Trimethylenemethane and Related α, α′ - Disubstituted Isobutenes*

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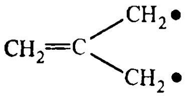
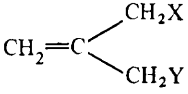
1 Introduction

Formally, trimethylenemethane is a diradical (1), with one methylene group attached to the central carbon atom by a double bond, the other two being single bonded and bearing an unpaired electron. It thus constitutes the backbone of compounds of general structure (2) and (3), which are α, α′-disubstituted derivatives of isobutene.



(1)



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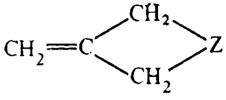

(3)

Trimethylenemethane has received much theoretical attention. It has been found by calculation[1] and experiment[2] to be in a triplet ground state, with a strongly delocalised 4π-electron system. The interesting consequence of the threefold symmetry of the structure is that all the resonance structures are equivalent diradical species, which distinguishes this π system either from the related straight chain 4π-electron system of butadiene (4), an isomer of (1), forming two conjugated double bonds as a stable resonance structure, or from the cyclic 4π-electron system of cyclobutadiene (5). The latter presents a triplet diradical character but can also appear in the form of two double bonds (Scheme 1).

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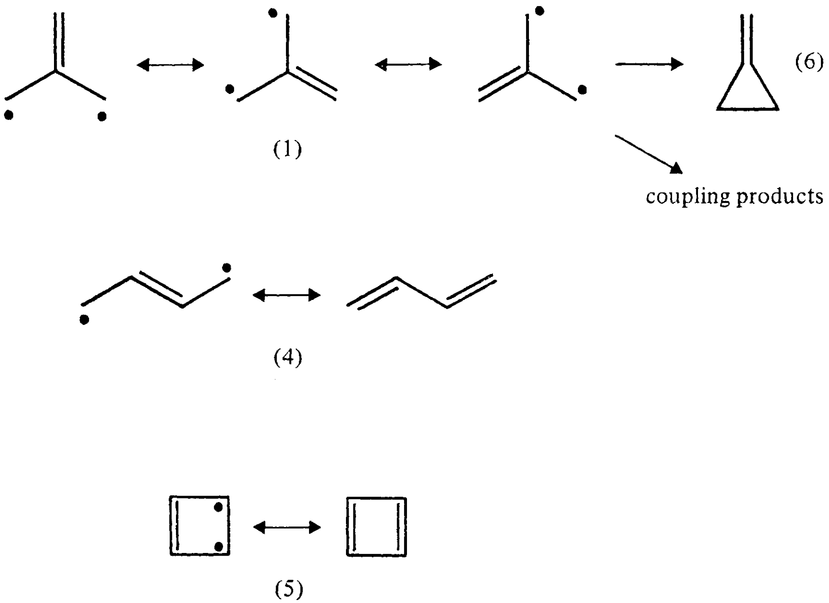
*This article is based on lectures given at Manchester, Symposium on 'New Olefin Reactions', on June 26, 1968, at Mülheim, Ruhr, on November 21, 1968, and at Strasbourg, on March 14, 1969.

[1] (*a*) W. E. Moffitt, footnote in C. A. Coulson, *J. Chim. phys.*, 1948, **45**, 243; (*b*) W. Moffitt, *Trans. Faraday Soc.*, 1949, **45**, 373; (*c*) H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265; (*d*) H. H. Greenwood, *Trans. Faraday Soc.*, 1952, **48**, 677; (*e*) J. D. Roberts, A. Streitwieser, jun., and C. M. Regan, *J. Amer. Chem. Soc.*, 1952, **74**, 4579; (*f*) J. D. Roberts, 'Notes on Molecular Orbital Calculations,' W. A. Benjamin, New York, 1961, p. 56; (*g*) A. Streitwieser, jun., 'Molecular Orbital Theory for Organic Chemists', J. Wiley, New York, 1961, p. 43, 57; (*h*) H. M. McConnell, *J. Chem Phys.*, 1961, **35**, 1520; (*i*) A. D. McLachlan, *Mol. Phys.*, 1962, **5**, 51; (*j*) D. P. Chong and J. W. Linnett, *ibid.*, 1964, **8**, 541; *J. Chem. Soc.*, 1965, 1798; (*k*) J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.*, 1954, 1201.

[2] (*a*) P. Dowd, *J. Amer. Chem. Soc.*, 1966, **88**, 2587; (*b*) P. Dowd and K. Sachdev, *ibid.*, 1967, **89**, 715; (*c*) P. Dowd, A. Gold, and K. Sachdev, *ibid.*, 1968, **90**, 2715.



Scheme 1

Equivalency of diradical resonance structures will disappear by unsymmetrical substitution of one or more hydrogens in (1).

The only way for (1) to achieve stabilisation is by forming σ-bonds with the unpaired electrons, thus losing the 4π-electron structure. Depending upon the electronic structure, the σ-bond may be formed intramolecularly, leading to methylenecyclopropane (6), or intermolecularly, giving various coupling products. Species of this kind have been postulated as intermediates both in the formation and also in several rearrangements of methylenecyclopropanes.[3] But, like other highly reactive compounds, *e.g.* cyclobutadienes,[4] trimethylene-

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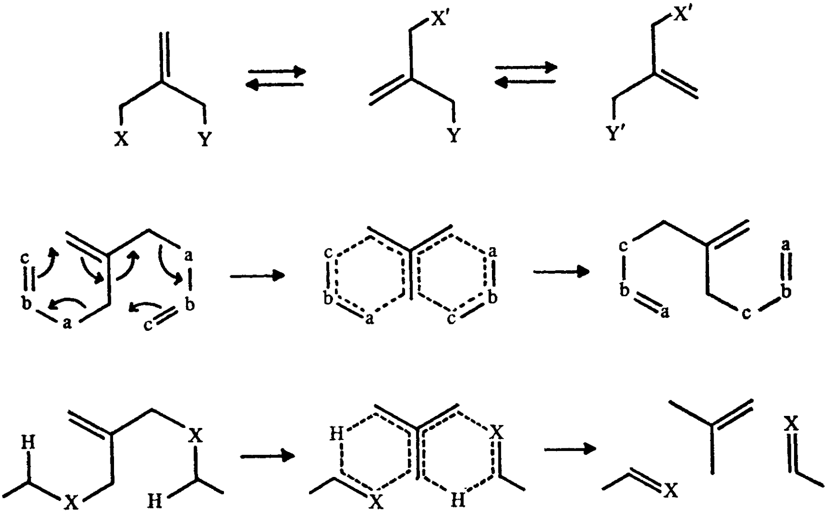
[3] (*a*) E. F. Ullman, *J. Amer. Chem. Soc.*, 1959, **81**, 5389; 1960, **82**, 505; (*b*) E. F. Ullman and W. S. Fanshawe, *ibid.*, 1961, **83**, 2379; (*c*) H. M. Frey, *Trans. Faraday Soc.*, 1961, **57**, 951; (*d*) J. P. Chesick, *J. Amer. Chem. Soc.*, 1963, **85**, 2720; (*e*) T. C. Shields, B. A. Shoulders, J. F. Krause, C. L. Osborn, and P. D. Gardner, *ibid.*, 1965, **87**, 3026; (*f*) A. C. Day and M. C. Whiting, *J. Chem. Soc.* (*C*), 1966, 464; *Proc. Chem. Soc.*, 1964, 368; (*g*) S. D. Andrews and A. C. Day, *Chem. Comm.*, 1966, 667; (*h*) J. K. Crandall and D. R. Paulson, *J. Amer. Chem. Soc.*, 1966, **88**, 4302; (*i*) R. J. Crawford and D. M. Cameron, *ibid.*, 1966, **88**, 2589; (*j*) T. Sanjiki, H. Kato, and M. Ohta, *Chem. Comm.*, 1968, 496; (*k*) W. R. Dolbier, jun., *Tetrahedon Letters*, 1968, 393; (*l*) J. J. Gajewski, *J. Amer. Chem. Soc.*, 1968, **90**, 7178; (*m*) T. Sanjiki, M. Ohta, and H. Kato, *Chem. Comm*, 1969, 638.

[4] (*a*) G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, **87**, 131; (*b*) M. P. Cava and M. J. Mitchell, 'Cyclobutadiene and Related Compounds', Academic Press, New York, London, 1967.

methane species can be successfully trapped in complexes with transition-metal compounds,[5] a field of investigation which raises considerable interest.

Outstanding characteristics of compounds (2) are the allylic nature of both substituents, and their 1,3 relative position, which allows a number of addition, substitution and cyclisation reactions. But the combination of these structural features sometimes entails unusual behaviour. Thus a number of cyclisation reactions of 1,3-substituted compounds to small ring compounds, while being easy with saturated derivatives, fails with compounds of type (2).[6] The threefold symmetry of (1), from which they are precursors, gives to compounds (2) and (3) very interesting possibilities in the numerous reactions involving allylic rearrangement. This comes from the fact that principally a double rearrangement can occur, since, if we consider a stepwise sequence, the first rearrangement displaces the double bond to a position which is equivalent to the original one, so that a second rearrangement can take place with the other substituent (Scheme 2). Such rearrangements seem to have both synthetic and mechanistic value,



Scheme 2

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[5] (*a*) G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1966, **88**, 3172; (*b*) A. Almennigen, A. Haaland, and K. Wahl, *Chem. Comm.*, 1968, 1027; (*c*) M. R. Churchill and K. Gold, *ibid.*, 1968, 693; (*d*) A. C. Day and J. T. Powell, *ibid.*, 1968, 1241; (*e*) R. Noyori, T. Nishimura, and H. Takya, *ibid.*, 1969, 89; (*f*) K. Ehrlich and G. F. Emerson, *ibid.*, 1969, 59; G. F. Emerson, K. Ehrlich, W. P. Giering, and D. Ehntholt, *Trans. New York Acad. Sci.*, 1968, **30**, 1007.

[6] (*a*) D. E. Applequist and J. D. Roberts, *J. Amer. Chem. Soc.*, 1956, **78**, 4012; (*b*) I. D'Yakonov, *J. Gen. Chem.* (*U.S.S.R.*), 1940, **10**, 402; (*c*) J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Amer. Chem. Soc.*, 1953, **75**, 3344; (*d*) R. G. Doerr and P. S. Skell, *ibid.*, 1967, **89**, 3062; P. S. Skell and R. G. Doerr, *ibid.*, 1967, **89**, 4688.

especially in the case of cyclic rearrangements like Cope and Claisen[7] rearrangements, or 1,5-transfers of hydrogen atoms.[8]

Scheme 2 indicates the scope of this chemistry and emphasises its specific interest. Despite this obvious interest, the chemistry of trimethylenemethane and related compounds has been little studied until recent years, so that the available knowledge is still fragmentary, a situation which should stimulate further work.

2 Nomenclature

No name can adequately express the true structure of three methylene groups of equal resonance and the absence of a free valence at the central carbon atom. The systematic name 2-methylenetrimethylene discriminates between the three peripheral CH_2 groups, whilst trismethylenemethyl suggests some reactivity at the central carbon atom. The completely trivial name, trimethylenemethane is therefore used in this article as being without structural significance.

Compounds (2) are 2-methylene-1,3-substituted propanes, or 2,3-substituted propenes, while compounds (3) are methylene-substituted heterocyclic compounds. Yet, these systematic names do not suggest the close relationship, nor do they point out the real structural characteristics of these compounds. They are to be considered as α,α'-disubstituted isobutenes, and this term may be a generic one for this class of compounds.

3 Preparation of α,α'-Disubstituted Isobutenes

Allyl halides and allyl alcohol are the basic intermediates from which most other allyl compounds can be obtained by a proper substitution reaction. In the same way the dichloroisobutene (8) and the isobutenediol (15) are convenient intermediates for the preparation of other α,α'-disubstituted isobutenes.

The methods of preparation can therefore be divided into two groups, those involving building up the structure and those which are simple substitution reactions starting from other α,α'-disubstituted isobutenes. The latter group will be more conveniently discussed in the section on chemical properties.

The simplest method of preparing these compounds is from isobutene itself by substituting each methyl group. This can be done by chlorination, either directly,[9] or better in two steps, *via* methallyl cloride (7).[10] However, even the two-step method gives poor results, because the chlorination of methallyl chloride is unselective, giving only 20–30% of (8),[11] together with equal amounts

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[7] (*a*) F. Weiss and A. Isard, *Bull. Soc. Chim. France*, 1967, 2033; (*b*) A. Isard and F. Weiss, *ibid.*, 1967, 2038; (*c*) J. P. Schirmann, A. Isard, and F. Weiss, *Tetrahedron*, 1968, **24**, 6475.

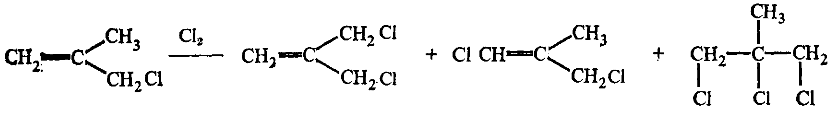
[8] (*a*) F. Weiss, A. Isard, and R. Bensa, *Bull. Soc. chim. France*, 1965, 1358; (*b*) J. M. Morgen, Thèse, Université de Strasbourg, 1966.

[9] (*a*) A. O. Rogers and R. E. Nelson, *J. Amer. Chem. Soc.*, 1936, **58**, 1029; (*b*) I. D'Yakonov and D. Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*), 1939, **9**, 1258.

[10] (*a*) J. Burgin, G. Hearne, and F. Rust, *Ind. Eng. Chem.*, 1941, **33**, 385; (*b*) L. F. Hatch, J. J. Russ, and L. B. Gordon, *J. Amer. Chem. Soc.*, 1947, **69**, 2614; (*c*) W. S. Ropp, C. W. Gould, H. M. Engelmann, and G. E. Hulse, *ibid.*, 1951, **73**, 3024; (*d*) See also ref. 6*a*, 6*c*, 6*d*, and 60.

[11] For Toxicity of (8) see V. V. Stankevitch, *Gig. Tr. Prof. Zabol.*, 1968 **12**, (1), 33-7 (*Chem. Abs.*, 1968, **68**, 8254).

of the close-boiling isomeric 1,3-dichloro-2-methylpropene (9) and of the saturated trichloro-compound (10).



(7) (8) (9) (10)

Several routes based on degradation reactions of pentaerythritol halohydrins[12] and of tri(hydroxymethyl)nitromethane[13] may be used to prepare (8) or (15), but they are often cumbersome and give low yields.

A three-step method giving good overall yields, starts from acrolein (11), which is first treated with cyclopentadiene (12)[14] to give the Diels–Alder adduct (13). The unreactive α-hydrogen atom of acrolein becomes reactive in (13), while the double bond is protected, and this permits a crossed Cannizzaro reaction with formaldehyde giving 2,2-di(hydroxymethyl)-5-norbornene (14).[15] Isobutenediol (15) (2-hydroxymethyl-2-propen-1-ol) is finally obtained by pyrolysis of (14) with recovery of the cyclopentadiene[16] (Scheme 3). Other dienes can be used instead of cyclopentadiene, for example anthracene,[16] which will give the adduct (17), or even acrolein itself.[17] The di(hydroxymethyl) adduct (17) can also be prepared by reducing the anthracene adduct of diethyl methylenemalonate (16) with lithium aluminium hydride.[6a]

The adducts (14) and (17) can be converted into a number of derivatives, such as carboxylic esters, ethers, acetals, *etc.* as a route to the corresponding isobutenediol derivatives for the pyrolysis step.[16] Applequist and Roberts[6a] have thus prepared 3-methyleneoxetan (19) by pyrolysing the oxetan (18), which was obtained from (17), instead of small ring compounds in attempts to cyclise α,α′-disubstituted isobutenes (Scheme 4).

Little indication exists as to the suitability of these methods for making homologues, which seems to be limited by the decreasing reactivities in the different steps. Thus, only moderate yields of 2-hydroxymethyl-2-buten-1-ol (20) are obtained when crotonaldehyde is used instead of acrolein.[16]

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[12] (*a*) A. Mooradian and J. B. Cloke, *J. Amer. Chem. Soc.*, 1945, **67**, 942; (*b*) R. Lukes and J. Plesek, *Chem. listy*, 1955, **49**, 1826 (*Chem. Abs.* 1956, **50**, 9288); (*c*) C. Issidorides and A. I. Matar, *J. Amer. Chem. Soc.*, 1955, **77**, 6382; (*d*) A. S. Matlack and D. S. Breslow, *J. Org. Chem.*., 1957, **22**, 1723; (*e*) F. Nerdel, *Ber.*, 1958, **91**, 938; (*f*) K. Watanabe, T. Sugihara, and M. Tanaka, *Yuki Gosei Kagaku Kyokai Shi*, 1966, **24**, 651 (*Chem. Abstr.*, 1965, **65**, 20082); K. Watanabe and T. Sugihara, *Makromol. Chem.*, 1966, **99**, 141.

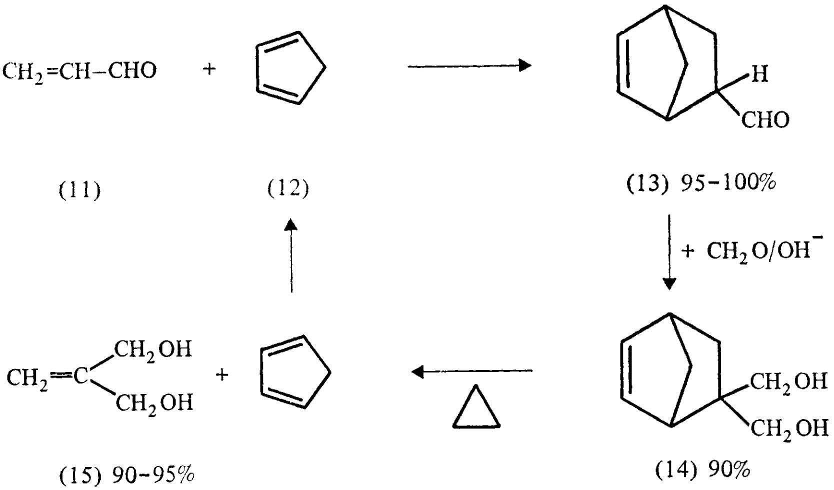
[13] H. Kleinfeller, *Ber.*, 1929, **62** B, 1582, 1590.

[14] O. Diels and K. Alder, *Annalen*, 1928, **460**, 98.

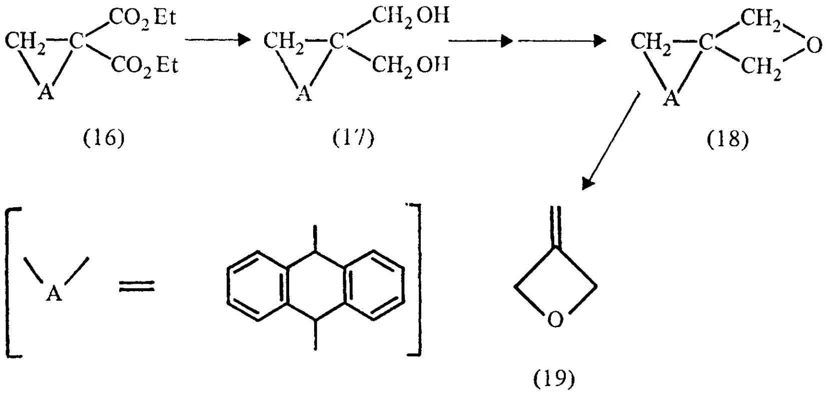
[15] H. A. Bruson, W. D. Niederhauser, and H. Iserson, U.S. P. 2,417,100/1947 (*Chem. Abs.* 1947, **41**, 3819).

[16] F. Weiss, A. Isard, and R. Bensa, *Bull. Soc. chim. France*, 1965, 1355; Ugine Kuhlmann, F. P. 1,350,723/1962 and 1,387,099/1963.

[17] C. W. Smith, 'Acrolein', J. Wiley, New York, 1962, p. 198.



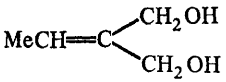
Scheme 3



Scheme 4

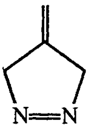
Another precursor of (1), 4-methylene-1-pyrazoline (21), can be prepared by the reaction of diazomethane with allene, at room temperature.[2a,3i,18] This product is highly sensitive to water, heat, light, and oxygen, and is best handled *in vacuo*.[2a] Similarly, 3-substituted 4-methylene-1-pyrazolines (22) can be obtained from substituted diazomethanes and allene.[3m]

[18] I. D'Yakonov, *J. Gen. Chem.* (*U.S.S.R.*), 1945, **15**, 473.



$MeCH{=}C(CH_2OH)_2$

(20)



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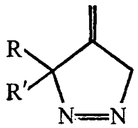
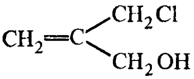


(22)

4 Substitution and Addition Reactions

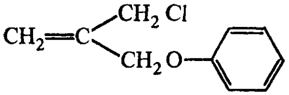
Practically no kinetic or mechanistic studies of the reactions of α,α′-disubstituted isobutenes have been published so far. Broadly speaking, substitution and addition reactions will be normal for allylic compounds of this kind and will give, in the case of substitution, the new disubstituted product. It appears also possible to limit some reactions to monosubstitution and thus to obtain mixed disubstituted isobutenes.

For example 2-chloromethyl-2-propen-1-ol (23) can be prepared in fairly good yield from gaseous hydrogen chloride with (15) in dioxan,[19a] and (2-chloromethyl)allyl phenyl ether (24) is obtained from stoicheiometric amounts of (8), phenol, and sodium hydroxide.[19b]



$CH_2{=}C(CH_2Cl)(CH_2OH)$

(23)



(24)

Various intramolecular eliminations which should give small 3- or 4-membered ring compounds are difficult, or even impossible. The problem of the synthesis of 3-methyleneoxetan (19) has been mentioned, and that of methylenecyclopropane will be considered later. There is a strong difference with saturated 1,3-disubstituted compounds which readily undergo such cyclisation reactions. How the double bond of α,α′-disubstituted isobutenes obstructs the cyclisation step is a problem which remains to be studied: the large bond angle of 120° on the central carbon atom,[6a] as well as resonance structures of the intermediates certainly are important factors.

Substitution reactions which have been described include halogen exchange,[6d,20] hydrolysis,[12a] and etherification[16] reactions of dichloroisobutene (8), and esterification,[12c,16] or polyesterification,[21] of isobutenediol (15). Hydrogen cyanide reacts with (8)[22] or (15)[19a] to give 3-methyleneglutaronitrile (25). Dichloroisobutene's reactions with metals and organometallic compounds will be considered in detail in section 5. Two alkylation reactions should be mentioned: the reaction of (8) with cyclopentadienylsodium gives the biscyclo-

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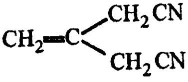
[19] (*a*) A. Isard and F. Weiss, unpublished results; (*b*) F. Pt. 1,503,900/1966.

[20] N. V. de Bataasche Petr. Maat., B. P. 672,757/1952.

[21] (*a*) T. W. Evans, U.S. P. 2,435,429/1948; (*b*) W. Gumlich and G. Schaefer (Hüls) G. P. 1,012,457/1957; (*c*) K. W. Doak and H. N. Campbell, *J. Polymer Sci.*, 1955, **18**, 215.

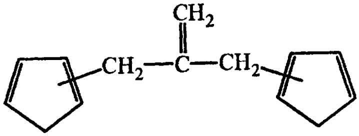
[22] (*a*) R. C. Schreyer, U.S. P. 2,609,385/1952; (*b*) P. Kurtz and O. Bayer, G. P. 925,774/1955.

pentadienylisobutene (26), which is in thermal equilibrium with one or more intramolecular Diels–Alder adducts.[23] In a similar manner (8) reacts with π-allylnickel complexes [e.g. (27)] to give products like (28).[24]



$CH_2{=}C(CH_2CN)_2$

(25)



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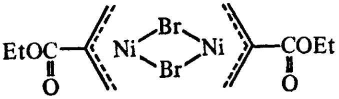

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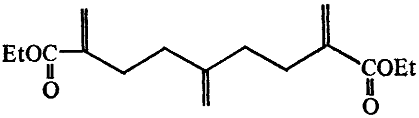
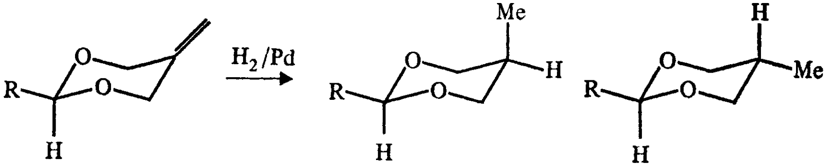


(28)

Hydrogenation of (8)[13] and (15)[25] proceed normally, but catalytic hydrogenaation of 5-methylene-1,3-dioxans (29) over palladium has been reported to be stereoselective, giving the less stable *cis*-isomer rather than the *trans*-isomer of the saturated dioxan (30) (Scheme 5).[26] A co-ordination of the oxygen atoms to the catalyst probably causes this selectivity.



cis (93–95%) *trans* (5–7%)

(29) (30)

R = Me, Bu^t, Ph

Scheme 5

Chlorine and bromine add on to the double bond of (8)[13] or (15)[19a] but with a marked steric hindrance effect. Thus, the following relative rates of halogena-

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[23] A. Lakodey and F. Weiss, unpublished results.

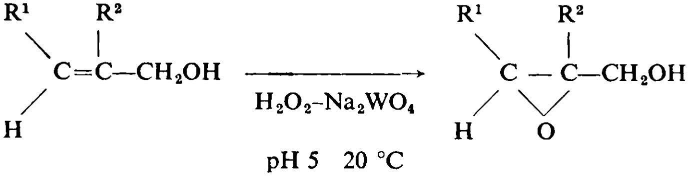
[24] E J. Corey and M. F. Semmelhack, *Tetrahedron Letters*, 1966, 6237.

[25] F. Weiss and A. Lantz, F. P. 1,398,960/1964.

[26] J. E. Anderson, F. G. Riddell, J. P. Fleury, and J. M. Morgen, *Chem. Comm.*, 1966, 128.

tion have been determined:[27] ethylene 1, allyl chloride 0·45, (8) 0·0055. In reverse, epoxidation is faster than for unsubstituted allyl compounds. Dichloroisobutene (8) is easily epoxidised by carboxylic peracids (*e.g.* *p*-nitroperbenzoic acid[19a] and performic acid[28]), to 2-chloromethylepichlorhydrin (31), while 2-(hydroxymethyl)glycidol (34) is obtained in 90% yield by epoxidation, in solution, of (15) with aqueous hydrogen peroxide and sodium tungstate.[29] The value of the rate constant for epoxidation of (15) is close to the published values for crotyl and methallyl alcohols,[30] showing a similar activating effect of hydroxymethyl and methyl groups (Table 1).

Table 1



R^1	R^2	k_1 (min^{-1}) × 10^4	Ref.
H	H	3·2	30
Me	H	71	30
H	Me	45	30
H	CH_2OH	58	29

Chloromethylepichlorhydrin (31), which can be also obtained by the reaction of diazomethane with 1,3-dichloro-2-propanone,[31] reacts with potassium cyanide to give 3-cyanomethyl-3-hydroxy-glutaronitrile (33),[31] and can be polymerised to a high molecular weight crystalline polyether (32) with triethylaluminium catalysts.[32] Hydrolysis of (34) and direct hydroxylation of (15) with hydrogen peroxide and tungstic(VI) acid[33] easily yield isoerythritol (35), which is formed also, but impure, in the hydrolysis of by-products from the chlorination of methallyl chloride.[34]

The Prins reaction with formaldehyde in acid works well with (8) and gives 4,4-di(chloromethyl)-1,3-dioxan (36),[35] whereas with (15), which is of poor

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[27] B. E. Swedlung and P. W. Robertson, *J. Chem. Soc.*, 1947, 630.

[28] A. Isard and F. Weiss, F. P. 1,464,139/1965.

[29] A. Lakodey, A. Isard, and F. Weiss, unpublished results.

[30] (*a*) Z. Raciszewski, *J. Amer. Chem. Soc.*, 1960, **82**, 1267; (*b*) H. C. Stevens and A. J. Kaman, *ibid.*, 1965, **87**, 734.

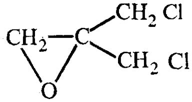
[31] F. Johnson, J. P. Panella, and A. A. Carlson, *J. Org. Chem.*, 1962, **27**, 2241.

[32] S. Kambarra and A. Takahashi, *Makromol. Chem.*, 1962, **58**, 226.

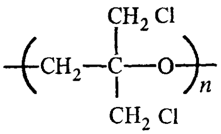
[33] F. Weiss and A. Isard, *Bull. Soc. Chim. France*, 1965, 1364.

[34] G. Hearne and H. W. de Jong, *Ind. Eng. Chem.*, 1941, **33**, 940.

[35] E. Steininger, U.S. P. 3,176,026/1962; *Chem. Abs.* 1965, **63**, 1775.

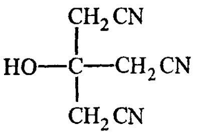


(31)



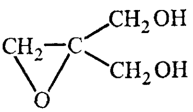
$$-\!\left(CH_2-\underset{CH_2Cl}{\overset{CH_2Cl}{C}}-O\right)_n-$$

(32)

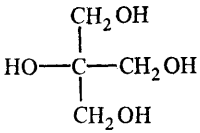


$$HO-\underset{CH_2CN}{\overset{CH_2CN}{C}}-CH_2CN$$

(33)



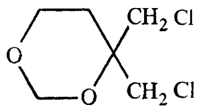
(34)



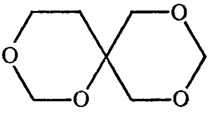
$$HO-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2OH$$

(35)

stability in strong acid, complex mixtures are obtained, in which the spirobisdioxan (37) has been identified.[19a]

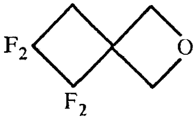


(36)

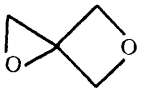


(37)

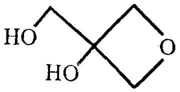
3-Methyleneoxetan (19) has a planar structure, according to the infrared and Raman spectra.[36] Berezin[37] studied its chemical properties, particularly the thermal cycloaddition of tetrafluoroethylene, giving the fluorinated oxetan (38), the epoxidation with carboxylic peracids to the epoxyoxetan (39), and the hydroxylation with hydrogen peroxide to the diol (40), which was oxidised with periodic acid to the very reactive 3-oxetanone (41).



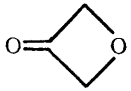
(38)



(39)



(40)



(41)

Almost nothing is known about free-radical reactions in this field. Polymerisation certainly is difficult, as it is for most allylic compounds. Benzoylperoxide-induced reaction of the dichloroisobutene (8) mainly gives a dimer, in 33% yield, and trimers, in 43% yield; this is probably due to steric hindrance and

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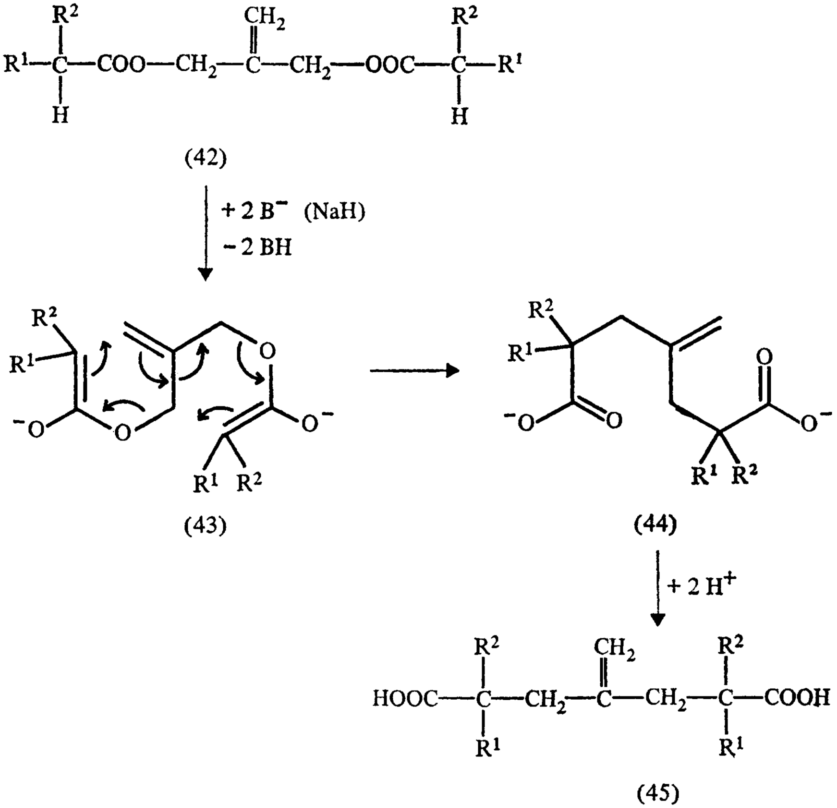
[36] J. R. Durig and A. C. Morrissey, *J. Chem. Phys.*, 1966, **45**, 1269.

[37] G. H. Berezin, S 161, *152nd ACS Meeting, Sept. 1966*, Abstracts of Papers; U.S. P. 3,297,719/1967.

to chain-transfer.[10c] Extremely low yields are found, on the other hand, in the free-radical additions of carbon tetrachloride to isobutenediol (15),[38] and of butyraldehyde to the diacetate of (15).[39] Nevertheless polyesters of (15) are said to be crosslinked by copolymerisation with styrene.[21b]

5 Allylic Rearrangements

A. Claisen-type Double Rearrangements.—While these reactions can occur step-wise by two successive normal rearrangements, there is an intriguing



$R^1 = R^2 = Me$: 38% yield
$= Ph$: 68% ”
$R^1 + R^2 = CH_2{-}CH{=}CH{-}CH_2CH_2$: 50% ”

Scheme 6

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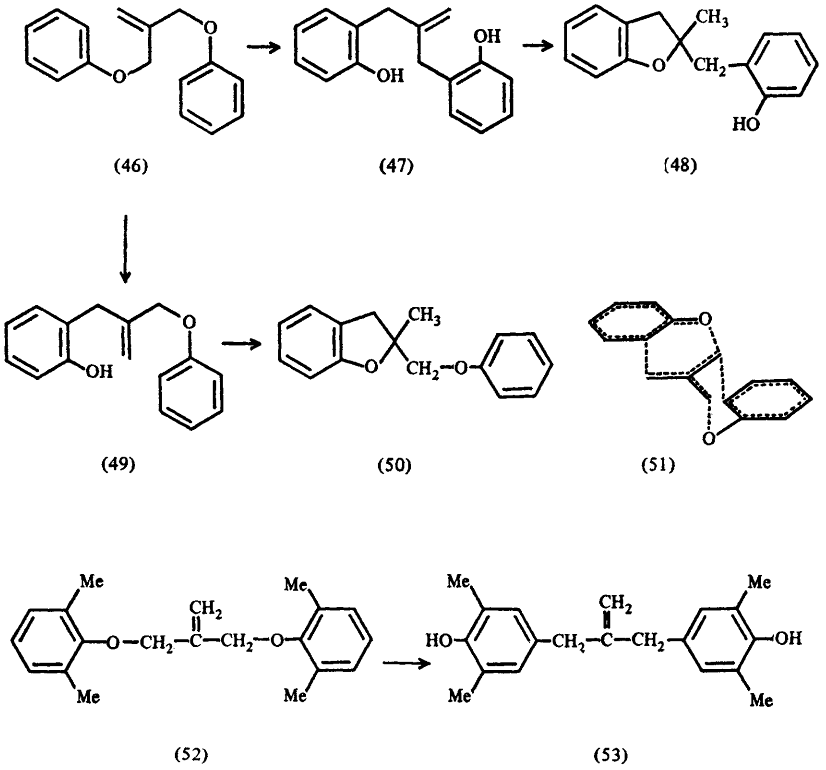
[38] A. Lantz and F. Weiss, unpublished results.
[39] B. P. 635,934/1950; *Chem. Abs.* 1950, **44**, 7867.

possibility that compounds of structure (2) might undergo a direct double rearrangement through the single bicyclic transition state suggested in Scheme 2, which is related to the 'trimethylenemethane' structure of the skeleton. Mechanistic studies should be done to elucidate this interesting point. The ease with which the reactions already investigated proceed, and some qualitative arguments, suggest that such a one-step process may occur, at least in part.

The known rearrangement of allyl carboxylic esters to γ-ethylenic acids by reaction with sodium metal,[40] or sodium hydride,[41] has been successfully extended to the rearrangement of isobutenediol carboxylates (42) to γ-methylenepimelic acids (45).[7b] Reaction of the esters (42) with sodium hydride presumably gives the bis-sodium enolates (43) which rearrange to the sodium pimelates (44). Acidification of the reaction mixture then liberates the free acids (Scheme 6).



Scheme 7

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[40] R. T. Arnolds and S. Searles, *J. Amer. Chem. Soc.*, 1949, **71**, 1151.

[41] (*a*) K. C. Brannock, H. S. Pridgen, and B. Thompson, *J. Org. Chem.*, 1960, **25**, 1815; (*b*) S. Julia, M. Julia, and C. Linstrumelle, *Bull. Soc. Chim. France*, 1966, 3499.

Thermal rearrangement of α,α′-bisaryloxyisobutenes[7a] is an application of the well known Claisen rearrangement of allyl phenyl ethers.[42] By heating α,α′-diphenoxyisobutene (46) at 200 °C in N,N-dimethylaniline, α,α′-bis-*o*-hydroxyphenylisobutene (47) is obtained in 66% yield. In the absence of a basic solvent an 80% yield of coumaran (48) is obtained, by a cyclisation of (47) during the treatment. This clean and rapid cyclisation, which compares with those often observed during allyl phenyl ether rearrangements,[42a,43] could also occur with a monorearrangement product (49) to give a coumaran (50) and thus prevent the rearrangement of the second phenyl ether group (Scheme 7). As no appreciable amounts of monorearrangement products are formed, one can infer that both steps are closely related and may very well merge into one another with a *quasi*-chair–chair bicyclic transition state (51) which appears to favour easy migration, according to recent stereochemical studies of the Claisen rearrangement.[42b,44]

Double *para*-rearrangement occurs as expected when the *ortho*-positions are substituted. Thus the bis-(2,6-dimethylphenoxy)isobutene (52) gives the *para-para′*bisphenol (53) in 73% yield.[7a,45]

In 3-methylene-1,5-benzodioxepan (54) the allylic double bond is blocked by the seven-membered ring at a distance from the aromatic ring which makes unlikely a concerted bond breaking and formation process. Nevertheless the rearrangement proceeds smoothly at 200 °C to give the cyclohexadienone derivative (56), which suggests a step-wise Claisen rearrangement *via* a diradical (55).[7c,46] The intermediate (56) has not been isolated; it reacts during the treatment with starting compound (54) to give an adduct (57), or with other dienophiles if the reaction is effected in their presence [*e.g.* with acrylonitrile, giving (58), or maleic anhydride, giving (59) (Scheme 8)].

When the product (54) is heated at 450 °C in the vapour phase, 2-(4′-methyl-2′-furyl)-2-cyclopenten-1-one (63) and 3*a*,4,7,7*a*-tetrahydro-5-methyl-1,7-indenedione (64) are formed, in 39 and 10% yields, respectively.[7c] This result has been interpreted in terms of a secondary free-radical rearrangement of the cyclohexadienone (56) (Scheme 8). The diradical (60) resulting from ring opening cyclises to give the diradical (61) which can proceed to structure (63) by mere hydrogen shifts, and to structure (64) by cyclisation and hydrogen shift. Thus the mechanism of this reaction would be closely related with that of thermal and

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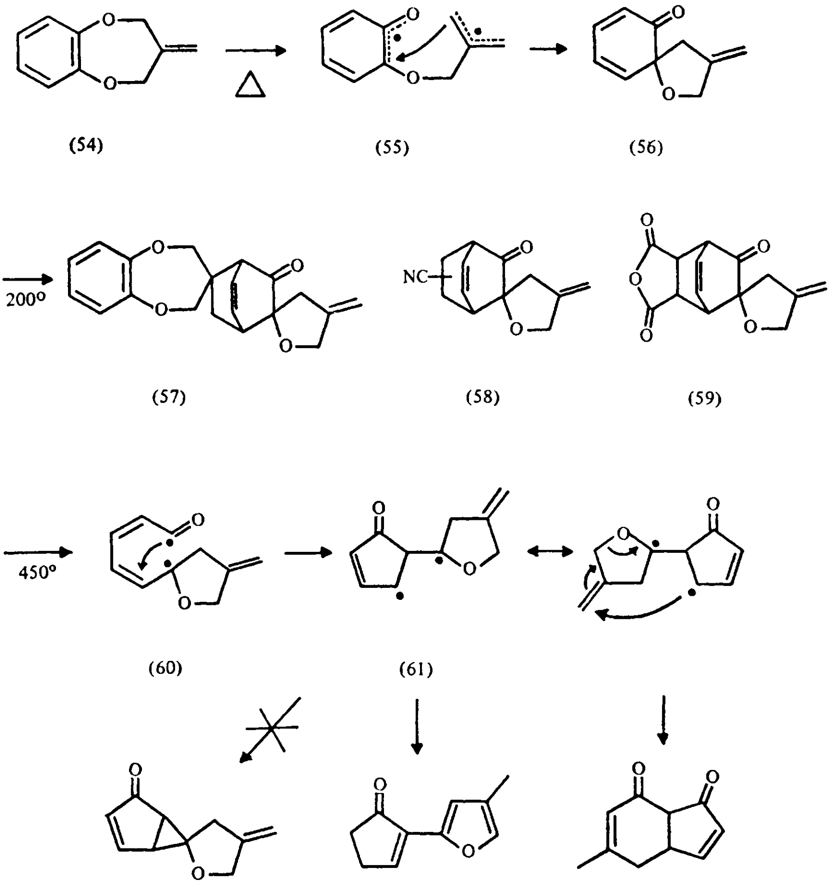
[42] (*a*) D. S. Tarbell, 'The Claisen Rearrangement in Organic Reactions', ed. R. Adams, J. Wiley, New York, 1944, vol. II, p. 1; (*b*) S. J. Rhoads, 'Rearrangements Proceeding through "No Mechanism Pathways",' in 'Molecular Rearrangements', ed. P. de Mayo, Interscience, New York, 1963, vol. I, p. 655.

[43] C. D. Hurd and W. A. Hoffmann, *J. Org. Chem.*, 1940, **5**, 212.

[44] B. Capon, M. J. Perkins, and C. W. Rees, 'Organic Reactions Mechanisms (1965),' Interscience, London, 1966, p. 173.

[45] For a similar double *para* rearrangement of bis-1,4-(2,6-dimethylphenyl)-2-butene, the linear isomer of (52), see: B. S. Thyagarajan, K. K. Balasubramanian, and R. Bhima Rao, *Chem. and Ind.*, 1967, 401.

[46] For an interesting case of a retro-Claisen rearrangement in a similar system, see: (*a*) M. F. Ansell and V. J. Leslie, *Chem. Comm.*, 1967, 949; (*b*) A. Jefferson and F. Scheinmann, *Quart. Rev.*, 1968, **22**, 409.



Scheme 8

photochemical isomerisations of *o*-cyclohexadienones to bicyclo[3,1,0] hexenones.[47] A bicyclo[3,1,0]hexenone (62) has, however, not been found; its formation at high temperatures is unlikely, but it may be an intermediate in the reaction to (63). Ring opening of (56) to a keten which would be a resonance structure of (60) could also be considered, although such a keten has not been detected during pyrolysis in the presence of methanol.[7c]

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[47] (*a*) A. J. Waring, in 'Advances in Alicyclic Chemistry', ed. H. Hart and G. J. Karabatsos, Academic Press, New York, 1966, vol. I, p. 241; (*b*) J. Griffith and H. Hart, *J. Amer. Chem. Soc.*, 1968, **90**, 3297.

B. Rearrangements involving Hydrogen Transfer.—Double 1,5-hydrogen transfers of the type indicated in Scheme 2 have not so far been reported; probably they should occur, for instance in the thermolysis of dialkyl ethers of (15) (compare, the thermolysis of simple alkyl allyl ethers.[48]

Several types of hydrogen transfer occur during the thermolysis, at 400—600 °C, of 5-methylene-1,3-dioxans (29) and (67), depending on the substituents present.[8] High yields of isomeric methallyl esters (65) are obtained from the acetals [29; R = hydrogen, or an aliphatic or an aromatic group (Table 2)]. Since the conversion of various acetals into esters is known to be a free-radical reaction, induced by peroxides,[49] u.v.-light,[50] or heat,[51] a free-radical mechanism such as (A) can be considered as operating here too (Scheme 9). However, since saturated 1,3-dioxans are very heat-stable in these conditions,[8b] or undergo other types of rearrangement,[52] the effect of the double bond has to be taken in account. Steric hindrance should prevent a normal hydrogen transfer through a six-membered transition state, unless it can be assumed that the intramolecular process (B) begins with the homolytic cleavage of an allylic bond in the ring, giving a diradical (66a). A kinetic study, now in progress, should elucidate this point.[53]

Table 2 *Thermolysis of* 5-*methylene*-1,3-*dioxans at* 450—550 °C

	R	*R'*	*% Dioxan reacted*	*Ester* (65) *% yield**	*Dialdehyde* (72) *% yield**
(29a)	H	—	26	62	—
(29b)	Me	—	11	85	—
(29c)	Et	—	40	80	—
(29d)	t-C_4H_9	—	92	70	—
(29e)	Ph	—	59	79	—
(29f)	$CH_2{=}CH$—	H	74	26	46
(29g)	$CH{=}C(CH_3)$—	Me	48	38	22
(67a)	Me	—	22	—	—
(67b)	†	—	0	—	—

* % of the theoretical yield, based on consumed dioxan
† R + R' = $[CH_2]_5 <$ (ketal of cyclohexanone)

The diradical (66) can split to the parent carbonyl compound and a diradical (68) which rearranges to methacrolein (69). In fact, methacrolein and the parent carbonyl compound are normally by-products of these thermolyses, and are the

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[48] (*a*) R. A. Malzahn, *Diss. Abs.*, 1963, **23**, 2698; (*b*) R. C. Cookson and S. R. Wallis, *J. Chem. Soc.* (*B*), 1966, 1245.

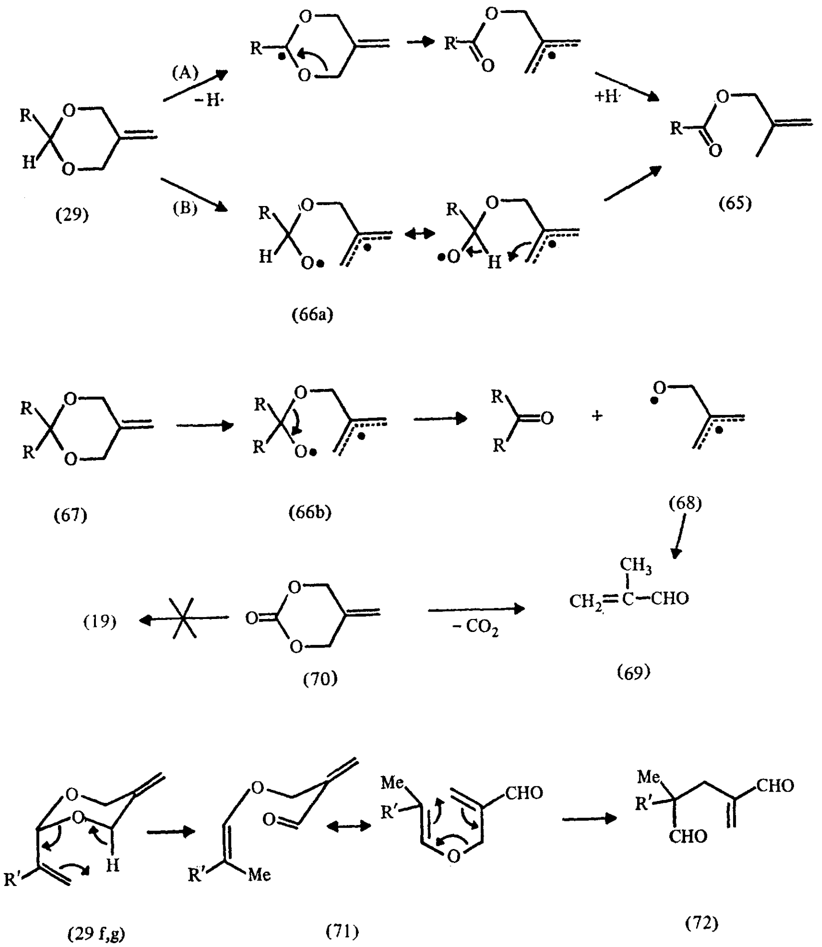
[49] (*a*) L. P. Kuhn and C. Wellman, *J. Org. Chem.*, 1957, **22**, 774; (*b*) E. S. Huyser and D. T. Wang, *ibid.*, 1964, **29**, 2720; (*c*) E. S. Huyser and Z. Garcia, *ibid.*, 1962, **27**, 2716.

[50] D. Elad and R. D. Youssefyeh, *Tetrahedron Letters*, 1963, 2189.

[51] (*a*) J. H. Davies and P. Kirby, *Chem. and Ind.*, 1964, 194; (*b*) H. Chafetz, U.S. P. 3,079,429/1961; *Chem. Abs.*, 1963, **59**, 2654.

[52] C. S. Rondestvedt and G. J. Mantell, *J. Amer. Chem. Soc.*, 1962, **84**, 3307, 3320.

[53] F. Mutterer, Thesis, Strasbourg, 1969; F. Mutterer, P. Baumgrrten, and J. P. Fleury, *Bull. Soc. Chim. France*, in the press.



Scheme 9

sole, if any, products from thermolysis of the ketals (67), which cannot give esters and are rather resistant to thermolysis. This behaviour compares with that of 5-methylene-1,3-dioxan-2-one (70), which at 200 °C over potassium carbonate gives methacrolein (69) instead of the expected 3-methyleneoxetan (19).[54]

When R in the dioxan (29) is a vinylic group a third rearrangement appears, concurrent with the former two, which leads to 4-methyl-2-methyleneglutaraldehydes (72). This reaction is easily interpreted as the result of a concerted

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[54] P. E. Throckmorton and S. Searles, S 102, *152nd ACS Meeting, Sept. 1966*, Abstracts of Papers.

transfer of a hydrogen on C-4 to the vinylic double bond and a subsequent Claisen rearrangement of the intermediate allyl vinyl ether (71) (Scheme 9).[8,55]

6 Trimethylenemethane

A. Structure.—Trimethylenemethane is important in theoretical chemistry because its central carbon atom has the maximum bond order, $N=1{\cdot}732$, and the minimum free valence index, $F=0$, possible for an sp^2 carbon atom; [1b,1d,1e] these values are the basis of the calculations of free-valence indexes of carbon compounds. This molecule has been used as a model in calculations of negative spin densities in triplet states,[1h,1i] in comparison of different methods for calculating the energy of π systems,[1j] and for estimation of the energy involved in the ring opening of cyclopropanone.[1k,56] Molecular-orbital calculations[1f,1g] predict that trimethylenemethane will have a triplet ground state (Figure 1) with a strong delocalisation energy of 1·46 β relative to the classical structure of one double bond and two localised electrons (1). The complete configuration interaction treatment of (1) also predicts a triplet ground state.[1j]

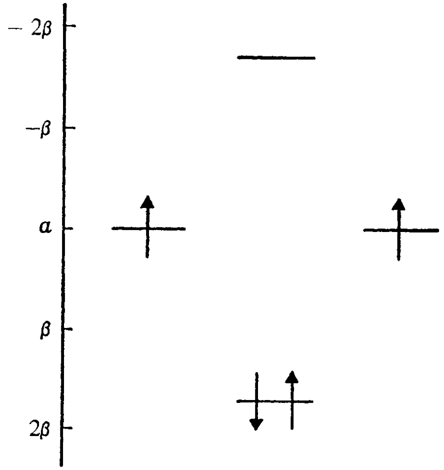

Figure 1 *HMO π energy levels of trimethylenemethane*

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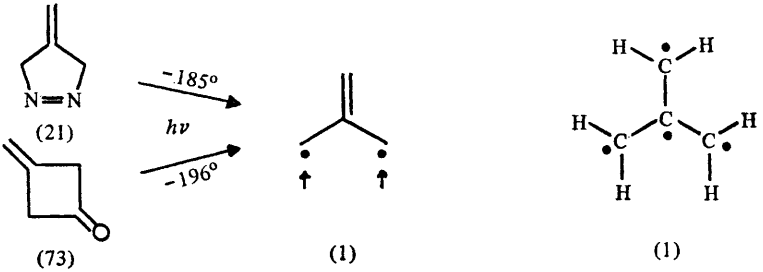
[55] F. Mutterer, J. P. Fleury and F. Weiss, *Tetrahedron Letters*, 1968, 4225.

[56] For a recent review on cyclopropanones see: N. J. Turro, *Accounts Chem. Res.*, 1969, 2, 25.

Recently, Dowd and his co-workers prepared trimethylenemethane by matrix photolysis of 4-methylene-1-pyrazoline (21) at − 185 °C[2a] and of 3-methylenecyclobutanone (73) at − 196 °C[2b] (Scheme 10). The e.s.r. spectrum then confirmed that trimethylenemethane has a triplet ground state. The proton hyperfine splitting of the e.s.r. spectrum observed with an irradiated crystal of 3-methylenecyclobutanone (73)[2c] is maximum when the magnetic field is perpendicular to the molecular plane. In this orientation all of the hydrogens are equivalent with respect to the magnetic field, and each of the two major lines is split into seven, and only seven, hyperfine lines, the intensities of which are close to the expected binomial coefficient ratios for an electron interacting whith six equivalent protons. The splitting between the peaks is 8·9 G, which agrees with the value calculated on the basis of valence-bond theory.[1h]



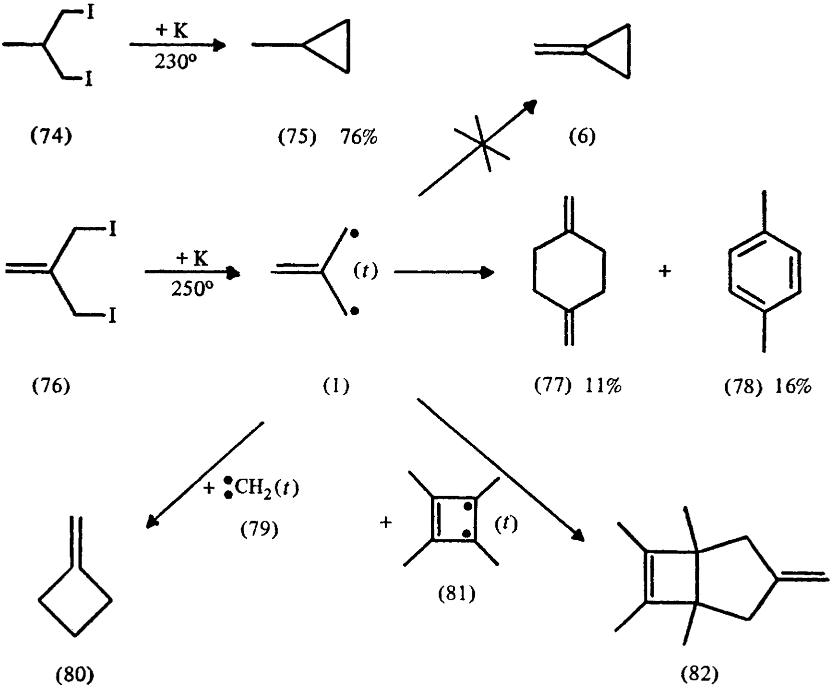
Scheme 10

The e.s.r. spectrum is stable for a month after termination of the irradiation,[2a] provided that the temperature of the sample is maintained at the boiling point of nitrogen; this indicates a remarkable stability for a simple aliphatic diradical. The peaks of the triplet disappear immediately, and irreversibly, if the temperature is raised to − 150 °C.

B. Trimethylenemethane as a Radical Intermediate.—The problem is to understand the behaviour of this diradical, and to deduce its structure from the course of the reactions in which it is thought to be an intermediate.

Skell and Doerr,[6d] studying the production of trimethylenemethane by the reaction of potassium vapour with 3-iodo-2-iodomethylpropene (76), obtained 1,4-dimethylenecyclohexane (77), and *p*-xylene (78) as a secondary product from (77), virtually no methylenecyclopropane (6) being formed. In contrast, a 76·7% yield of methylcyclopropane (75), but no coupling products, was obtained from reaction of the corresponding saturated di-iodide (74) under the same conditions (Scheme 11).

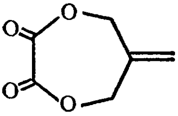
This suggests the intermediacy of triplet trimethylenemethane, and its unusual behaviour compared with that of other 1,3-radicals has been explained by the large delocalisation energy which makes it the favoured state, but renders its cyclisation to triplet methylenecyclopropane endothermic by *ca.* 25—50 kcal/mole whilst its cyclisation to singlet methylenecyclopropane (*ca.* 20 kcal/mole exothermic) is strongly spin-forbidden.[6d] Thus, since no favourable unimolecular path is available, trimethylenemethane (1) accumulates until its concentration becomes high enough for bimolecular coupling to give 1,4-dimethylenecyclohexane (77). Coupling with other triplet species provides further evidence for the triplet state for (1): the reaction of potassium vapour with a mixture of 3-iodo-2-iodomethylpropene (76) and di-iodomethane gives some methylenecyclobutane (80) by addition of trimethylenemethane (1) to triplet methylene (79), and with a mixture of (76) and di-iodotetramethylcyclobutene an adduct (82) of trimethylenemethane (1) and the triplet cyclobutadiene (81) is obtained (Scheme 11).[6d]

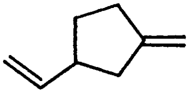


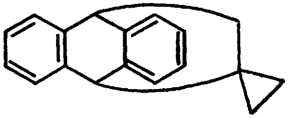
Scheme 11

1,4-Dimethylenecyclohexane (77), but not methylenecyclopropane (6), was also obtained in the high-temperature pyrolysis of the oxalate (83),[57] suggesting the same triplet (1) intermediate. Lastly, trimethylenemethane, formed by photolysis of 3-methylenecyclobutanone (73), has also been shown to give the dimethylenecyclohexane (77), and further undergoes a photochemical 1,2-cycloaddition to butadiene, giving the 1-methylene-3-vinylcyclopentane (84).[58] However, cycloaddition to ethylene was not observed under thermolysis conditions,[6d] which is consistent with the triplet structure of (1) (see, for example the study by Day and Powell, Scheme 15).

In contrast to these facts, trimethylenemethane species have been considered as intermediates both in formation and in rearrangements of cyclopropanes.[3]


(83)


(84)


(85)

Obviously it will not then have the same structure. The outstanding contrast is given by the results of decomposition of 4-methylene-1-pyrazoline (21) which, while giving the triplet trimethylenemethane by photolysis,[2a] quantitatively gives methylenecyclopropane (6) by thermolysis.[3i]

Deuterium labelling showed in this case that the original methylene group in the pyrazoline was at least partially equilibrated with the methylene groups in the cyclopropane ring. A similar equilibration was observed in the formation of alkylidenecyclopropanes from the photolysis and pyrolysis of 4-alkylidene-1-pyrazolines,[3f,3g,3j,3m] and in the rearrangement of substituted alkylidenecyclopropanes.[3a,3b,3d,3h]

Borden[59] rationalised these results by discussing the correlation diagrams of the photolytic and thermal decompositions of 4-methylene-1-pyrazoline (21). In the photolysis, the allowed $n \rightarrow \pi^*(N{=}N)$ transition gives rise to a state which is correlated with the lowest antisymmetric state of trimethylenemethane in a conrotatory mode and with a symmetric state in a disrotatory reaction. Intersystem crossing then leads to the ground state triplet of trimethylenemethane. These trimethylenemethane species are themselves correlated with excited states of methylenecyclopropane of higher energies, so that ring closure cannot occur. The thermally produced singlet trimethylenemethane, by decomposition of

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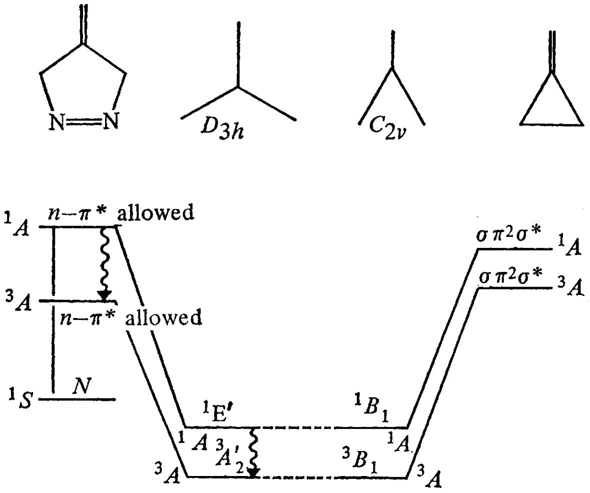
[57] J. P. Schirmann and F. Weiss, *Tetrahedron Letters*, 1967, 5164.

[58] P. Dowd, G. Sengupta, and K. Sachdev, ORGN 147, *156th ACS Meeting, Sept. 1968*, Abstracts of Papers.

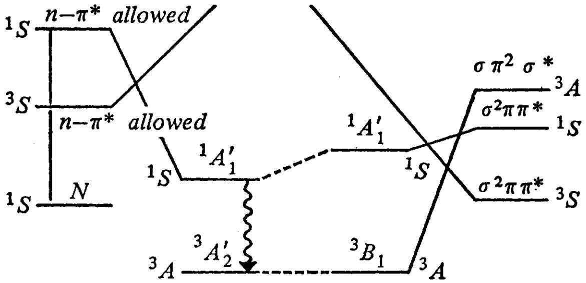
[59] W. T. Borden, *Tetrahedron Letters*, 1967, 259.

S symmetric to C_2
A antisymm 〃 〃



Controtatory photolysis

S symmetric through plane
A antisymm 〃 〃



Disrotatory photolysis

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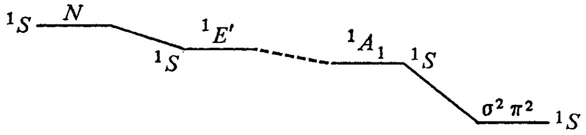
Jahn-Teller distortion



Con- and Dis- rotatory thermolysis

Figure 2 *Partial Correlation Diagrams* ground-state pyrazoline, might undergo intersystem crossing to the ground-state triplet too, but this competes with the ring closure to the ground-state methylenecyclopropane, which is possible in either a conrotatory or disrotatory fashion. Moreover the Jahn–Teller distortion of the $^1E'$ state from D_{3h} to C_{2v} symmetry can move two of the carbon atoms together and orient the molecule favourably to a quick disrotatory closure to methylenecyclopropane (Figure 2).

C. Non-radical Trimethylenemethane Intermediates.—The synthesis of methylenecyclopropane (6) has long been an elusive problem, because of the difficulties of cyclisation to small rings, already mentioned. Thus, the classical halogen elimination from 1,3-dihalogeno-compounds with zinc, which gives a 91% yield of methylcyclopropane (75) with 1,3-dihalogeno-2-methylpropane, failed to give any methylenecyclopropane with dichloroisobutene (8)[6b,6c] (see also results of Skell). On the other hand, the method involving the preparation and retrodienic cracking of Diels–Alder intermediates also failed with the anthracene adduct (85) of methylenecyclopropane, which appeared to be thermally stable.[6a] The first successful synthesis of methylenecyclopropane (6) was realised by Gragson *et al.*[6c] who obtained a 17% yield by the reaction of dichloroisobutene (8) with magnesium. This low yield was later improved to *ca.* 30% by Anderson,[60a] by using tetrahydrofuran as solvent (see also ref. 60*b*).

Recent re-examination[61] of the reaction has confirmed that 1,4-dimethylenecyclohexane (77) is in fact the main product. The yield may rise as high as 60% but has poor reproductibility, apparently because of the great versatility of the reaction. Interestingly, a full range of macrocyclic 'oligomers of trimethylenemethane' were found also, *e.g.* 1,4,7-trimethylenecyclononane (86) 1,4,7,10-tetramethylenecyclododecane (87), 1,4,7,10,13-pentamethylenecyclopentadecane (88), and 1,4,7,10,13,16-hexamethylenecyclooctadecane (89). Each of these cyclic compounds is accompanied by a small amount of the open-chained analogue, *e.g.* (90)—(94). Yields from a typical experiment are shown in Scheme 12.

This reaction thus appears to be both an intramolecular and an intermolecular cyclisation by a Würtz procedure, and macrocyclisation may be favoured by the 'rigid' structure of the dihalide (8). This compares with the similar behaviour of α,α′-dihalogenoxylenes in coupling reactions with sodium.[62] The mechanism possibly is a step-wise formation of successive Grignard intermediates, having a pseudocyclic structure by intramolecular co-ordination of the magnesium atom with the second chlorine atom.

This process would consist in an intermolecular elimination of magnesium chloride, which results in an insertion of a trimethylenemethane unit to give the

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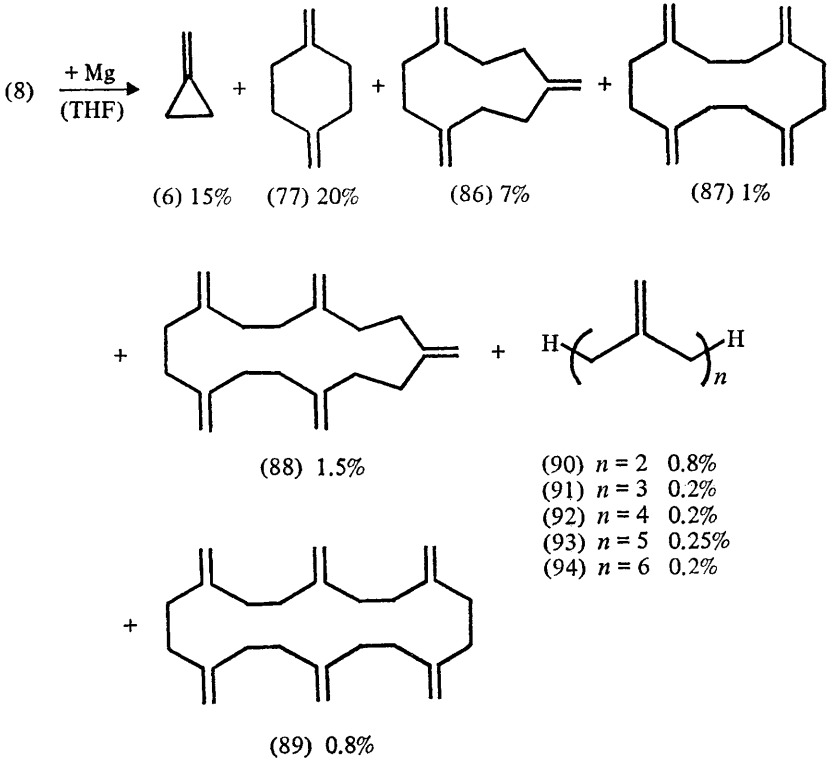
[60] (*a*) B. C. Anderson, *J. Org. Chem.*, 1962, **27**, 2720; (*b*) Methylenecyclopropane can be prepared also in 60% yield from diazomethane and allene; see: A. T. Bloomquist and D. J. Connolly, *Chem. and Ind.*, 1962, 310.

[61] A. Lakodey, G. Bonnard, and F. Weiss, to be published.

[62] K. Ziegler, in Houben Weyl, 'Methoden der Organischen Chemie', G. Thieme, Stuttgart, 1955, vol. IV, part 2, p. 733.



Scheme 12

next higher intermediate Grignard structure (95) → (96) → (97) → (98), *etc.*[63] (Scheme 13). Two competing reaction pathways can then take place with each intermediate, an intramolecular elimination giving the corresponding cyclic hydrocarbon, or reaction with magnesium to give the cyclic magnesium compound, *e.g.* (99), which is postulated to form the open-chain hydrocarbons in the subsequent hydrolysis of the mixture.

An analogous cyclisation, by a mechanism not discussed, has been discovered by Corey and Semmelhack[24] in the reaction of dichloroisobutene (8) with nickel carbonyl, which affords a 54% yield of the trimethylenecyclononane (86), together with 11% of (77) and 5% of 3,6-dimethylenecycloheptanone (100). No higher 'oligomers' are mentioned.

A good preparative method for methylenecyclopropane (6) may finally have

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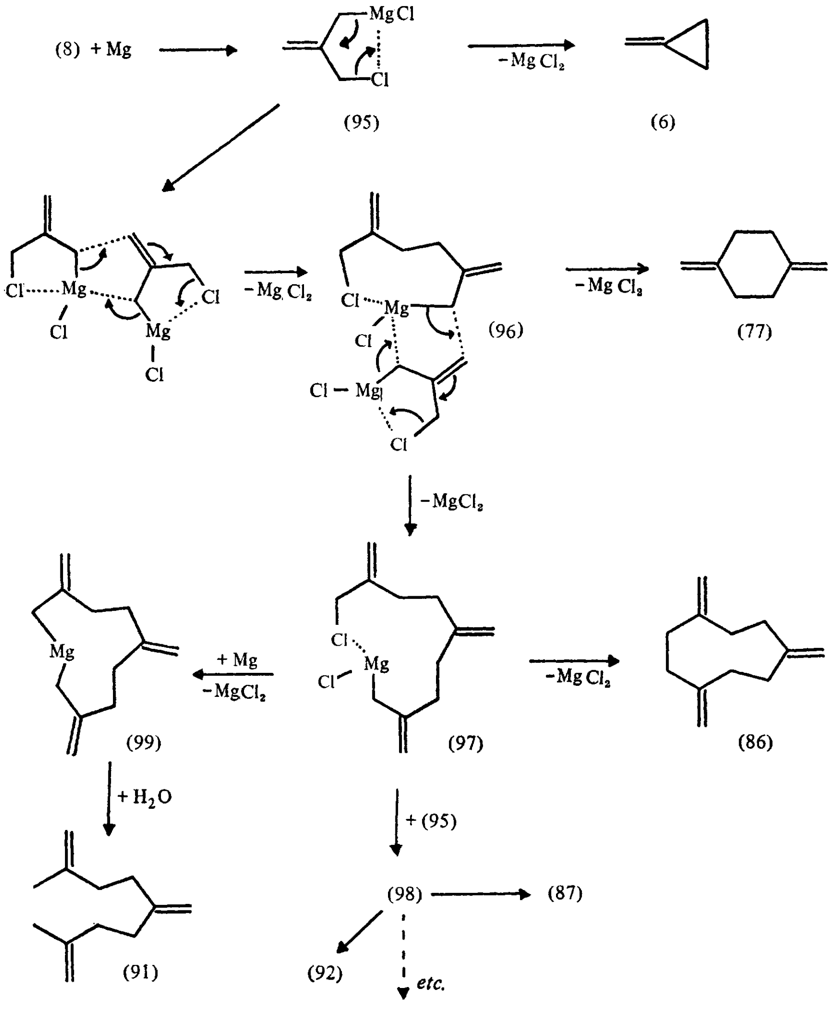
[63] These allylic Grignard intermediates possibly are in a dynamic equilibrium (see: J. E. Nordlander and J. D. Roberts, *J. Amer. Chem. Soc.*, 1959, **81**, 1769), but this should not affect the qualitative course of the reaction, for symmetry reasons.



Scheme 13

been found in the reaction, recently described by Köster *et al.*,[64] of methallyl chloride (7) with potassium amide in tetrahydrofuran, which affords a 36% yield of (6). The reaction with sodium amide, formerly reported to give 1-methylcyclopropene (101),[65] has been found to give a mixture of (6) and (101). As

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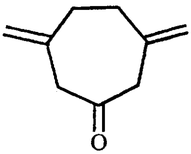
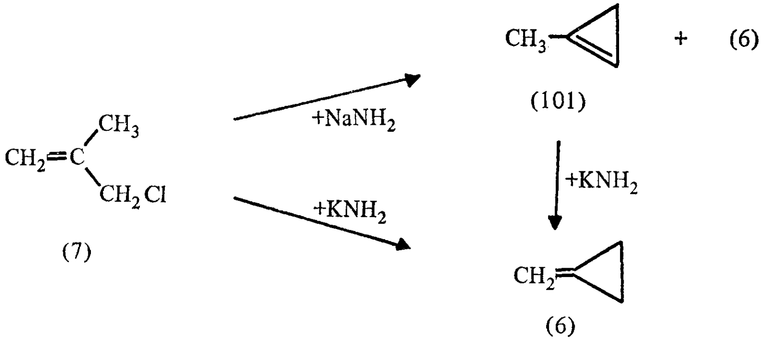
[64] R. Köster, S. Arora, and P. Binger, *Angew. Chem.*, 1969, **81**, 186; *Angew. Chem. internat. Edn.*, 1996, **8**, 205.

[65] F. Fisher and D. E. Applequist, *J. Org. Chem.*, 1965, **30**, 2089.



(100)

potassium amide quantitatively isomerises (101) to (6), the former may well be an intermediate in this case (Scheme 14).



Scheme 14

D. Iron Tricarbonyl Complexes.—A number of molecules which are unstable in the free state can be stabilised as ligands in transition metal π-complexes, for example cyclobutadienes,[4] cyclopentadienone,[66a,b] 2,4-cyclohexadienone,[66c] carbene,[66d] *o*-quinodimethane,[66e] and benzyne.[66f] Trimethylenemethane, like cyclobutadiene, having an unfilled nonbonding orbital, has also proved to be an excellent acceptor in transition-metal complexes.

A tricarbonyl-π-allyl(acyl)iron complex (102) is formed when iron enneacarbonyl reacts with isobutenediol (15)[67] whereas the reaction of iron enneacarbonyl with 3-chloro-2-chloromethylpropene (8) gives the tricarbonyl-(trimethylenemethane)iron (103) in 30% yield.[5a] More recently Ehrlich and Emerson[5f] observed that (103) could also be formed in a disproportionation of tricarbonyl-2-methallyliron chloride (105), and found a convenient one-step synthesis of (103) in the reaction of an excess of 2-methallyl chloride (7) with iron enneacarbonyl, followed by fractional distillation, without isolation of the

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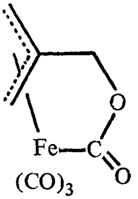
[66] (*a*) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1960, 989; (*b*) E. Weiss, R. Merényi, and W. Hübel, *Chem. and Ind.*, 1960, 407; (*c*) A. J. Birch, P. E. Cross, J. Lewis, and D. A. White, *ibid.*, 1964, 831; (*d*) E. O. Fischer and A. Maasböl, *Chem. Ber.*, 1967, **100**, 2445; (e) W. R. Roth and J. D. Meier, *Tetrahedron Letters*, 1967, 2053; (*f*) E. W. Gowling, S. F. A. Kettle, and G. M. Sharples, *Chem. Comm.*, 1968, 21.

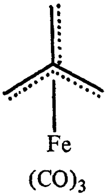
[67] H. D. Murdoch, *Helv. Chim. Acta*, 1964, **47**, 936.

intermediate (105), which gives a yield of 14—20% of theory based on $Fe_2(CO)_9$.

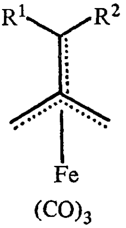
Several substituted trimethylenemethaneiron complexes have been prepared by these authors, using the same procedure with substituted allyl halides: the tricarbonyl(phenyltrimethylenemethane)iron (104*a*) was obtained in 32% yield from 3-chloro-2-methyl-1-phenylpropene, while 36% of a 1 : 3 mixture of tricarbonyl(methyltrimethylenemethane)iron (104*d*) and tricarbonyl(isoprene) iron (106*b*) were obtained by reaction of an excess of $Fe_2(CO)_9$ with a mixture of 1- and 3-chloro-2,3-dimethylpropene. Substituted tricarbonyl(trimethylenemethane)iron complexes [(104*a*), (104*b*), and (104*c*)] can also be prepared by reaction of $Fe_2(CO)_9$ with 2-substituted methylenecyclopropanes (107*a*), (107*b*), and (107*c*), in 40—60% yield.[5e]



(102)

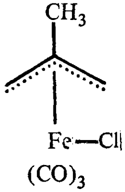


(103)

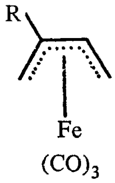


(104)

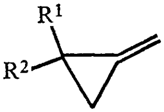
(*a*) R^1=H; R^2=Ph
(*b*) R^1=Me; R^2=Ph
(*c*) R^1=R^2=Ph
(*d*) R^1=H; R^2=Me
(*e*) R^1=H; R^2=Br



(105)



(106) (*a*) R=H
(*b*) R=Me



(107)

Methylenecyclopropane (6) itself, however, gives tricarbonyl(butadiene)iron (106*a*), *ca.* 2%, rather than tricarbonyl(trimethylenemethane)iron (103), in the same conditions.[5e] In contrast, methylenecyclopropane (6) and the 2,2-diphenyl derivative (107*c*) react with palladium chloride to give the π-allylpalladium complexes (108) and (109), respectively.[68]

Gas-phase electron-diffraction investigation of tricarbonyl(trimethylenemethane)iron (103)[5b] and single-crystal *X*-ray diffraction study of (104*a*)[5c] show a close similarity in molecular conformation of the two complexes. The iron

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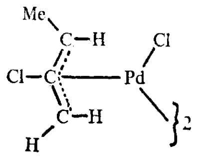
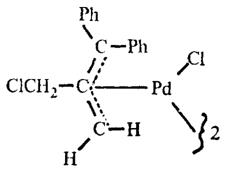
[68] R. Noyori and H. Takaya, *Chem. Comm.*, 1969, 525.

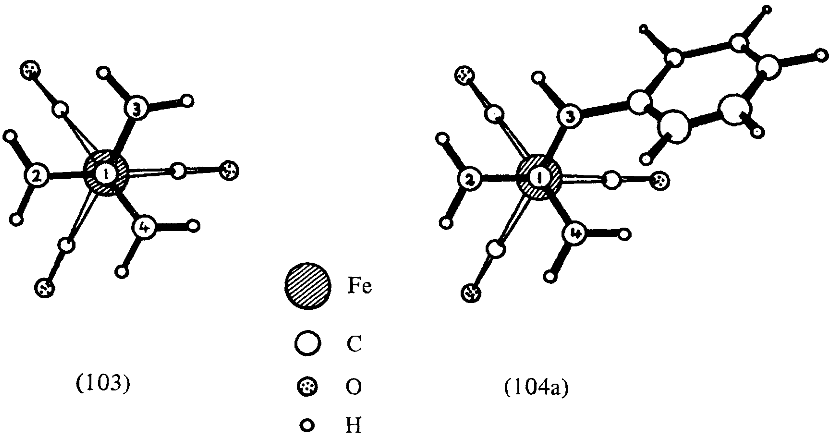


(108)



(109)

atom is located directly beneath the central atom C^1 of the trimethylenemethane skeleton (the Fe—C_1 distances being respectively 1·938 and 1·929 Å) and is π-bonded to all four carbon atoms of this ligand. The carbon skeleton of the ligand forms a tetrahedron, with C^1 displaced away from the iron atom relative to the C^2–C^3–C^4 plane, by *ca.* 0·34 Å for (103) and by 0·31 Å for (104*a*). The trimethylenemethane ligand and the Fe$(CO)_3$ moiety adopt a mutually staggered conformation, forming a trigonal antiprism (Figure 3). It also appears that the plane of the phenyl ring makes an angle of *ca.* 59° with the plane defined by C^2–C^3–C^4, which seems to indicate that there is little conjugation between phenyl and trimethylenemethane systems. This seems to be the case even in solution, according to the i.r. spectra.[5e]



(103)

(104a)

Figure 3

Preliminary studies of some reactions of tricarbonyl(trimethylenemethane)iron (103) have been made. Protonation of the ligand occurs in strong acids, as with tricarbonyl(butadiene)iron and derivatives,[69] and treatment of (103) with sulphuric acid, followed by concentrated hydrochloric acid gives rise to complex (105) in high yield.[5a] Addition of bromine to (103) gives the complex (110),

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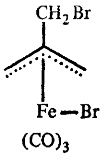
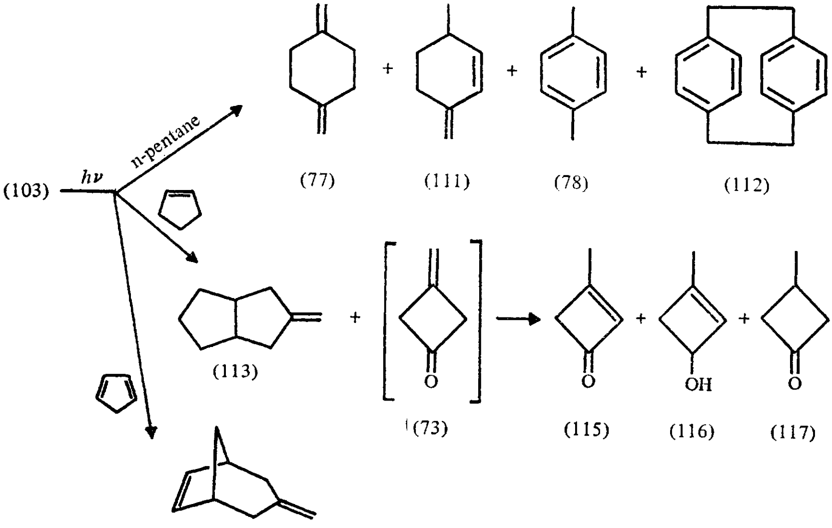
[69] G. F. Emerson and R. Pettit, *J. Amer. Chem. Soc.*, 1962, **84**, 4591.



(110)

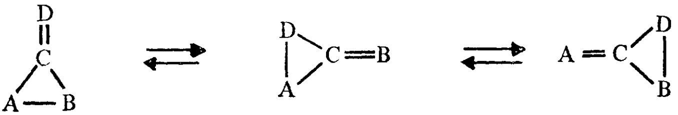
which disproportionates to re-form (103), instead of yielding complex (104*e*) as would be expected from a reaction similar to the disproportionation of (105).[5f]

Day and Powell[5d] studied the photolysis of (103) in several solvents, as a possible method of generating (1) and obtained results which strongly suggest the intermediacy of free trimethylenemethane in some of the reactions (Scheme 15). In pentane dimers of (1), *e.g.* (77; 6%), and isomers like (111; 9%) as well as *p*-xylene (78; 20%), and even 3% of [2,2]paracyclophane (112), were formed, a result which is similar to those obtained by Skell and Doerr[6d] (*cf.* Scheme 11). In cyclopentene and in cyclopentadiene the formation of these dimerisation products and derivatives was completely suppressed, and cycloaddition of (1) to the olefins occurs: (113) was obtained in *ca.* 5% yield in cyclopentene [*cf.* Dowd's[58] result with butadiene → (84)], and (114) was obtained in 23% yield in cyclopentadiene. The main products of these complex photolyses, in cyclopentene, were the three cyclobutane derivatives (115; 29%), (116; 11%), and (117; 3%), which were probably formed by carbonylation of (1) to a primary product believed to be 3-methylenecyclobutanone (73). These carbonylation products [*cf.* (8) → (100) in the presence of nickel carbonyl] are probably formed within the ligand sphere of the iron atom, and not at the expense of free trimethylenemethane (1).

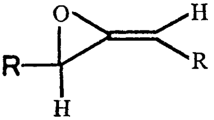


Scheme 15

E. Heteroanalogues of Trimethylenemethane.—Although it will not be discussed here, the possible existence of heteroanalogues of trimethylenemethane (1) is mentioned, without implication as to their electronic structures. They may occur, for example, in the isomerism depicted in Scheme 16, in which, if A = B = C = D = carbon, we have the isomerism of methylenecyclopropanes. The much discussed valence tautomerism of allene oxides (118) and cyclopropanones (119)[56] recently received experimental support,[70a] and substituted diaziridine imines (120) have been shown to be in thermal equilibrium, possibly through structure (121).[70b]



Scheme 16



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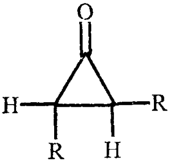

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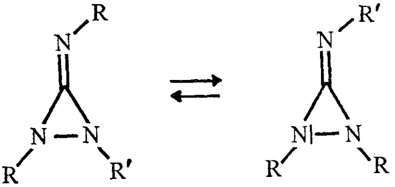

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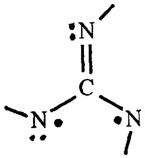

(121)

7 Conclusion

This article aims to provide an introductory review of a new field of organic chemistry, which already promises much interest. The close relation of trimethylenemethane and cyclobutadiene clearly demands a comparison of the two systems, their reactivities, analogies and differences. Study of complexes with

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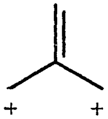
[70] (*a*) R. L. Camp and F. D. Greene, *J. Amer. Chem. Soc.*, 1968, **90**, 7349; J. K. Crandall and W. H. Machleder, *ibid.*, 1968, **90**, 7347; (*b*) H. Quast and E. Schmitt, *Angew. Chem.*, 1969, **81**, 429; *Angew Chem. internat. Edn.*, 1969, **8**, 449; *Chem. Ber.*, 1970, **103**, 1234.

transition-metal compounds, the syntheses and chemistry of complexes with metals other than iron, with substituted trimethylenemethanes, study of ligand transfers, *etc.*, should be particularly fruitful. The possibility of producing ionic trimethylenemethane species like the dication (122), the dianion (123) and especially the 1,3-dipolar species (124) also deserves attention. The chemistry of α,α′-disubstituted isobutenes in general, whether or not trimethylenemethane itself is implicated as an intermediate, should continue to find both synthetic and mechanistic interest, especially in the broad field of reactions involving some allylic rearrangement. In all cases the influence of various substituents on the properties of the systems, for example on the stability of trimethylenemethane species, should be investigated for a better understanding of this chemistry.



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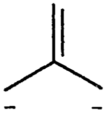

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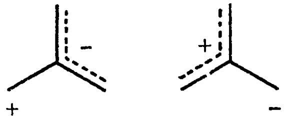
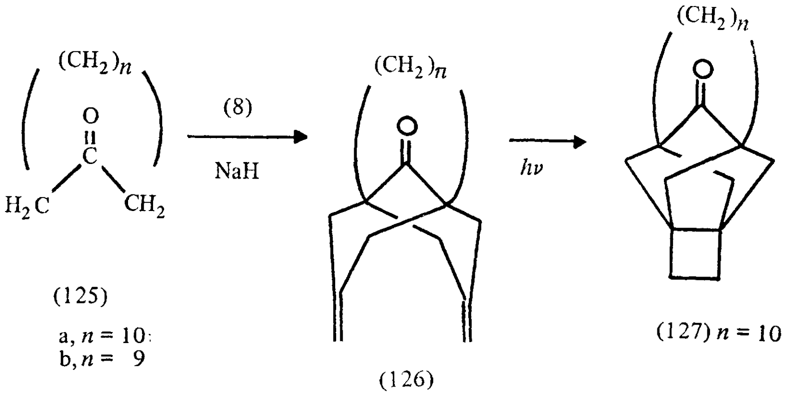


(124)

Note added in Proof. — Several recent papers on these subjects deserve mention. Photochlorination of methylenecyclopropane (6) gives dichloroisobutene (8) in 42% yield, among a variety of chlorinated products, but not the expected 2-chloromethylenecyclopropane.[71] Condensation of (8) and large-ring cycloalkanones (125) in the presence of sodium hydride provides substantial yields of 1,5-polymethylene-bridged 3,7-dimethylenebicyclo[3,3,1]nonan-9-ones (126),



(125)

a, n = 10;
b, n = 9

(126)

(127) n = 10

Scheme 17

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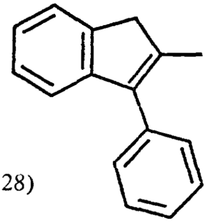
[71] A. J. Davidson and A. T. Bottini, *J. Org. Chem.*, 1969, 34, 3642.

and u.v.-irradiation of (126a) causes a smooth intramolecular cycloaddition to cage compounds (127) (Scheme 17).[72]

Conformational studies[73a,73b] and additional data on the thermal rearrangement[73b,73c] of 5-methylene-1,3-dioxans (29) and (67) have been published. A recent calculation indicates a positive value for the zero field splitting parameter *D* of trimethylenemethane (1).[74]

The closely related thermal rearrangements of 2,2-diphenyl-1-methylenecyclopropane (107*c*) to 2-methyl-3-phenylindene (128), [75a] and of 1-methylene-2-vinylcyclopropane (129) to 3-methylenecyclopentene (130), [75b,75c] may well proceed through trimethylenemethane intermediates.[75a]



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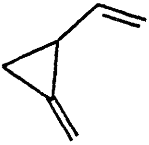

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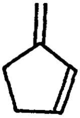
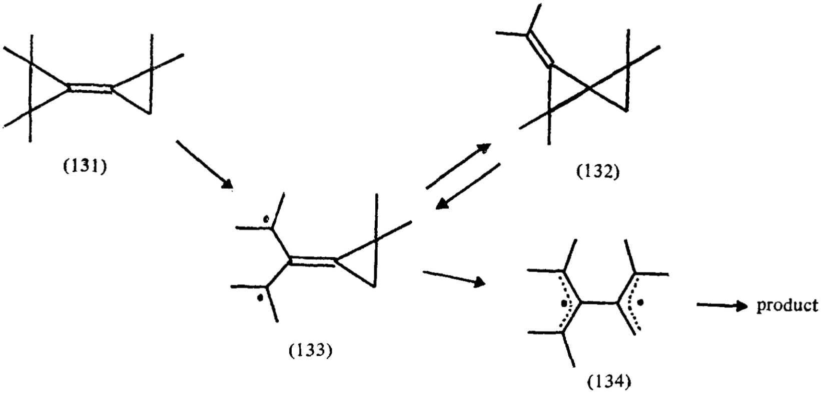


(130)

The thermal behaviour of the more complex cyclopropylidenecyclopropane (131) and the related methylenespiropentane (132) is also interpreted by a mech-



Scheme 18

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[72] T. Mori, K. Kimoto, M. Kawanisi, and H. Nozaki, *Tetrahedron Letters*, 1969, 3653.

[73] (*a*) Ph. Desaulles, Thèse, Strasbourg, 1969; (*b*) F. Mutterer, J. M. Morgen, J. M. Biedermann, J. P. Fleury, and F. Weiss, *Bull. Soc. chim. France*, 1969, 4478; *Tetrahedron*, 1970, **26**, 477; (*c*) J. M. Biedermann, J. P. Fleury, and F. Weiss, *Bull. Soc. chim. France*, 1970, 1187.

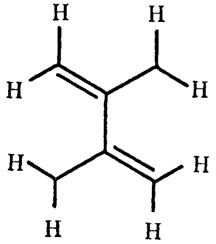
[74] A. Gold, *J. Amer. Chem. Soc.*, 1969, **91**, 4961.

[75] (*a*) J. Maitland jun., M. E. Hendrick, J. C. Gilbert, and J. R. Butler, *Tetrahedron Letters*, 1970, 845; (*b*) T. C. Shields, W. E. Billups, and A. R. Lepley, *J. Amer. Chem. Soc.*, 1968, **90**, 4749; T. C. Shields and W. E. Billups, *Chem. and Ind.*, 1969, 619; (*c*) H. D. Roth, PETR 2, Abstracts of Papers. 159th ACS National Meeting, Feb. 1970.

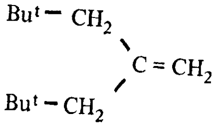
anism based on trimethylenemethane-type intermediates (*e.g.* 133), as summarized in Scheme 18.[76]

The bis-allyl diradical (134a) ('tetramethylene ethane') has been observed recently by Dowd[77] in the low-temperature photolysis of 3,4-dimethylenecyclopentanone, and of its perdeuteriated derivative. The e.s.r. spectrum confirmed the ground-state triplet structure of (134a), which was predicted,[1c] and which determines a close relation between this species and trimethylenemethane (1) (see references cited in ref. 77, for example).

Irradiation of tricarbonyliron complexes, (103) and the bromo-analogue of (105), in t-butylbromide gives mainly the hydrocarbon (135), which is a dialkylation product of trimethylenemethane.[78]



(134 a)



(135)

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