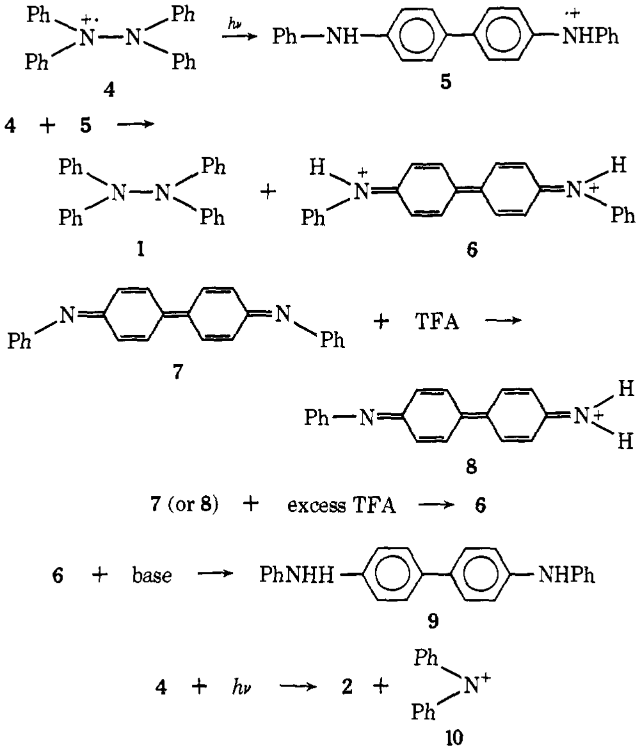
Scheme I



methane shows a reversible two electron oxidation indicating that **5** is more easily oxidized than **9** and thus disproportionation is to be expected.

It seems reasonable to suggest that excitation of **4** results in a unimolecular rearrangement to **5**. If the first step were fragmentation to **2** and **10** some reduction of **2** to **3** would be expected. Furthermore, formation of **10**, a high-energy species, should be unfavorable.

The work reported here on the photo reactions of **4** and **1** illustrates the differences in photo reactions of cation radicals and their precursors and thus opens a new area of photochemistry to study. Our recent report[12] of the synthesis of cation radical salts by electrolysis in trifluoroacetic acid provides a route to a variety of new cation radicals, the photochemistry of which is now being investigated.

(12) O. Hammerich, N. S. Moe, and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, 156 (1972).

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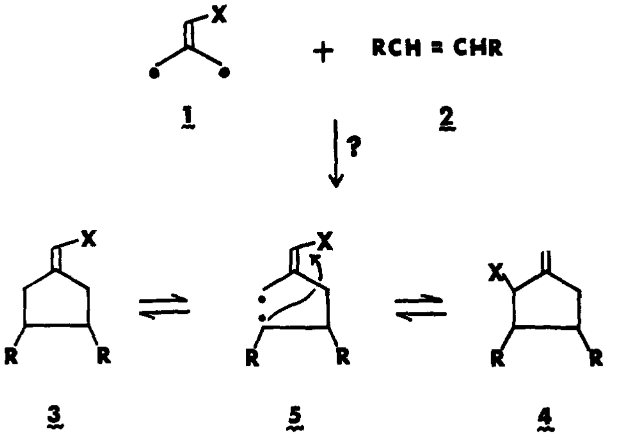
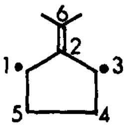
Direct Formation of Methylenecyclopentanes by Cycloaddition of a Trimethylenemethane to Olefins[1]

Sir:

Among several reasons for mechanistic interest in the cycloadditions of trimethylenemethanes and olefins (*e.g.*, **1** + **2** → **3** + **4**) is the speculation that the properties of the hypothetical intermediate **5** in the cycloaddition might serve as a model for the behavior to be expected of similar "diradical" species generated in a nonconcerted 1,3-sigmatropic rearrangement (*e.g.*, **3** → **5** → **4**). Moreover, the cycloadditions are of potential importance in synthesis as a direct route to methylenecyclopentanes.



Although there are scattered reports of formal cycloadditions of trimethylenemethane itself (TMM, **1**, X = H) to olefins, the yields usually are low.[2] One reason for this is the frequent occurrence of an intramolecular side reaction, the formal ring closure of TMM to methylenecyclopropane.[3] One might hope to suppress the ring closure by the imposition of a strain barrier, for example, by incorporation of the TMM system in a relatively small ring, thus giving the intermolecular cycloaddition a better opportunity to occur. We now report that the cyclic TMM, 2-isopropylidenecyclopentane-1,3-diyl (**6**),[4] which would give the highly strained hydrocarbon **7** upon cyclization,[5] does indeed give high yields of cycloadducts with many olefins.



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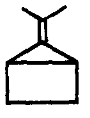
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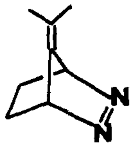

8

The cycloadditions are carried out by the slow thermal (40–60°) decomposition of the azo compound **8**[4] in a large excess (neat liquid or concentrated solution) of the olefinic acceptor. These conditions almost completely suppress the formation of the four character-

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(1) This work was supported in part by the National Science Foundation (GP11017X), the National Institute of General Medical Sciences (GM16962), and the Hoffmann-LaRoche Foundation.

(2) (a) Photolysis of 3-methylenecyclobutanone in 1,3-butadiene gives 35% of 1-methylene-3-vinylcyclopentane: P. Dowd, G. Sengupta, and K. Sachdev, *J. Amer. Chem. Soc.*, **92**, 5726 (1970). (b) Photolysis of TMM–Fe(CO)$_3$ in cyclopentene gives a 5% yield of 3-methylenebicyclo[3.3.0]octane, and in cyclopentadiene it gives 23% of 3-methylenebicyclo[3.2.1]oct-6-ene: A. C. Day and J. T. Powell, *Chem. Commun.*, 1027 (1968). (c) The action of potassium vapor on a mixture of 3-iodo-2-iodomethylpropene and diiodotetramethylcyclobutene gives a 7% yield of 3-methylene-1,5,6,7-tetramethylbicyclo[3.2.0]hept-6-ene [R. G. Doerr and P. S. Skell, *J. Amer. Chem. Soc.*, **89**, 3062 (1967)], although no methylenecyclopentane is formed in the reaction of 3-iodo-2-iodomethylpropene, potassium, and ethylene: P. S. Skell and R. G. Doerr, *ibid.*, **89**, 4688 (1967). (d) Oxidation of TMM–Fe(CO)$_3$ with Ce(IV) ion in the presence of tetracyanoethylene gives a 4% yield of 4-methylene-1,1,2,2-tetracyanocyclopentane: J. S. Ward and R. Pettit, *Chem. Commun.*, 1419 (1970).

(3) R. J. Crawford and D. M. Cameron, *J. Amer. Chem. Soc.*, **88**, 2589 (1966); J. J. Gajewski, A. Yeshurun, and E. J. Bair, *ibid.*, **94**, 2138 (1972).

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

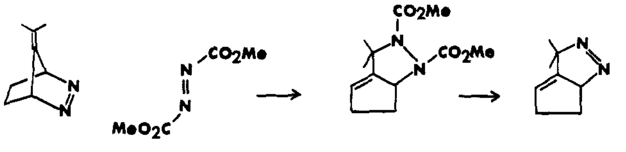
(5) Previous studies[4] already have shown that **7** reverts readily to **6**.

istic $C_{16}H_{24}$ dimers of **6**, which are formed in high yield in the absence of a trapping agent.[4]

The efficiency of the cycloaddition, as measured by the competition between adduct formation and dimerization of **6**, is greater with conjugated olefins than with simple ones. 1,3-Cyclohexadiene, 2,4-hexadiene, methyl acrylate, acrylonitrile, fumaronitrile, and crotononitrile all form adducts in high yield, whereas cyclohexene, dihydropyran, and 1,2-diethoxyethylene do not.

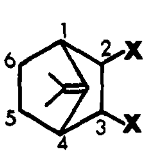
Conjugated acetylenes do not seem to be good trapping agents. Decomposition of **8** in the presence of dimethyl acetylenedicarboxylate gives no adduct and a substantial amount of a polymeric product; in the presence of diphenylacetylene, **8** gives only the four $C_{16}H_{24}$ dimers of **6**.

The reaction of azo compound **8** with dimethyl azodicarboxylate **9** provides an example of an "azo transfer" reaction. The resulting cycloadduct **10**[6] can be converted by a hydrolysis–decarboxylation–oxidation sequence to the fused azo compound **11**, isomeric with bridged azo compound **8**. Thermal decomposition of **11** gives the same four $C_{16}H_{24}$ dimers[4] formed from **8**. The dimers are formed in proportions identical with those observed[4] in other reactions leading to the diyl **6**.

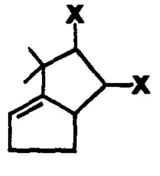


8 **9** **10** **11**

Either *cis*- or *trans*-1,2-dichloroethylene gives about a 10% yield of an approximately 1:1 mixture of bridged (**12**) and fused (**13**) cycloadducts, whereas fumaronitrile gives a high yield (83% isolated) of the fused adducts **14**.[6] The stereochemistry of these adducts is not yet known. Cycloadditions of dimethyl maleate and dimethyl fumarate give 95–100% yields of mixtures of fused[6] and bridged cycloadducts. A typical product composition from maleate consists of the two fused adducts (**15**) with cis carbomethoxy groups (27 and 36%), the corresponding fused adducts **15** with trans carbomethoxy groups (11 and 8%), and the bridged adducts (**16**), endo-cis (1%) and trans (17%). Fumarate gives almost exclusively the trans adducts, fused (**15**, 57 and 33%) and bridged (**16**, 10%).[7]



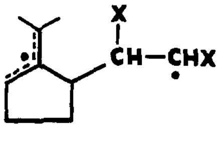
12, X = Cl
16, X = CO2CH3



13, X = Cl
14, X = CN
15, X = CO2CH3

The stereochemical assignments in the bridged series **16** rest upon independent syntheses from or direct comparisons with known[8] compounds, obtained from Diels–Alder reactions of 6,6-dimethylfulvene. The cis compounds in the fused series (**15**) are identified by their preparation from the corresponding anhydrides, which are formed by the decomposition of azo compound **8** in molten maleic anhydride, and by their epimerization to mixtures of the two trans isomers with methanolic sodium methoxide.

Although some cis → trans crossover does occur in the maleate cycloaddition, it is clear that any intermediates in this and the corresponding fumarate reaction cannot be formulated as a single long-lived diradical (*e.g.*, **17**), since that would produce identical adduct mixtures from each.



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We hope to complete soon a quantitative ranking of the diylophilic reactivities of various olefins. In an accompanying paper,[9] we report evidence on the mechanism of these cycloadditions.

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[6] Elemental analysis and spectroscopic properties establish the molecular formula and structure.

[7] Analyses of product compositions by vapor chromatography.

[8] K. Alder and R. Rühmann, *Justus Liebigs Ann. Chem.*, **566**, 1 (1950).

[9] J. A. Berson, D. M. McDaniel, and L. R. Corwin, *J. Amer. Chem. Soc.*, **94**, 5509 (1972).

[10] Postdoctoral Fellow of the National Institute of General Medical Sciences, No. 1 FO2 GM37,585.

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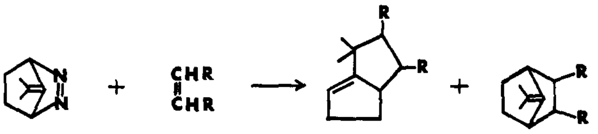
On the Mechanism of the Reaction of 7-Isopropylidene-2,3-diazanorborn-2-ene with Olefins. Evidence for a Symmetrical, Nitrogen-Free Intermediate[1]

Sir:

When a mixture of 7-isopropylidene-2,3-diazanorborn-2-ene (**1**) and an appropriate olefin is kept at 40–60°, high yields of nitrogen and the cycloadducts **2** and **3** are formed.[2]



1 **2** **3**

We record here experiments that establish the following features of the mechanism of these reactions.

(1) The rate-determining step involves the conversion of the azo compound **1** to an intermediate which then

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[1] This work was supported in part by the National Science Foundation (GP 11017X), the National Institute of General Medical Sciences (GM 16962), and the Hoffmann-LaRoche Foundation.

[2] J. A. Berson, D. M. McDaniel, L. R. Corwin, and J. H. Davis, *J. Amer. Chem. Soc.*, **94**, 5508 (1972).