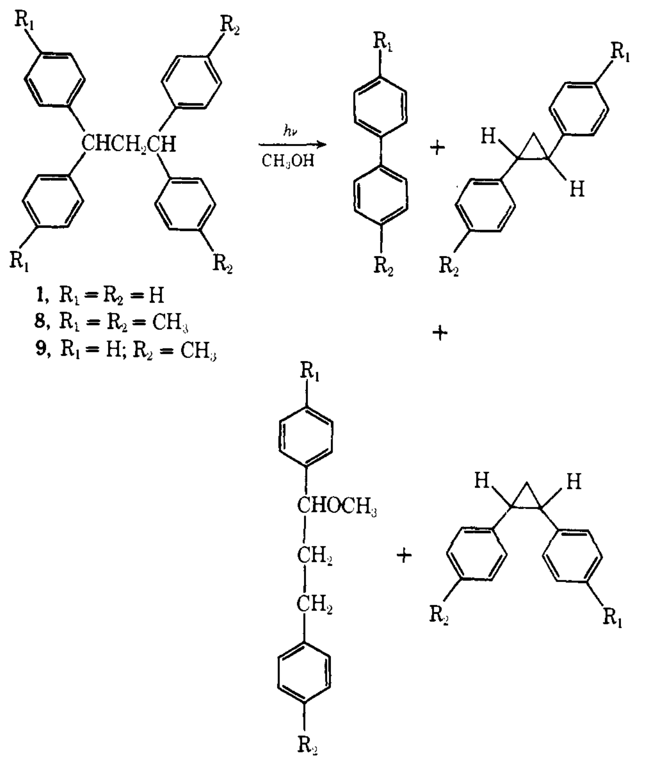
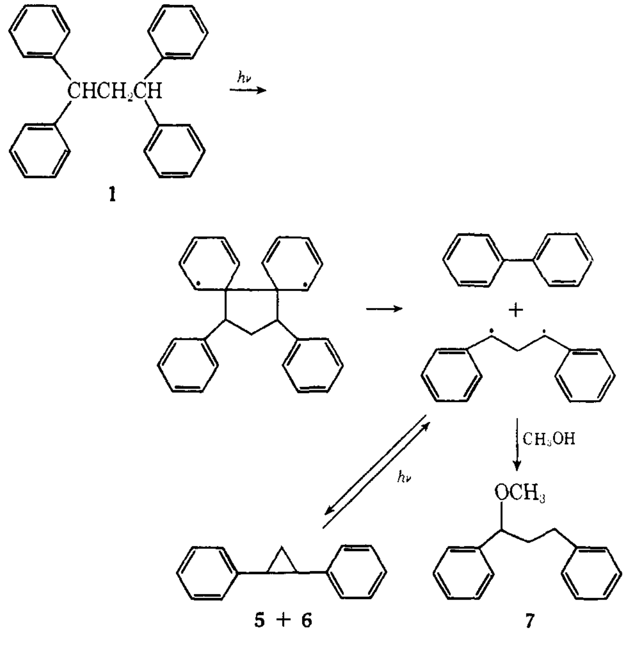


1, $R_1 = R_2 = H$
8, $R_1 = R_2 = CH_3$
9, $R_1 = H; R_2 = CH_3$

anism shown as an explanation for this reaction process (Scheme I). In connection with the proposed mechanism it is worthwhile to note that *trans*-1,2-diphenylcyclopropane (**5**) has been reported to form 1,3-diphenyl-1-methoxypropane (**7**) upon photolysis.[8] This reaction has been verified to occur under our reaction conditions. Also of interest is the fact that the ratio of the yield of **7** to the combined yields of **5** and **6** does not approach zero at short photolysis times, thus suggesting that the cyclopropanes are not necessarily intermediates in the formation of the methyl ethers.

Scheme I. Proposed Di-π-propane Reaction



The photolyses of 1,1,4,4-tetraphenylbutane (**2**) and 1,1,5,5-tetraphenylpentane (**3**) assumed a quite different pathway from that followed by 1,1,3,3-tetraphenylpropane (**1**). The irradiations of both **2** and **3** were characterized by a rapid formation of a deep yellow color in the reaction mixture accompanied by the coating of the immersion well with an insoluble material. Chromatography of the reaction mixtures resulted in the isolation of unreacted starting material along with small amounts (less than 2% each) of 1,1-diphenylethylene and diphenylmethane. No other identifiable materials could be eluted from the chromatography columns.

Until further testing of these π-interaction processes is complete, the reason for the failure to observe the di-π-butane and pentane reactions remains unknown. The simple explanation that sufficient separation of reactive centers prevents π-interaction reactions is an attractive hypothesis. Molecular models indicate that preferred conformers of unreactive molecules, unlike their reactive counterparts, have potentially interacting π systems well separated.

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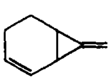
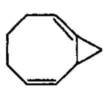
[8] C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinsson, C. S. Aaron, G. W. Griffin, and G. J. Roudreaux, *J. Amer. Chem. Soc.*, **88**, 5675 (1966).

Synthesis and Pyrolytic Transformations of 7-Methylenebicyclo[4.1.0]hept-2-ene and Bicyclo[6.1.0]nona-1,6-diene

Sir:

Substituted trimethylenemethane diradicals as reaction intermediates are of current interest, especially with respect to the choice between this mechanism and one-step concerted mechanisms.[1] Substituents containing double bonds can modify the normal reaction course.[2] We report the syntheses and rearrangements of two substances **1** and **2** for which such intermediates can be proposed.


1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1[3] was produced in 50% yield by adding 8,8-di-

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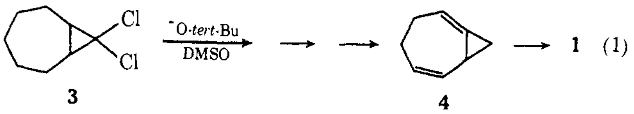
[1] A relevant discussion is W. von E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970).

[2] H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

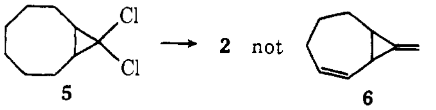
[3] Structures are based primarily on nmr, ir, uv, and mass spectral evidence. **1** has a molecular weight of 106 (mass spectrum). The methylenecyclopropane feature is from a strong ir absorption at 11.28 μ, and the remaining features are from the proton nmr [δ 0.9–2.2 (6 H), 5.20–6.25 (4 H)] and the ^{13}C nmr (eight distinct signals, one unattached to hydrogen). **2** has a molecular weight of 120 from the mass spectrum. Reduction to bicyclo[6.1.0]nonane, identical with the sodium in ammonia reduction product of **5** (M. S. Baird and C. B. Reese, *Chem. Commun.*, 1519 (1970)) confirms the skeleton; the double bonds are assumed not to be moved far from the cyclopropane ring, and cyclopropenes are not considered since they are unstable to the reaction conditions. The uv spectrum eliminates 1,3-dienes; the proton nmr is consistent with the structure [δ 0.5–0.85 (1 H), 1.05–2.83 (8 H), 5.6 (m, 2 H), 5.89 (m, 1 H)]; the ^{13}C nmr shows nine signals, one for carbon not attached to hydrogen. The uv of **7** shows the diene structure, λ_{max} 238 nm ($\epsilon \approx 15{,}000$), the proton nmr is well resolved [δ 1.5–2.7 (m, 4 H), 3.24 (m, 2 H), 4.62 (1 H), 4.76 (1 H), 6.2 (2 H)],

chlorobicyclo[5.1.0]octane (**3**)[4] to a cold solution of potassium *tert*-butoxide in dimethyl sulfoxide. The flash-distilled reaction product was over 90% pure, and further purification was accomplished by preparative scale gas chromatography. The skeletal rearrangement might arise from the intermediacy of the highly strained compound **4**, formed by the normal[5] elimination route, which then suffers a methylenecyclopropane rearrangement, as shown in eq 1.[6]



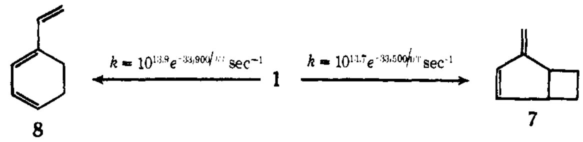
3 **4** (1)

Compound **2** was similarly prepared by the elimination from 9,9-dichlorobicyclo[6.1.0]nonane[4] (**5**). The rearranged product analogous to **1**, compound **6**, was not obtained, as shown by the reduction to bicyclo[6.1.0]nonane. Presumably **2** is, by virtue of the larger ring size, far less strained than **4**, accounting for the preparation of **2** and not of **6** by this method, eq 2.



5 **6** (2)

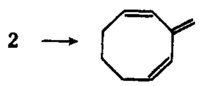
The study of the thermolysis is summarized by eq 3.



8 **7** (3)

The rates were followed in the gas phase using the diffusively stirred flow system.[7] Both reactions followed a first-order course with the indicated rate constants; the ratio of **7** to **8** was 1.15 ± 0.05 at all temperatures.[8]

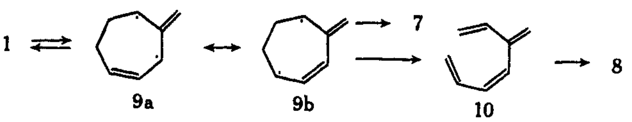
Compound **2** rearranges in dimethylformamide to **11**, 3-methylene-1,4-cyclooctadiene, by a first-order process, followed by nmr, giving $k = 10^{11}e^{-29,000/RT}$ sec^{-1}, eq 4.



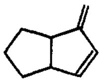
11 (4)

Scheme I conveniently accounts for both **7** and **8** from **1**. The formation of **7** suggests this biradical path, since a one-step thermally allowed 1,3-sigmatropic shift requires an inversion at the migrating center,[9] leading to an unknown trans-fused ring system, and the 3,3-sigmatropic shift, adequate for the parent compound,[5] is impossible. The formation of **7** from **8** is accounted for through the fission[10] of the "1,4" diradical **9b** to the tetraene **10** followed by facile cyclization to **8**. Activation energies sometimes eliminate a diradical mechanism, but the activation energy should be roughly that of *trans*-2-thujene isomerization (44 kcal)[11] less the allyl resonance energy (13 kcal), or 31 kcal,[12] not helpfully different from the observed 33.5 kcal. The same diradical, **9**, is required for the assumed reaction **4** → **1**, and the good yield of **1** requires that **9** have a lower barrier leading to **1** than to **7** or **8**.

Scheme I



The reaction **2** → **11** must involve a hydrogen migration. It may occur by the sequence **2** → **6** → **11**, or by a hydrogen migration in the diradical. An argument against the intermediary of **6** is that its expected rearrangement product, **12**, is undetected.



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and the last two signals for the olefinic hydrogens are virtually identical with those of 3-methylene-4-methylcyclopentene. **8** is a known compound (W. Ziegenbein, *Angew. Chem., Int. Ed., Engl.*, **4**, 70 (1965)). Its uv maxima absorption is indistinguishable from that kindly supplied by Dr. Ziegenbein, and the nmr spectrum is consistent. The conjugation of **11** is shown by the λ_{max} 250 nm and the skeleton by hydrogenation to methylcyclooctane, and the nmr is too simple to allow a structure of lesser symmetry [δ 1.44 (m, 2 H), 2.25 (m, 4 H), 4.93 (s, 2 H), 5.33 (double t, 2 H), 6.24 (d, 2 H)].

(4) The dichlorocyclopropanes were prepared following P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 3409 (1956).

(5) T. C. Shields, W. E. Billups, and A. R. Lepley, *ibid.*, **90**, 4749 (1968).

(6) An alternative rearrangement is to homotropylidene, but this product was not found.

(7) E. S. Lewis and J. T. Hill, *J. Amer. Chem. Soc.*, **91**, 7458 (1969).

(8) Another compound, not identified, was produced in <3% yield.

(9) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

(10) P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968).

(11) R. H. Eastman, Final Technical Report, AFOSR Contract No. AF-49-638-1272.

(12) J. S. Swenton and A. Wexler, *J. Amer. Chem. Soc.*, **93**, 3066 (1971).

Unusual Water Exchange Behavior in Copper(II)- and Nickel(II)-β,β',β''-Triaminotriethylamine Complexes

Sir:

In the course of studying, by means of ^{17}O nmr, the kinetics of a number of water exchange processes in substituted aquo metal ions, we have found unique behavior for Cu(II)- and Ni(II)-tren (β,β',β''-triaminotriethylamine) complexes.

Among the considerable number of Ni(II) complexes studied, we have observed in any given case only one apparent exchange rate for bound water in the partly substituted species. For the Ni(II)-tren species, however, two distinct rates are observed.[1] While the

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(1) A similar result has apparently been found for the Ni(II)-NTA system: private communication from Drs. J. Vriesenga and R. E. Connick.