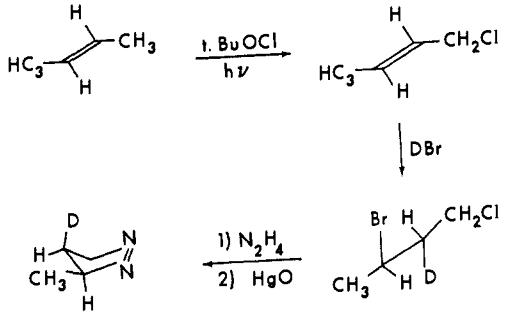
resulting pyrazolidine with mercuric oxide,[6] produced a pyrazoline whose nmr spectrum (100 MHz) lacked the proton at τ 9.01. This signal was previously assigned[5] to the hydrogen on C_4 *cis* to the methyl group. The over-all sequence is indicated in Scheme I. The *trans* isomer IV was similarly produced from *cis*-2-butene and lacked the proton signal at τ 7.92.

Scheme I



The pyrazolines III and IV were pyrolyzed in a conditioned stainless-steel reactor at 218.0°[7] using an initial pressure of 100 torr. The hydrocarbon products were then separated by preparative gas chromatography.[8] Careful integration of the nmr spectrum of each of the olefins produced the data in Table II and allows one to calculate the mole per cent N_a of olefin produced by hydrogen migration *vs.* that produced by deuterium migration, N_b.

Table II. Nmr Analysis of Olefins Produced (Solvent $CDCl_3$)

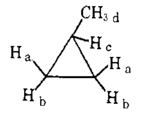
Source		1-Butene	*cis*-2-Butene	*trans*-2-Butene
III	R^a	0.80 ± 0.02	4.4 ± 0.4	4.1 ± 0.5[c]
	% N_a	78	72	63
	% N_b	22	28	37
	k_H/k_D	3.5 ± 1.0	2.7 ± 1.0	1.7 ± 0.6
IV	R^a	0.78 ± 0.02	4.1 ± 0.4[b]	4.2 ± 0.4[b]
	% N_a	75	63	65
	% N_b	25	37	35
	k_H/k_D	3.0 ± 0.6	1.7 ± 0.6	1.9 ± 0.6

[a] *R* is the ratio of integrated areas of allylic to vinyl protons. [b] An impurity in the deuteriochloroform at τ 8.45 prevented a more accurate integration of the methyl signal. [c] Spectra run in carbon tetrachloride.

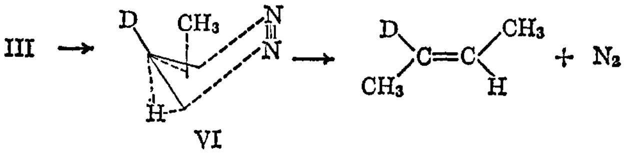
The nmr spectrum of methylcyclopropane in chloroform is as indicated in Table III. Integration of the spectrum of samples of methylcyclopropane derived from III and IV indicated an equimolar mixture of *cis*- and *trans*-2-deuteriomethylcyclopropane.

The data in Tables I–III are entirely consistent with the intermediate V and do not allow for the possibility of a concerted migration of only that hydrogen transoid to the departing nitrogen as in VI. McGreer[9] has recently demonstrated such a participation in the pyrolysis of 3-carbomethoxy-4-alkylpyrazolines, thus demonstrating the existence of a different mechanism when electron-withdrawing groups are present on C_3.

Table III. Nmr Analysis of Methylcyclopropane in $CDCl_3$ at 100 MHz ($CHCl_3$ Used as Internal Standard)

	Proton	τ	Known	Integrated areas[a] From III	Integrated areas[a] From IV
	H_a	10.06	2.00	1.51	1.51
	H_b	9.60	2.02	1.49	1.49
	H_c	9.35	0.99	1.00	1.01
	H_d	9.02	3.00	3.00	3.00

[a] $J_{ab}(gem)$ = 2.5 Hz; J_{ac} = 4.0 Hz; J_{bc} = 7.5 Hz; J_{cd} = 6.5 Hz. Integration accuracy ±2%.



VI

Acknowledgment. The authors are grateful to the Petroleum Research Fund of the American Chemical Society and to the National Research Council of Canada for support of this work. They are also grateful to Professor D. E. McGreer for a preprint of ref 9 prior to publication.

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[6] R. J. Crawford, A. Mishra, and R. J. Dummel, *J. Am. Chem. Soc.*, **88**, 3959 (1966).

[7] Rate constants for III and IV compared with I yield k_H/k_D values of 1.07 ± 0.04 and 1.05 ± 0.04, respectively.[1]

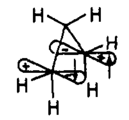
[8] A 20-ft silver nitrate and propanediol column was used to separate the methylcyclopropane and *trans*-2-butene from the *cis*-2-butene and 1-butene. A 20-ft dimethylsulfolane on Chromosorb WAW column, cooled to −25°, was used to separate the latter two hydrocarbons.

[9] D. E. McGreer and W-S. Wu, *Can. J. Chem.*, **45**, 461 (1967).

Thermolysis of *cis*- and *trans*-3,4-Dimethyl-1-pyrazoline

Sir:

Previous studies of the thermolysis of alkyl- and vinyl-1-pyrazolines have demonstrated the existence of a nitrogen-free intermediate which is capable of conversion to alkenes and cyclopropanes.[1] This intermediate, most probably an antisymmetric singlet having the geometry I,[2] has the same stoichiometry and spin state as a possible adduct of singlet methylene to ethylene.[3]



I

The most thoroughly studied example of singlet methylene addition to an olefin is that using *cis*- and *trans*-2-butene as a substrate.[4] This has lead to the speculation that the two carbon–carbon bonds are formed

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[1] (a) R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **88**, 3963 (1966); (b) R. J. Crawford and G. Erickson, *ibid.*, **89**, 3907 (1967); (c) R. J. Crawford and D. M. Cameron, *Can. J. Chem.*, **45**, 691 (1967).

[2] R. Hoffmann, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Paper 109K.

[3] For an excellent discussion of this problem see (a) P. Gasper and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, Inc., New York, N. Y., 1964, p 235; and (b) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964).

[4] F. A. L. Anet, R. F. W. Bader, and A. Van der Auwera, *J. Am. Chem. Soc.*, **82**, 3217 (1960); H. M. Frey, *ibid.*, **82**, 5947 (1960); D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962); R. F. W. Bader and J. I. Generosa, *ibid.*, **43**, 1631 (1965).

simultaneously.[3,5] We have undertaken a study of the pyrolysis of *cis*- and *trans*-3,4-dimethyl-1-pyrazoline (II, III) in an attempt to see whether or not the singlet species, like I, derived from these compounds may be playing a role in the singlet methylene addition process.

The pyrazolines II and III were prepared by the cycloaddition of diazomethane to *cis*- and *trans*-2-butene. In a typical run a solution of 6 g of diazomethane in 150 ml of ether was added, at −10°, to 25 ml of dry *cis*-2-butene in a pressure vessel. After 1 week at room temperature the solution was fractionally distilled to give 6 g of II, bp 32° (4 mm), $n^{25}\text{D}$ 1.4320. The nuclear magnetic resonance spectrum of II (and III) at 100 MHz was consistent with the stereospecific cycloaddition, as demonstrated earlier by other olefin cycloadditions.[6] The addition to *trans*-2-butene required 10 days[7] and resulted in a product, bp 31.5° (4 mm), $n^{25}\text{D}$ 1.4286. Dideuteriodiazomethane was used to prepare *cis*- and *trans*-3,4-dimethyl-1-pyrazoline-5,5-d_2 (II-d_2 and III-d_2).

The kinetics of the thermolysis reaction are described in Table I and indicate that the thermolysis of II and III proceeds with an activation energy similar to those of previously studied pyrazolines.[1] The secondary kinetic isotope effects observed imply that the primary carbon to nitrogen bond is also breaking in the rate-determining step.[1c,8] The products produced by thermolysis of II and III and their proportions are indicated in Table II. We judge from Table II and the data in the next paragraph that the thermolysis *is not* stereospecific and that the intermediates IV and V produced *are not* on the reaction coordinate in the singlet methylene addition to *cis*- and *trans*-2-butene.[8a]

Table I. Kinetic Parameters at 100 Torr

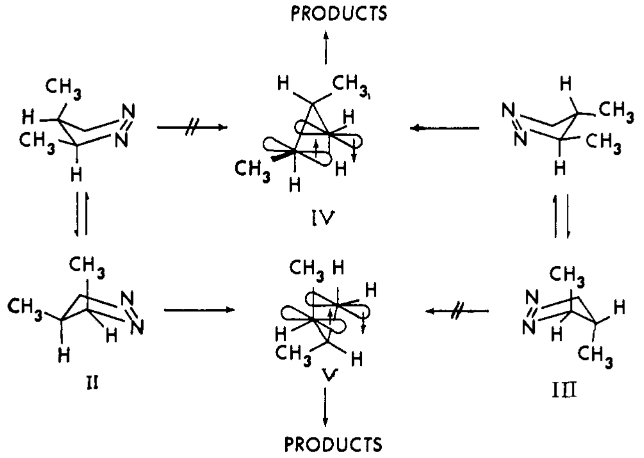
	Temp, °C ±0.1°	10^4K, sec^{-1}	
II (*cis*)	210.4	5.30[a]	$E_a = 39.0 \pm 0.6$
	220.9	12.	$\log A = 14.23 \pm 0.50$
	229.8	27.9	
II-d_2	220.9	10.8	$k_H/k_D = 1.19 \pm 0.05$
III (*trans*)	210.4	4.05	
	220.9	9.66	$E_a = 41.3 \pm 0.3$
	229.8	20.4	$\log A = 15.36 \pm 0.15$
III-d_2	220.9	8.02	$k_H/k_D = 1.21 \pm 0.05$

[a] The rate constants are accurate to about ±2%.

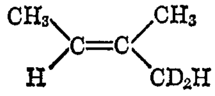
Table II. Products of Thermolysis of II and III

	II,[a] %	III, %
cis-Dimethylcyclopropane[b]	45.4 ± 0.1[c]	46.0 ± 0.5
trans-Dimethylcyclopropane	33.0 ± 0.6	21.8 ± 0.3
2-Methyl-2-butene	14.3 ± 0.3	16.3 ± 0.3
2-Methyl-1-butene	7.2 ± 0.4	15.8 ± 0.2

[a] Errors expressed as standard deviations from three runs. [b] The products were identified by collecting each peak and obtaining its nmr spectrum. [c] Analysis carried out using a 10-ft 20% dimethylsulfolane on Chromosorb W column in tandem with a 24-ft silver nitrate–propylene glycol on Chromosorb Column.

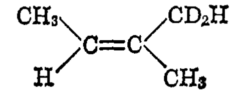


If the thermolyses of II and III produce intermediates of the type I, then two discrete intermediates[1] IV and V may be produced from each, depending upon which conformation is preferred in the transition state. Upon thermolysis II-d_2 would produce *trans*-2-methyl-2-butene-1,1-d_2 (VI) *via* the intermediate IV and *cis*-2-methyl-2-butene-1,1-d_2 (VII) *via* V. Similarly, III-d_2 would produce VI or VII depending upon the preferred conformation in the transition state. The 100-MHz nmr spectrum of 2-methyl-2-butene indicates a doublet at τ 8.53 strongly coupled to the olefinic proton and singlets at τ 8.49 and 8.39. The assignment of the latter two peaks was made by using the stereospecific synthesis of *cis*-2-methyl-2-butene-1,1,3-d_4 from 2-butanone-1,1,1,3,3-d_5 by Cornforth's elegant method.[9] Thus the methyl group *cis* to the hydrogen on C_3 was found to be the one at lowest field. Careful integration of the nmr spectrum of 2-methyl-2-butene-d_2 indicated that the olefin derived from II-d_2 was greater than 94% VII and that III-d_2 produced 2-methyl-2-butene of greater than 96% VI. This is consistent with the suggestion that the second methyl group at C_4 in 4,4-dimethyl-1-pyrazoline leads to steric crowding in the rate-determining transition state.[10]



$$(CH_3)HC{=}C(CH_3)(CD_2H)$$

VI



$$(CH_3)HC{=}C(CD_2H)(CH_3)$$

VII

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(5) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956); P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956).

(6) For an excellent review of cycloadditions see R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, p 739.

(7) Satisfactory mass, infrared, and ultraviolet spectral data were obtained for all new compounds mentioned herein.

(8) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 2625 (1961); S. Seltzer and F. T. Dunne, *ibid.*, **87**, 2628 (1965).

(8a) Note Added in Proof. Professor Roald Hoffman has recently sent us a preprint of a paper dealing with trimethylene and the addition of methylene to ethylene, wherein he comes to the same conclusions from extended Hückel MO calculations. These calculations also indicate that the geometry I for the trimethylene intermediate is the only minimum on the potential surface other than cyclopropane.

(9) J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 112 (1959).

(10) R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **87**, 3768 (1965).