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.

(18) K. von Auwers and E. Cauer, *J. Prakt. Chem.*, **126**, 166 (1930).
(19) A. A. Petrov and A. V. Fedorova, *Russ. Chem. Rev.*, **33**, 1 (1964).

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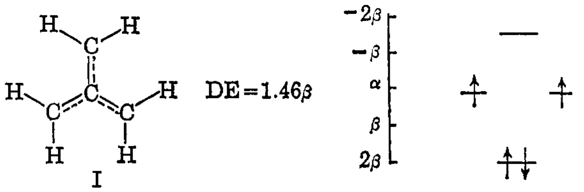
Evidence for Trimethylenemethane as an Intermediate in a Pyrolysis Reaction

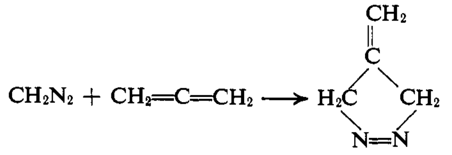
Sir:

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).



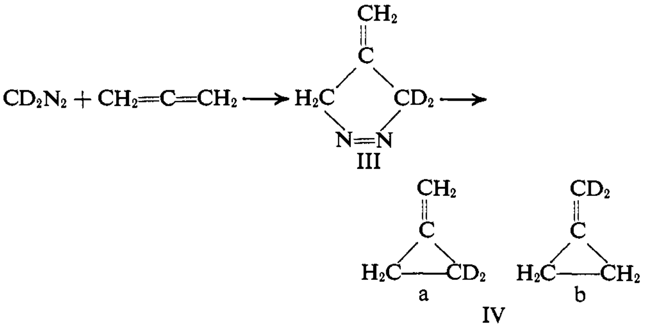
II

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	$E_a = 32.6 \pm 0.2$ kcal mole^{-1}
2	170.3	15.0 ± 0.1	
3	176.5	25.0 ± 0.2	$\Delta S^* = -1.1 \pm 0.5$ 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]

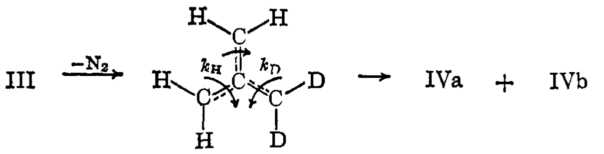
To check that a symmetrical intermediate was involved in the reaction we prepared 4-methylene-1-pyrazoline-3,3-d_2 (III) by the addition of diazomethane-d_2 to allene. Such a species would *a priori* be expected to produce methylenecyclopropane with two-thirds of the deuterium in the ring and one-third 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.



IV

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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(1) A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. I, Pergamon Press, Oxford, 1965, p 1; J. D. Roberts, "Molecular Orbital Calculations," W. A. Benjamin Inc., New York, N. Y., 1962, pp 56–58.

(2) (a) J. P. Chesick, *J. Am. Chem. Soc.*, **85**, 2720 (1963); (b) H. M. Frey, *Trans. Faraday Soc.*, **57**, 951 (1961).

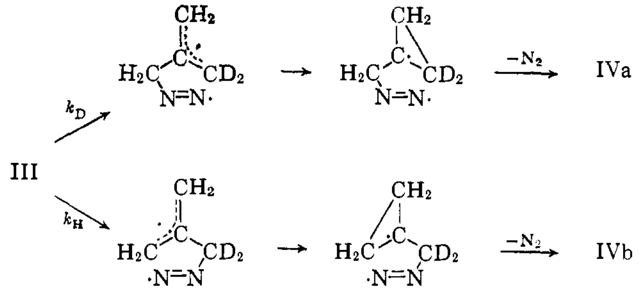
(3) A. D'Yakonov, *J. Gen. Chem. USSR*, 473 (1945); *Chem. Abstr.*, **40**, 4718 (1946).

(4) R. J. Crawford, R. J. Dummel, and A. Mishra, *J. Am. Chem. Soc.*, **87**, 3023 (1965).

(5) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co. Inc., New York, N. Y., 1960, p 256.

then a k_H/k_D value of 1.37 ± 0.05 is derived from the values observed in the above experiment. Mechanism B consists of the breaking of carbon–nitrogen bonds in an unsymmetrical fashion and of a secondary kinetic isotope effect of 1.47 ± 0.06, resulting in the observed ratio of IVa to IVb.[6]

Mechanism B



A decision between these two mechanisms is possible on the basis of the nmr ring to vinyl ratio of the isomer mixture resulting from pyrolysis of 4-methylene-1-pyrazoline-3,3,6,6-d_4 (V) prepared by the addition of diazomethane to allene-d_4. Using the above values for mechanisms A and B, the predicted percentages of VIa and VIb were calculated and are shown in Table II. The observed value from pyrolysis at 175° is such as to confirm mechanism A, the observation of trimethylenemethane as an intermediate.

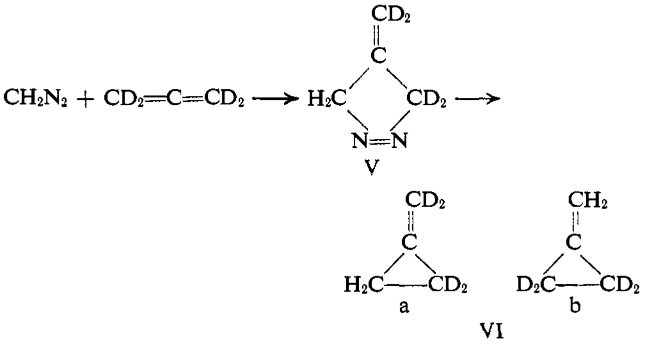


Table II

Predicted	R^a	VIa, %	VIb, %
Mechanism A	2.73	73.2 ± 2.0	26.8 ± 2.0
Mechanism B	1.47	59.3 ± 2.0	40.7 ± 2.0
Observed	2.82^b ± 0.10	73.8 ± 0.8	26.2 ± 0.8

[a] R = ratio of integrated areas of the ring to vinyl protons.
[b] Result of four measurements taken at different times and checked with a pure sample of methylenecyclopropane, R = 2.01 ± 0.03.

The value of k_H/k_D for rotation about the symmetry axis of I is such that $\Delta\Delta F^* = 286$ cal mole^{-1} and is larger in magnitude than most secondary isotope effects. An important contribution may arise from the ponderal effect of the deuterium as the CD₂ group will have twice the moment of inertia of the CH₂ group. Further attempts to observe the intermediate spectroscopically are currently under investigation.

Acknowledgement. The authors are grateful to the Petroleum Research Fund of the American Chemical Society (Grant 1770-A4) and to the National Research Council of Canada for support of this work.

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(6) S. Seltzer and F. T. Dunne, *J. Am. Chem. Soc.*, 87, 2628 (1965).

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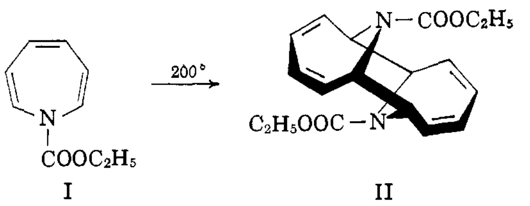
The Thermal Dimerization of N-Carbethoxyazepine[1]

Sir:

As part of our broad interest in the ground-state[2] and electronically excited-state[3] behavior of medium-sized unsaturated heterocycles, we have investigated the thermal behavior of N-carbethoxyazepine (I) and wish to describe the unusual mode of self-condensation which occurs under these conditions.

When I[4] was heated in a sealed tube for 5–10 min at 200°, there resulted in 75% yield a highly crystalline white solid, mp 196–197°,[5] $\lambda_{\max}^{\mathrm{EtOH}}$ 232 (ϵ 14,100) and 237.5 mμ (ϵ 14,800). The dimeric nature of the latter substance was apparent from its mass spectrum which displayed a molecular ion peak at *m/e* 330. The nmr spectrum of this dimer (in CDCl₃) was suggestive of a highly symmetrical species [two completely superimposable ethoxy groups at δ 4.08 (4 H, quartet, J = 7.5 cps, $-O-CH_2-$) and 1.29 (6 H, triplet, J = 7.5 cps, CH_3-), a pseudo-singlet absorption for the vinyl protons[6] at δ 5.88, and a broad doublet (4 H, J = 8.5 cps) for the bridgehead protons], and was fully compatible with structure II. This formulation (II) was corroborated further by its dipole moment (0.91 D., in dioxane) and by its Raman spectrum which displayed an intense band near 1620 cm^{-1} which was strongly depolarized by a parallel filter, thereby implicating a symmetrical diene vibration. Further, II has been correlated chemically with a dimer of N-cyanoazepine of similar structure.[7]



Catalytic hydrogenation of II (Adams catalyst, 740 mm) proceeded with the uptake of 4 equiv of hydrogen to give IIIa, mp 87–88°,[5] which with lithium aluminum hydride in dioxane afforded IIIb, mp 148–150°.[5] Diamine IIIc, mp 60–61° (sealed tube),[5] resulted from the

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(1) Unsaturated Heterocyclic Systems. XXV. For paper XXIV of this series, refer to L. A. Paquette and J. H. Barrett, *J. Am. Chem. Soc.*, **88**, 1718 (1966).

(2) For a review of certain aspects of this work, see L. A. Paquette, *Proc. N. Y. Acad. Sci. U.S.*, **28**, 387 (1966).

(3) See particularly footnote 9 of ref 1.

(4) R. J. Cotter and W. F. Beach, *J. Org. Chem.*, **29**, 751 (1964).

(5) Satisfactory analyses were obtained for all new compounds described.

(6) The appearance of a group of vinyl protons, which *a priori* would be expected intuitively to possess differing chemical shifts, as a simple pseudo-singlet nmr absorption is not unique to II, but has been reported for a number of polyunsaturated cyclic systems such as 1,3,5-cyclooctatriene [W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain, and R. B. Williams, *J. Am. Chem. Soc.*, 78, 5448 (1956)] and the cyclooctatetraene dimer mp 53° [G. Schröder and W. Martin, *Angew. Chem. Intern. Ed. Engl.*, 5, 130 (1966)].

(7) A. L. Johnson and H. E. Simmons, *J. Am. Chem. Soc.*, **88**, 2591 (1966).