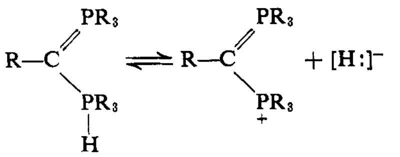
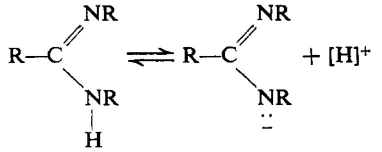


14



15

These considerations lead to the formulation of a new function in phosphorus chemistry, the "geminal alkylidenediphosphorane" function **14**, analogous to the amidine function **15**.

The adduct **3** is merely the "zwitterion" of the conjugate acid and base forms of these two functions **14** and **15**, respectively. Further work based on this hypothesis is under way.

The description of the pyrolysis reaction **3** → **4** involves simply the migration of a formal phenonium ion $(C_6H_5)^+$ from the positive phosphorus to the negative nitrogen, forming a single bond using one of the sets of lone-pair electrons on nitrogen, with neutralization of the formal charges.

# π-Interaction Photochemistry. Relationship between Photochemical Reaction in Tetraphenylalkanes and the Separation of Interacting π Systems[1]

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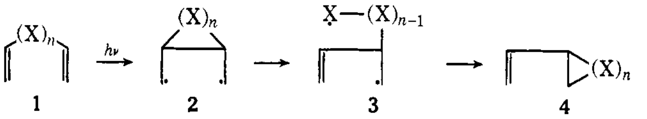
*Contribution from the Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115.* *Received April 3, 1972*

**Abstract:** A general photochemical reaction type, named the π-interaction process, is described and discussed using examples to show the variety of photochemical processes which are understandable as π-interaction reactions. To explore the relationship between reactivity and separation of intereacting π systems in this reaction, a series of tetraphenylalkanes, 1,1,2,2-tetraphenylethane (**5**), 1,1,3,3-tetraphenylpropane (**6**), 1,1,4,4-tetraphenylbutane (**7**), and 1,1,5,5-tetraphenylpentane (**8**), were studied. Both **5** and **6** undergo π-interaction reaction (previously, **5** had been shown to participate in the process); however, **7** and **8** do not experience this photochemical change. For those systems which do react (**5** and **6**), the quantum yields were measured and a triplet assignment was made to the reactive excited state. The reason for the difference in reactivity among these compounds (**5**–**8**) and the significance of the nature of the excited state are discussed.

One of the problems facing organic photochemistry today is that the increase in the number of light-initiated reactions being discovered and investigated during the past few years is sufficiently great to make their proper assimilation and evaluation difficult. This situation creates a need for an organization of information in such a way that the importance of new reactions can be better assessed and the most desirable direction for further work more clearly understood. A possible solution to a portion of this organization problem is offered here in the form of a name and a definition for a type of photochemical process which brings together a wide variety of existing photochemical reactions under a common reaction type. This reaction type is called a π-interaction process and is defined as a photochemical reaction between nonconjugated π systems which passes through one or more of the following stages.



$X = CH_2$, NH, O, . . .
$n = 1, 2, 3, \ldots$

There are basically four ways in which π-interaction reactions may differ from each other. The first of these is in the nature of the interacting π systems. The π systems shown in the definition are simple double bonds; however, a variety of other π systems are possible (aromatic rings, dienes, . . ). A second potential difference arises from the fact that a molecule need not travel through the entire reaction pathway. It is possible for a reactant to be diverted into a new pathway at an intermediate stage (*i.e.*, **2** or **3**). The final two ways in which π-interaction reactions may differ from each other is that the number and nature of the atoms forming the bridging chain between the interacting π systems may vary; that is, *n* may assume different values and X may represent different atoms or groups of atoms.

The specific goal of the research described here is to investigate the π-interaction process between two aromatic rings to determine the effect on reactivity of systematically lengthening the bridging carbon chain. The four compounds selected for study are the four tetraphenylalkanes (**5**–**8**). The first of these, 1,1,2,2-tetraphenylethane (**5**), has previously been shown to undergo

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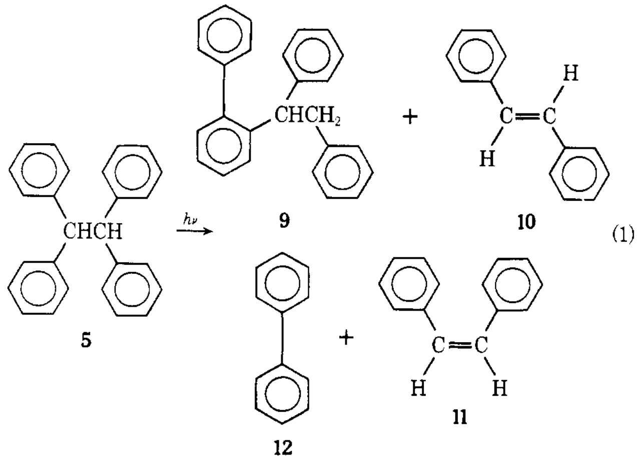
(1) A preliminary communication of a portion of this work has appeared: R. W. Binkley and W. C. Schumann, *J. Amer. Chem. Soc.*, **94**, 1769 (1972).

**Table I.** Quantum Yields from the Photolysis of Tetraphenylalkanes **5**–**8**

| Compound | Solvent | Sensitizer | $\Phi^a$ | Quantum yields for product formation<br>**12** | <br>**10, 11** | <br>**9** | <br>**13** | <br>**14** |
|---|---|---|---|---|---|---|---|---|
| 1,1,2,2-Tetraphenylethane (**5**) | Methanol | None | 0.20 | *b* | *b* | 0.12 | | |
| | Acetone | Acetone | 0.09 | *b* | *b* | 0.05 | | |
| 1,1,3,3-Tetraphenylpropane (**6**) | Methanol | None | 0.07 | 0.06 | | | 0.06 | *b* |
| | Acetone | Acetone | 0.02 | 0.02 | | | 0.01 | 0.01 |
| 1,1,4,4-Tetraphenylbutane (**7**) or 1,1,5,5-tetraphenylpentane (**8**) | Methanol | Methanol | 0.01 | | | | | |

[a] Quantum yield for disappearance of starting material. [b] Chemical yield sufficiently small to prevent reliable determination at the conversions used.

a $\pi$-interaction reaction[2] (eq 1); thus, it was necessary to determine whether increasing the length of the bridging chain would still permit reaction and, if so, what the reaction would be.

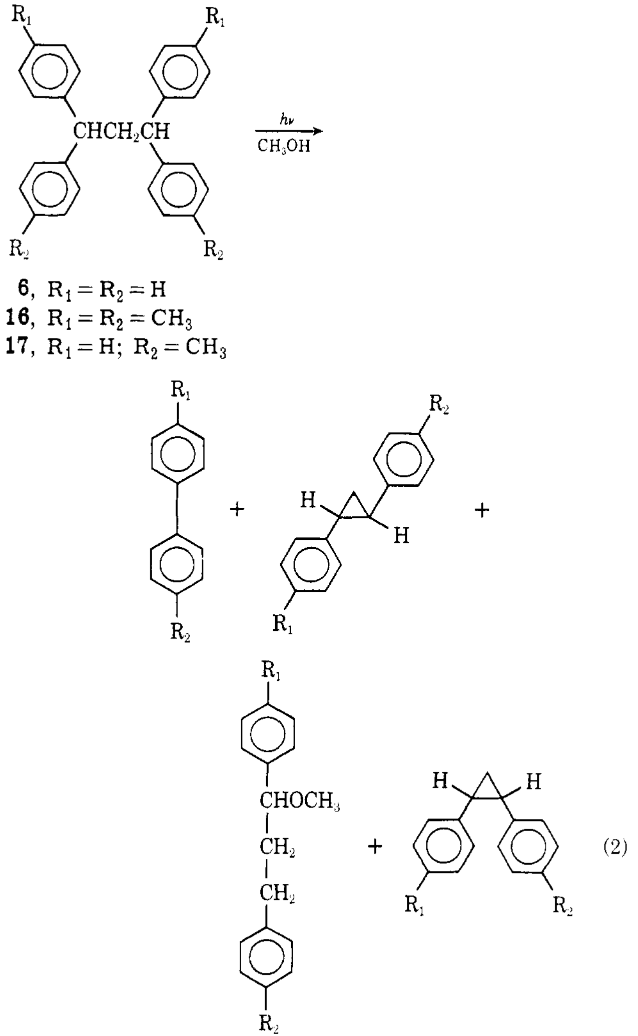


**5** **9** **10** **11** **12** (1)

## Results

Vycor-filtered irradiation of 1.00 mmol of 1,1,2,2-tetraphenylpropane (**6**) in 350 ml of methanol for 1 hr wiith a 450-W Hanovia mercury-vapor lamp under nitrogen (eq 2) caused the reaction of 43% of the starting material to produce, after chromatographic separation on Florisil, biphenyl (**12**, 93%), *cis*- and *trans*-1,2-diphenylcyclopropane (**13**, 24%, and **14**, 23%), and 1,3-diphenyl-1-methoxypropane (**15**, 44%).

Similar irradiations of 1,1,4,4-tetraphenylbutane (**7**) and 1,1,5,5-tetraphenylpentane (**8**) produced a much different result with the starting material in each case gradually disappearing but only low yields of 1,1-diphenylethylene (2%) and diphenylmethane (1%) arising from chromatographic isolation. No other products could be isolated. The nmr spectra of the crude reaction mixtures prior to chromatography showed broad absorption in the region from $\tau$ 5 to 8 but no distinct peaks appeared. During these irradiations the immerision well slowly became coated with an insoluble material.



**6**, $R_1 = R_2 = H$
**16**, $R_1 = R_2 = CH_3$
**17**, $R_1 = H$; $R_2 = CH_3$

(2)

The photochemical reactions of 1,1,3,3-tetra-*p*-tolylpropane (**16**) and 1,1-diphenyl-3,3-di-*p*-tolylpropane (**17**) were also studied. The general features of these reactions were the same as those of 1,1,3,3-tetraphenylpropane (eq 2). From the photolysis of **16** the only biphenyl formed was 4,4′-dimethylbiphenyl while the only cyclopropanes were the cis and trans isomers of 1,2-di-*p*-tolylcyclopropane. During the irradiation of 1,1-diphenyl-2,2-di-*p*-tolylpropane (**17**), aside from methyl ethers, only 4-methylbiphenyl and *cis*- and *trans*-1-phenyl-2-*p*-tolylcyclopropane were formed.

Using ferrioxalate actinometry and a cobalt sulfate–nickel sulfate filter solution (see Experimental Section for details), the quantum yields in methanol for the disappearance of each of the four tetraphenylalkanes **5**–**8** were determined (Table I). It was necessary to keep the extent of conversion small (less than 7%) for these reactions owing to light absorption of the photoproducts becoming significant. Those quantum yields

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(2) W. C. Schumann, D. B. Vashi, J. A. Ross, and R. W. Binkley, *J. Org. Chem.*, 37, 21 (1972).

for product formation which could be determined[3] are also shown in Table I.

Sensitization of the photoreactions of **5** and **6** using acetophenone as a sensitizer was attempted but proved to be unsuccessful. Irradiations of these two tetraphenylalkanes (**5** and **6**) using acetone as a sensitizer (acetone absorbing greater than 99% of the light) did lead to reaction in each case. The sensitized reactions produced the same products in essentially the same yields as in the unsensitized reactions with the only differences being more rapid interconversion of the photoproduct cyclopropanes in the photolysis of **6** and greater isomerization of the substituted biphenyl[2] **9** in the case of **5**. The quantum yields for the acetone sensitized reactions of **5** and **6** are given in Table I.

Quenching and phosphorescence studies on the reactions of 1,1,2,2-tetraphenylethane (**5**) and 1,1,3,3-tetraphenylpropane (**6**) were both informative. The reaction of each of these compounds at 298°K was quenched by the presence of piperylene. In each case a linear relationship between the quencher concentration and the reciprocal of the quantum yield was observed (Figure 1). Triplet energies of the four tetraphenylalkanes (**5**–**8**), determined at 77°K using methanol or EPA as a solvent, were found to be 82 kcal/mol for each system. Observable phosphorescence of these compounds (at 77°K) was totally quenched by a 0.2 *M* concentration of piperylene.

## Discussion

One of the first observations arising from the results just described is that in the systems studied the π-interaction process does not occur if the bridging carbon atom chain between two aromatic rings is longer than three atoms. A π-interaction process takes place in 1,1,3,3-tetraphenylpropane (a di-π-propane reaction) analogous to the di-π-ethane reaction observed in 1,1,2,2-tetraphenylethane[2] (**5**) and the di-π-methane reaction in tetraphenylmethane.[4] Further members in this series, the di-π-butane and di-π-pentane reactions, are not observed, as evidenced by the slow and largely uncharacterizable photochemical decay of 1,1,4,4-tetraphenylbutane (**7**) and 1,1,5,5-tetraphenylpentane (**8**).

To be certain that a di-π-propane process was responsible for the reaction of 1,1,3,3-tetraphenylpropane (**6**), it was necessary to demonstrate that 1–3 related benzene rings were interacting and that this interaction was between the number one carbon atoms in each ring. The latter of these two necessary conditions was satisfied by irradiating 1,1,3,3-tetra-*p*-tolylpropane (**16**), since in this reaction the only biphenyl formed was 4,4′-dimethylbiphenyl and the only cyclopropanes were *cis*- and *trans*-1,2-di-*p*-tolylcyclopropane; hence, only the number one carbons on each ring were interacting. That 1–3 related benzene rings were interacting was demonstrated by the irradiation of 1,1-diphenyl-3,3-di-*p*-tolylpropane (**17**) for in this reaction only 4-methylbiphenyl and 1-phenyl-2-*p*-tolylcyclopropane were formed.

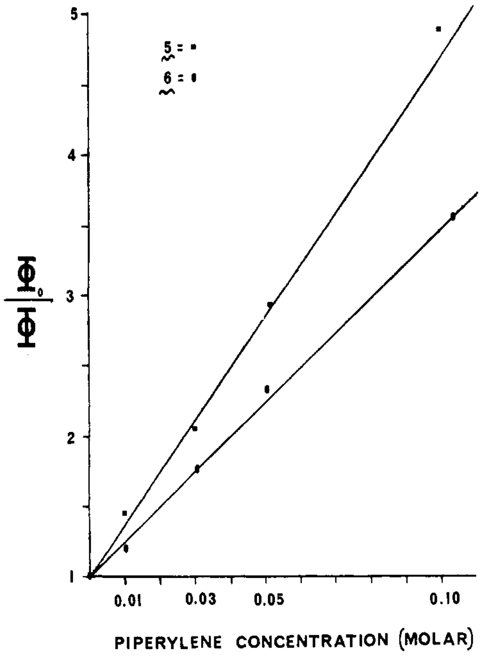
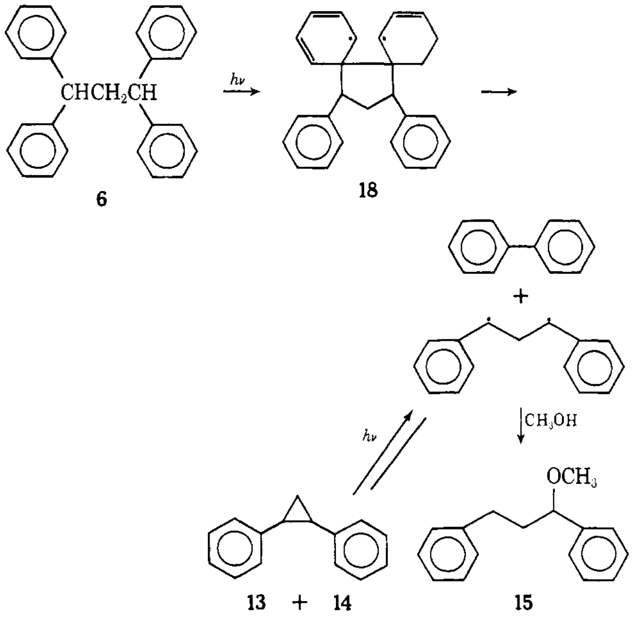


Figure 1. Quenching of tetraphenylalkane photoreaction.

When the information resulting from the photochemical reactions of these three propane derivatives, **6**, **16**, and **17**, is combined, it suggests the mechanism shown in Scheme I as an explanation for this reaction process.

**Scheme I.** Mechanism for Photoreaction of 1,1,3,3-Tetraphenylpropane (**6**)



In connection with the proposed mechanism it is worthwhile to note that *trans*-1,2-diphenylcyclopropane (**14**) has been reported to form 1,3-diphenyl-1-methoxypropane (**15**) upon photolysis.[5] This reaction has been verified to occur under the reaction conditions used here.

A second observation which arises from an analysis of the results of this work concerns the nature and reactivity of the excited state responsible for the π-interaction process. Quantum yields (Table I) for the direct irradiation of these systems show that this reaction is a

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(3) It was not possible with the detection procedure employed to determine with reliability the quantum yields for the formation of those photoproducts produced in low chemical yields.

(4) T. D. Walsh and D. R. Powers, *Tetrahedron Lett.*, 3855 (1970).

(5) (a) C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinsson, C. S. Aaron, G. W. Griffin, and G. J. Boudreaux, *J. Amer. Chem. Soc.*, **88**, 5675 (1966); (b) S. S. Hixon, *ibid.*, **93**, 5293 (1971).

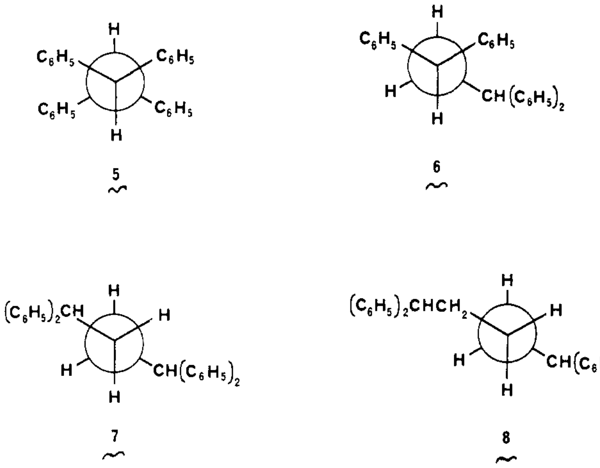

Figure 2. Conformational formulas for tetraphenylalkanes.

reasonably efficient one when the interacting centers are on adjacent or 1–3 related carbon atoms but that this reactivity drops rapidly as the benzene rings are further separated. In the last two members of the series the quantum yields for the $\pi$-interaction process are actually much less than 0.01 since no detectable amount of product formation can be attributed to this type of reaction.

The most reasonable explanation for the decrease in reactivity in passing from compound **5** to **8** is related to the nearness of approach of the interacting $\pi$ systems. If one examines molecular conformations for the four tetraphenylalkanes **5**–**8** (Figure 2), a clear difference between reactive and unreactive systems appears. For 1,1,2,2-tetraphenylethane (**5**) and 1,1,3,3-tetraphenylpropane (**6**) no conformation exists in which at least two $\pi$ systems on different atoms are not held in close proximity. The more reactive of these two (**5**) contains $\pi$ systems held more closely together. For 1,1,4,4-tetraphenylbutane (**7**) and 1,1,5,5-tetraphenylpentane (**8**) the situation is quite different, for here the favored conformations have the aromatic rings situated on opposite sides of the molecule, hence, well separated. The conclusion drawn is simply that unreacting molecules have $\pi$ systems which are too remote for interaction.[6]

Turning next to the question of the nature of the reactive excited state in these $\pi$-interaction processes, one finds there are three types of information which have bearing on this question. The first of these has to do with sensitization experiments. Clearly in the systems where it occurs, the $\pi$-interaction reaction is sensitized by acetone although the sensitization is an inefficient process as evidenced by the fact that the sensitized quantum yields are less than those arising from direct irradiation (Table I). If this reaction is a triplet state process, a fact suggested but not proved by acetone sensitization, it is logical that the transfer of energy would be possible but inefficient due to the triplet energy of the tetraphenylalkanes **5** and **6** ($E_t$ = 82 kcal/mol) being slightly higher than acetone ($E_t$ = 80 kcal/mol).[7] The observation that a lower energy sensitizer, acetophenone ($E_t$ = 73 kcal/mol),[8] is completely ineffective in sensitizing this reaction is consistent with the proposal of a high-energy, reactive triplet state participating in this reaction and argues against the possibility of a lower energy, nonspectroscopic triplet being responsible for this process. Sensitization involving energy transfer between the spectroscopic singlet state of acetone and the tetraphenylalkanes **5** and **6** is quite unlikely on an energetic basis due to the fact that the acetone singlet state is considerably lower in energy (more than 10 kcal/mol) than the corresponding state in the tetraphenylalkanes. The *a priori* possibility of a nonspectroscopic singlet state responsible for reaction is compatible with the sensitization findings.

Further information about the nature of the excited state in these reactions arises from the study of the quenching of the photoreactions of 1,1,2,2-tetraphenylethane (**5**) and 1,1,3,3-tetraphenylpropane (**6**) by piperylene. Examination of the results pictured in Figure 1 (see Experimental Section for details) reveals that piperylene is an effective quenching agent for this reaction even at relatively low quencher concentrations and that a linear relationship exists between the quencher concentrations and the reciprocal of the quantum yield. The latter observation means that, unless there is an accidentally equal quenching of two different excited states, only one state is responsible for the $\pi$-interaction process.[9]

When an analysis of the sensitization and quenching experiments is made, it appears to be consistent with a reactive triplet exicted state which is either the same triplet observed spectroscopically or one near to it in energy. This conclusion derives from the following considerations. Two types of excited states would explain the acetone sensitization, a triplet state, either the spectroscopic triplet or one energetically similar, or a singlet state whose energy is well below the energy of the spectroscopic singlet. Of these two possibilities, the triplet state should be easily quenched by piperylene ($E_t < 60$ kcal/mol).[10] A singlet state, whose energy was well below that of the corresponding state for **5** or **6**, should not transfer excitation to the piperylene singlet whose singlet energy is above that of the tetraphenylalkanes; hence, a triplet state is more consistent with the observed experimental data.[11]

Further support for the triplet assignment to the reactive state in the $\pi$-interaction processes under study arises from the observation that the phosphorescence of both **5** and **6** is totally quenched by a 0.2 *M* concentration of piperylene. This same piperylene concentration is also sufficient to cause essentially complete quenching of the photochemical reaction.

It is of interest to compare the fact that a triplet excited state is responsible for the reactions observed

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(6) We are investigating further systems where di-$\pi$-butane and di-$\pi$-pentane reactions may be possible owing to forcing the interacting systems into closer proximity.

(7) R. F. Borkmann and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

(8) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(9) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N Y., 1967, pp 94–95.

(10) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," New York, N. Y., 1967, p 509.

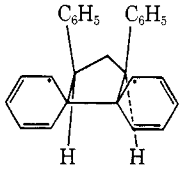
(11) The possibility of singlet quenching by piperylene involving a nonspectroscopic singlet state cannot be completely excluded; however, it is minimized here by the need for only low quencher concentration[12] and the use of a low reactivity diene quencher (piperylene).[13]

(12) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665 (1966).

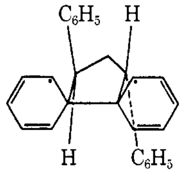
(13) R. R. Hautala and N. J. Turro, *ibid.*, **93**, 559 (1971).

here with related findings on the nature of excited states in similar reactions. Zimmerman has noted that in the di-$\pi$-methane rearrangement acyclic systems react *via* singlet pathways while bicyclic systems prefer triplet processes.[14] He has further proposed that the lack of reactivity for acyclic triplets is due to a free rotor process dissipating the excitation energy.[15] The observed triplet reactivity for **5** and **6**, which do not have the free rotor deactivation available due to the constraint of the $\pi$ systems to aromatic rings, is in agreement with the Zimmerman proposal. The fact that the di-$\pi$-ethane and di-$\pi$-propane reactions observed in **5** and **6** follow the pattern described by Zimmerman raises the possibility that this principle may apply to an even broader group of photochemical reactions.

The final aspect to the findings reported here which merits consideration concerns the fact that in low conversion irradiations of 1,1,3,3-tetraphenylpropane (**6**) the only cyclopropane detectable was *trans*-1,2-diphenylcyclopropane (**14**). Although the reason for this stereoselectivity may be associated with an as yet unknown factor, we would like to suggest a possible explanation for this phenomenon based on a consideration of the ease of formation of two possible diradical intermediates. The diradical **18** actually represents either a cis (**18a**) or trans (**18b**) isomeric form. Loss of biphenyl from the cis isomer (**18a**) would lead most easily to *cis*-1,2-diphenylcyclopropane (**13**) while a similar loss from **18b** would proceed more readily to the trans isomer (**14**). If the factor controlling stereochemistry in cyclopropane formation is whether **18a** or **18b** is produced from excitation of **6**, the relative positioning of groups in the excited state of **6** as $\pi$ interaction begins becomes the important stereochemical factor. The formation of **18b** should have a lower energy pathway than **18a** since as **18a** is being formed the noninteracting benzene rings are being forced into increasing closer proximity while in **18b** the noninteracting rings move to opposite sides of the molecule during formation. This difference in steric interaction could lead to a favored formation of **18b**, hence, *trans*-1,2-diphenylcyclopropane (**14**).[16]



**18a**



**18b**

## Experimental Section

**Vicor-Filtered Irradiation of 1,1,3,3-Tetraphenylpropane (6).** In a typical run 348 mg (1.00 mmol) of 1,1,3,3-tetraphenylpropane[17] (**6**) in 350 ml of methanol was irradiated for 1 hr with a 450-W Hanovia high-pressure mercury-vapor lamp which had been lowered into a water-cooled quartz immersion well. Prepurified nitrogen was passed through the solution for 1 hr prior to irradiation and a slow stream of nitrogen was continued during photolysis.

After irradiation, the solvent was removed by distillation *in vacuo* below 25°, producing a distillate which exhibited the uv spectrum of biphenyl and leaving a residual yellow oil. The residual oil was chromatographed on a 90 × 2.5 cm Florisil column slurry packed in 1:9 ether–hexane; 60 ml fractions were collected. The column was eluted as follows: 0.5 l. of hexane, 0.5 l. of 1:49 ether–hexane, and 0.75 l. of 1:24 ether–hexane.

Fraction 7 afforded 63 mg (0.42 mmol, 93%) of biphenyl (**12**), mp 68°, identical in ir and nmr spectra with a known sample.[18] Fractions 8–10 gave 49 mg of a mixture of compounds. The nmr of this mixture indicated it to be equal amounts of *cis*- and *trans*-1,2-diphenylcyclopropane (**13** and **14**). Rechromatography of these fractions under the same conditions separated them into 20 mg (0.11 mmol, 23%) of *trans*-1,2-diphenylcyclopropane (**14**), identified by comparison with an authentic sample,[19] and 21 mg (0.11 mmol, 24%) of *cis*-1,2-diphenylcyclopropane, also identified by comparison with an authentic sample.[5] Fractions 21–25 yielded 195 mg (0.57 mmol) of unreacted 1,1,3,3-tetraphenylpropane (**6**). Fractions 26–28 gave 44 mg (0.19 mmol, 44%) of 1,3-diphenyl-1-methoxypropane (**15**), identified by comparison with known sample.[5]

**Vycor-Filtered Irradiations of 1,1,4,4-Tetraphenylbutane (7) and 1,1,5,5-Tetraphenylpentane (8).** The irradiation and isolation procedures were the same as employed in the Vycor-filtered irradiation of **6**. The photolysis time was extended to 4 hr in each case.

From chromatography of 1,1,4,4-tetraphenylbutane[17] (**7**) fraction 7 yielded 3 mg (0.005 mmol, 1%) of diphenylmethane, identified by nmr and ir spectroscopy. Fraction 8 yielded 7 mg (0.001 mmol, 2%) of 1,1-diphenylethylene, also identified by ir and nmr spectroscopy. Fractions 20–25 afforded 180 mg (0.50 mmol) of unreacted 1,1,4,4-tetraphenylbutane (**7**). No other materials could be eluted from the chromatography column.

From chromatography of 1,1,5,5-tetraphenylpentane[17] (**8**), fraction 7 gave 3 mg (0.005 mmol, 1%) of diphenylmethane. Fractions 20–25 produced 190 mg (0.50 mmol) of unreacted 1,1,5,5-tetraphenylpentane (**8**). No other materials could be obtained from the chromatography column.

**Synthesis of 1,1,3,3-Tetra-*p*-tolylpropane (16).** The 1,1,3,3-tetra-*p*-tolylpropane (**16**) was synthesized according to the procedure of Hauser, Hauser, and Hamrick[17] for the synthesis of 1,1,3,3-tetraphenylpropane (**6**), the only difference being the substitution of di-*p*-tolylmethane for diphenylmethane. From this reaction mixture a nearly quantitative yield of 1,1,3,3-tetra-*p*-tolylpropane was obtained: mp 150–152°; nmr ($CCl_4$) $\tau$ 3.07 (16 H, s), 6.40 (4 H, t), 7.42 (4 H, t), and 7.80 (12 H, s).

*Anal.* Calcd for $C_{31}H_{32}$: C, 92.01; H, 7.99. Found: C, 92.00; H, 7.92.

**Vicor-Filtered Irradiation of 1,1,3,3-Tetra-*p*-tolylpropane.** The irradiation and isolation procedures were the same as in the Vycor-filtered irradiation of **6**. Fraction 8 gave 69 mg (0.42 mmol, 93%) of 4,4′-dimethylbiphenyl, identified by comparison with an authentic sample.[18] Fractions 9 and 10 contained a mixture showing the same nmr spectrum as the mixture of *cis*- and *trans*-1,2-diphenylcyclopropane obtained from the Vycor-filtered irradiation of **6** except for two 3 H absorptions at $\tau$ 7.95 and 7.80. Rechromatography of these fractions under the same conditions separated them into two colorless oils. The first of these was identified as *trans*-1,2-di-*p*-tolylcyclopropane (22 mg, 0.11 mmol, 23%) on the basis of nmr absorptions at $\tau$ 3.05 (10 H, s), 7.80 (6 H, s), 7.92–8.14 (2 H, m), and 8.68–8.89 (2 H, m) and its independent synthesis from 4,4′-dimethylstilbene.[19] The second oil from the rechromatography of fractions 9 and 10 was found to be *cis*-1,2-di-*p*-tolylcyclopropane, based on its nmr ($CCl_4$) absorptions at $\tau$ 2.80–3.26 (10 H, m), 7.70 (2 H, t), 7.95 (6 H, s), and 8.75 (2 H, t) and independent synthesis *via* isomerization of the trans isomer.[5] Fractions 21–26 from the 1,1,3,3-tetra-*p*-tolylpropane (**16**) irradiation mixture afforded 216 mg (0.58 mmol) of unreacted **16**. Fractions 27–28 gave 48 mg of a slightly yellow oil identified as 1,3-di-*p*-tolyl-1-methoxypropane by comparison with an authentic sample obtained

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(14) H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969).

(15) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 1409 (1970). An exception to this rule has recently been described by Z. Goldschmidt and A. S. Kende, *Tetrahedron Lett.*, 4625 (1971).

(16) As has been described in ref 5 and verified under our reaction conditions, *cis*-1,2-diphenylcyclopropane (**13**) arises from photolysis of the trans isomer (**14**).

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

(18) Aldrich Chemical Co., Milwaukee, Wis.

(19) Authentic samples of the trans isomers of the cyclopropane photoproducts were synthesized *via* a modification of the Simmons–Smith reaction as reported by S. Sawada, J. Oda, and Y. Inouye, *J. Org. Chem.*, **33**, 2141 (1968).

from the photochemical addition of methanol to *trans*-1,2-di-*p*-tolylcyclopropane.[6]

**Synthesis of 1,1-Diphenyl-3,3-di-*p*-tolylpropane (17).** The synthesis of 1,1-diphenyl-3,3-di-*p*-tolylpropane was the same as that for **6**[17] except that 2,2-diphenylethyl chloride[20] replaced methylene chloride and di-*p*-tolylmethane replaced diphenylmethane in the synthesis. From this reaction a nearly quantitative yield of a colorless oil was obtained. Although attempted crystallization of this material was unsuccessful, spectroscopic and chromatographic analysis showed to to be homogeneous. It was assigned the structure 1,1-diphenyl-3,3-di-*p*-tolylpropane on the basis of the following data: nmr ($CCl_4$) $\tau$ 2.88 (10 H, s), 3.00 (8 H, s), 6.28 (2 H, t), 7.34 (2 H, t), and 7.83 (6 H, s).

*Anal.* Calcd for $C_{29}H_{28}$: C, 92.55; H, 7.45. Found: C, 92.26; H, 7.50.

**Vycor-Filtered Irradiation of 1,1-Diphenyl-3,3-di-*p*-tolylpropane (17).** The irradiation and isolation procedures were the same as in the Vycor-filtered irradiation of **6**. Fraction 8 gave 65 mg (0.42 mmol, 92%) of 4-methylbiphenyl, identified by comparison with an authentic sample.[18] Fractions 9 and 10 consisted of a mixture of two compounds which were separated by rechromatography to give *trans*-1-phenyl-2-*p*-tolylcyclopropane (22 mg, 0.11 mmol, 23%), identified by nmr and ir comparison with a sample synthesized from *trans*-4-methylstilbene *via* the Simmons–Smith reaction.[19] The second of the two compounds in fractions 9 and 10 was identified as *cis*-1-phenyl-2-*p*-tolylcycloproapne by nmr and ir comparison with a sample obtained by isomerization of *trans*-1-phenyl-2-*p*-tolylpropane.[5] Fractions 21–25 from the 1,1-diphenyl-3,3-di-*p*-tolylpropane (**17**) irradiation mixture afforded 200 mg (0.57 mmol) of unreacted **17**. Fractions 26–28 gave a mixture of methoxy ethers which are thought to be 1-methoxy-1-phenyl-3-*p*-tolylpropane and 1-methoxy-3-phenyl-1-*p*-tolylpropane; however, it was not possible to separate them. An identical mixture of methoxy ethers was obtained from photolysis of *trans*-1-phenyl-2-*p*-tolylcyclopropane.

**Sensitized Irradiation of 1,1,3,3-Tetraphenylpropane (6).** The irradiation and isolation procedures were the same as employed in the Vycor-filtered irradiation of **6**. The only differences were that acetone was used as the solvent and the reaction time was extended to 3 hr.

Fractions 7 and 8 yielded 45 mg (0.29 mmol, 90%) of biphenyl. Fractions 9–11 gave, as in previous chromatographies, a mixture of *cis*- and *trans*-1,2-diphenylcyclopropanes which were separated into pure isomers by rechromatography to yield 25 mg (0.13 mmol, 41%) of the trans and 39 mg (0.17 mmol, 53%) of the cis isomers. Fractions 21–26 gave 239 mg of unreacted starting material. No 1,3-diphenyl-1-methoxypropane was observed.

**Quantum Yield Determinations.** The quantum yields were determined using a 100-W Hanovia high-pressure mercury-vapor lamp which had been lowered into a quartz immersion well.[21] Between the light source and the reaction mixture a Corex filter was placed (Pyrex in sensitized irradiations) and a solution which was 2 *M* in both nickel and cobalt sulfates was circulated, providing both a temperature control (25°) and a light filter for the reaction. The light measurements were conducted using a jacketed cell[21] which always contained the actinometer, potassium ferrioxalate,[22] in the outer chamber to detect light not captured by the contents of the inner chamber. All direct irradiations required some correction for light not absorbed by the tetraphenylalkanes in the inner chamber. The inner chamber alternately was filled with actinometer, irradiation mixture, then actinometer, thus measuring the light emitted both before and after irradiation. The irradiations were run to slightly less than 7% conversion to minimize the light absorption by the products. Each quantum yield obtained represented an average of three determinations (see Table I).

Chromatographic isolation of the products as described in the preparative irradiations was employed. In certain cases (see Table I) the product yields were too low at the conversion used for reliable measurement under these low-conversion conditions. The quantum yield photolyses differed from the preparative irradiations in one respect: irradiation of 1,1,3,3-tetraphenylpropane (**6**) gave no measurable amount of *cis*-1,2-diphenylcyclopropane (**13**) but showed an increase in the trans isomer (**14**). (At low conversions the secondary isomerization of **14** to **13** had not had a chance to occur to any measurable extent.)

**Quenching of the Photoreactions of 1,1,2,2-Tetraphenylethane (5) and 1,1,3,3-Tetraphenylpropane (6) by Piperylene.** Quenching studies on the photoreactions of **5** and **6** were conducted using piperylene as a quenching agent. The apparatus and procedure for determining quantum yields described above were also used in the quenching experiments. The results of these experiments are listed in Table II and shown in Figure 1.

**Table II.** Quenching of Photoreaction of **5** and **6** by Piperylene

| Compd | Quencher concn, *M* | Quantum yield |
|---|---|---|
| **5** | 0.00 | 0.20 |
| **5** | 0.01 | 0.14 |
| **5** | 0.03 | 0.10 |
| **5** | 0.05 | 0.07 |
| **5** | 0.10 | 0.04 |
| **6** | 0.00 | 0.07 |
| **6** | 0.01 | 0.06 |
| **6** | 0.03 | 0.04 |
| **6** | 0.05 | 0.03 |
| **6** | 0.10 | 0.02 |

Several aspects of the quenching experiments are worth noting. The percentage of the light absorbed by piperylene at 0.10 *M* concentration, the highest concentration used, was not significant (3%). The variation in individual quantum yields determined at a given piperylene concentration increased from less than 10% at low quencher concentrations to 25% at the highest concentration. The quantum yields used were based on disappearance of starting material and were determined by nmr analysis of the crude irradiation mixtures as well as actual isolation of unreacted starting material.

**Triplet Energies of the Four Tetraphenylalkanes 5–8.** The triplet energies of each of the four compounds **5–8** were determined on an Aminco-Bowman spectrofluorometer with a phosphorescence attachment at 77°K in methanol or EPA (ethyl ether–isopentane–ethanol 2:2:1). Each of the four was found to have a triplet energy of 82 kcal/mol. This phosphorescence was totally quenched by 0.20 *M* piperylene.

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(20) K. E. Hamlin, A. W. Weston, F. E. Fischer, and R. J. Michaels, Jr., *J. Amer. Chem. Soc.*, **71**, 2734 (1949).

(21) Ace glass, Inc., photochemical immersion well (No. 6515) and jacketed photochemical reaction vessel (No. 6522) were used in the quantum yield determinations.

(22) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser., A*, **235**, 518 (1956).