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THE PHOTOCHEMICAL REARRANGEMENT OF 1,1,2,2-TETRAPHENYLETHANE. A DI-π-ETHANE REACTION.

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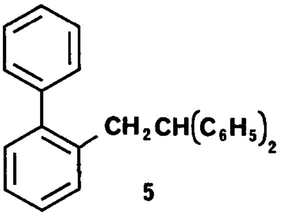
We would like to report our findings concerning a new reaction arising from the photolysis of 1,1,2,2-tetraphenylethane (1)[2]. The significance attached to this reaction lies not only in the formation of an unusual photochemical rearrangement product but also in the discovery of a new type of photochemical process, a di-π-ethane reaction[3].

Vycor filtered irradiation of 1.00 mmol of 1,1,2,2-tetraphenylethane (1) in 400 ml of methanol under nitrogen for 15 min with a 450-W Hanovia mercury vapor lamp caused the rapid disappearance of the starting material and the formation of four photoproducts, isolated by chromatography on Florisil. The three minor products were identified as cis-stilbene (2, 16%), biphenyl (3, 10%)[5], and trans-stilbene (4, 5%) by comparison with known samples[2]. Structural assignment to the major photoproduct (65%, mp 79-81°) rests upon the following spectroscopic and chemical evidence. The major photoproduct 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 (CCl_4) showed absorptions at 3.10 (19 H, m), 5.67 (1 H,t), and 6.81 (2 H, d) τ. These data suggested that the photoproduct possessed a substituted biphenyl structure. The fact that the uv spectrum showed only end absorption was in accord with a biphenyl system which possessed an ortho substitution pattern[6]. Spectroscopic analysis, therefore, was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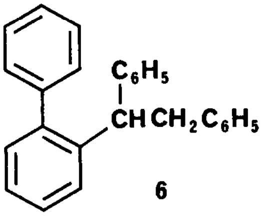
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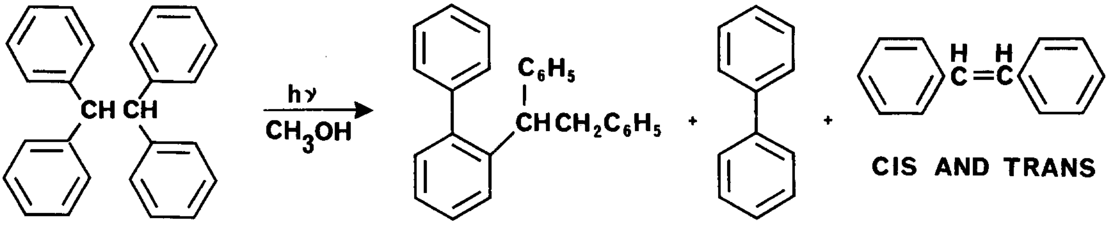
consistent with two possible photoproduct structures, 2-(2-biphenylyl)-1,1-diphenylethane (5) and 1-(2-biphenylyl)-1,2-diphenylethane (6). Assignment of structure 6 to the major photoproduct was made on the basis of its independent synthesis from 1-bromo-1,2-diphenylethane and 2-bromobiphenyl in the presence of magnesium. The photochemical reaction of 1,1,2,2-tetraphenylethane (1) is described by the following equation:



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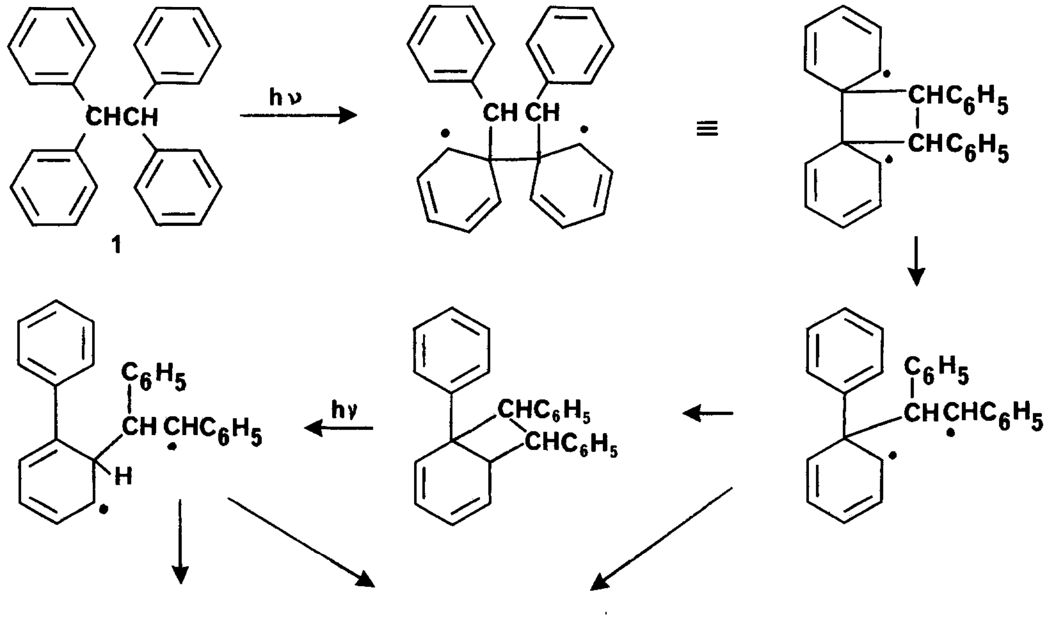
We propose the following mechanism to account for the observed photochemical reaction.

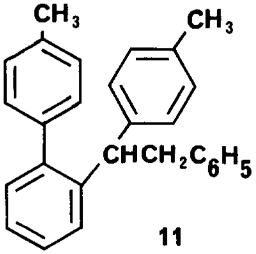


6 2,3,4

In order to test this mechanistic proposal 1,1-diphenyl-2,2-ditolylethane (7)[7] was irradiated using the same photolysis procedure as with 1. Chromatography on Florisil separated the reaction mixture into two mixtures of photoproducts. The first mixture contained only stilbenes and simple (methyl substituted) biphenyls while the second consisted of methyl substituted biphenyls corresponding to 1-(2-biphenylyl)-1,2-diphenylethane (6) obtained from photolysis of 1. Preparative vpc analysis (5 ft x 0.25 in column packed with 20% SE30 on Chromosorb P) of the first photoproduct mixture separated it into 4-methylbiphenyl[2] (8, 22%), and *cis*- and *trans*-4-methylstilbene[8] (9, 16% and 10, 5%). No other stilbenes or methylbiphenyls were detected even though experiments with the other possible stilbenes and simple biphenyls showed that they would have been in this mixture and would have been detected by vpc analysis[9].

The formation of 4-methylbiphenyl (8) from the photolysis of 1,1-diphenyl-2,2-ditolylethane (7) requires, as the proposed mechanism postulates, that the biphenyl formed by photolysis of 1 result from bonding together of two aromatic rings originally located on adjacent carbons and that this bonding occur at the number one position on each ring. The *cis*- and *trans*-4-methylstilbene (9 and 10) formed confirm the interaction of aromatic rings on adjacent carbons in biphenyl formation; thus, the mechanism proposed for formation of biphenyl (3) and *cis*- and *trans*-stilbene (2 and 4) from photolysis of 1,1,2,2-tetraphenylethane (1) appears to describe well this reaction.

The second fraction isolated from photolysis of 7 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 11 and 12 which would be expected from the proposed mechanism; unfortunately, however, this photolysis mixture proved to be an inseparable one. Vpc analysis resulted in decomposition. Absorption chromatography using Florisil, silica gel, and alumina as well as several types of liquid-liquid partition chromatography were unsuccessful. No conclusion, therefore, can be drawn from this work regarding the mechanism of formation of the



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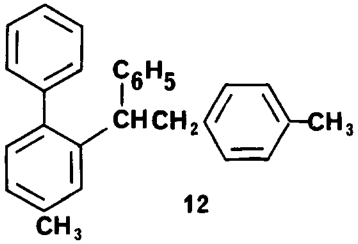

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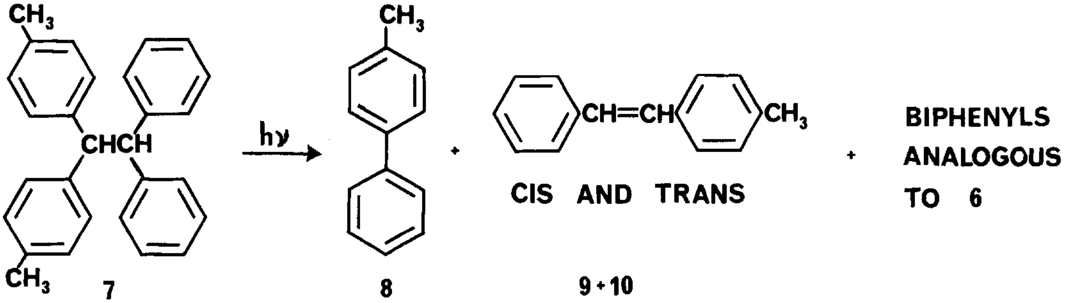
substituted biphenyl (6) from the photolysis of 1,1,2,2-tetraphenylethane (1). We are presently investigating other systems in an effort to observe a reaction analogous to substituted biphenyl formation in a system where mechanistic studies of this reaction will be more successful.



The results from this study may be summarized by stating that the photolysis of 1,1,2,2-tetraphenylethane (1) produces biphenyl (3), cis- and trans-stilbene (2 and 4) and 1-(2-biphenylyl)-1,2-diphenylethane (6). Mechanistic studies have shown that the first three of these photoproducts result from a di-π-ethane reaction. The final product may also result from such a process; however, for this compound the mechanistic studies are inconclusive.

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REFERENCES:

1. Author to whom inquires should be addressed.

2. Aldrich Chemical Co., 940 W. St. Paul Ave., Milwaukee, Wisconsin 53233.

3. The di-π-ethane reaction derives its name from analogy to the di-π-methane rearrangement, a rearrangement which has been extensively studied by Zimmerman and coworkers[4].

4. H. E. Zimmerman and A. C. Pratt, J. Amer. Chem. Soc., 92, 6267 (1970) and references therein.

5. The uv spectrum of the methanol distilled from the reaction mixture had an absorption spectrum identical to biphenyl; thus, it is likely that some biphenyl was lost during evaporation of the solvent.

6. H. H. Jaffe' and M. Orchin, "Theory and Applications of ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, 1964, p 397. Both 5 and 6 have considerably larger ortho substituents than any of the compounds whose uv is described in this reference (ref 6). This is probably the reason for the unusually large shift in the uv maximum.

7. Synthesized according to the method of W. E. Bachmann, J. Amer. Chem. Soc., 55, 3859 (1933).

8. A. Ramart, Ann. de Chim. [10] 8, 315.

9. The stilbenes and biphenyls considered "possible" included biphenyl, 2- and 3-methylbiphenyl, 4,4'-dimethylbiphenyl, cis- and trans-stilbene, and cis- and trans-4,4'-dimethylstilbene.