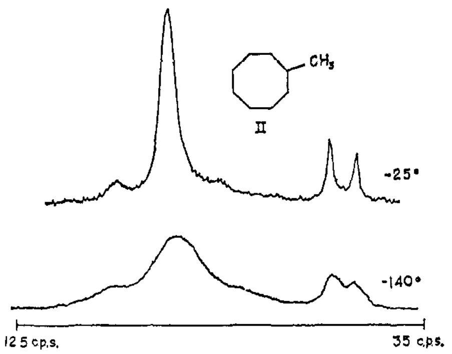

Figure 1. Proton nmr spectra (60 Mcps) of II, at various temperatures. The scale is in cycles per second downfield from tetramethylsilane.

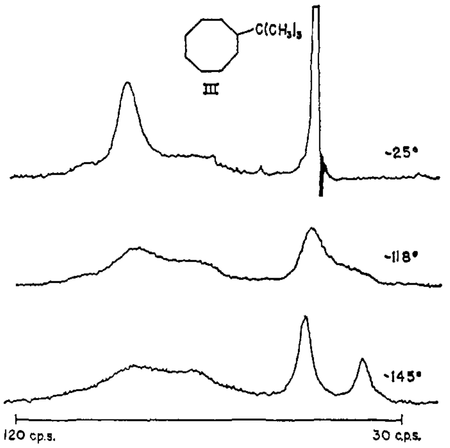

Figure 2. Proton nmr spectra (60 Mcps) of III at various temperatures. The scale is in cycles per second downfield from tetramethylsilane.

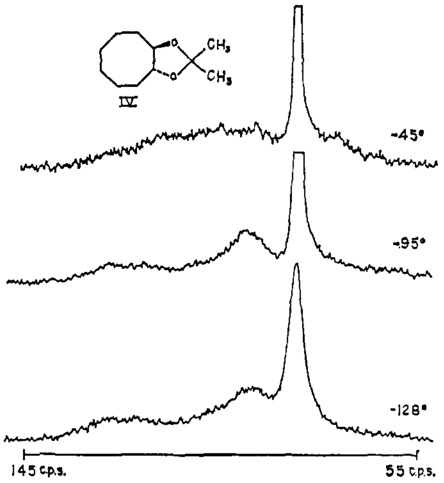

Figure 3. Proton nmr spectra (60 Mcps) of IV at various temperatures. The scale is in cycles per second downfield from tetramethylsilane.

the others are then "axial." The eight "equatorial" bonds are shown in V.

The pseudo-rotation or wagging process mentioned above results in the formation of two sets of bonds: let set A be [1e, 2e, 3e, 4a, 5a, 6a, 7e, 8e]; then set B is [1a, 2a, 3a, 4e, 5e, 6e, 7a, 8a]. Only ring inversion will mix set A with set B. A large group can be accommodated in set A (positions 1e, 2e, 3e, 7e, or 8e) or in set B (positions 4e, 5e, or 6e). Therefore, the low-temperature nmr spectrum of an alkylcyclooctane should show two conformational isomers, even if the sole ring conformation is the boat-chair. Also it is possible to have two equatorial substituents on adjacent carbon atoms in either set A or set B, and therefore *trans* fusion to another ring also allows two conformational isomers to be present. It can also be seen that conversion of a group from set A to set B and *vice versa* is analogous to ring inversion in cyclooctane itself, except that it should lead, at high temperatures, to a relatively narrow band for the methylene protons instead of a single sharp line as with cyclooctane.[7]

Thus, the present evidence points to the boat-chair as the major conformation in cyclooctane and monosubstituted cyclooctanes. The assignment[8] of configurations to the 5-*t*-butylcyclooctanols, made on the basis of a crown conformation, is therefore not convincing, but it is not easy to predict the relative proportions of boat-chair and crown forms for these compounds. Further work on the conformations of eight-membered rings is in progress.

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[7] A mechanism for inversion which is satisfactory for II, III, and IV, as well as for cyclooctane itself, involves stretching out C_8 and C_7 in V to give a centrosymmetrical ring "conformation" (conformation V in ref 5a) as a transition state.

[8] N. L. Allinger and S. Greenberg, *J. Am. Chem. Soc.*, **84**, 2394 (1962).

[9] Holder of a National Research Council of Canada scholarship.

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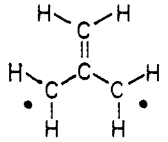
Trimethylenemethane

Sir:

Trimethylenemethane (I) is important in theoretical chemistry by virtue of the fact that the central carbon atom of this molecule attains the maximum π bond order possible for any carbon atom.[1] The magnitude of the bond order thus obtained (4.732) is the base for numerous calculations of free valence indexes of carbon compounds. In addition, this molecule has been used as a model in theoretical calculations of negative spin density in triplet states[2] and in a comparison of different methods useful in theoretical calculations of the energies of π systems.[3]



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[1] (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. Am. Chem. Soc.*, **74**, 4579 (1952); (d) H. H. Greenwood, *Trans. Faraday Soc.*, **48**, 677 (1952); (e) J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, Inc., New York, N. Y., 1961, p 56; (f) A. Streitwieser Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 43, 57.

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[3] D. P. Chong and J. W. Linnett, *ibid.*, **8**, 541 (1964).

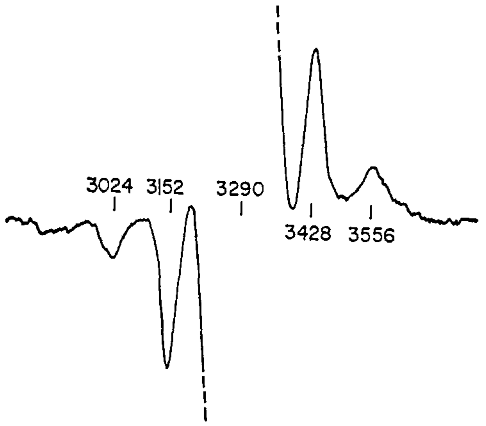


Figure 1. Esr spectrum of trimethylenemethane in hexafluorobenzene. The base line of this spectrum has been corrected for slight nonlinearity.

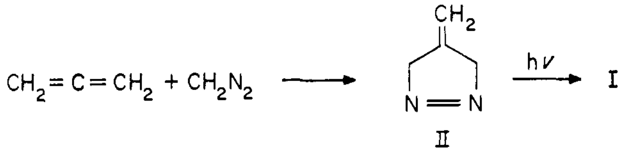
Derivatives of trimethylenemethane are implicated as possible intermediates in both rearrangement[4] and formation[5] of methylenecyclopropanes.

Trimethylenemethane is predicted by theory[1,6] to be a ground-state triplet. Thus, one should be able to detect this triskelion molecule and study its properties using electron spin resonance spectroscopy.[7] In addition to being an attempt to confirm an important prediction of the theory, such an experiment is made even more attractive because of the close structural relationship between trimethylenemethane and its oxygen analogs which have been discussed in connection with the photolyses of cyclobutanediones[8] and in connection with the Favorskii rearrangement.[9] That is, it was felt that if one could find means of producing and detecting trimethylenemethane, then the problem of testing the cyclopropanone diradical hypothesis might be somewhat simplified.

The following experiments leading to a new detectable intermediate in organic chemistry have been performed. Photolysis of dilute hexafluorobenzene or perfluoromethylcyclohexane solutions[10] of 4-methylene-Δ^1-pyrazoline (II) at −185° for 24 hr with light of wavelength 315–335 mμ yielded the esr spectrum shown in Figure 1. Peaks are found at 3024, 3152, 3428, and 3556 gauss, with, in addition, a strong monoradical absorption at 3290 gauss ($g = 2$). It is assumed, since this spectrum can be fitted to a Hamiltonian, that the spectrum is due to the presence of a triplet-state species. The zero-field parameters are readily derived from the spectrum:[11] $D = 0.024$ cm^{-1} and $E < 0.001$ cm^{-1}. This result definitely implies that the triplet has a threefold (or higher) axis of symmetry. The spectrum is stable for a period of a month after the termination of irradiation, as long as the temperature of the sample is maintained at the boiling point of liquid nitrogen. If the temperature is raised to −150°, the peaks due to the triplet disappear immediately and irreversibly. The stability of the spectrum at liquid nitrogen temperature strongly implies that one is dealing with a ground-state triplet.

If one assumes a carbon–carbon bond length of 1.427 A[12] it may be calculated using Hückel molecular orbitals that for trimethylenemethane $D = 0.057$ cm^{-1}. The discrepancy between the Hückel value and the value found is, almost certainly, due to negative spin density on the central carbon atom.[2] When allowance is made for negative spin density as, for example, in the calculations of McLachlan,[2] the result is $D = 0.037$ cm^{-1}. The valence bond method seems to overestimate the contribution of negative spin density to D.[13] Using this approach McConnell[2] has calculated $D \cong 0$ for trimethylenemethane.[14] It is important to note that even the simple Hückel calculation gives a result which is in fair agreement with the value found. These results constitute the first direct physical evidence for the existence of such a 1,3 diradical.[15] Experiments to trap this reactive species chemically are currently in progress.

The parent 4-methylene-Δ^1-pyrazoline was prepared by the reaction of diazomethane with allene.[16] This reaction was carried out in a sealed tube using dry allene as solvent. The reaction is complete after 24 hr at room temperature. The product pyrazoline II is sensitive to water, heat, and light and oxygen; it is most easily handled on a vacuum line.[17]



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(12) This number corresponds roughly to that which one would estimate from the bond order–bond length plot given in ref 1e, p 55.

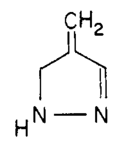
(13) *Cf.* E. Wasserman, *J. Chem. Phys.*, **42**, 3739 (1965).

(14) The author wishes to thank Professor Martin Karplus for the Hückel calculation of D, for the values of the integrals which are necessary in the evaluation of McLachlan's results, and for very helpful conversations on the interpretation of the magnitude of the zero-field splitting constant D.

(15) N. C. Yang and A. J. Castro, *J. Am. Chem. Soc.*, **82**, 6208 (1960), have reported a highly conjugated, stable derivative of trimethylenemethane obtained by oxidation of the quinone methide derived from tris(3,5-di-*t*-butyl-4-hydroxyphenyl)methane. The esr spectrum of this diradical has been reported by R. Kreilich, *J. Chem. Phys.*, **43**, 308 (1965).

(16) I. A. D'yakanov, *Zh. Obsch. Khim.*, **15**, 473 (1945); *Chem. Abstr.*, **40**, 4718^4 (1946).

(17) If the allene is not properly dried (passage through P_2O_5) and if the product II is allowed to stand at room temperature for any appreciable length of time, the result is isomerization to a complex mixture of products of which the chief component appears to be 4-methylene-Δ^2-pyrazoline (i). The nmr spectrum of this conjugated isomer shows a one-proton vinyl singlet at τ 3.0, a one-proton vinyl methylene triplet (J = 4 cps) at τ 4.95, a one-proton vinyl methylene triplet (J = 4 cps) at τ 5.05, and a two-proton aliphatic methylene triplet (J = 4 cps) at τ 6.0. The ultraviolet spectrum of the mixture shows λ_{max} 289 mμ (ε 2100) in cyclohexane. Compound i has not been isolated in pure form.



i

The structure of the adduct II of allene and diazomethane, heretofore not known, was established by its nmr spectrum (neat): two-proton vinyl methylene quintuplet (J = 2.1 cps) at τ 4.95 and four-proton aliphatic triplet (J = 2.1 cps) at τ 5.15; its ultraviolet spectrum: $\lambda_{\max}^{n\text{-hexane}}$ 324 mμ (ϵ 500) and 329 mμ (ϵ 500); and its mass spectrum: exact mass of molecular ion found, 82.0530; calcd for $C_4H_6N_2$, 82.0531. Furthermore, treatment of the methylenepyrazoline II with Pd–C in ethyl acetate in the presence of hydrogen yielded 4-methylpyrazole (70%) identical in all respects with an authentic sample.[18] The 4-methylpyrazole is easily distinguished from 3-methylpyrazole by nmr. No trace of the latter could be detected in the total crude Pd–C isomerization reaction product. It follows that the reaction of diazomethane with allene is completely orientation specific, showing that the addition of 1,3-dipoles to allene proceeds in the same sense as do ionic reagents such as hydrogen bromide.[19] This result is of considerable general interest.

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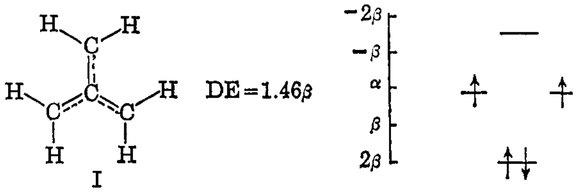
Received April 18, 1966

Evidence for Trimethylenemethane as an Intermediate in a Pyrolysis Reaction

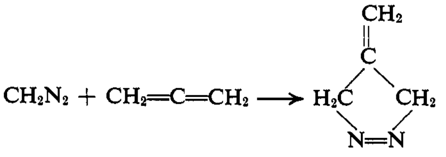
Sir:

Trimethylenemethane (I), a species for which Hückel molecular orbital calculations[1] predict a triplet ground electronic state, has been the subject of mechanistic speculation.[2] We have thus undertaken a study of the pyrolysis of 4-methylene-1-pyrazoline (II) as a source of this species.



I

Addition of allene to an ethereal solution of diazomethane, free from acid or base, in a Teflon-lined cylinder gives, after 18 hr, a product, $C_4H_6N_2$, bp 48° (33 mm), $n^{27}D$ 1.4714, $\lambda_{\max}$ 322 mμ (ϵ 490, C_2H_5OH),[3] the nmr spectrum of which shows a quintet at τ 4.87 (J = 2.6 cps) and a triplet at τ 5.12 (J = 2.6 cps) of integrated areas 1:2, consistent with the structure 4-methylene-1-pyrazoline (II).



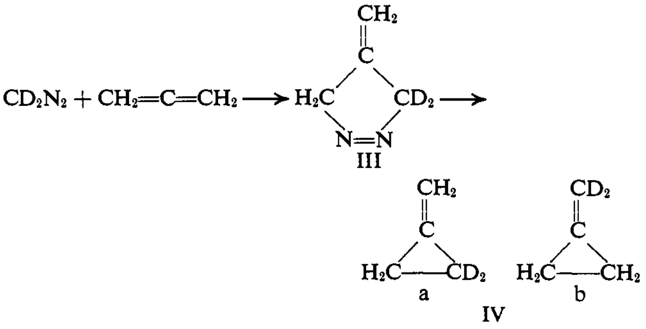
II

Table I. Kinetics of Pyrolysis of 4-Methylene-1-pyrazoline (II)

Expt	Temp, °C	10^4k, sec^{-1}	
1	165.3	9.84 ± 0.09	E_a = 32.6 ± 0.2 kcal mole^{-1}
2	170.3	15.0 ± 0.1	
3	176.5	25.0 ± 0.2	ΔS^* = −1.1 ± 0.5 eu
4	184.9	49.4 ± 0.5	
5	187.9	61.7 ± 0.6	

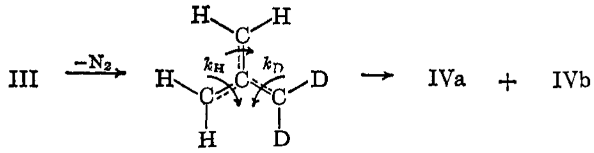
Gas-phase pyrolysis[4] (100–200 mm) data allowed the calculation of the first-order rate constants and activation parameters indicated in Table I. The pyrazoline was quantitatively converted to a single hydrocarbon, C_4H_6, having physical properties, boiling point, infrared, nmr, and mass spectra identical with those of methylenecyclopropane. The activation energy for the pyrolysis of II on comparison with 1-pyrazoline (E_a = 42.2, ΔS^* = + 11.2 eu)[4] is seen to be lower by 9.6 kcal mole^{-1}; most noticeable is the decrease in ΔS^* for the 4-methylene-1-pyrazoline, consistent with the lower probability of formation of the triplet species.[5]

To check that a symmetrical intermediate was involved in the reaction we prepared 4-methylene-1-pyrazoline-3,3-d_2 (III) by the addition of diazomethane-d_2 to allene. Such a species would *a priori* be expected to produce methylenecyclopropane with two-thirds of the deuterium in the ring and one-third at the vinyl position. Integration of the nmr spectrum of the mixture (IVa and IVb) would thus give a 2.00:1.00 ratio of ring to vinyl protons. The value observed upon pyrolysis at 175° was (2.37 ± 0.04):1.00, indicating a nonstatistical mixture of isomers (equivalent to 59.3 ± 0.7% IVa and 40.7 ± 0.7% IVb). Thus there must be a mechanistic reason for the preference of the dideuteriomethylene for the *exo* position.



Two reasons come to mind: in mechanism A that the symmetrical species has been produced, but by virtue of secondary isotope effect in the product-determining step the dideuteriomethylene group is slower to rotate into the ring conformation than are the diprotiomethylene groups. If we partition the formation of the product into rate constants k_H and k_D,

Mechanism A



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