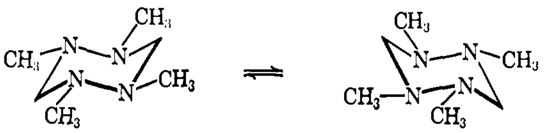
Table I. Spectral Parameters of N,N′,N″,N‴-Tetramethylhexahydrotetrazine in Cyclopropane Solution

	NCH_2N group	NCH_3 group
Chemical shift,[a] 37°	3.25	2.20
Chemical shift,[a] −87°	2.85	1.95
	3.52	2.36
Relative chemical shift,[b] −87°	40.3	24.3
Geminal coupling constant,[b] −87°	11.6	
Coalescence temperature, deg	−24	−35
Free energy of activation at coalescence temperature, kcal/mole	11.8	11.6

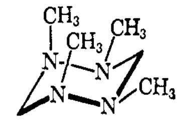
[a] From protons of the cyclopropane used as solvent; in parts per million. [b] In hertz.

methyl groups (see Table I for a summary of the spectral data). The nonequivalence observed for the ring methylenes is indicative of slow ring inversion, for which somewhat similar examples have recently been reported with several six-membered rings containing N-methyl groups.[3] The 1:1 doublet obtained for the N-methyl groups rules out the possibility that **1** exists as a mixture of conformations **2** and **3** with equivalent equatorial methyl groups which are interconverted rapidly at room temperature and slowly at −87° by a ring inversion and four nitrogen inversions.



2 **3**

To account for the two equally intense N-methyl resonances, a conformation with two axial N-methyl groups and two equatorial methyl groups is required, and **4**, **5**, and **6** are the possibilities. It is likely that



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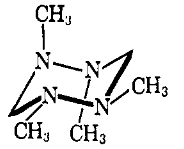

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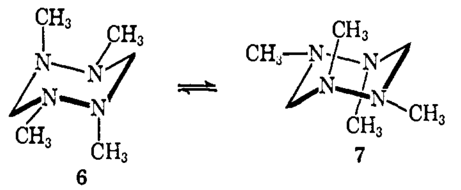
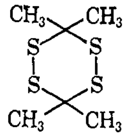


6 **7**

4 can be excluded because of the substantial 1,3 interaction between its axial methyl groups. A decision as to whether **5** or **6** is more favorable is less simple, but it seems reasonable to choose **6** on the basis that **6** has identical interaction between the members of each pair of vicinal N-methyl groups. Other grounds for favoring **6** over **5** will be presented elsewhere—the important point is that the unusual features of the low-temperature pmr spectrum of **1** to which we call attention here are independent of the choice between **5** and **6**.

An alternate conformation of a different kind is a boat-type arrangement which Bushweller[4] has recently reported to be important for duplodithioacetone (**8**). However, the mobility of boat-type conformations in the absence of bridging groups is likely to be much too great to permit observation of two kinds of methylene hydrogens and two kinds of methyl groups for **1** at −87°.



8

For **6**, inversion of each of the four nitrogens gives conformation **7**, in which the axial and equatorial methyl groups have been interchanged but not the axial and equatorial methylene hydrogens. Clearly, observation of two N-methyl resonances at −87° means that the **6** $\rightleftharpoons$ **7** equilibration which results by nitrogen inversion must also be slow at this temperature. Occurrence of slow nitrogen inversion in simple six-membered rings has only been reported previously for 4,4-difluoropiperidine[5] and in acid solutions.[6]

The free energies of activation corresponding to the coalescence points of the methyl and methylene signals are both about 11.7 kcal/mole. The methylene hydrogens only become equivalent on the nmr time scale when ring inversion is fast, so that the barrier to ring inversion is 11.7 kcal/mole. The N-methyl resonances are expected to coalesce when either ring inversion or nitrogen inversion is fast, so that the barrier to nitrogen inversion must be greater than or equal to 11.7 kcal/mole.

In summary, **1** is remarkable because two of its methyl groups prefer to occupy axial positions and because nitrogen inversion is relatively slow.

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[3] (a) N-Methylpiperidine: J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *J. Am. Chem. Soc.*, 89, 3761 (1967); (b) N,N′-dimethylpiperazine: R. K. Harris and R. A. Spragg, *Chem. Commun.*, 314 (1966); (c) N,N′-dimethylhexahydropyrimidine: F. G. Riddell, *J. Chem. Soc.*, *B*, 560 (1967); (d) N,N′-dimethylpiperidazine: J. E. Anderson and J. M. Lehn, *Bull. Soc. Chim. France*, 2402 (1966); (e) N,N′,N″-trimethylhexahydrotriazine: J. M. Lehn, F. G. Riddell, B. J. Price, and I. O. Sutherland, *J. Chem. Soc.*, *B*, 387 (1967).

[4] C. H. Bushweller, *J. Am. Chem. Soc.*, 89, 5978 (1967).

[5] G. A. Yousif and J. D. Roberts, submitted for publication.

[6] See the very recent work of J. J. Delpuech and M. N. Deschamps, *Chem. Commun.*, 1188 (1967), and J. L. Sudmeier and G. Occupati, *J. Am. Chem. Soc.*, 90, 154 (1968). Some analogy to the present results can be found in bridged diaza ring systems; see J. E. Anderson and J. M. Lehn, *ibid.*, 89, 81 (1967), and E. L. Allred, C. L. Anderson, R. L. Miller, and A. L. Johnson, *Tetrahedron Letters*, 525 (1967), and also in fused-ring compounds; see B. Junge and H. A. Staab, *ibid.*, 709 (1967).

[7] Harkness Fellow of the Commonwealth Fund of New York, 1966–1968.

J. Edgar Anderson,[7] John D. Roberts
Contribution No. 3678
Gates and Crellin Laboratories of Chemistry
California Institute of Technology, Pasadena, California 91109

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Evidence for a Concerted Mechanism for Allene Cycloaddition

Sir:

The Woodward–Hoffmann "selection rules" for electrocyclic reactions predict that concerted 2 + 2 cycloaddition should not be symmetry allowed from the ground state and that thermal cyclobutane-forming reactions must therefore proceed *via* multistep (*e.g.*, biradical) mechanisms.[1] The experimental support

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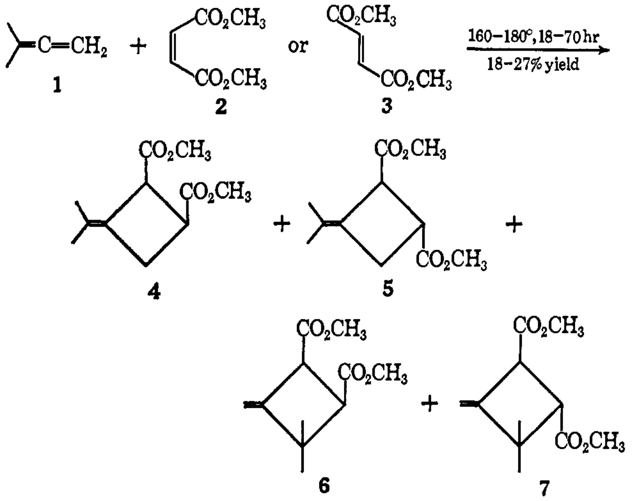
[1] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 87, 2046 (1965).

provided by the careful study by Bartlett and coworkers of the thermal cycloaddition of fluoroolefins with 1,3-dienes[2] and by recent investigations of the thermal rearrangements of methylenecyclobutanes[3] would appear to have disposed of the issue, and in fact the "accepted"[4] two-step mechanism for 2 + 2 cycloaddition has already been placed in the arsenal of criteria applicable to the continuing attack on the presumably more subtle Diels–Alder mechanism.[4]

Given the conceptual validity of the Woodward–Hoffmann rules, the idea that "any merging of one-step and two-step mechanisms into one another is limited to the type of cycloaddition where the concerted mechanism is "allowed","[2a] is indeed attractive, but may in fact be experimentally undemonstrable. We wish to present evidence which appears to favor a concerted mechanism for the well-known thermal cycloaddition reaction of allenes and to argue therefrom that the accepted experimental criteria for distinguishing one- and two-step reactions[2–5] are no more rigorous in dealing with nonallowed processes than with allowed ones.

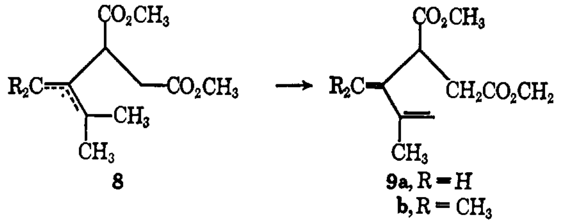
Reaction of 1,1-dimethylallene (**1**) with dimethyl maleate (**2**) or fumarate (**3**) can lead to four possible cycloadducts, **4**–**7**.[6] The reaction of **1** and **3** was found to be at least 99% stereospecific, giving only **5** and **7** in the ratio 11.5.[7,8] Reaction of **1** and **2** produced all four adducts in a ratio (**4** + **5**):(**6** + **7**) = 5–6, but was also greater than 90% stereospecific, and quite possibly >99%, since both **2** and **6** were found to isomerize somewhat under the reaction conditions.[9]



The possibility that charge-transfer or dipolar forces could be responsible for this stereospecificity is rendered unlikely by the fact that the rate of cycloaddition of **1** and acrylonitrile, which may be reasonably assumed to proceed by a similar mechanism,[8] varies by less than a factor of two in a series of solvents ranging in polarity from cyclohexane to dimethyl sulfoxide.[10]

The cycloaddition of **1** and **3** was found by direct competition to be faster than that of **1** and **2** by a factor of 9.3 at 170°, which is the same order (though less than half the magnitude) observed in the concerted Diels–Alder reaction of **2** and **3** with cyclopentadiene[11] and opposite to that found by Bartlett in the two-step fluoroolefin–hexadiene addition.[2c]

The reaction of **2** and **3** with tetramethylallene under the same conditions takes a different course, producing only an acyclic adduct (**9b**) analogous to those obtained by pyrolysis of dimethylallene cycloadducts of structural type **6** and **7** at 600–650°.[12] We suggest[13] that this behavior characterizes a true biradical of type **8** and that cycloadducts **4**–**7** are formed by an alternate pathway which is, at least to some degree, concerted. No evidence for the formation of **9a** could be found (though it could easily have polymerized under the reaction conditions).



If allene cycloaddition is to be considered a counterexample to the Woodward–Hoffmann selection rules,[1] it is not difficult to construct a rationale along the lines developed by Brauman and Golden for the disrotatory ring opening of bicyclo[2.1.0]pentene,[14] using thermochemical data available in the literature and the penetrating mechanistic analysis provided by Doering and Gilbert.[3c] The cornerstone of such a treatment is a comparison of the exceptionally high energy barrier to formation of a perpendicular allylic radical with the relatively high nucleophilicity of the terminal positions of ground-state allenes. This discussion, along with

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(2) (a) J. S. Swenton and P. D. Bartlett, *J. Amer. Chem. Soc.*, **90**, 2056 (1968); (b) P. D. Bartlett, *Science*, **159**, 833 (1968); (c) P. D. Bartlett and L. K. Montgomery, *J. Amer. Chem. Soc.*, **86**, 628 (1964), and preceding papers.

(3) (a) J. J. Gajewski and C. N. Shih, *ibid.*, **89**, 4532 (1967); (b) W. von E. Doering and W. R. Dolbier, Jr., *ibid.*, **89**, 4534 (1967); (c) W. von E. Doering and J. C. Gilbert, *Tetrahedron Suppl.*, **7**, 397 (1966).

(4) J. C. Little, *J. Amer. Chem. Soc.*, **87**, 4020 (1965).

(5) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(6) It has only recently come to our attention that this experiment was specifically suggested by Doering and Gilbert (ref 3c, footnote 44) more than a year after the present work was completed. We wish to thank these authors for providing the incentive to communicate our comparatively primitive results.

(7) Compounds **4**–**7** were separated by glpc (20 ft × 0.25 in., 20% Apiezon L on 60–80 Chromosorb W, 200°) and readily distinguished by their ir and nmr spectra, though stereochemical assignments were based ultimately on those of the ester precursors. Spectral data for a number of closely related cycloadducts have been described.[8]

(8) H. N. Cripps, J. K. Williams, and W. H. Sharkey, *J. Amer. Chem. Soc.*, **81**, 2723 (1959).

(9) The **4**:**5** ratio varied from 6 to 10 and was not affected by prolonged heating, but **6** was somewhat unstable under the reaction conditions, leading to consistently lower ratios of **6**:**7**. It could not be positively determined that the small amount of *trans* adduct **5** did not arise entirely from prior isomerization of **2** to the more reactive **3**. When carefully purified and dried, only 0.5% of **2** isomerized in 72 hr at 170°, but the isomerization was found to be strongly accelerated by traces of acid or moisture such as might have been present during the cycloaddition reactions due to cooling of the vessels in Dry Ice before sealing.

(10) E. F. Kiefer and M. A. Khaleque, unpublished results. The stereospecific cycloaddition of 2,3-dicyanohexafluoro-2-butene to electron-rich olefins is faster by $>10^4$ in more polar solvents: S. Prokow, H. E. Simmons, and T. L. Cairns, *J. Amer. Chem. Soc.*, **85**, 2341 (1963).

(11) J. Sauer, D. Lang, and H. Wiest, *Z. Naturforsch.*, **17b**, 206 (1962).

(12) J. J. Drysdale, H. B. Stephenson, and W. H. Sharkey, *J. Amer. Chem. Soc.*, 81, 4908 (1959).

(13) A convincing proof of this point has been elusive, due to the propensity of tetramethylallene to isomerize and/or dimerize above 150° (*cf.* D. R. Taylor and D. B. Wright, *Chem. Commun.*, 434 (1968)). A plausible mechanism leading directly to **9b** by a concerted hydrogen transfer can also be visualized.

(14) J. I. Brauman and D. M. Golden, *J. Amer. Chem. Soc.*, **90**, 1920 (1968).

further experimental details, will be presented in a full paper.

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(15) National Science Foundation Undergraduate Research Participant, 1964–1965.

Edgar F. Kiefer, Melvin Y. Okamura[15]
Department of Chemistry, University of Hawaii
Honolulu, Hawaii 96822

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Free-Radical Intermediates in Chromic Acid Oxidation

Sir:

A previous report from this laboratory[1] noted a small amount of polymerization of acrylonitrile added to a chromic acid oxidation of phenyl-*t*-butylcarbinol (2,2-dimethyl-1-phenyl-1-propanol). The polymerization occurred under conditions which lead to the formation of relatively large ($\sim 50\%$) amounts of the "cleavage" products, benzaldehyde and *t*-butyl alcohol. It was noted that the conversion to polymer was low (approximately 0.020 g for 20 ml of 0.025 M CrO$_3$ solution) and the product ratios were unchanged from oxidations under the same conditions but without acrylonitrile. The source and nature of the radicals initiating the polymerization could not be identified. We have now found that these radicals result from the oxidation of benzaldehyde by an intermediate Cr(IV) [most probable] or Cr(V) species.

No polymer could be detected in the oxidation of 2-propanol under the same conditions. However, the dropwise addition of 10 ml of a solution of CrO$_3$ (0.05 M in 85% aqueous acetic acid) to a solution containing 1 ml of 2-propanol, 1 ml of benzaldehyde, 5 ml of acrylonitrile, and 15 ml of the 85% aqueous acetic acid led to precipitation of the polymer within 15 min. The precipitation continued as long as the addition was continued (about 6 hr). Two grams of film-forming polymer was isolated. In the absence of the 2-propanol, polymer precipitation was delayed for several hours and only poor conversions were obtained over 48 hr (0.050 g). Omission of the benzaldehyde under the above conditions led to no polymer formation. These data suggest that the intermediate Cr(IV) or Cr(V) species formed in the oxidation of the alcohol[2] was responsible for the radical products and that the oxidation of benzaldehyde was involved in the initiation. These Cr(IV) and Cr(V) species are formed much more slowly in the oxidation of benzaldehyde than in the oxidation of a secondary alcohol.

When extra benzaldehyde was added to the oxidation of phenyl-*t*-butylcarbinol, the benzaldehyde was oxidized at a much greater rate than was observed for Cr(VI) alone. The extent of this secondary oxidation was dependent on the amount of benzaldehyde added. This is characteristic of previously observed "induced oxidations" by Cr(IV) and Cr(V).[2-4] As would be expected for this interpretation, the polymerization reaction was completely eliminated by the addition of Ce(III) to the oxidation. The Ce(III) removes the lower oxidation states of chromium from the reaction.[2,5]

In view of the above, it should be noted that Wiberg and Richardson[3] reported that $\sim 30\%$ yields of carbon monoxide could be obtained by the Cr(VI) oxidation of triphenylacetaldehyde, probably by decarbonylation of the radical formed by attack of Cr(IV) on the triphenylacetaldehyde.

In a full publication which is in preparation, we will relate these observations to the mechanisms of chromic acid oxidations of alcohols and aldehydes. The one-electron reagent is identified as Cr(IV) in the above cases. If Cr(V) acted as a one-electron reagent (reaction 1), the reaction would be an autocatalytic chain reaction due to reaction 2. Since these aldehyde oxidations are not autocatalytic,[3,6,7] this process cannot occur to any appreciable extent.

$$\mathrm{Cr(V)} + \text{substrate} \longrightarrow \mathrm{Cr(IV)} + \text{radical} \qquad (1)$$

$$\mathrm{Cr(IV)} + \mathrm{Cr(VI)} \longrightarrow 2\mathrm{Cr(V)} \qquad (2)$$

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(1) W. A. Mosher, W. H. Clement, and R. L. Hilliard, "Selective Oxidation Processes," Advances in Chemistry Series, No. 51, American Chemical Society, Washington, D. C., 1965, pp 81–88.

(2) J. Hampton, A. Leo, and F. H. Westheimer, *J. Am. Chem. Soc.*, 78, 306 (1956).

(3) K. B. Wiberg and W. H. Richardson, *ibid.*, 84, 2800 (1962).

(4) J. Rocek and A. Riehl, *Tetrahedron Letters*, 1437 (1966).

(5) The quenching of Cr(IV) and Cr(V) reactions by Ce(III) is more complicated than previously indicated. This subject will be included in a future publication.

(6) K. B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, 80, 3022 (1958).

(7) G. T. E. Graham and F. H. Westheimer, *ibid.*, 80, 3030 (1958).

William A. Mosher, G. L. Driscoll
Department of Chemistry, University of Delaware
Newark, Delaware 19711

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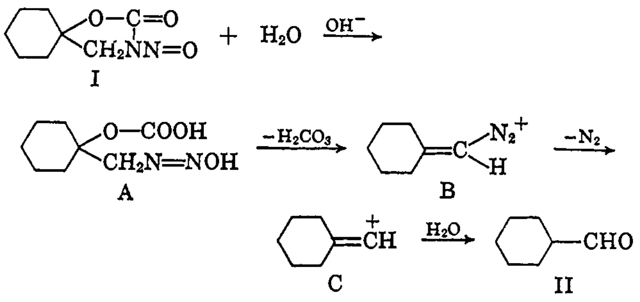
Unsaturated Carbenes Formed by Reaction of Nitrosooxazolidones with Bases

Sir:

Some time ago a mechanism was proposed to account for the products produced in the alkaline decomposition of nitrosooxazolidones in which an unsaturated carbonium ion was the key intermediate.[1] This mechanism is illustrated below in the reaction of 3-nitroso-1-oxa-3-azaspiro[4.5]decan-2-one (I) with hydroxide ion to yield formylcyclohexane (II). The hypothetical species involved were A, B, and C.



All of the products isolated in this and other cases[2,3] could be satisfactorily accounted for by assuming that unsaturated carbonium ions similar to C were involved. In his book,[4] Hine suggested that by a different mechanism A could decompose *via* an unsaturated diazo compound (E) to yield an unsaturated carbene (F) which could then give rise to products.

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(1) M. S. Newman and A. Kutner, *J. Am. Chem. Soc.*, 73, 4199 (1951). As in the present paper, the timing of proton movements was ignored.

(2) M. S. Newman and W. M. Edwards, *ibid.*, 76, 1840 (1954).

(3) M. S. Newman and A. E. Weinberg, *ibid.*, 78, 4654 (1956).

(4) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964, pp 89–90.