The Photochemistry of 1,1,2,2-Tetraphenylethane. A Di- π -ethane Reaction

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The photolysis of 1,1,2,2-tetraphenylethane (1) has been found to result in the formation of 1-(2-biphenyly)-1,2-diphenylethane (6), biphenyl (3), and *cis*- and *trans*-stilbene (2 and 4). Mechanistic studies involving the photolysis of 1,1-diphenyl-2,2-ditolylethane (8) were conducted. The results from these studies require that three of the four photoproducts (2, 3, and 4) from irradiation of 1,1,2,2-tetraphenylethane (1) arise through an interaction of the number one positions of two benzene rings attached to adjacent carbon atoms. This type of reaction is termed a di- π -ethane reaction in analogy to the well-known di- π -methane rearrangement. The mode of formation of the fourth photoproduct is still unknown.

We have recently isolated 1,1,2,2-tetraphenylethane (1) as one of the photoproducts from the photolysis of benzophenone azine.² There was a clear indication from the products in this reaction that 1,1,2,2-tetraphenylethane (1) was itself photolabile. We have now investigated the photochemistry of 1 and wish to describe the unusual fragmentation and rearrangement processes it undergoes as well as to report the discovery of a new type of photochemical process, a di- π -ethane reaction.

Results

Vycor-filtered irradiation of 3.00 mmol of 1,1,2,2tetraphenylethane (1) in 1200 ml of methanol under nitrogen for 45 min with a 450-W Hanovia mercury vapor lamp caused the disappearance of 0.93 mmol of starting material as well as a yellowing of the reaction mixture. Distillation of the solvent and chromatography of the photolysis mixture on Florisil separated it into four fractions in addition to unreacted starting material. The three minor products were identified as cis-stilbene (2, 16%), biphenyl³ (3, 10%), and trans-stilbene (4, 5%) by comparison with known samples. Structural assignment to the major photoproduct (65% yield, mp 79-81°) rests upon the following spectroscopic and chemical evidence. The major product was found to be isomeric with the starting material (1) by elemental analysis and molecular weight determination. The ir spectrum showed only absorptions characteristic of an alkyl aromatic system. The nmr spectrum (CCl₄) showed absorptions at τ 3.10 (19 H, m), 5.67 (1 H, t), and 6.81 (2 H, d). These data suggested that the photoproduct possessed a substituted biphenvl structure. The fact that the uv spectrum exhibited only end absorption was in accord with a biphenyl system which possessed an ortho substitution pattern.⁴ Spectroscopic analysis, therefore, was consistent with two possible photoproduct structures, 2-(2-biphenylyl)-1,1-diphenylethane (5) and 1-



(1) Author to whom inquiries should be addressed.

(2) R. W. Binkley and J. Gorse, III, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., 1971, No. ORGN 128.
(3) The uv spectrum of the methanol distilled from the reaction mixture had an absorption spectrum identical with that of biphenyl; thus, it is likely that some biphenyl was lost during evaporation of the solvent.
(4) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1964, p 397.

(2-biphenylyl)-1,2-diphenylethane (6). Assignment of structure 6 to the major photoproduct was made on the basis of its synthesis from 1-bromo-1,2-diphenyl-ethane and 2-bromobiphenyl in the presence of magnesium. The photochemical reaction of 1,1,2,2-tetraphenylethane (1) is described by eq 1.

Irradiation of 1,1,2,2-tetraphenylethane (1) under the same conditions as described above except for a longer photolysis time (3 hr) followed by the same chromatographic procedure resulted in similar yields of *cis*-stilbene (2, 16%), biphenyl⁸ (3, 11%), and *trans*stilbene (4, 7%); however, the yield of 1-(2-biphenylyl)-1,2-diphenylethane (6) was reduced to 22% and a new photoproduct was formed in 39% yield. The



new photoproduct was also isomeric with the starting material (1) and nearly identical with 6 in ir and nmr spectral data [nmr (CCl₄) $\tau 2.85$ (19 H, m), 5.79 (1 H, t), 6.66 (2 H, d)]; however, the uv spectrum exhibited a maximum at 251 nm (ϵ 10,000), indicating a biphenyl system which was not ortho-substituted. On the basis of this spectral information the most probable structure for the photoproduct was 1-(3-biphenylyl)-1,2-diphenylethane (7). Confirmation of this structural assignment was achieved by synthesis of 7 from 1-bromo-1,2-diphenylethane and 3-bromobiphenyl via a Grignard coupling reaction.

The two reactions of 1,1,2,2-tetraphenylethane (1) described above clearly suggested that 1-(2-biphenyly)-1,2-diphenylethane (6) was an intermediate in the formation of 1-(3-biphenyly)-1,2-diphenylethane



(7). Photolysis of 6 under the same conditions as 1 led quantitatively to 7.5

1,1-Diphenyl-2,2-ditolylethane (8) was irradiated using the same photolysis procedure as with 1. Chromatography on Florisil separated the reaction mixture into two mixtures of photoproducts. Preparative vpc analysis of the first photoproduct mixture separated it into 4-methylbiphenyl (9, 22%) and cis- and trans-4-methylstilbene (10, 16% and 11, 5%). No other stilbenes or methylbiphenyls were detected even though experiments with biphenyl, 2- and 3-methylbiphenyl, 4,4'-dimethylbiphenyl, and cis- and trans-4,4'-dimethylstilbene showed that they would have been in this mixture and would have been detected by vpc analysis.

The second fraction isolated from photolysis of 8 exhibited an nmr spectrum which was clearly a mixture of compounds related to 1-(2-biphenylyl)-1,2-diphenylethane (6). The nmr spectrum was consistent with an essentially equal combination of 12 and 13; unfortunately, however, this photolysis mixture proved to be an inseparable one. Vpc analysis resulted in decomposition. Adsorption chromatography using Florisil, silica gel, and alumina as well as several types of liquid-liquid partition chromatography were unsuccessful.



The photochemical reaction of 1,1-diphenyl-2,2ditolylethane (8) is described in eq 2.



biphenyls analogous to 6 (2)

Discussion

There are several interesting questions raised by the results from the photolysis of 1,1,2,2-tetraphenylethane (1). Perhaps the most intriguing of these deals with the mechanism of the reaction process, although a knowledge of the types of systems which will undergo this reaction is certainly of interest. Even though further experimentation is necessary before complete mechanistic determinations can be made, the results from this study give important insight into understanding this reaction and the new mechanistic process which controls it. In considering possible mechanisms for the photoreaction of 1,1,2,2-tetraphenylethane⁶ (1), two fundamental reaction types, the di- π -methane and the di- π -ethane (Scheme I), appear possible. A di- π -methane





reaction in this system (Scheme II) would be initiated



by bond formation between the substituted positions of two geminal benzene rings and lead to the intermediate 14. The diradical thus produced could stabilize itself by rearrangement to the cyclobutane 16, which upon further excitation would either fragment the two ring bonds to produce biphenyl (3) and cis- and trans-stilbene (2 or 4) or break only a single cyclobutane ring bond to lead, after hydrogen migration, to 1-(2-biphenylyl)-1,2-diphenylethane (6). It is worth noting that although the proposed reaction process (Scheme II) is identical with the di- π -methane rearrangement throughout the first segment of the reaction course, it takes a different turn at an intermediate stage. In the normal di- π -methane reaction the diradical 15 would have formed a norcaradiene

⁽⁵⁾ This type of rearrangement has been studied by a number of workers. Most recent is the thorough examination of methylbiphenyls by V. Mende, J. L. Laseter, and G. W. Griffin, *Tetrahedron Lett.*, 3747 (1970).

⁽⁶⁾ The most extensive studies of the di- π -methane reaction have been by H. E. Zimmerman and A. C. Pratt, J. Amer. Chem. Soc., **92**, 6267 (1970), and references cited therein.

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structure; instead, however, it undergoes a phenyl migration before ring closure.

A second mechanistic possibility is shown in Scheme III. This process proposes a di- π -ethane reaction to



account for the transformations of 1.1.2.2-tetraphenylethane (1). Such a mechanism differs from the di- π -methane reaction in that it describes the interaction of π systems attached to adjacent carbon atoms. This type of interaction and rearrangement in the case of 1 leads through intermediate diradicals 17 and 18 to the cyclobutane derivative 16. Possible reaction of this intermediate (16) was discussed in the previous paragraph and is pictured in Scheme III.

A decision between the two proposed mechanistic pathways (di- π -methane and di- π -ethane) can be made for three of the four products (2, 3, and 4) from photolysis of 1 based upon the results from irradiation of 1,1-diphenyl-2,2-ditolylethane (8). Excitation of 8 yields 4-methylbiphenyl (9) as the only simple biphenyl and cis- and trans-4-methylstilbene (10 and 11) as the only stilbenes formed (Scheme IV). This result excludes the di- π -methane pathway but is completely consistent with the di- π -ethane proposal. Experimental difficulties (see Results) prevented any conclusion from being drawn regarding the mechanism of formation of the substituted biphenyl 6.

The apparent demonstration that a di- π -ethane type of interaction is taking place in the photolysis of 1 raises a number of questions related to the photochemistry of unsaturated systems. For example: What are the molecular structural requirements for a di- π -ethane reaction to occur? What factors control whether a di- π -methane or di- π -ethane reaction will take place in a particular system where both are possible? Is there a series of related reactions involving the photochemical interaction of π systems in which the two processes discussed here (the di- π -methane and di- π -ethane rearrangements) represent only the



first two members? These and other questions are currently under investigation in our laboratories.

Experimental Section

Vycor-Filtered Irradiation of 1,1,2,2-Tetraphenylethane (1).---In a typical run 999 mg (3.00 mmol) of 1,1,2,2-tetraphenyl-(1) in 1200 ml of methanol was irradiated for 45 min with ethane a 450-W Hanovia high-pressure mercury-vapor lamp which had been lowered into a water-cooled guartz 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 residue consisting of crystals mixed with a yellow oil. The residual oil was chromatographed Initial 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 0.751. of 1:24 ether-hexane.

Fraction 7 afforded 15 mg (0.09 mmol) of crystalline biphenyl, mp 68-69°, identical in ir spectrum and giving no mixture melting point depression with a known sample.7 Fractions 8 and 9 gave 27 mg (0.15 mmol) of cis-stilbene, identical in ir and nmr spectra with an authentic sample.⁷ Fractions 10 and 11 produced 9 mg (0.06 mmol) of crystalline *trans*-stilbene, mp 118–122°, identical in ir spectrum and showing no mixture melting point depression with a known sample.⁷ Fractions 14-18 yielded 234 mg of a clear oil which crystallized on standing to give a material melting at 69-81°. Identification of this material is described in the following paragraph. Fractions 21-25 afforded 690 mg (2.07 mmol) of unreacted 1,1,2,2-tetraphenylethane (1).

Recrystallization of fractions 14-18 from hexane afforded 204 mg (0.60 mmol) of colorless crystals identified as 1-(2-biphenylyl)-1,2-diphenylethane (6) on the basis of the following black: mp 79-81°; ir λ_{max}^{neat} 3.18-3.43 (s), 6.24 (s), 6.68 (s), 6.76 (s), 6.89 (s), 9.33 (m), 9.70 (m), 9.92 (m), 13.30 (vs), and 14.35 nm (vs); nmr (CCl₄) τ 3.10 (19 H, m), 5.67 (1 H, t), 6.81 (2, H, d). Anal. Calcd for C₂₅H₂₂: C, 93.38; H, 6.62. Found: C,

93.39; H, 6.77.

1-(2-Biphenylyl)-1,2-diphenylethane (6) was synthesized from 1-bromo-1,2-diphenylethane⁸ and 2-bromobiphenyl⁹ in the pres-

Aldrich Chemical Co., Milwaukee, Wis. 53233.
 (8) E. S. Wallis and F. H. Adams, J. Amer. Chem. Soc., 55, 3849 (1933).

(9) G. Schultz, Justus Liebigs Ann. Chem., 207, 353 (1881).

ence of magnesium according to the procedure of Bachmann.¹⁰ This material was found to be identical with the photoproduct, thus confirming the assignment of structure 6 to the major photoproduct from the photolysis of 1,1,2,2-tetraphenylethane (1).

Extended Vycor-Filtered Irradiation of 1,1,2,2-Tetraphenylethane (1).—The irradiation and isolation procedures were the same as those described above except that the irradiation time was extended to 3 hr.

Fraction 7 afforded 45 mg (0.30 mmol) of crystalline biphenyl, mp 67-69°. Fractions 8 and 9 gave 78 mg (0.42 mmol) of *cis*stilbene, identified by ir spectroscopy. Fractions 10 and 11 produced 33 mg (0.19 mmol) of *trans*-stilbene, mp 119-120°. Fractions 14-18 yielded 240 mg of a crystalline material, mp 70-80°, recrystallized from hexane to give 198 mg (0.60 mmol) of 1-(2biphenylyl)-1,2-diphenylethane (6), mp 79-80°. Fractions 19 and 20 afforded 352 mg of a clear oil whose identification is described in the following paragraph. Fractions 21-23 gave 99 mg (0.31 mmol) of unreacted 1,1,2,2-tetraphenylethane (1).

The unknown photoproduct from fractions 19 and 20 was identified as 1-(3-biphenylyl)-1,2-diphenylethane (7) on the basis of the following spectral data as well as its independent synthesis from 1-bromo-1,2-diphenylethane and 3-bromobiphenyl¹¹ in the presence of magnesium:¹⁰ ir λ_{max}^{neat} 3.18-3.43 (s), 6.25 (s), 6.68 (s), 6.76 (m), 6.89 (s), 9.33 (m), 9.70 (m), 13.25 (vs), and 14.30 nm (vs); nmr (CCL) τ 2.85 (19 H, m), 5.79 (1 H, t), and 6.66 (2 H, d).

Vycor-Filtered Irradiation of 1-(2-Biphenylyl)-1,2-diphenylethane (6).—The irradiation and isolation procedures were the same as those described above except that the irradiation was conducted for only 5 min and 50 mg (0.15 mmol) of 6 was irradiated.

Fractions 19 and 20 afforded 45 mg of 1-(3-biphenylyl)-1,2diphenylethane (7), identified by nmr spectroscopy.

Synthesis of 1,1-Diphenyl-2,2-ditolylethylene.—Magnesium (3.00 g, 0.125 g-atom) and benzhydrol bromide⁷ (24.7 g, 0.125 mol) were added to 50 ml of anhydrous ether. After the initial reaction had subsided, the mixture was refluxed for 1 hr, followed by the dropwise addition of 21 g (0.100 mol) of 4,4'-dimethylbenzophenone in 100 ml of anhydrous ether and a second 1-hr reflux period. The ether was removed *in vacuo* below 25° and 25 ml of a 48% solution of hydrogen bromide in acetic acid was carefully added, precipitating a white solid. This solid was

washed with water and recrystallized twice from chloroformhexane to give 9.7 g of 1,1-diphenyl-2,2-ditolylethylene: mp 141-145°; nmr (CDCl₃) τ 3.05 (10 H, s), 3.18 (8 H, s), and 7.80 (6 H, s).

Anal. Calcd for C₂₈H₂₄: C, 93.30; H, 6.70. Found C, 93.41; H, 6.71.

Synthesis of 1,1-Diphenyl-2,2-ditolylethane.—1,1-Diphenyl-2,2-ditolylethylene (3 g) was reduced by the method of Bachman¹⁰ to give 2.1 g of 1,1-diphenyl-2,2-ditolylethane: mp 129–130°; nnr (CDCl₃) τ 2.6–3.1 (18 H, m), 5.15 (2 H, s), and 7.88 (6 H, s).

Anal. Caled for $C_{25}H_{25}$: C, 92.45; H, 7.55. Found: C, 92.40; H, 7.13.

Vycor-Filtered Irradiation of 1,1-Diphenyl-2,2-ditolylethane (8).—The irradiation and isolation procedures were the same as those described in the Vycor-filtered irradiation of 1,1,2,2-tetraphenylethane (1) except that 1.00 g of 8 was irradiated and the irradiation time was extended to 35 min.

Fractions 7-9 afforded 68 mg of a mixture of materials whose separation is described below. Fractions 10 and 11 yielded 10 mg (0.05 mmol) of *trans*-4-methylstilbene, mp 178° (lit.¹² mp 180°), identical with an authentic sample. Fractions 14-19 afforded a second mixture of compounds which, unfortunately, proved to be inseparable. Various types of absorption and partition chromatography were unsuccessful at separating this mixture. Fractions 22-27 gave 698 mg of unreacted starting material (8).

Preparative vpc analysis of fractions 7-9 on a 5 ft \times 0.25 in. column packed with 20% SE-30 on Chromosorb P at 140° separated them into two components. The first of these represented 55% (37 mg, 0.22 mmol) of the mixture and was found by comparison with an authentic sample⁷ to be 4-methylbiphenyl. The second component was found to be *cis*-4-methylstilbene (31 mg, 0.16 mmol) also by comparison with a known sample.¹⁹ No other materials could be detected in this mixture.

Registry No.—1, 632-50-8; 6, 32298-37-6; 7, 32298-38-7; 8, 32298-39-8; 1,1-diphenyl-2,2-ditolyl-ethylene, 32298-40-1.

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(12) A. Ramart, Ann. Chim. (Paris), [10] 8, 315 (1938).

(13) cis-4-Methylstilbene was obtained by the Pyrex-filtered photoisomerization of the trans isomer in benzene.

⁽¹⁰⁾ W. E. Bachmann, J. Amer. Chem. Soc., 55, 3859 (1933).

⁽¹¹⁾ M. Gomberg and W. W. Bachman, J. Amer. Chem. Soc., 46, 2343 (1924).