The Photochemical Conversion of *o*-Terphenyl into Triphenylene

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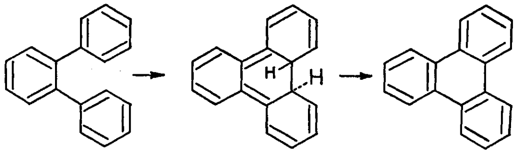
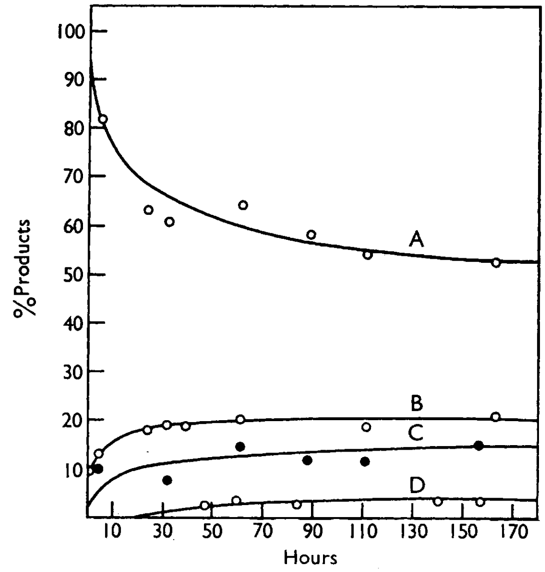
IN the course of their elegant studies of the photocyclisations of stilbenes to phenanthrenes, Mallory and his co-workers[1] found that under the irradiative conditions which readily permitted the cyclodehydrogenations of stilbenes, *o*-terphenyl (I) did not yield triphenylene. Theoretical considerations concerning the unlikelihood of the cyclisation were suggested. While the photolytic conversion of (I) into (III), presumably *via* an intermediate as (II), has thus been questioned, photocyclisations of substances such as the bianthrones and related structures, as well as of diphenylamines and of azobenzenes have now been reported, and good evidence has been presented for an intermediate of type (II) in the case of the stilbenes.[1,2]



(I) (II) (III)

Using an efficient source of ultraviolet radiation,[3] we have found, however, that *o*-terphenyl is converted smoothly into triphenylene when photolysed in benzene solution, in the required presence of iodine. *o*-Terphenyl (1·02 g.), in benzene (170 ml.) containing iodine (0·67 g.), gave triphenylene (71%). When the photolysis of *o*-terphenyl was followed by quantitative gas chromatography, *complete* conversion into triphenylene was found, using 1·00 g. of iodine to 1·02 g. of *o*-terphenyl and 130 hr. photolysis. Without iodine, conversion into (III) failed, and with smaller amounts of iodine conversion was slower and incomplete. The conditions which allowed conversion of (I) into (III) are those we have also found generally effective for synthesis of biaryls by photolysis of iodoaromatic compounds in benzene.[3] It was also found that *op*-quaterphenyl was converted smoothly, in benzene solution with iodine present, into 2-phenyltriphenylene. Identity of the latter was fully confirmed.[4]

The present work relates also to that of Kampmeier and Hoffmeister[5] on the photolysis of 1,2-di-iodobenzene and of 2-iodobiphenyl. In an independent study, concurrent with that of Kampmeier and Hoffmeister (*cf.* footnote 14, Ref. 5), we had found that *o*-terphenyl, together with other products, was formed by photolysis of either 1,2-di-iodobenzene, or of 2-iodobiphenyl in benzene; but we had not detected triphenylene, whose presence was fully demonstrated by Kampmeier and Hoffmeister. We have now re-examined the photolyses of 1,2-di-iodobenzene and of 2-iodobiphenyl, in benzene, and our overall results are in excellent agreement with those of Kampmeier and Hoffmeister, and also with our earlier



Typical run for photolysis of 2-*iodobiphenyl in benzene:* A, *unreacted* 2-*iodobiphenyl;* B, o-*terphenyl;* C, *biphenyl;* D, *triphenylene. The starting concentration was* 1·24 *g. of* 2-*iodobiphenyl in* 170 *ml. of benzene.*

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[1] F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, 1964, **86**, 3094. *Cf.* also C. S. Wood and F. B. Mallory, *J. Org. Chem.*, 1964, **29**, 3373; C. E. Loader, M. V. Sargent, and C. J. Timmons, *Chem. Comm.*, 1965, 127.

[2] F. R. Stermitz, in "Aspects of Organic Photochemistry," edited by O. L. Chapman; Marcel Dekker, Publisher, N.Y. (in press).

[3] W. Wolf and N. Kharasch, *J. Org. Chem.*, 1961, **26**, 283; 1965, **30**, in press. N. Kharasch, W. Wolf, T. Erpelding, P. G. Naylor, and L. Tokes, *Chem. and Ind.*, 1962, 1720.

[4] D. D. Lawson and C. M. Buess, *J. Org. Chem.*, 1960, **25**, 272.

[5] J. A. Kampmeier and E. Hoffmeister, *J. Amer. Chem. Soc.*, 1962, **84**, 3767.

finding that *o*-terphenyl is present in each of the photolysates. As is seen in the Figure, photolysis of 2-iodobiphenyl, in benzene, followed for each of the components by gas chromatography, clearly shows the early formation of *o*-terphenyl, the somewhat later appearance of triphenylene, attended by levelling off of the *o*-terphenyl formation, as well as the concurrent formation of biphenyl. We therefore conclude that *o*-terphenyl is the most logical immediate precursor of triphenylene in the photolysis of 1,2-di-iodobenzene and of 2-iodobiphenyl, in benzene, under the conditions of our work, as well as in the study of Kampmeier and Hoffmeister.

Attempted photocyclisation of 1,2,3-triphenylazulene, (IV),[6] similarly as with *o*-terphenyl, gave no conversion. This was expected, since in (IV) no two of the vicinal phenyl groups can apparently become sufficiently coplanar to permit cyclisations.

The Figure also illustrates the formation of biphenyl and the incompleteness of photolysis of 2-iodobiphenyl even after long irradiation. These observations, which have also been made by Kampmeier and Hoffmeister[5] are of mechanistic interest and have received further detailed study in this laboratory.

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[6] S. J. Assony and N. Kharasch, *J. Amer. Chem. Soc.*, 1958, **80**, 5978.