

Trimethylenemethane

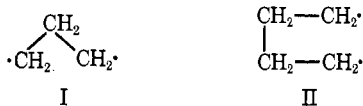
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In recent years there has been a revolution in the study of reactive intermediates in organic chemistry. Discoveries in this area have arisen from two general sources. The more recent, illustrated by the carbonium ion studies of Mackor and McLean, Birchall and Gillespie, and Olah, and by the triplet state studies of Hutchison, van der Waals and de Groot, and Wasserman, has resulted from the introduction of magnetic resonance into organic chemistry. The second, chemical trapping, is less a sudden break with the past, but rather a technique which has grown and come to fruition with the benzyne studies of Wittig, Roberts, and Huisgen and the dichlorocarbene trapping studies of Doering. The particular examples cited are only a few of those to which one might refer, but they attest admirably to the power and heuristic value of such experiments.

A group of suspected reactive intermediates that had proved to be very elusive was that of aliphatic diradicals. The two simplest members of this class are trimethylene (I) and tetramethylene (II). Such inter-



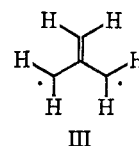
mediates, their derivatives, and their higher homologs have been postulated to be important in such diverse reactions as pyrolytic and photochemical opening and isomerization of small rings, triplet methylene additions to olefins, photochemical decomposition of ozonides, certain cycloaddition reactions, electrochemical and alkali metal reductions of 1,3- and 1,4-dihaloalkanes, photochemical decarbonylations of cyclic ketones, and photochemically induced release of nitrogen from cyclic azo compounds.

Until recently, no member of this general class of aliphatic diradical had been observed spectroscopically or trapped by chemical means. Indeed, since such molecules carry internally the seeds of their own destruction and are expected to undergo ring-closure reactions at very high rates, one had no assurance that *any* means could be found which would result in the direct observation or trapping of such species. Thus, for many of the reactions cited above, the diradical intermediate has simply been suggested as one of a number of mechanistic possibilities.

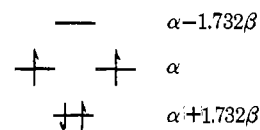
Paul Dowd graduated from Harvard College in 1958, and then went to Columbia, where he received the M.A. and Ph.D. degrees. His thesis was written under the direction of Ronald Breslow and dealt with approaches to the sym-triphenylcyclopropenyl anion. He then returned to Harvard for a year of postdoctoral work with R. B. Woodward, followed by 6 years on the staff. He is now Associate Professor at the University of Pittsburgh, and is an Alfred P. Sloan Fellow.

Trimethylenemethane: Electron Spin Resonance Experiments¹⁻³

Trimethylenemethane (III) was chosen as the



opening wedge with which to effect entry into this area for a number of reasons. It is predicted⁴ to be a ground-state triplet. This conclusion follows upon examination of its simple Hückel π -electron molecular orbital energy levels, of which two are degenerate and nonbonding.



This molecule is of further theoretical interest because the central carbon atom attains the highest possible mobile bond order for an sp^2 carbon atom; it is the base for all Hückel molecular orbital calculations of bond order and spin density.⁴ The molecule has also been used extensively in testing various theoretical methods of calculating energies and spin densities in π systems.^{4f-k,5} Trimethylenemethane (III) has been postulated to be the reactive intermediate in a number of reactions involving the formation and rearrangement of methylenecyclopropanes.

Since trimethylenemethane (III) was expected to be a ground-state triplet, the decision was made to search for it using electron spin resonance spectroscopy.⁶ The first requirement was the choice and preparation of

(1) P. Dowd, *J. Amer. Chem. Soc.*, **88**, 2587 (1966).

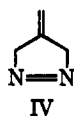
(2) P. Dowd and K. Sachdev, *ibid.*, **89**, 715 (1967).

(3) P. Dowd, A. Gold, and K. Sachdev, *ibid.*, **90**, 2715 (1968).

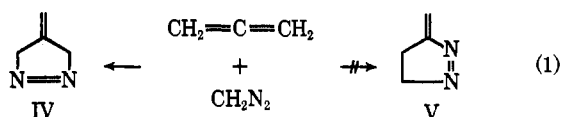
(4) (a) W. E. Moffitt, footnote to C. A. Coulson, *J. Chim. Phys.*, **45**, 243 (1948); (b) W. Moffitt, *Trans. Faraday Soc.*, **45**, 373 (1949); (c) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Amer. Chem. Soc.*, **74**, 4579 (1952); (d) H. H. Greenwood, *Trans. Faraday Soc.*, **48**, 677 (1952); (e) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950); (f) J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, New York, N. Y., 1961, p 56; (g) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 43, 57; (h) J. N. Murrell, S. F. A. Kettle, and K. M. Tedder, "Valence Theory," Wiley, New York, N. Y., 1965, p 263; (i) H. M. McConnell, *J. Chem. Phys.*, **35**, 1520 (1961); (j) A. D. McLachlan, *Mol. Phys.*, **5**, 51 (1962); (k) D. P. Chong and J. W. Linnett, *ibid.*, **8**, 541 (1964); *J. Chem. Soc.*, 1798 (1965); (l) J. G. Burr and M. J. S. Dewar, *ibid.*, 1201 (1954).

(5) A. Gold, *J. Amer. Chem. Soc.*, **91**, 4961 (1969).

(6) (a) C. A. Hutchison, Jr., and B. W. Mangum, *J. Chem. Phys.*, **29**, 952 (1958); **34**, 908 (1961); (b) J. H. van der Waals and M. S. de Groot, *Mol. Phys.*, **2**, 333 (1959); **3**, 190 (1960); (c) W. A. Yager, E. Wasserman, and R. M. R. Cramer, *J. Chem. Phys.*, **37**, 1148 (1962).

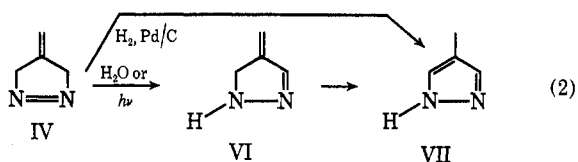


a proper precursor. 4-Methylene- Δ^1 -pyrazoline (IV) seemed ideally suited for this purpose since it presented an azo group which was expected to be both accessible and labile photolytically. In addition, one had the advantage of knowing from the work of D'yakanov⁷ that diazomethane forms an adduct with allene. The structure of the adduct was not known, but it appeared likely that it was the desired pyrazoline IV. This surmise was based on knowledge that electrophilic species add to the terminus of the allene system. Thus, one had reason to expect that the dipolar diazomethane would exhibit similar behavior with respect to allene, leading to the desired 4-methylene- Δ^1 -pyrazoline (IV) to the exclusion of the alternative 3-methylene- Δ^1 -pyrazoline (V) (eq 1). What one could not know was



the ease with which IV would undergo prototypic rearrangement to VI and then, ultimately, to the stable heteroaromatic 4-methylpyrazole (VII).

In the event,¹ the desired pyrazoline IV was the only product isolated in the reaction between allene and diazomethane. However, it was necessary to maintain strictly anhydrous and oxygen-free conditions in order to minimize rearrangement to VI and oxidation to undesirable by-products (eq 2).



The structure of the pyrazoline IV was easily established spectroscopically and also by mild catalytic (H_2 , Pd/C) rearrangement to 4-methylpyrazole (VII). As is implied above, the rearrangement of IV to VI is catalyzed by traces of moisture. The reaction also takes place upon photolysis in solution at ambient temperatures⁸ (eq 2).

Irradiation¹ of 4-methylene- Δ^1 -pyrazoline (IV) at -196° in dilute glassy solution yielded the epr spectrum shown in Figure 1. The outer lines are identified with the triplet trimethylenemethane (III). These four lines are stable, with only slight loss of intensity, for several months as long as the sample is maintained at the boiling point of liquid nitrogen. If the temperature

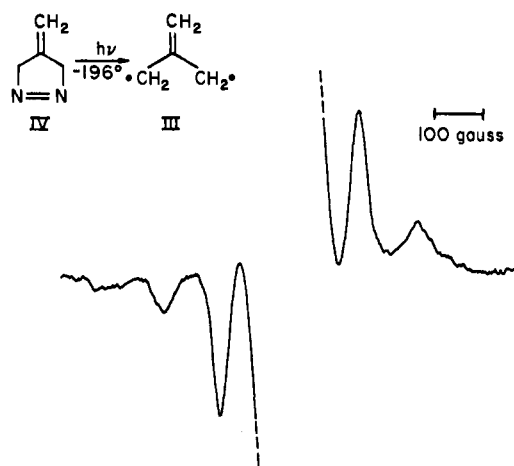


Figure 1. ESR spectrum of trimethylenemethane in hexafluorobenzene. The base line of this spectrum has been corrected for slight nonlinearity.

is raised to -150° , the lines due to the triplet vanish completely after only a few minutes. This is one feature which distinguishes the outer four lines from the intense central line. The latter is quite stable over this temperature range and appears to be due to relatively stable monoradicals produced in the course of the photolysis. The splitting between the two outermost lines (D value) is 0.025 cm^{-1} . This is significantly smaller than the splitting found in, for example, diphenylmethylene ($D = 0.40 \text{ cm}^{-1}$) or triplet naphthalene ($D = 0.10 \text{ cm}^{-1}$) and strongly supports the hypothesis that one has, for the first time, directly observed a 1,3 diradical. Thus, since the D value is a measure of the interaction between the two unpaired electrons, it is expected to diminish as the electrons become more remote from one another. Further evidence is provided by the symmetry of the spectrum which shows only four out of a possible six lines (two lines corresponding to each of the cartesian coordinates x , y , and z). This is consistent with two of the axes being equivalent, as is required for the molecule trimethylenemethane, which must have at least C_3 symmetry and which is quite probably D_{3h} in its triplet state.

In order to approach the reactive triplet (III) from an independent precursor, 3-methylenecyclobutanone (VIII) was prepared.² Irradiation of this substance yielded the particularly strong, clean spectrum shown in Figure 2. Of special note is the virtual absence of the central impurity line. The spectrum obtained with ketone VIII was sufficiently strong that it permitted the observation of the $\Delta m = 2$ line at 1590 G which is a most important and useful characteristic of the epr spectra of triplet-state molecules.^{6b}

The choice of 3-methylenecyclobutanone (VIII) as a precursor was a fortunate one since it was later discovered that one could grow a single crystal of this compound.³ When this crystal was irradiated with ultraviolet light and then properly oriented in the magnetic field, the proton hyperfine spectrum shown in Figure 3 was obtained. The presence of only seven lines with intensity ratios very close to the expected binominal

(7) I. A. D'yakanov, *Zh. Obshch. Khim.*, **15**, 473 (1945); *Chem. Abstr.*, **40**, 4718⁴ (1946). See also A. C. Day and M. C. Whiting, *J. Chem. Soc. C*, 464 (1966); *Proc. Chem. Soc. London*, 368 (1964), who had prepared a substituted pyrazoline in a similar fashion and decomposed it photochemically to the corresponding methylenecyclopropane. A trimethylenemethane intermediate was proposed for the latter reaction.

(8) P. S. Engel, unpublished results.

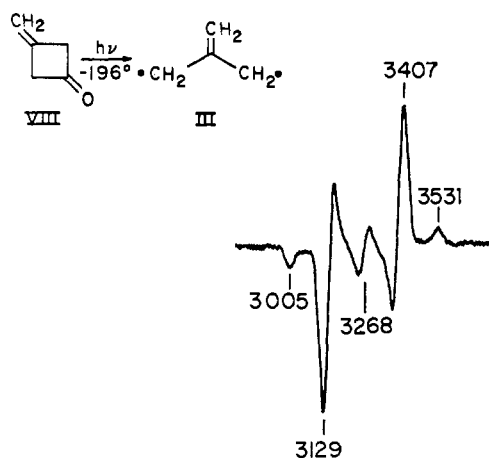


Figure 2. ESR spectrum of trimethylenemethane from photolysis of 3-methylenecyclobutanone in perfluoromethylcyclohexane. The peak positions were measured at a klystron frequency of 9149.7 MHz.

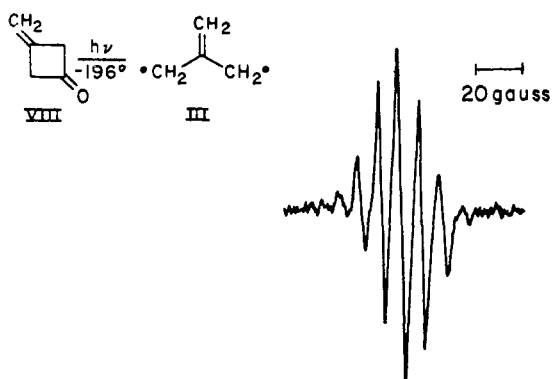


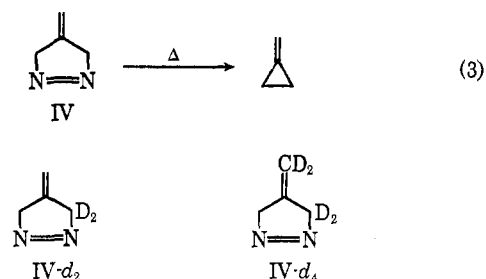
Figure 3. Single-crystal ESR spectrum of trimethylenemethane. The septet shown, one of two, is the low-field peak. It is centered at 2940 G (klystron frequency 9150 MHz).

ratio of 1:6:15:20:15:6:1 must arise through the interaction of six equivalent protons with the unpaired electrons. The magnitude of the splitting between the peaks is 8.9 G, very close to that which is calculated on the basis of valence-bond theory. Hückel molecular orbital theory does not take account of negative spin density on the central carbon atom and predicts the lower splitting value of 7.1 G. The latter spectrum constitutes the strongest present support for the existence and skeletal structure of trimethylenemethane. Although it might seem reasonable to assume that this molecule is planar (D_{3h}) and this assumption would be consistent with prior theoretical discussion, this point has not been verified experimentally. The establishment of the shape of this molecule is clearly essential if one hopes to establish a correlation (or lack of one) between the EPR results and the highly interesting, stereospecific, thermal rearrangements of methylenecyclopropanes which are discussed at a later point in this article.

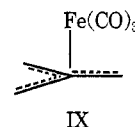
Alternative Approaches

Simultaneously with the photochemical EPR work, a study of the thermal decomposition of 4-methylene- Δ^1 -pyrazoline (IV) was undertaken by Crawford and

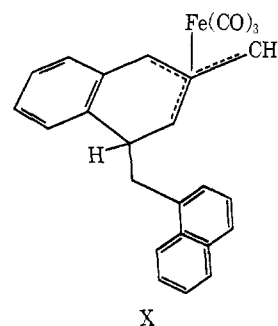
Cameron. They found that the sole product of thermal decomposition was methylenecyclopropane (eq 3). The intermediacy of trimethylenemethane was postulated on the basis of isotopic scrambling of molecules appropriately labeled by synthesis from, in one case (IV- d_4), allene- d_4 and diazomethane and, in the other (IV- d_2), allene and diazomethane- d_2 .⁹ It seems probable that this pyrolysis is a singlet-state reaction.¹⁰



Shortly thereafter a trimethylenemethane-iron tricarbonyl complex (IX) was reported by Emerson and



his coworkers.¹¹ The structure of this molecule is supported by electron-diffraction studies.¹² In addition, the crystalline phenyltrimethylenemethaneiron tricarbonyl has been synthesized by Emerson and its structure firmly established by X-ray analysis.¹³ The iron complex IX may also be prepared by reaction of methylenecyclopropane with iron enneacarbonyl.¹⁴ Iron enneacarbonyl reacts with a mixture of α - and β -bromomethylnaphthalenes in a most interesting fashion, yielding the trimethylenemethane complex X.¹⁵



(9) R. J. Crawford and D. M. Cameron, *J. Amer. Chem. Soc.*, **88**, 2589 (1966). An unusually large secondary deuterium isotope effect was postulated for these decomposition reactions.

(10) W. von E. Doering, J. C. Gilbert, and P. A. Leermakers, *Tetrahedron*, **24**, 6863 (1968); W. T. Bordon, *Tetrahedron Lett.*, 259 (1967). The existence of both singlet and triplet modes of reaction is indicated by the work of S. D. Andrews and A. C. Day, *Chem. Commun.*, 667 (1966), who found that the product distribution in the photolysis of a substituted pyrazoline depended upon whether the irradiation was conducted directly or in the presence of triplet sensitizers. But see also T. Sanjiki, M. Ohta, and H. Kato, *ibid.*, 638 (1969); T. Sanjiki, H. Kato, and M. Ohta, *ibid.*, 496 (1968).

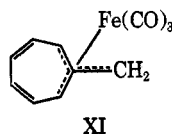
(11) G. F. Emerson, K. Ehrlich, W. P. Gierind, and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **88**, 3172 (1966).

(12) A. Almennigen, A. Halland, and K. Wahl, *Chem. Commun.*, 1027 (1968).

(13) M. R. Churchill and K. Gold, *ibid.*, 693 (1968).

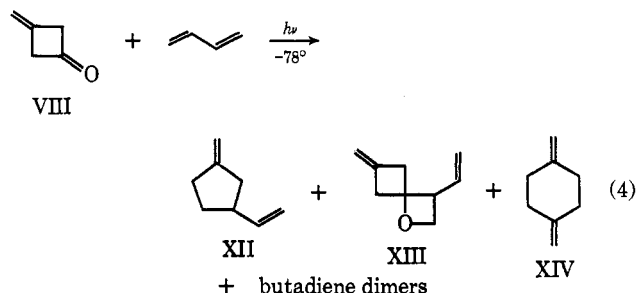
(14) R. Noyori, T. Nishimura, and H. Takaza, *ibid.*, 89 (1969).

In a similar fashion hydroxymethylcycloheptatriene reacts to yield an iron tricarbonyl complex of heptafulvene.¹⁶ The trimethylenemethane complex XI has been suggested for the structure of this molecule.



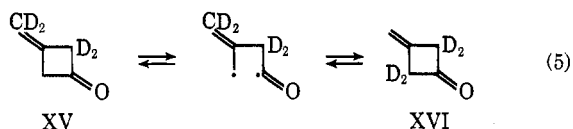
Chemical Reactivity and Trapping Reactions

Part of the original plan was to attempt the chemical interception of a 1,3 diradical. It was especially attractive to be able to use, as precursors, molecules for which firm spectroscopic evidence indicated the ready formation of the desired reactive intermediate. Accordingly, the photolysis of 3-methylenecyclobutanone (VIII) in the presence of olefinic trapping agents was undertaken. Negative results were obtained with cyclopentene, 1,1-diphenylethylene, 1,1-dimethoxyethylene, furan, and cyclopentadiene (for the most part, these reactions were dominated by oxetane formation, *vide infra*). However, photolysis in butadiene at -78° (eq 4) yielded (35%) a new product identified



spectroscopically as 3-vinylmethylcyclopentane (XII). The structure of this molecule was unequivocally established by synthesis.¹⁷

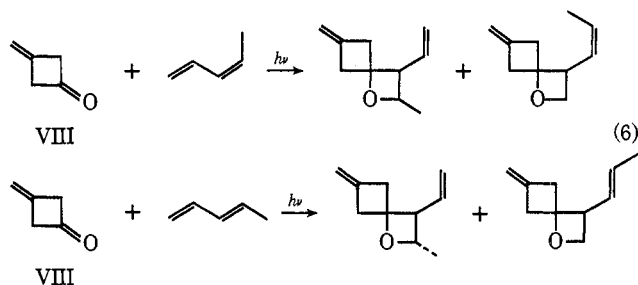
An attempt was made to single out trimethylenemethane (from several possibilities) as the reactive intermediate in this reaction by deuterium labeling. Thus, the deuterated ketone XV was prepared and ir-



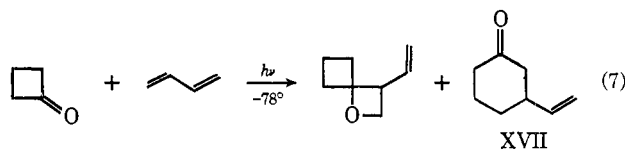
radiated in butadiene at -78° . Isolation of 3-vinylmethylcyclopentane- d_4 , with the deuterium atoms statistically scrambled among the three carbon atoms which formally correspond to the peripheral carbons of trimethylenemethane, established that half of this product (XII) arises from butadiene, while the other half arises from the ketone XV.¹⁸ The fact that the deuterium is completely scrambled in the hydrocarbon product (XII) is, however, not necessarily indicative of

the intermediacy of trimethylenemethane in the photolysis. It was found that deuterium was also completely scrambled in the starting ketone, reisolated from a reaction carried 75% to completion. One possibility for this change is the sequential opening, bond rotation, and reclosure of the cyclobutanone ring as shown above, XV \rightleftharpoons XVI (eq 5).

The formation of the oxetane XIII (eq 4) was unexpected on the basis of the common assumptions one makes about the ease of intersystem crossing of excited-state ketones and the ordinarily facile transfer of triplet energy from triplet ketones to conjugated dienes. Further investigation¹⁹ using *cis*- and *trans*-piperylene (eq 6) showed that oxetane formation, in this instance,



was stereospecific.²⁰ On this basis the oxetane is postulated to arise through the excited singlet state of the ketone VIII. An analogous reaction (eq 7) occurs



with the parent cyclobutanone, but not, under the reaction conditions, with cyclopentanone or cyclohexanone. The latter behave in the expected manner, transferring triplet energy to butadiene and leading to high yields of butadiene dimers.

An additional unexpected result was the isolation of 3-vinylcyclohexanone (XVII) from the photolysis of cyclobutanone in butadiene (eq 7).²¹ This product has been tentatively postulated to arise through the intermediacy of the 1,4 diradical XVIII. If this hy-



pothesis can be verified by independent experiment, this will be the first trapping of a type of reactive intermediate which has long been assumed to be of fundamental importance in the photochemistry of cyclic ketones.

A minor product in the 3-methylenecyclobutanone

(15) A. N. Nesmayanov, I. S. Astakhova, G. P. Zol'nikova, I. I. Kritskaya, and Yu. T. Struchkov, *Chem. Commun.*, 85 (1970).

(16) D. J. Ehntholt and R. C. Kerber, *ibid.*, 1451 (1970).

(17) P. Dowd, G. Sengupta, and K. Sachdev, *J. Amer. Chem. Soc.*, 92, 5726 (1970).

(18) This is not a completely punctilious observation. H. Muller, D. Wittenberg, H. Siebt, and E. Scharf, *Angew. Chem., Int. Ed. Engl.*, 4, 327 (1965), have reported the isolation 3-vinylmethylcyclopentane (XII) from a nickel-catalyzed dimerization of butadiene.

(19) P. Dowd, A. Gold, and K. Sachdev, *ibid.*, 92, 5725 (1970).

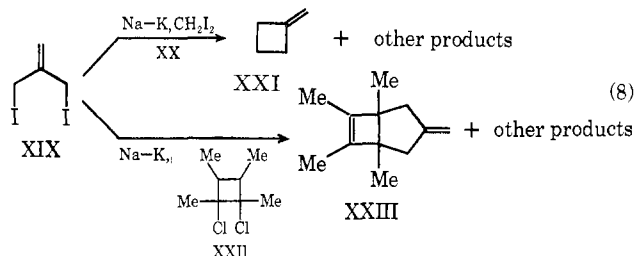
(20) Cf. D. R. Arnold, *Advan. Photochem.*, 6, 301 (1968).

(21) P. Dowd, A. Gold, and K. Sachdev, *J. Amer. Chem. Soc.*, 92, 5724 (1970).

photolysis (eq 4) was 1,4-dimethylenecyclohexane (XIV). This substance has also been observed by Weiss and Schirmann,²² as the sole hydrocarbon product, in their studies of the thermal decomposition of the polyoxalates of 2-methylenepropane-1,3-diol. No methylenecyclopropane could be detected in their reaction. By contrast, methylenecyclopropane was one of the products of the photolysis of 3-methylenecyclobutanone (VIII) and could be detected under most of the conditions studied.

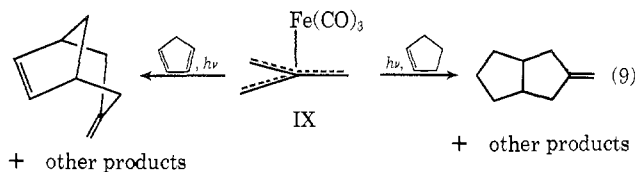
Ward and Pettit²³ have treated trimethylenemethaneiron tricarbonyl with Ce^{4+} in the presence of tetracyanoethylene and succeeded in isolating a 1:1 adduct, 3,3,4,4-tetracyanomethylenecyclopentane. They also report the isolation of molybdenum and chromium complexes of trimethylenemethane.

At 250° potassium vapor reacts with 1,3-diiodo-2-methylenepropane (XIX), yielding 1,4-dimethylenecyclohexane (XIV). In the presence of methylene iodide (XX) and dichlorotetramethylecyclobutene (XXII) the products XXI and XXIII, respectively, have been isolated (eq 8).²⁴ It is maintained²⁴ that



this represents a trapping of trimethylenemethane since for the corresponding saturated compound, 2-methyl-1,3-diiodopropane, no dimeric products were isolated under the reaction conditions. In such a complex system, one may ask whether any compound may be found which serves as an adequate model.

An intriguing approach to the problem of trapping and chemical reactivity has been reported by Day and Powell,²⁵ who subjected trimethylenemethaneiron tricarbonyl (IX) to photolysis and obtained adducts with a variety of olefins including cyclopentene and cyclopentadiene (eq 9). It is possible that the iron carbonyl plays a role in this reaction.

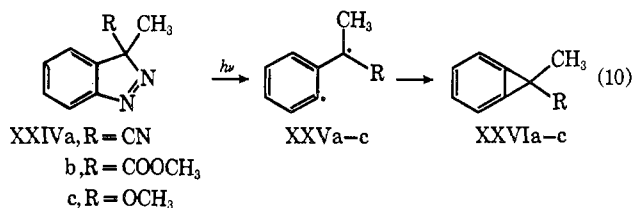


Recent Developments

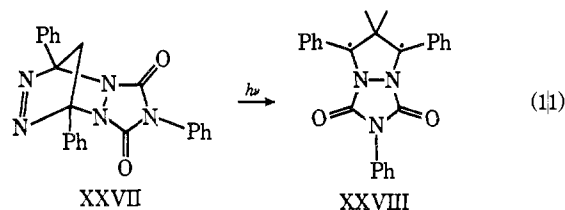
The ground-state triplet nature of trimethylenemethane has recently been confirmed by the experiments of Dewar and Worley,²⁶ who have measured and

analyzed the photoelectron spectrum of trimethylenemethaneiron tricarbonyl (IX). The second ionization potential was found to be remarkably close to that predicted for the triplet ground state of trimethylenemethane.

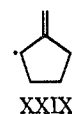
There have now been reported several observations, using esr, of 1,3 diradicals. One instance is the series of diradicals XXV²⁷ which result from photolysis of the benzopyrazoline precursors XXIV to the benzocyclopropenes XXVI (eq 10). The diradical XXIVa has been trapped with butadiene at -70° .²⁷



In a second instance, photolysis of the azo compound XXVII has led to the esr detection of the diradical XXVIII.²⁸ (eq 11). Very recently Berson, *et al.*,²⁹



completed an elegant series of experiments delineating the properties and chemical reactivity of the distorted trimethylenemethane XXIX. They demonstrated the



existence of this reactive species by low-temperature esr spectroscopy. They have also demonstrated the direct involvement of the triplet ground state in the formation of dimeric products using chemically induced dynamic nuclear polarization.³⁰ A dimeric product postulated to arise from a similarly constituted diradical has been isolated by Kobrigh and Heinemann.³¹

Cyclopropanone

Part of the initial interest in the trimethylenemethane system arose from the general feeling that the very high reactivity associated with the cyclopropanones might be understood in terms of an open diradical form (the open dipolar form was a more widely discussed

(26) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **51**, 1672 (1969).

(27) G. L. Closs, L. R. Kaplan, and V. I. Bendell, *J. Amer. Chem. Soc.*, **89**, 3376 (1967).

(28) D. R. Arnold, A. B. Evin, and P. H. Kasai, *ibid.*, **91**, 784 (1969).

(29) J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, *ibid.*, **93**, 1544 (1971).

(30) See also G. L. Closs, *ibid.*, **93**, 1546 (1971).

(31) G. Kobrigh and H. Heinemann, *Chem. Commun.*, 493 (1969).

(22) J. P. Schirmann and F. Weiss, *Tetrahedron Lett.*, 5163 (1967).

(23) J. S. Ward and R. Pettit, *Chem. Commun.*, 1419 (1970).

(24) R. G. Doerr and P. S. Skell, *J. Amer. Chem. Soc.*, **89**, 3062 (1967); P. S. Skell and R. G. Doerr, *ibid.*, **89**, 4688 (1967).

(25) A. C. Day and J. T. Powell, *Chem. Commun.*, 1241 (1968).

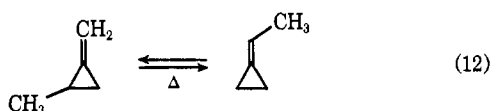
possibility). An attempt was made to observe such a diradical using esr following photolysis of both tetramethyl-1,3-cyclobutanedione and 1,3-cyclobutanedione, but the results in both instances were negative.³² Definitive experiments were performed by Turro and Hammond³³ using nmr spectroscopy. They demonstrated that ground-state cyclopropanone (XXX) is



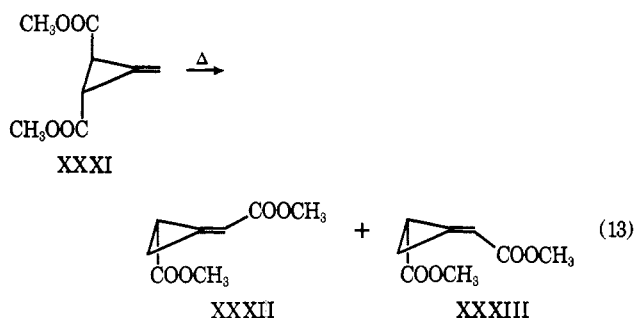
best described by a closed three-membered-ring structure. This conclusion has been confirmed by microwave spectroscopy.³⁴

Thermal Rearrangements of Methylene cyclopropanes

Methylene cyclopropane undergoes a degenerate thermal rearrangement, the degeneracy being lifted and the reaction revealed when substituents are present. An early example, the ethylenecyclopropane-methylmethylene cyclopropane interconversion, studied by Chesick,³⁵ is shown in eq 12.

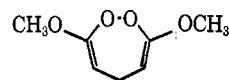


The existence of such a rearrangement was first discovered in the course of studies which yielded the presently accepted structures of the dimethyl ester of Feist's acid XXXI and its thermal rearrangement products XXXII and XXXIII.³⁶ The thermal rearrangement of Feist's ester is shown in eq 13.



The crucial inner workings of the Feist ester rearrangement were first revealed by the pioneering experiments of Ullman³⁷ and are twofold in their importance to the understanding of the thermochemistry of methylenecyclopropane. First, Ullman observed a certain amount of racemization of the optically active, starting trans-diester XXXI and postulated the intermediacy of a (dipolar) trimethylenemethane-like intermediate, which is, of course, achiral. Leaving open the possible

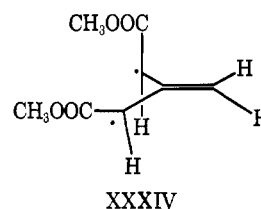
intermediacy of a trimethylenemethane intermediate in this reaction, Doering and Roth³⁸ have suggested a new alternative, 3,6-dimethoxy-4,5-dioxamethylenecycloheptadiene. This intermediate was particularly di-



rected toward an explanation of the exceptional ease of racemization of the syn-diester rearrangement product XXXII. In a study similar to Ullman's, Gajewski postulated the intermediacy of a trimethylenemethane intermediate in order to account for a moderate amount of racemization in the thermolysis of the optically active *trans*-2,3-dimethylmethylene cyclopropane.³⁹

Second, racemization is only a part of this reaction. Both Ullman and Gajewski observed substantial retention of optical activity in the rearranged products. Further, Doering and Roth have elegantly demonstrated that the absolute configuration of the starting *trans*-ester XXXI is retained in both the *anti* (XXXIII) and the *syn* (XXXII) products.

These are most interesting observations which demand for their explanation either a concerted, symmetry allowed $2_s + 2_a$ rearrangement⁴⁰ or a trimethylenemethane of the orthogonal type shown below (XXXIV). Here three of the carbon atoms are joined



in allylic array while the fourth, designated the pivot,³⁸ is perpendicular to them. Doering and Roth have noted that the energetics of this reaction may be satisfactorily explained without the intervention of concert. They have also suggested a mode of attack which promises to distinguish between the two alternatives. One awaits the outcome of these experiments with great interest.

In addition to the results cited above dealing directly with the possible configurations of trimethylenemethane during the course of its rearrangement, numerous studies provide further examples of the methylenecyclopropane rearrangement.⁴¹ Many of these have been interpreted in terms of nonplanar intermediates such as that discussed above or as concerted reactions. All of the systems examined thus far are sterically encumbered to some extent. Thus it is possible to state *a priori* that the mode of rearrangement discussed immediately

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(33) N. J. Turro, and W. B. Hammond, *Tetrahedron*, **34**, 6017 (1968). See also N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

(34) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, **90**, 1072 (1968).

(35) J. P. Chesick, *ibid.*, **85**, 2720 (1963).

(36) M. G. Ettliger, *ibid.*, **74**, 5805 (1952).

(37) E. F. Ullman, *ibid.*, **82**, 505 (1960).

(38) W. von E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970).

(39) J. J. Gajewski, *J. Amer. Chem. Soc.*, **90**, 7178 (1968).

(40) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, GmBH, Weinheim/Bergstr, 1970, p 121.

