for several days, a 14.1% yield of a bis-hydroxamic acid complex (90) was obtained. The structure of the product was assigned on the basis of its elemental analysis ($C_{10}H_{16}N_2O_6Mo$), its mass spectrum (M^+ 358,356,355) and infrared spectrum ($\nu C{=}O$ 1595 for complexed C=O). On addition of a sample of the product to ethanolic ferric chloride solution, a deep cherry-red colour characteristic of hydroxamic acids developed slowly (5-10 seconds). Further proof for the structure of the complex (90) came from its synthesis by addition of N-hydroxy-2-piperidone to a mixture of molybdenum trioxide and hydrogen peroxide.

The oxidation reaction promises to be an important new method for the synthesis of hydroxamic acids.



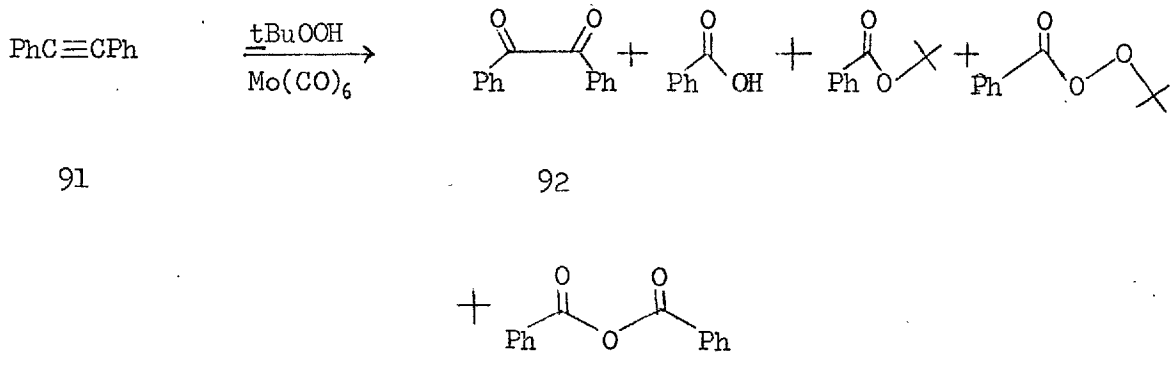
90

2.6. Oxidation of acetylenes: metal-ketocarbene complexes.

Investigations of the molybdenum-catalysed oxidations of acetylenes were carried out. The course of the peracid oxidation of acetylenes (Section 2.1.) is well interpreted in terms of the reactions of an intermediate ketocarbene (rearrangement, enone

formation, addition of "HX") and there seems no reason to doubt that in the absence of metals a ketocarbene-oxiren equilibrium[78] prevails. The question then arises whether oxirens might be intermediates in the molybdenum-catalysed oxidation of acetylenes, particularly since oxirens are isoelectronic with cyclobutadiene and might therefore be stabilised in a similar manner by complexation to a transition metal.

Treatment of diphenyl acetylene (91) with $Mo(CO)_6$ and a large excess of t-butyl hydroperoxide in refluxing benzene produced a slow and incomplete oxidation of the acetylene. Four principal products, as well as unchanged starting material and traces of benzoic anhydride, were isolated by preparative tlc (Scheme 29).



91 92

Scheme 29.

It appeared that benzil was the primary reaction product and that all the other products were derived from it by further oxidation. Good evidence for this came from the observation that treatment of benzil with tBuOOH under identical conditions to the acetylene oxidation produced a very similar mixture of reaction products (Table 5).

Product	Diphenyl acetylene oxidation[a].		Benzil oxidation[a]	
	%based on conversion[b]	Ratio[d]	%based on conversion[c]	Ratio[d]
Benzil	35	-	42	-
t-butyl benzoate	6	1	11	1
t-butyl perben-zoate	11	1.83	20	1.82
Benzoic Acid	31	5.17	63	5.73

a. Reaction conditions: 5.0 hours reflux. 16.67 eq. of tBuOOH.

b. Conversion of acetylene = 54%. Material recovery = 91%.

c. Conversion of benzil = 58%. Material recovery = 97%.

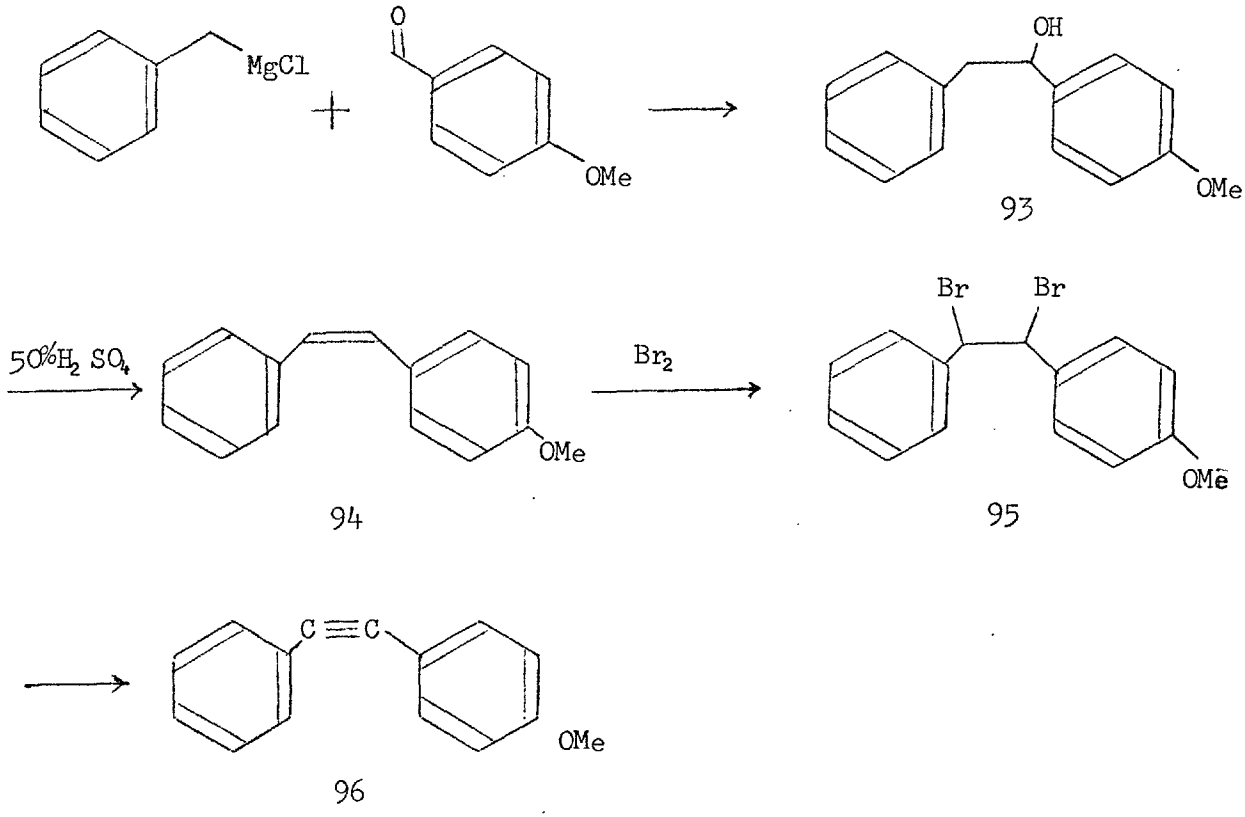
d. Relative to t-butyl benzoate formed.

Table 5. Tolane and Benzil oxidations.

Oxidation of diphenylacetylene with two moles of MoO_5 HMPT gave a 17.6% conversion of the tolane after seven days. Benzil, isolated in 57% yield based on the conversion (total recovery of material = 92%) was the only detectable product.

Thus, in contrast to the peracid oxidation (Section 2.1.), none of the products is derived from Wolff rearrangement of an intermediate ketocarbene. In order to examine this point further, the oxidations of p-methoxy-tolane (96) were carried out, it being reasoned that any disposition of an intermediate ketocarbene to rearrange would be enhanced by the presence of the p-methoxy group. The synthesis of p-methoxy-tolane was attempted by the method of

Orekhoff and Tiffeneau (Scheme 30).[106]

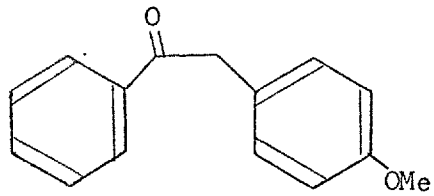


Scheme 30.

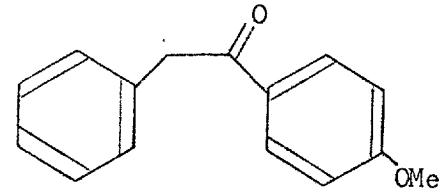
The first three stages all went in good yields, giving the dibromide (95) m.p. 172-3° (Lit: 175-6°) in two crops. The first, main crop was shown by NMR to be predominantly one isomer of the dibromide, contaminated with a small amount of the other isomer. The proportions of these two isomers were reversed in the second, minor crop. Presumably the major isomer results from trans-addition to the p-methoxy-stilbene (94) whilst the minor one comes from cis-addition.

When the dibromide (95) was refluxed with K_2CO_3 in water according to the literature method for the synthesis of the acetylene (96), a product was obtained (ca 40% yield after recrystallisation) having m.p. 85-6° (Lit: 89-90°). On examination

this proved to be a mixture of the olefin (94) and the ketone (97) (83% of the latter by NMR estimation). Examination of the mother-liquors of the reaction by tlc revealed only trace quantities of the desired acetylene (96).



97



98

Final proof of the structure of the ketone (97) come from the synthesis of the isomeric ketone (98) by manganese dioxide oxidation of the alcohol (93) and comparison of the IR spectra (97: $\nu C{=}O$ 1690cm^{-1}; 98: $\nu C{=}O$ 1675cm^{-1}) and NMR spectra (97:aromatic H 1.7-3.2, no specially intense signals; 98:aromatic H 1.8-3.3, with very sharp singlet at 2.75 for phenyl in a benzyl group). Katritzky[107] has also reported that treatment of the dibromide (95) with aqueous potassium carbonate gives a ketone as the major product and suggested the structure (97) for it on the basis of its i.r. spectrum. The olefin (93) isolated with the ketone (97) probably comes from a thermal elimination of bromine, since it is reported that this reaction of the dibromide (95) will occur in refluxing acetone.[106]

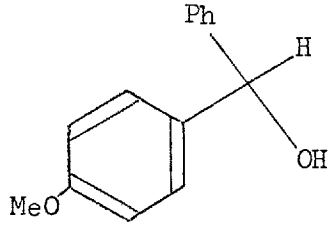
The conversion of the dibromide (95) to p-methoxy-tolane was successfully achieved by heating with KOH in trigol at 140-50° and careful crystallisation of the crude product.

On standing for four days with one mole of MoO_5 HMPT in dichloromethane, p-methoxy-tolane was oxidised to p-methoxybenzil as the only detectable product (21.0% conversion; 76.8% yield based on conversion; 95% recovery of material). The reactivity of p-methoxy-tolane is hence much greater than that of diphenyl acetylene (8%

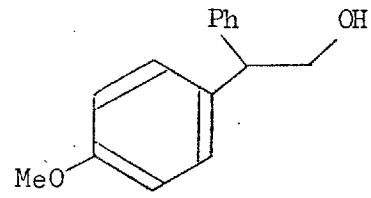
conversion after four days).

Oxidation of p-methoxy-tolane with a large excess of tBuOOH in the presence of $Mo(CO)_6$ gave a complex mixture of products which were partially separated by preparative tlc into four fractions. Each fraction was carefully examined by NMR, and in no case could a signal be detected at τ 5.0, where the tertiary proton in 2[p-methoxyphenyl]-phenylacetic acid or its derivatives would be expected.

A second oxidation of p-methoxy-tolane under the same conditions as above was carried out and the entire reaction mixture reduced with a large excess of $LiAlH_4$. The NMR of the reduced mixture was carefully examined and revealed no signals at τ3.5-5.0 (benzhydrol showes a signal at τ4.23(1H)) or at τ5.7-6.1 (2,2-diphenyl ethanol shows a signal at τ5.9(3H)) from which it may be concluded that neither of the substituted alcohols (99) or (100) was present in the mixture.



99

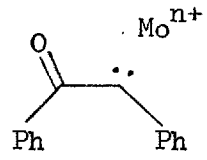


100

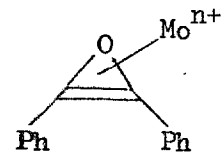
Examination of the reduced reaction mixture by mass spectrometry showed intense peaks for anisyl alcohol (M^+138) and benzyl alcohol (M^+108) and in addition two very weak peaks at 213 and 227 which might represent M^+-1 for the methoxy-alcohols (99) and (100) respectively. Their combined intensities suggested a maximum of ca. 5% rearranged products.

Taking into account the NMR evidence, it can be concluded that the oxidation of p-methoxy-tolane under the above conditions proceeds almost exclusively via the formation of p-methoxy-benzil and that a maximum of 5% Wolff rearrangement is involved in the reaction.

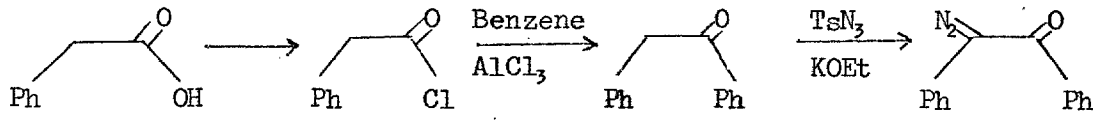
Hence the intermediacy of a free ketocarbene in the molybdenum-catalysed oxidations of acetylenes can be excluded. In view of the known ability of metals such as copper to form stabilised carbene complexes (Section 2.1.) it was conjectured that the present oxidations involved a molybdenum-bound ketocarbene intermediate (101). In order to examine this possibility, azibenzil (103) was synthesised by a series of standard reactions (Scheme 31) and subjected to the conditions of the oxidation reactions.



101



102



103

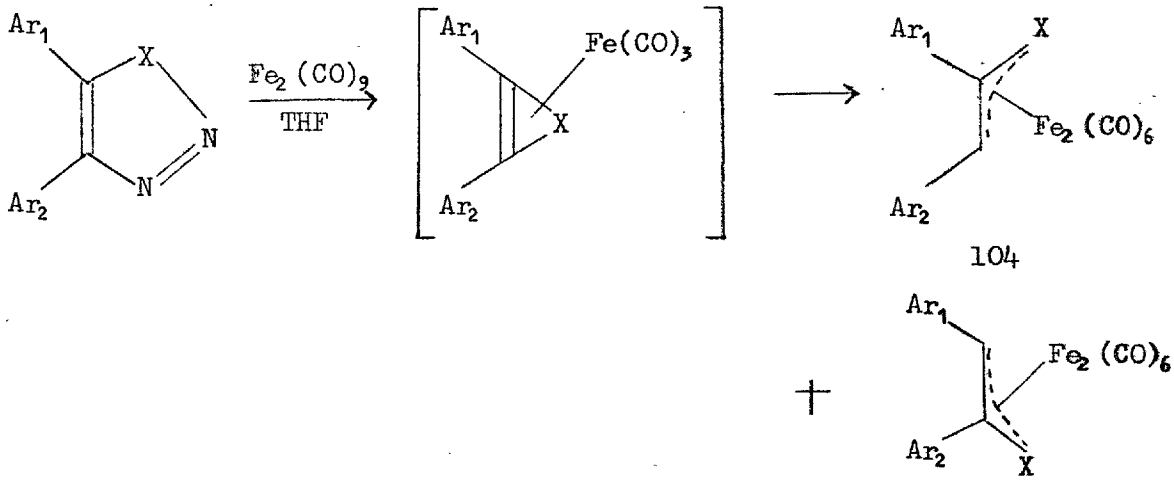
Scheme 31.

Reaction of azibenzil with one mole of MoO_5 HMPT for several days in dichloromethane gave a 79% yield of benzil (based on starting azibenzil). Chromatography of the reaction mixture yielded only one significant product band apart from the benzil. IR showed this to be a mixture of HMPT and an aromatic acid (1700cm^{-1}) together with

traces of an anhydride (1790cm^{-1}). NMR indicated that the acid was benzoic rather than diphenylacetic (broad aromatic region, rather than the sharp singlet shown by diphenylacetic acid) and from the ratio of the HMPT:aromatic protons a yield of 5-6% of benzoic acid was indicated.

When azibenzil was heated for five hours in the presence of $Mo(CO)_6$ and tBuOOH, complete decomposition of the diazoketone occurred and benzil (36.7%), tbutyl benzoate (2.4%), tbutyl perbenzoate (8.5%) and benzoic acid (18.7%) were isolated. In addition, ca. 20 weight % of a mixture of unidentified products was obtained. The NMR spectrum of each of the reaction products showed no traces of any diphenylacetic acid or its derivatives. Although the material recovery is not very good for this reaction (66% of identified products), it is clear that no Wolff rearrangement occurred and that the principal pathway is conversion of the azibenzil to benzil and further oxidation of this in the expected manner.

The two oxidations of azibenzil described above provide strong evidence that the same intermediate is involved as in the oxidations of diphenylacetylene and strongly suggest that this intermediate is a molybdenum-ketocarbene complex (101). However, the alternative molybdenum-oxiren complex (102) cannot be entirely ruled out at this stage, since although the ketocarbene-oxiren equilibrium is completely inhibited by metals such as copper and silver (Section 2.2.), Rees[108] has very recently reported that thiocarbene-thiiren and selenocarbene-seleniren interconversions will take place in the presence of Fe when diarylthiadiazoles and selenadiazoles are decomposed by $Fe_2(CO)_9$ (Scheme 32).



Ar_1, Ar_2 = C_6H_5 , pBu^tC_6H_4 .

X = S 104:105 = 70:30.

X = Se 104:105 = 75:25.

Scheme 32.

It was therefore decided to apply the test for oxirens[78] developed above (Section 2.2.) to the case of molybdenum-catalysed diazoketone decompositions. On heating 3-diazoheptan-4-one (26) with $Mo(CO)_6$ in benzene, only cis- and trans-hept-2-en-4-ones (30) and (31) were formed together with traces of heptan-4-one and heptan-3,4-dione. No trace of hepten-3-one derived from oxiren rearrangement could be detected. Similarly, 2,2-dimethyl-4-diazohexan-3-one (40) gave only cis- and trans-2,2dimethylhex-4-en-3-ones (41) and (42); no 2,3dimethylhex-2-en-4-one was formed in the presence of $Mo(CO)_6$.

Reaction of 3-diazoheptan-4-one with MoO_2 HMPT produced a 55:45 mixture of heptan-3,4-dione and hept-2-en-4-ones; again no oxiren-derived products were detected.

These tests provide compelling evidence that the molybdenum-

catalysed decompositions of α-diazoketones and oxidations of acetylenes proceed by way of molybdenum-ketocarbene intermediates and that equilibration of the ketocarbene with the corresponding oxiren is completely inhibited.

In view of these results the reactions reported by Rees for the sulphur and selenium analogues (Scheme 32) merited further consideration.

Azibenzil was rapidly decomposed by di-iron nonacarbonyl in THF, but no organometallic complexes could be isolated. 3-diazoheptan-4-one (26) was decomposed more slowly and gave only hepten-4-ones (28%): no oxiren-derived products could be detected. Strikingly, the principal product was the cis-enone (c:t = 82:18), which implicates an iron-carbonyl complex as intermediate since general metal catalysis would have produced an equal mixture of cis- and trans-enones (c.f. Ag, Cu and Mo). Since, in iron-diene complexes, the olefin has almost invariably the trans-trans configuration whenever possible,[109] it was considered feasible that more of the trans-hept-2-en-4-one had actually been formed, but that it remained bound in an iron complex. Since it is known that addition of triphenylphosphine to iron-diene complexes displaces the diene ligand,[109] PPh_3 was added to the reaction mixture of the diazoketone decomposition and the results monitored by G.L.C. The absolute yield of enones remained essentially constant (27%) after seven days, whilst the cis-trans ratio altered dramatically (10:90), indicating that no trans-enone was complexed but that an isomerisation was occurring.

The disparity between these results and Rees' must be attributed to differences between oxygen and sulphur or selenium. Presumably in the latter cases the longer bonds to carbon, the

greater availability of lone pairs and the ability to enter into $d\pi$ bonding with the Fe make possible the formation of thiiren and seleniren complexes. It appears to be very much more difficult to form oxirens in the presence of metals.

Experimental.

I.r. spectra were recorded on a Unicom SP200 spectrometer and u.v. spectra on a Unicom SP800 spectrometer. Mass spectra were determined with an AEI MS9 or Perkin-Elmer 270 machine. G.L.C. analyses were carried out on a Perkin-Elmer F11 gas chromatograph using the following columns: 2m. 15-85 PEGS on Chromosorb P, o.d. $\frac{1}{8}$"; 2m. 15-85 carbowax on Chromosorb W, o.d. $\frac{1}{8}$"; 4m. 2.5:97.5 silicone gum on AW DMCS on Chromosorb G, o.d. $\frac{1}{8}$"; or 6 ft. 15-85 squalane on Chromosorb P, o.d. $\frac{1}{4}$". Preparative G.L.C. separations were performed on a Pye 105 gas Chromatograph using a 12 ft. column of 15-85 E30 on diatomite C. Combined G.L.C. - mass spectral analyses were performed on a Perkin-Elmer 270 mass spectrometer using one of the above analytical columns. When estimated by G.L.C., absolute yields of products were determined by calibration of the G.L.C. system using an internal reference, generally o-methyl anisole, and comparison of the peak areas with calibration graphs constructed using pure samples of the products.

Unless otherwise stated, all photolyses were carried out with a Pyrex filter and using a 450 W medium-pressure mercury lamp. Solutions were degassed with dry, O_2-free nitrogen for at least 10 minutes before photolyses. ^1H n.m.r. spectra were generally determined with either a Varian A60 or T60 spectrometer, with deuteriochloroform as solvent and tetramethylsilane as internal reference.

Melting-points and boiling points are uncorrected. Unless otherwise stated, literature values quoted are taken from I. Heilbron, "Dictionary of Organic Compounds" Eyre and Spottiswoode, London, 4th Ed. 1965

3-Diazoheptan-4-one (26). - Small pieces of sodium (3.75g; .163M) were dissolved in anhydrous ethanol (50 ml.) under reflux, and the solution then evaporated to give sodium ethoxide (11.1g; 0.163M). This was suspended in anhydrous ether and stirred, whilst cooling it in an ice-salt bath, as a mixture of heptan-4-one (15.0g; 0.131M) and ethylformate (12.0g; 0.162M) was added dropwise over 30 min. After a further 3 hr. stirring in the cooling bath, the mixture was allowed to warm to room temperature overnight and then diluted with dry ether (500 ml.). A yellow gum separated, which was washed with dry ether, dissolved in sulphuric acid (400 ml; 2 ½%) and the solution then extracted with ether (2x100 ml.). The ethereal phase was washed with water (2x25 ml.), dried over Na_2SO_4 and evaporated to give a pale yellow oil. Distillation under reduced pressure afforded 3-formylheptan-4-one, b.p. 115°/80 mm. (Lit:[110] 115°/80 mm.), 11.1g; 60%. νmax. (film), 3300 bw, 1735, 1710, 1650-1600 bs. Deep violet colour with aqueous ferric chloride solution. It crystallised to a low-melting solid on storing in the refrigerator.

To 3-formylheptan-4-one (1.56g; 0.011M) and triethylamine (2.0g; 0.02M) in dichloromethane (25 ml.), stirred in an ice-bath, was added tosyl azide (2.0g; 0.01M) dropwise over one minute. After stirring 90 minutes, the reaction mixture was extracted with a solution of potassium hydroxide (1g) in water (25 ml.), washed with water (3x25 ml.), dried (Na_2SO_4) and evaporated to give 3-diazoheptan-4-one[11] (1.05g; 75%), νmax (film) 2070, 1640cm^{-1}. (Lit: 2075 cm-1), 7.60 (4H,m), 8.3 (2H,m), 8.9(3Ht, J7Hz), 9.05(3Ht,J7Hz).

Cis-(31) and Trans-hept-2-en-4-one (30). - 3-diazoheptan-4-one (.31g; .0022M) was stirred with a suspension of silver oxide (20 mg.) in 1:5 aqueous dioxan (6 ml.) at room temperature for 3 hours.

Combined G.L.C.-mass spectral analysis (PEGS column) showed the formation of four products: cis-hept-2-en-4-one (31) (30%), trans-hept-2-en-4-one (30) (33%), heptan-4-one (1%) and heptan-3,4-dione (2%). By carrying out the reaction on a larger scale in ether followed by preparative G.L.C.$_0$ authentic samples of the cis- and trans-enones were isolated. The trans-isomer[111] had νmax ($CHCl_3$) 1690(S), 1625(m) cm^{-1}; τ 9.1(3Ht J7Hz), 8.4 (2Hm), 8.1 (3Hdd, J1.5,6Hz), 7.6(2Ht, J7Hz), 4.0(1Hdq, J1.5, 16Hz), 3.3(1Hdq, J6,16Hz); m/e 112(M^+)(2), 97(20), 83(8),71(5), 69(100), 55(5), 43(15), 41(45), and 39(20). cis-hept-2-en-4-one showed νmax ($CHCl_3$) 1690(sh), 1665(S), 1635(S) and 985(S)cm^{-1}; τ 9.1(3Hm), 8.4(2Hm), 8.0 (3Hm), 7.6(2Hm) and 3.9(2Hm). Double irradiation of the peak at τ 3.9 caused collapse of the multiplet at 8.0 to a singlet. INDOR experiments showed that the multiplets at 9.1, 8.4 and 7.6 were due to the propyl group; m/e 112(M^+)(15), 97(8), 83(5), 71(5), 69(100), 55(5), 43(15), and 39(20).

Trans-Hept-4-en-3-one (32). Methyl ethyl ketone (21.6g; 0.30M) in anhydrous ether (50 ml.) was added to a suspension of freshly-prepared sodamide (from 15.2g, 0.66 M sodium in anhydrous ether (300 ml.) over 10 min., before heating the mixture to reflux for 5 min and then adding ethyl propionate (61.2g; 0.60M) in anhydrous ether (50 ml.). The reaction mixture was stirred and refluxed for two hours, cooled, poured onto ice-water (300 ml.), acidified and the aqueous phase extracted with ether (3x100 ml.). The combined ethereal phases were evaporated to afford a brown oil (60g) which was dissolved in hot methanol (75 ml.) and added to a hot solution of copper acetate (40g) in water (350 ml.). After cooling, the blue precipitate was collected, washed with light petroleum (100 ml.) and dried in vacuo to give copper (II) dipropionylmethanate (25g; 52%), m.p. (EtOH) 209° (subl.)

(lit.[112] m.p. 209-210°). The copper complex (20g) was shaken with dilute suphuric acid (400 ml.) and ether (200 ml.) and the ether solution dried (Na_2SO_4) and evaporated to give, after distillation, dipropionylmethane (12.4g., 77%) b.p. 78-80°/30 mm. n_D^{23} 1.4563 (lit.[112] b.p. 78-80°/30 mm).

To a suspension of lithium aluminium hydride (4.0g; 0.105M) in anhydrous ether (75 ml.) was added a solution of dipropionylmethane (10.0g; 0.078M) in ether (25 ml.) over 1 hour at room temperature.

The mixture was heated to reflux for a further 1 hr. to give, after work-up, hept-4-en-3-ol (6.75g; 76%) b.p. 76-77°/30 mm, n_D^{24} 1.4355. Manganese dioxide oxidation of the allylic alcohol (3.42g; 0.03M) in ether (100 ml.) at room temperature gave, after work-up, pure trans-hept-4-en-3-one (32)[72] (1.65g, 50%), b.p. 56-9°/30 mm. νmax (film) 1690(S), 1635(S)cm^{-1}, τ 8.9 (6Hm), 7.6 (4Hm), 3.9 (1H broadened, J16Hz), 3.1 (1Hm); m/e 112(M^+)(15), 83(100), 69(10), 55(50), 43(10), 41(10), 39(15).

Photolysis of a sample of the trans-hept-4-en-3-one in ether under the standard conditions gave a rapid photo-equilibration with the corresponding cis-isomer (33), m/e 112(M^+)(35), 83(100), 57(20), 55(50), 43(20), 41(10, 39(15) and the cis- and trans-hept-5-en-3-ones (34) and (35) m/e 112(M^+)(15), 83(5), 69(10), 57(100), 55(30), 43(15), 41(10), 39(15).

Decompositions of 3-Diazoheptan-4-one (26). -

a). Photolysis. The diazoketone (.30g) in anhydrous ether (40 ml.) was photolysed for 90 minutes, the reaction being followed by disappearance of the i.r. band at 2070cm-1. o-Methyl anisole (.300g) was added as internal standard and the solution concentrated by

removal of solvent at room temperature. The reaction mixture, analysed by combined G.L.C. mass spectrometry using both the PEGS and Silicone gum columns, contained the following products: hexan-3-one (27) m/e 100(M^+), 71,57,43, identical to an authentic sample; heptan-3,4-dione (29) m/e 128(M^+), 71,57,43 (the bis-2,4-dinitrophenylhydrazone of this diketone was isolated by preparative tlc from the crude reaction mixture, m.p. 263-264° (lit.[113] m.p. 264°), and the brick-red solid went purple with alcoholic KOH); hept-2-en-4-ones (30) and (31), identical in all respects to authentic samples; hept-4-en-3-ones (32) and (33) also identical to authentic samples; hept-5-en-3-ones (34) and (35) as a mixture, identical with the minor fraction obtained by photolysis of trans-hept-4-en-3-one; heptan-4-one, identical to an authentic sample. Yields are tabulated (Scheme 16 and Table 1).

b). Thermal. These were carried out in refluxing cyclohexane and vapour-phase pyrolyses were carried out in the injection port of the F11 analytical G.L.C. instrument by varying the inlet temperature and maintaining the column temperature constant (90°) using the PEGS and Silicone gum columns. Results for the PEGS column are given in Figure 1.

3-Methoxyheptan-4-one. 3-diazoheptan-4-one (26) (0.702g; .005M) and copper oxide (.702g) in anhydrous methanol (15 ml.) were refluxed together for 2 hours. The mixture was cooled, poured into water (50 ml.), extracted with ether (2x50 ml.) and the ethereal phase washed with water (3x20 ml.) dried over Na_2SO_4 and evaporated to give 3-methoxyheptan-4-one,[77] (0.584g, 81%) νmax 1710cm^{-1}, τ6.5 (1H tJ7Hz), 6.6(3H s), 7.6(2Ht, J7Hz), 8.4(4Hm), 9.1(6Ht, J7Hz).

1-Diazoheptan-2-one[80] (36). - n-Hexanoyl chloride (2.80g, 0.02M) in anhydrous ether (25 ml.) was added dropwise to a solution of

diazomethane (0.1M) in ether (100 ml.) at 0°. Evaporation gave the diazoketone as a yellow oil (2.9g). νmax 3100(S), 2150(S), 1640(S) cm^{-1}. τ 9.1-8.7(9Hm), 7.6(2Hm), 4.7(1Hs). Photolysis of the diazoketone, under standard conditions in ether (40 ml.), for 60 minutes was followed by addition of o-methylanisole (0.051g), evaporation to small bulk and G.L.C.-mass spectral analysis (PEGS and Silicone gum columns) which showed the presence of hept-2-enal (4%), identical to an authentic sample. A small amount of heptan-2-one was also detected in the reaction mixture, m/e 114(M^+), 99,85, 71,68 and 43.

Hept-2-enal (37). - Ethyl hydrogen malonate (22g; 0.17M) and n-pentanal (10.32g; 0.12M) in dry pyridine (50 ml.) and piperidine (0.2 ml.) were refluxed gently together for 6 hr. and poured into water (250 ml.). After extraction with ether (2x50 ml.), the organic phase was washed with hydrochloric acid (5x50 ml; 15%), saturated $NaHCO_3$ solution (50 ml.), dried over Na_2SO_4, evaporated and the residue distilled to afford ethyl 2-heptenoate (14.6g, 78%), b.p. 88-91°/16 mm., νmax 1720(S), 1655(M)cm^{-1}, τ 3.0(1Hm J20Hz), 4.2(1Hm J20Hz), 5.8(2Hq), 8.3-9.2(12Hm). The ester (11.7g, .075M) in ether 50 ml.) was added dropwise to an ice-cooled, stirred suspension of lithium aluminium hydride (5.7g; .15M) in ether (200 ml.) over 1 hour. After stirring for a further 1 hr, work-up afforded hept-2-en-1-ol (8.6g), νmax 3350(S), 1660(W), 1640(W). The alcohol (8.0g, 0.07M) and MnO_2 (30g, 0.35M) were stirred in dry ether (100 ml.) for 24 hours. Filtration and evaporation afforded 5g. of crude product which was purified via the sodium metabisulphite addition compound to give 0.5g hept-2-enal νmax 2075(W), 1690(S), 1640(M) cm^{-1}; 2,4DNP, m.p. 130° (lit.[81] 131-132°) m/e 112(M^+)(10), 97(10), 83(72), 71(13), 70(39), 69(40), 68(39), 57(60), 56(52), 55(68), 43(46), 42(23), 41(100), 39(40).

1-Diazo-3-phenylpropan-2-one (39). - The diazoketone (2.0g; 0.0125M), m.p. 46-7° (lit.[82] m.p. 48-9°), was photolysed in 1:9 aqueous dioxan (40 ml.) for 3 hr. The reaction mixture was extracted with 10% aqueous sodium carbonate solution (3x25 ml.), which on re-acidificaton yielded 3-phenylpropionic acid (1.43g; 76%) m.p. 49-50° (light petrol) (lit. 48.5°), τ 7.2(4Hm), 2.80(5Hm), -0.2(1Hs). G.L.C.-mass spectral analysis of the neutral fraction from the ether extract confirmed the presence of cinnamaldehyde (< 5%), identical to an authentic sample. A pyrolysis, in refluxing cyclohexane, of the diazoketone (39) also gave traces of cinnamaldehyde.

2,2-Dimethyl-4-diazohexan-3-one (41). - Pivaloyl chloride (4.82g, .04M) in anhydrous ether (25 ml.) was added dropwise, over 1 hr. with stirring, to a solution of diazopropane (0.086M) and triethylamine (0.08M) in ether (600 ml.) at -20°. After a further 3 hr. the solution was warmed to room temperature, washed with water, sodium carbonate solution, and finally water. After drying (Na_2SO_4) the solution was evaporated to give a pale orange oil. Purification by preparative tlc (SiO_2 G, 1:9 acetone-light petroleum) gave the diazoketone (3.08g, 50%), νmax (film) 2100(S), 1635(S) cm^{-1}, τ 8.8 (3Ht, JBHz), 8.7 (9H s), 7.6(2Hq, J 8Hz), (Found : C, 62.6; H, 9.1; N, 17.8 ($C_8H_{14}N_2O$ requires C, 62.3; H, 9.1; N, 18.2%).

2,3-Dimethylhex-2-en-4-one (44). - Propionyl chloride (18.5g, .02M) and trimethylethylene (21.0g, .03M) was slowly treated with stannic chloride (2.5g) with cooling to 0°. After addition the reaction mixture was allowed to warm to room temperature, left for 10 min., and then treated with dilute hydrochloric acid (4N, 100 ml.). The organic phase was re-washed with acid, then water before drying (Na_2SO_4) and distilling to give 2,3-dimethylhex-1-en-4-one[83]

(3.9g, 15%), b.p. 80-90° at 50 mm Hg. The residue, which was mainly 2-chloro-2,3dimethylhexan-3-one (30g) was treated with potassium hydroxide (25g) in ethanol (250 ml.). The mixture was left at room temperature for 15 min. before extraction with water and ether. The organic extract was washed with water before drying (Na_2SO_4) and removal of ether. Distillation afforded 2,3-dimethylhex-2-en-4-one, (12g, 48%) b.p. 161-165°/770 mm., νmax, 1690, 1620, 980 cm^{-1}, characterised as its semicarbazone, m.p. (EtOH) 189-190°, νmax 3400, 3300, 1685, 1630 cm^{-1}, τ 9.0 (3Ht, J 8 Hz), 8.3 (9 H, broad s), 7.70 (2Hq, J 8 Hz), 4.40 (2H broad s) and 2.0 (1H broad s), m/e 183 (M^+) (Found: C, 58.65; H, 9.5, N, 23.2. $C_{,}H_{17}N_3O$ requires C, 58.95; H.9.4; N, 22.9%).

Photolysis of 2,2-Dimethyl-4-diazohexan-3-one (14). - The photolyses (Table 2) were carried out by the standard procedure, the product being washed with aqueous sodium carbonate solution and water before drying (Na_2SO_4) and careful evaporation to small bulk. G.L.C.-mass spectral analysis of the photolyses showed the presence of three main products, identified by comparison to authentic samples. One of these was 2,3-dimethylhex-2-en-4-one (17), m/e 126 (M^+) (20), 97 (73), 69(100), 57(15), 41(90). The two other major components were identical to the cis- and trans-2,2-dimethylhex-4-en-3-ones produced in the silver oxide catalysed decomposition of the starting material: m/e 126 (M^+) (10), 69(100), 57(80), 41(75), 39(35) and m/e 126 (M^+) (10), 97(13), 83(10), 69(100), 57(50), 41(55), 39(25).

2-Diazocyclodecanone (47). - Diethylsebacate (129g; 0.50M) in dry xylene (80 ml.) was added dropwise to a rapidly stirred mixture of finely dispersed, molten sodium (46g; 2.0M) in dry xylene (500 ml.) under reflux under dry, O_2-free nitrogen. After addition (3 hr.) the mixture was refluxed for 45 min., then cooled to below 20°

and dry methanol (100 ml.) added over 20 min. The solution was then acidified by dropwise addition of sulphuric acid (ca. 400 ml., 30%). The organic phase was washed with water (2x100 ml.), saturated $NaHCO_3$ solution (2x100 ml.), water (2x100 ml.), dried over Na_2SO_4 and evaporated. Distillation of the residue afforded 2-hydroxycyclodecanone[114] (19.2g; 23%), b.p. 125-137°/13 mm. νmax 3,500(S), 2,900(S), 1700(S).

The acyloin fraction (18.5g; 0.109M) in acetic acid (50 ml.) was added to zinc dust (20g; 0.3M) in acetic acid (50 ml.) and conc. hydrochloric acid (50 ml.). The mixture was heated on a steam bath and three further portions of hydrochloric acid (50 ml.) added at 30 min. intervals, then the cooled mixture was poured into water (250 ml.) and extracted with ether (2x100 ml.). The organic phase was washed with sodium carbonate solution (2x100 ml; 10%), water (2x100 ml), dried and evaporated. Distillation afforded cyclodecanone[114] (8.54g, 51%), b.p. 114-119°/14 mm. νmax (film) 1700(S) cm^{-1}. m/e 154(M^+).

Cyclodecanone (8.5g; .055M) was added to ethyl formate (8.0g; 0.11M) and sodium methoxide (7g) in dry ether (150 ml). After stirring overnight, the mixture was poured into ice-water (100 ml.) and the aqueous phase extracted with ether (50 ml.) and the ether phase with water (50 ml.). The aqueous phase was acidified with hydrochloric acid (50 ml; 20%) and extracted with ether (2x50 ml). The ethereal solution was dried and evaporated to afford, after distillation, 2-formylcyclodecanone[85] (8.50g, 85%) b.p. 120-130°/11 mm. νmax (film) 3400 (b), (1720(w), 1695(w), 1640-1580(b).

To a solution of 2-formylcyclodecanone (1.84g; 0.01M) and triethylamine (2.03g; .02M) in dichloromethane (10 ml.) cooled and

stirred at -20° was added tosyl azide (2.00g; .01M), over 2 min. The solution was stirred for 10 min. at -20°, then for 2 hr. at 0°. Evaporation afforded a yellow crystalline mass which was taken up in ether (20 ml.) and stirred with potassium hydroxide (0.6g) in water (10 ml.) for 5 min. The ethereal phase was washed with water (10 ml.) containing KOH (.05g), then water (10 ml.), dried over Na_2SO_4 and evaporated. The residue was recrystallised from absolute ethanol at -50° to give pure 2-diazocyclodecanone (1.16g; 64%), 56-7°, (lit.[84] 56-7°), νmax (Nujol) 2100(S), 1615(S) cm^{-1} (lit:[84] 2086, 1618 cm^{-1}).

The diazoketone (0.14g) in anhydrous ether (40 ml.) was photolysed under the standard conditions. After evaporation to small bulk, G.L.C. on the Carbowax and PEGS columns and G.L.C.-mass spec. on theCarbowax column showed cyclononanone, cyclodecenones and a mixture of two bicyclic ketons. Relative yields were estimated via the appropriate peak areas.

Cyclodec-2-enone (50). - 2-Diazocyclodecanone (0.27g) and silver oxide (0.25g) in dry ether (20 ml.) were stirred together in the dark for 24 hr. before filtering and evaporation. The residue was chromatographed (SiO_2 ; 1:9 acetone-light petroleum) to give cyclodec-2-enone[86] (0.18g, 79%) νmax 1690(S) 1635(M) cm^{-1}; τ 8.7 (8Hm), 8.1 (2Hm), 7.6 (4Hm), 4.30 (1H dt, J 8, 12 Hz), 3.60 (1Hd, J 12 Hz); m/e 152 (M^+) (6), 133 (9), 125 (7), 109 (18), 98 (52), 97 (14), 95 (36), 82 (41) 81 (100), 68 (63), 67 (29), 55 (46), 54 (21), 53 (23), 41 (44), 39 (31).

Cyclodec-3-en-1-one (53).- The enone (50) (0.17g), in dry ether (40 ml.) was photolysed for 75 min. under the standard conditions. Evaporation gave a colourless oil which was purified by preparative tlc to give the cyclodec-3-enone[87] (0.14g). νmax 1700(S), 1635(W)

cm^{-1} τ 9.0 - 7.1 (12H m), 6.8 (2H m), 4.3 (2H m). Double irradiation at 6.8 caused the multiplet at 4.3 to simplify, m/e 152 (m^+) (28), 109 (21), 98 (74), 95 (26), 84 (23), 83 (21), 81 (33), 79 (16), 70 (17), 68 (26), 67 (60), 56 (67), 55 (100), 54 (18), 45 (15), 42 (20), 41 (65), 39 (38).

Oct-2-ene Oxidation. - A mixture of $Mo(CO)_6$ (0.0059g), ClPh (3.0 ml), cis- and trans-oct-2-ene (3.0 ml; .018M) and t-BuOOH (1.0g; .011M) was heated and stirred on an oil bath at 90° for 1 hr. G.L.C. (4m. Silicone gum column) then showed complete disappearance of the t-BuOOH, a new peak for tBuOH and two peaks of long retention times which were identified by G.L.C.-mass spec. as 2,3-epoxyoctanes: m/e 128(M^+), 113, 112, 110, 99, 95, 85, 83, 82, 81, 71, 69, 67, 58, 57, 56, 45, 43 (100%), 41. The combined yield of epoxides (based on tBuOOH) was estimated as 88% by G.L.C.

Cholest-2-ene Oxidations. - The olefin (0.1848g; 4.99×10^{-4} M), $Mo(CO)_6$ (.0008g), benzene (0.25 ml.) and t-BuOOH (0.1 ml; 10^{-3} M) were refluxed together for 2 hr. and the mixture chromatographed on thick alumina p.l.c. plates using light petroleum (40-60°) to elute. Apart from starting material, the only product found was 2α,3α-epoxycholestane, (0.1046g, 54.3%), m.p. ($MeOH/Et_2O$) 107-8° (Lit: 2α,3α-epoxide m.p. 107-8°; 2β,3β-epoxide m.p. 91°).[115]

Hexa-1,5-diene Oxidation. - The diene (0.72g; 0.01M), $Mo(CO)_6$ (0.0056g), tBuOOH (1.0 ml; 0.01M) and benzene (2.0 ml.) were sealed in a carius tube and heated at 90° for 2 hr. G.L.C. (4m Silicone gum column) after this time showed, apart from t-butanol, one major new peak and one very minor one of much longer retention time. The major product was isolated by preparative G.L.C. and identified as 1,2-epoxy-hex-5-ene,[116] ν_{max} 3030, 995, 920cm^{-1} (C-H

of vinyl group); 1640 cm^{-1} ($C{=}CH_2$); 2990, 1260cm^{-1} (epoxide), m/e 98(M^+), τ 4.2 (1H m), 4.9 (2H m), 7.3 (2H m), 7.7 (3H m), 8.3 (2H m).

Octa-1,7-diene Oxidation. - The diene (1.10g; .01M), $Mo(CO)_6$ (.0024g) and tBuOOH (.01M) in chlorobenzene (2.0 ml.) were heated together at 95°& G.L.C. (Squalane columns) after 5 hr. showed two products in the ratio 6:1, formed in yields of 55% and 9% (estimated using the chlorobenzene as internal standard). The two products were isolated by prep. G.L.C. and the major one identified as 1,2-epoxyoct-7-ene,[116] m/e 126 (M^+) (weak), τ 4.3 (1H m), 5.0 (1H m), 7.2 (2H m), 7.6 (1H m), 7.9 (2H m), 8.5 (6H bs). The minor product was identified as 1(2),7(8)-diepoxyoctane,[116] m/e 142(M^+) (weak), τ 7.2 (4H m), 7.5 (2H m), 8.45 (8H bs).

Cycloocta-1,5-diene Oxidation. - The diene (1.09g; .01M), $Mo(CO)_6$ (.0101g) and t-BuOOH (.01M) in benzene (2.0 ml.) were heated under reflux on an oil bath at 90° for 3 hr. G.L.C. (4m Silicone gum column) showed two products in the ratio 8.4:1. Both were isolated by prep. G.L.C. and the major one identified as 1,2-epoxycyclooct-5-ene,[117] m/e 124 (M^+), τ 6.4 (2H m), 7.0 (2H m), 7.9 (8H m).
The minor product was 1(2),5(6)-diepoxycyclooctane,[117] m/e 140 (M^+) τ 7.05 (4H bs), 8.05 (8H bs).

Squalene Oxidations. - Squalene (.5178g; .0126M], purified immediately before use via its thiourea clathrate, was refluxed and stirred with $Mo(CO)_6$ (0.0055g) and t-BuOOH (0.013M) in dry benzene (1.0 ml.) on an oil bath at 95° for 2 hr. After cooling and evaporation under reduced pressure, the residue was chromatographed on silica (8:92 ethylacetate/light petrol). Some squalene (0.1631g, 31.5%) was recovered together with squalene-2,3-oxide (0.1007g; 27.2% based on converted squalene) m/e 426 (M^+), τ 4.85 (5H bs), 7.3 (1Ht), 8.0

(18Hd), 8.3 (bs) and 8.4 (bs) (2OH), 8.7 (6H d) and a mixture of squalene-6,7 and -10,11-oxides (0.0811g; 22.0% based on converted squalene) m/e 426 (M^+), τ 4.85 (5H bs), 7.3 (1Ht), 8.0 (18H bs), 8.3 (bs) and 8.4 (bs) (2OH), 8.7 (3H s).

The other oxidations of squalene (Table 4) were carried out in an analogous manner.

Methyl Sorbate Oxidations. - Method a). The ester (0.6257g; 4.97×10^{-3} M), $Mo(CO)_6$ (0.0065g) and t-BuOOH (.005M) in benzene (0.5 ml.) were refluxed and stirred together on an oil-bath at 95° for 2 hr., P.l.c. on silica eluted with 20:80 acetone/light petrol, yielded trans-4,5-epoxy-trans-hex-2-enoic acid methyl ester (0.292g, 41.4%),[101] m/e 142 (M^+) (5), 126(30), 111(45), 110(27), 98(43), 95(39), 83(78), 82(25), 81(15), 67(45), 59(35), 55(30), 53(18), 43(100), 41(44), 39(70), τ 8.58(3Hd, J 5Hz), 7.02(1Hq, J 5cps, 2Hz), 6.81(1Hq J 2Hz, 6.5Hz), 6.25(3Hs), 3.88(1Hd, J 16Hz), 3.25(1Hq, J 16Hz, 6.5Hz).

Method b). The ester (0.6377g; 5.06×10^{-3} M), $Mo(CO)_6$ (0.0085g) and tBuOOH (0.005M) in ClPh (.50 ml.) was heated together at 90°. A sample was removed after 2 hr. for G.L.C. analysis (squalene columns and more t-BuOOH (.50 ml.) added. Another sample was removed after two more hours and tBuOOH (0.50 ml.) again added. After a further 1 hr. a final sample was removed. G.L.C. estimates of conversion and yields were made by measurement of peak areasusing the ClPh as internal standard.

3-Methylindole Oxidation. The indole (2.6261g; .02M), $Mo(CO)_6$ (0.0094g), t-BuOOH (0.04M) and ClPh (5.0 ml.) were heated at 95° for 2 hours. Preparative chromatography on alumina plates (25:75 acetone/light petrol) gave 2-acetyl-N-formyl aniline (0.4219g, 13%) as bright yellow needles m.p. 75-7° (EtOH) (Lit:[119] m.p. 79°), νmax

(Nujol) 3250(m), 1680(s), 1645(s) cm^{-1}. m/e 163(38), 148(15), 135(50], 120(100), 77(12), 65(30), 43(24).

τ 1.1-1.6 (2H bm), 2.0-2.9 (4H m), 7.35 (3H s).

Triethyloxonium Fluoroborate. - In a 500 ml, 3-necked flask fitted with a stirrer, dropping funnel and condenser protected by a drying tube, was placed a solution of freshly distilled boron trifuoride etherate (71g; 0.5M. b.p. 82-4°/80 mm) in dry ether (125 ml). Freshly-distilled epichlorohydrin (35g; 0.46M. b.p. 115-116°) was added dropwise at such a rate that gentle reflux was maintained by the exothermic reaction. The mixture was then heated to reflux for a further 45 minutes and left at room temperature overnight. The ethereal phase was decanted off leaving a white crystalline mass which was washed with anhydrous ether (6x100 ml) and the pure triethyloxonium fluoroborate, 65g, 90%, was stored under anhydrous ether in a stoppered flask.

2-ethoxy-3,4,5,6-tetrahydropyridine. -

Cyclopentanone oxime (12g) was dissolved in chloroform (150 ml) and cooled to -5°. Thionyl chloride was added and the mixture swirled and allowed to warm until a vigorous exothermic reaction began, when the flask was rapidly cooled in an ice-salt bath. After standing for 1 hr. following completion of the reaction, the precipitate of 2-piperidone hydrochloride was filtered off and washed with a little ice-cold chloroform. Two further batches of cyclopentanone oxime were similarly treated, giving a total of 15.1g (32.8%) of 2-piperidone hydrochloride from the oxime (33.7g; .388M). The combined mother-liquors of the reaction were concentrated to ca. 100 ml. and filtered to give a further 3.0g of product. The filtrate was evaporated to dryness and the residue taken up in hot ethanol (100 ml.) which was cooled and diluted with ether (50 ml.) to give a brown precipitate.

This was collected and decolourised with charcoal (10g) in hot ethanol (100 ml.) to give a further quantity of product (4.7g). The combined yield of pure 2-piperidone hydrochloride was 49.5%, νmax (Nujol) 660,825,840,1300,1330,1365,1510,1660,2100-2600 cm^{-1}

To the hydrochloride (22.6g; .168M) in water (35 ml.) at 0° was added dropwise a solution of KOH (10g) in water 41 ml.) until the mixture was just alkaline. Extraction with chloroform (5x50 ml.) gave, after drying (Na_2SO_4) and evaporating, 2-piperidone, 15.1g; 91.4%, on a low-melting solid. νmax (film) 3200(m), 1660(bs), 1500(m), 760(bs) cm^{-1}. τ 2.3(1H bs), 6.7(2H bs), 7.7(2H bs), 8.2(4H m).

To a solution of 2-piperidone (15.1g;.153M) in dry dichloromethane was added with stirring a solution of triethyloxonium fluoroborate (45.5g; .245M) in dry dichloromethane (40 ml.). After stirring overnight the solution was added rapidly to a stirred, saturated solution of sodium bicarbonate in water (200 ml). The mixture was transferred to a separating funnel and cautiously shaken until effervescence ceased. The organic phase was then washed with water (50 ml.), dried over Na_2SO_4 and evaporated. Distillation of the residue afforded 2-ethoxy-3,4,5,6-tetrahydropyridine 11.86g, 61.2%, b.p. 117-119°/230 mm, as a foul-smelling liquid. νmax (film) 1680(s), 1225(s) cm^{-1}, τ 6.0(2H q, J 7Hz), 6.5(2Hm), 7.9(2H m), 8.4(4H m), 8.8(3Ht, j 7Hz).

Oxidation of 2-ethoxy-3,4,5,6-tetrahydropyridine.

The imino-ether (1.27g, 0.01M) in anhydrous methanol (50 ml.) was cooled and stirred in an ice-salt bath and m-chloroperbenzoic acid (0.01M) in anhydrous methanol (50 ml.) was added in 1 minute. After stirring a further 9 minutes (starch-iodide test positive),

hydrochloric acid (50 ml, 6N) was added and stirring continued for 5 minutes more. The methanol was then removed under reduced pressure and the solution extracted with dichloromethane (1x100 and 3x25 ml.) and continuously extracted with chloroform for 12 days to give 0.62g, 54%, N-hydroxy-2-piperidone, νmax (film) 3100(b,s) 1635(b,s), cm^{-1}, strong cherry-red colour with ferric chloride solution. Benzoate, m.p. 73-5° (Lit:[103] 77-8°).

The dichloromethane extract was washed with sodium carbonate solution (3x50 ml; 10%), dried over Na_2SO_4 and evaporated to give the nitrosoester dimer (82) (.174g; 11%), νmax (film) 1730 cm^{-1}.

N-Trimethylsilyl 2-Piperidone (89). - 2-piperidone (7.20g; 0.073M) and triethylamine (7.07g; 0.070M) in dry benzene (40 ml.) was refluxed and stirred as trimethylsilylchloride (7.60g; 0.070M) was added dropwise over 30 minutes. After a further 45 minutes reflux, the mixture was cooled, filtered and evaporated. The residue was distilled to give N-trimethylsilyl-2-piperidone,[104] 7.03g; 56%, b.p. 114-119°/100 mm. νmax 1635,1355,1305,860 cm^{-1} and 3250,1670 cm^{-1} for 2-piperidone. τ 6.2(.5H q), 6.8(2H m), 7.7(2.5H m), 8.3(4H m), 8.8(1H m), 9.8(9H s); estimated amount of 2-piperidone 20%. Re-treatment of the product (3g) with trimethylsilylchloride (3.5g) and triethylamine (4g) in benzene (15 ml.) gave N-trimethylsilyl-2-piperidone (3g) containing 10% 2-piperidone.

Molybdenum dioxide bis-hydroxamate. (90). Method a). N-trimethylsilyl-2-piperidone (.002M) and MoO_2 HMPT (.3554g; .001M) in dichloromethane (10 ml.) was stirred at room temperature for 2 days. The mixture was then concentrated and chromatographed on preparative silica plates eluted with 1:9 methanol-chloroform giving .14g yellow oil which was triturated with light petroleum and recrystallised fom

methanol to give 0.050g, 14.1% yellow crystals, m.p. 214°, νmax (Nujol) 1590(s), 1110(s), 940(s) 920(s), 885(s), 735(s) cm^{-1}, τ 6.1(2H bs), 7.4(2H bs), 8.1(4H bs), m/e 358, 356, 355 (M^+; Mo isotopes), found C 33.80%, H4.46%, N7.75%. Calculated for $C_{10}H_{16}N_2O_6Mo$, C 33.72%, H 4.53%, N 7.86%.

Method b). Hydrated molybdenum trioxide (1.2g; .0074M) was dissolved in hydrogen peroxide (7.5 ml, 28%) by stirring for 30 min. at 40°. N-hydroxy-2-piperidone (0.5g; .0043M) in water (1 ml.) was added, giving a clear yellow solution which was stirred for 1 hour and then continuously extracted overnight with chloroform. The yellow oil obtained by evaporation of the chloroform was chromatographed on silica (1:9 methanol-chloroform) to give 0.20g crude product which was recrystallised from methanol, affording 0.034g, 4.5% of the bis-hydroxamate complex, m.p. 210-11°, i.r. spectrum identical to the product in (a) above.

Diphenylacetylene Oxidations. a). The acetylene (0.1785g; 0.001M) and MoO_5 HMPT (.3613g; .001M) were stirred together in dichloromethane (5 ml.) at room temperature for 3 days. P.l.c. gave recovered acetylene (92.1%) and benzil, (.0094g, 4.6%), m.p. 89-92°, νmax (Nujol) 1670cm^{-1} (spectrum identical to an authentic sample).

b). Diphenyl acetylene (0.1781g; 0.001M), tBuOOH (1.67 ml; 0.0167M) and $Mo(CO)_6$ (0.0175g) in dry benzene (2.5 ml) were refluxed together for 5 hr. P.l.c. gave recovered acetylene (0.0824g; 46%), benzil (.0375 g) m.p. 94-5° (Lit 95°), m/e 210 (M^+), νmax 1670cm^{-1}, τ 3.4-4.2 only; benzoic acid (.0410g), m.p. 121-2° (Lit 122°), m/e 122 (M^+), νmax 1700(s) cm^{-1}; .0225g t butylperbenzoate, m/e 194(M^+), νmax (film) 1755cm^{-1}, λ_m (EtOH) 280(sh), 273, 230 nm. τ 1.9-2.7 (5H m), 8.63(9H s); a trace of benzoic anhydride, m/e 226.0637(M^+) - $C_{14}H_{10}O_3$ requires 226.0630; t-butylbenzoate (.0012g), m/e 178(M^+), νmax (film)

1700cm^{-1}, τ 1.85-2.7 (5H m), 8.4(9H s).

p-Methoxyphenyl Benzyl Carbinol (93). To benzyl magnesium chloride [from 12.05g (0.50M) magnesium and 65g (0.53M) benzyl chloride] in anhydrous ether (225 ml.) was added dropwise, with stirring, a solution of p-methoxybenzaldehyde (65g; 0.48M) in anhydrous ether (150 ml.) over 30 minutes. After refluxing 2 hr. and cooling the mixture was poured onto ice (1000g) and dilute sulphuric acid (250 ml; 10%). The aqueous phase was extracted with ether (200 ml.) and the combined organic extracts washed with water (200 ml.), dried and evaporated. The residue was recrystallised from light petrol (60-80°) to give the carbinol (103g, 94.5%), m.p. 58° (lit[106] 57-8°), νmax 3,300 cm^{-1} τ 3.0 (9Hm), 5.23(1H t, J 6.5 Hz), 6.28(3Hs), 7.0(2Hd, J 6.5Hz), 7.7(1Hbs).

p-Methoxystilbene (94). The carbinol (100g; .44M) and sulphuric acid (250 ml; 50%) were refluxed together for 2 hr. After cooling and pouring into water (1000 ml.) filtration and recrystallisation of the precipitate (HOAc, then EtOH) gave p-methoxystilbene 85g, 92%. M.p. 136-7° (lit[106] 135-6°). νmax (Nujol) 970cm^{-1} τ 6.20(3H s), 2.3-3.3(11H m).

p-Methoxystilbene Dibromide (95). Bromine (17.1g; 0.11M) in chloroform (50 ml.) was added dropwise to a stirred solution of p-methoxystilbene (21.0g; .10M) in chloroform (150 ml.) and the mixture stirred for 1 hour. The precipitate was filtered off and washed with a little cold chloroform to give p-methoxystilbene dibromide (16g) m.p. 172-3° (lit[106] 175-6°). τ 6.17 (intense S) and 6.05 (weak S) (3H), 4.57(weak S) and 4.50(strong S) (2H), 2.2-3.3(9H m). Further concentration of the mother-liquors gave a further quantity of the dibromide (6g) τ 6.15(weak S) and 6.07(intense S) (3H), 4.57 (intense S) and 4.50(weak S) (2H), 2.1-3.2 (9H m). Total yield,

22g, 60%.

p-Methoxybenzyl Phenyl Ketone (97). p-methoxystilbene dibromide (20.0g; .054M) and potassium carbonate (20 g) in water (400 ml.) were refluxed together for 4 hours. After cooling, the mixture was extracted with ether (2x100 ml.) and the organic phase dried and evaporated to give a yellow solid which was recrystallised from ethanol as white plates, 5.0g, m.p. 85-6°. νmax 1690(C=O), 965 (C=C) cm^{-1}. τ 1.8-3.25 (aromatic H m), 5.8(Ar$\underline{CH_2}$ COAr S), 6.2(Me$\underline{O}$Ar in 2 cpds, low-field peak smaller, d). From the ratio of CH_2 : Me protons (22:40) the amount of p-methoxystilbene present was estimated as 17%. The two components were separated by preparative thin-layer chromatography, giving p-methoxystilbene νmax 970cm^{-1} and p-methoxybenzylphenyl ketone (97)[107] νmax 1685 cm^{-1}, m.p. 91-3° (Lit: 94°).

p-Methoxyphenyl Benzyl Ketone (98). p-methoxyphenyl benzyl carbinol (0.229g; 0.001M) and manganese dioxide (0.87g) in ether (10 ml.) were stirred together for 3 hours. Filtration, evaporation and p.l.c. gave the ketone (0.1087g, 47.5%), νmax 1675 cm^{-1}, τ 1.9-3.2 (10H m), 5.8(2H S), 6.2(3H S).

p-Methoxytolane (96). To potassium hydroxide (20g; .36M) in trigol (25 ml.) stirred on an oil bath at 145-150° was added p-methoxy-stilbene dibromide (9.05g; .0245M). Rapid darkening of the solution occurred and a fine precipitate appeared. After stirring 10 minutes and cooling the reaction mixture was diluted with water (75 ml.) and extracted with ether (2x30 ml.). The ether phase was washed with water, dried and evaporated to give a brown solid (7g). This was fractionally crystallised from absolute ethanol to give p-methoxy-tolane,[107] 1.9g, 37.3%. m.p. 62-4° νmax 2205 cm^{-1}. τ 2.3-3.3(9H m),

6.2(3H s).

p-Methoxybenzil - p-Methoxytolane (.2085g; .001M) and MoO_5 HMPT (.3565g; .001M) were stirred together in dichloromethane (5 ml.) for 3 days. Preparative chromatography on silica ($CHCl_3$) yielded .0158g, 79.0% recovered acetylene and .0385g (77% based on acetylene converted) p-methoxybenzil. m.p. 58°(EtOH) (Lit: 58°) νmax 1670cm^{-1}.

Benzylphenyl ketone. - Phosphorous trichloride (17.5g; 0.125M) was added to phenylacetic acid (34g; 0.25M) and the mixture heated on a steam bath for 1 hour. After cooling to ca. 40° dry benzene (200 ml.) was added and the benzene solution decanted off the residual phosphoric acid into a flask containing $AlCl_3$ (37.5g; 0.28M). A vigorous reaction quickly developed which was controlled by intermittent cooling in an ice bath. After 15 minutes the reaction had subsided and the mixture was refluxed 1 hour, cooled and poured onto crushed ice (250g) and conc. hydrochloric acid (100 ml.). The benzene phase was separated off, and the aqueous phase washed with a mixture of benzene (50 ml.) and ether (50 ml.). The combined organic phases were washed with water (100 ml.), dried and evaporated to give a yellow oil which solidified on cooling. Recrystallisation from methanol afforded the ketone,[120] m.p. 55-56° (Lit 55-56°) 36.5g, 75%, νmax (Nujol) 1690(s) cm^{-1}.

Azibenzil (103). - Tosyl azide (4.1g; .021M) was added to an ice-bath cooled solution of benzyl phenyl ketone (4.0g; .020M) and KOH (1.16g; .021M) in absolute ethanol (40 ml.). After stirring 3-4 minutes, KOH (1.16g) in ethanol (40 ml.) was added, the mixture removed from the ice-bath, and stirring continued at room temperature for 10 minutes. Water (100 ml.) was added and the mixture extracted with ether (2x100 ml). The organic phase was washed with water

(3x50 ml.), dried over $MgSO_4$ and evaporated to give an orange crystalline product which was recrystallised from ether as find yellow-orange needles 2.65g, 58%, m.p. 77-78° (Lit:[10] 78°). νmax 2,100,1620cm^{-1}.

Azibenzil oxidations. - a). The diazoketone (.2203g; .0010M) and MoO_5 HMPT (.3545g; .0010M) in dichloromethane (5 ml.) were stirred together in the dark for 3 days. P.l.c. yielded benzil .1632g; 79.0% m.p. 92-4°. νmax 1670cm^{-1}.

b). Azibenzil (0.2255g; 0.001M), $Mo(CO)_6$ (0.o250g) and tBuOOH (0.01M) in dry benzene (2 ml.) were refluxed together for 5 hrs. Preparative t.l.c. gave t-butylbenzoate .0087g, 2.4% νmax 1700 cm^{-1}, t-butylperbenzoate (0.0330g, 8.5%), νmax 1755cm^{-1}, benzil (.0770g, 36.7%), m.p. 93-4°, νmax 1670 cm^{-1}, and benzoic acid (0.0457g, 18.7%), m.p. 119-121°, νmax 1700 b cm^{-1}.

Decomposition of 3-Diazoheptan-4-one (26) with $Mo(CO)_6$ -

The diazoketone (.1000g; 0.00071M) and $Mo(CO)_6$ (0.1006g) in dry benzene were refluxed and stirred for 4 hours. G.L.C. showed that only cis- and trans-hept-2-en-4-ones were formed.

The decomposition of 2,2dimethyl-4-diazohexan-3-one with $Mo(CO)_6$ was carried out in a similar manner.

Decomposition of 3-Diazoheptan-4-one with $Fe_2(CO)_9$. -

To the diazoketone (.1412g; 0.001M) in anhydrous THF (2.5 ml.) was added $Fe_2(CO)_9$ (0.2666g) and the mixture stirred for 48 hrs. to give a dark brown, viscous solution to which o-methyl anisole (.1136g) was added as internal standard. G.L.C. (PEGS and Silicone gum columns) showed a mixture (28% yield) of cis- and trans-hept-2-en-4-ones (ratio cis:trans 82:18). Triphenylphosphine (1.5860g; 6 moles per mole Fe) was added, and after 7 days stirring the yield of enones was 27% and the cis:trans ratio 10:90 respectively.

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