CD bands have shifted to longer wavelengths, and the net circular dichroism is now less positive. In dilute aqueous solution the CD spectrum of II is net negative, although a small positive component exists at 680 nm. Finally, a 2:1 pyridine adduct of II in nitromethane has a visible CD spectrum which is totally negative to 700 nm, the longest wavelength we can attain with the Jasco ORD/UV-5 instrument used in our investigations.

From models we find that for both I and II the sterically favored conformation of the chelate rings has the C^*-methyl groups equatorial. In this conformation of I the terminal methyl groups of the ethyl substituents which are on the same side of the coordination plane as the C^*-methyl groups lie directly above the metal ion.[3] With II, however, the z axis of the molecule is completely unobstructed.

The CD spectrum of monomeric II shown in Figure 2a has the form predicted by Richardson[5] for the first-order charge-transfer contribution to the total rotatory strength of four-coordinate trans copper–L-alanine complexes; *i.e.*, bands from $d_{xz} \leftarrow d_{x^2-y^2}$ and $d_{xy} \leftarrow d_{x^2-y^2}$ transitions having opposite signs, the long wavelength band being the more intense by a factor of 2. The nonbonded methyl groups near the z axis of I evidently perturb the copper d_{xz} orbital in such a way as to alter radically the CD band associated with it, even though the visible spectra of I and II are not appreciably different. In this connection it is also noteworthy that with II, changing the solvent from ethylene chloride to nitromethane alters the energy levels and/or the transition probabilities but not the CD spectrum.

With both I and II, as the coordination number of the metal increases from 4 the visible spectrum shifts to longer wavelengths, and with strong complexing agents the net CD sign becomes negative. The signs of the CD bands of II in aqueous solution are opposite to those of the corresponding bands of the copper complex with N-methyl-L-alanine in this medium.[2] If the same number of water molecules is bound to each complex, this result may be rationalized since the chelate ring conformation suggested by Wilson and Martin[2] for the monomethylated ligand is opposite to the one we propose for II.

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A New π-Interaction Process.[1]
A Di-π-propane Reaction

Sir:

During the last few years one of the most extensively studied photochemical processes has been the di-π-methane rearrangement.[2] Recently we have discovered that the photolysis of 1,1,2,2-tetraphenylethane leads to a di-π-ethane reaction,[3] a discovery which suggested that the di-π-methane rearrangement might be only the first in a homologous series of π-interaction processes.[1] We have now investigated the photochemical reactions of 1,1,3,3-tetraphenylpropane (**1**), 1,1,4,4-tetraphenylbutane (**2**), and 1,1,5,5-tetraphenylpentane (**3**),[4] compounds capable of experiencing the di-π-propane (compound **1**), di-π-butane (**2**), and di-π-pentane (**3**) reactions, and wish to report that the first of these processes is observed while the latter two do not take place in this series of compounds. These and earlier observations[3,5] establish that π-interaction processes in the tetraphenylalkanes can occur when the π systems are separated by one or more atoms but that there is a limit to the number of separating atoms which will allow reaction to proceed.

Vycor-filtered irradiation of 1.00 mmol of 1,1,3,3-tetraphenylpropane (**1**) in 350 ml of methanol for 1 hr with a 450-W Hanovia mercury vapor lamp under nitrogen caused the reaction of 43% of the starting material to produce biphenyl (**4**, 93%), *cis*- and *trans*-1,2-diphenylcyclopropane (**5**, 24%, and **6**, 23%), and 1,3-diphenyl-1-methoxypropane (**7**, 44%).[6] The identity of these photoproducts, as with all photoproducts described in this communication, was established by comparison with independently synthesized samples.[7]

Critical to the understanding of this reaction is a determination not only of the original position in the starting material of the various benzene rings present in the products but also of any change in point of attachment within a given benzene ring to the rest of the molecule. These determinations were achieved by studying the photochemical reactions of 1,1,3,3-tetra-p-tolylpropane (**8**) and 1,1-diphenyl-3,3-di-p-tolylpropane (**9**). The general features of these reactions were the same as those of 1,1,3,3-tetraphenylpropane (**1**). From the photolysis of **7** the only biphenyl formed was 4,4′-dimethylbiphenyl while the only cyclopropanes were the cis and trans isomers of 1,2-di-p-tolylcyclopropane. This experiment demonstrated that the number one carbon atoms in the benzene rings of the starting material retained their numbering in product molecules. During the irradiation of 1,1-diphenyl-2,2-di-p-tolylpropane, aside from methyl ethers, only 4-methylbiphenyl and *cis*- and *trans*-1-phenyl-2-p-tolylcyclopropane were formed, thus showing that the interacting phenyl groups were 1–3 related in the starting material.

Combining the information resulting from these three photochemical reactions, we suggest the mech-

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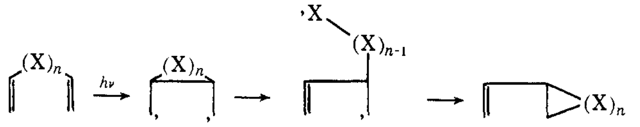
[1] A π-interaction process is a photochemical reaction between nonconjugated π systems which passes through one or more of the following stages.



X = CH$_2$, NH, O, etc.
n = 1,2,3 ...

[2] See H. E. Zimmerman, P. Hackett, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, 93, 3653 (1971), and references therein.

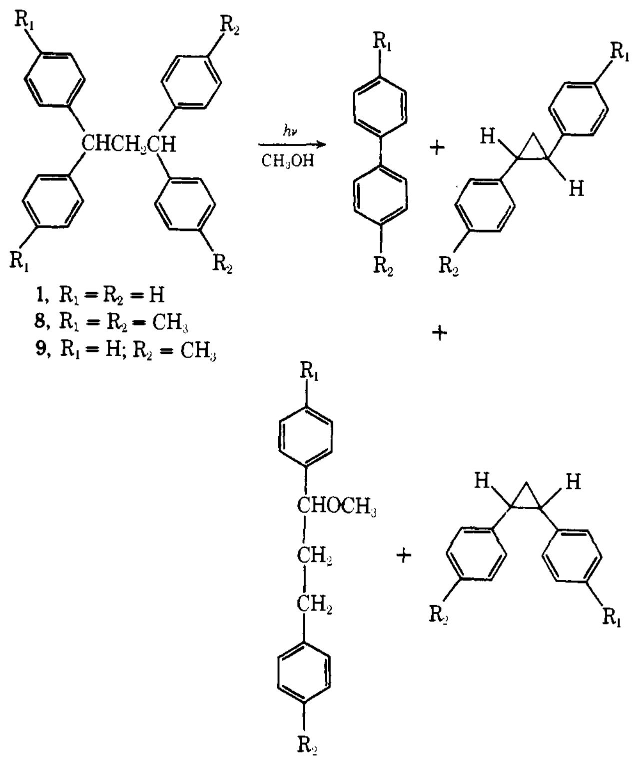
[3] J. A. Ross, W. C. Schumann, D. B. Vashi, and R. W. Binkley, *Tetrahedron Lett.*, 3283 (1971).

[4] C. R. Hauser, C. F. Hauser, and P. J. Hamrick, *J. Org. Chem.*, **24**, 397 (1959).

[5] T. D. Walsh and D. R. Powers, *Tetrahedron Lett.*, 3855 (1970).

[6] It is possible in this reaction to have a 100% yield of biphenyl (**4**) along with a combined 100% yield of the methyl ether 7 and cyclopropanes 5 and 6.

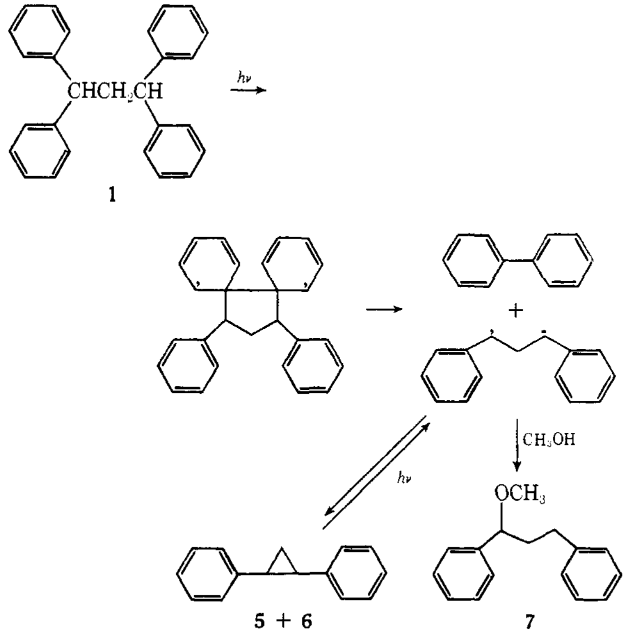
[7] The biphenyls were purchased from the Aldrich Chemical Co., Milwaukee, Wis. The cyclopropanes were synthesized by a modification of the Simmons–Smith reaction as reported by S. Savada, J. Oda, and Y. Inouye, *J. Org. Chem.*, 33, 2141 (1968). The methyl ethers were prepared by photolysis of the corresponding cyclopropanes in methanol (ref 8).



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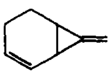
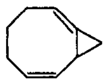
(8) C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinsson, C. S. Aaron, G. W. Griffin, and G. J. Roudreaux, *J. Amer. Chem. Soc.*, **88**, 5675 (1966).

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


2

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)],