Photochemical Reaction of 1,1-Diphenylethylene with Benzene

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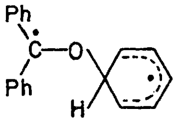
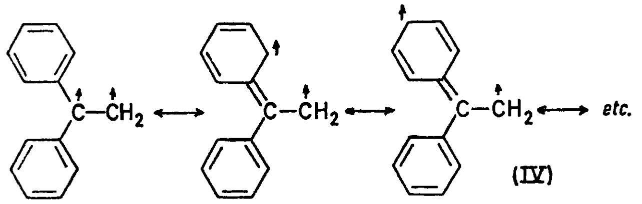
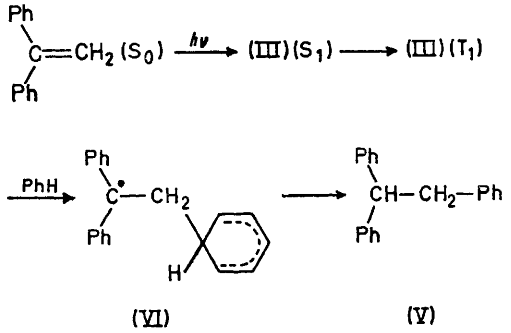
Summary Photoexcited 1,1-diphenylethylene reacts with benzene to give 1,1,2-triphenylethane.

RECENT kinetic studies revealed that the behaviour of the lowest triplet excited state of benzophenone (I) in benzene can be rationalized by reversible formation of a diradical adduct (II).[1] On the other hand, Rosenberg and Servé have shown that electronically excited 1,1-diphenylethylene (III) could react in a similar way as the triplet of (I), because of resonance stabilization, as shown in (IV), with an enhanced diradical reactivity.[2] Combining these two considerations, we felt that photoexcited (III) might be expected to alkylate benzene. We have shown this to be so.


(II)


(IV)

When a solution of (III) (0·04 M) in pure benzene was irradiated in a quartz vessel by means of a high pressure Hg lamp for 180 h, g.l.c. analysis of the reaction mixture showed the presence of a product (V) together with unchanged (III) (28% conversion). No other products such as the dimer of (III)[2] were detected. The compound (V) was isolated by preparative g.l.c. and its structure was firmly established as 1,1,2-triphenylethane by direct comparison with an authentic specimen.[3] The reaction can be visualized as shown in the Scheme, but the formation of triplet (III) by benzene sensitization cannot be ruled out.



SCHEME

The mechanistic details of the conversion of an intermediate (VI) into (V) cannot be easily understood at present since hydrogen migration can take place either intra- or inter-molecularly. The oxidation of (VI) by an external oxidant cannot be ruled out also because the rigorous exclusion of the dissolved oxygen was not carried out. However, to our best knowledge, this is the first example of alkylation of benzene by a photoexcited olefin to form alkylbenzene, although Bryce-Smith *et al.* reported the '1,4-ene-type' reaction between 2,3-dimethylbut-2-ene and benzene, which was obviously induced by excited benzene and intrinsically of different type from ours.[4]

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[2] H. M. Rosenberg and P. Servé, *J. Amer. Chem. Soc.*, 1970, **92**, 4746.
[3] A. Kloges, *Ber.*, 1904, **37**, 1455.
[4] D. Bryce-Smith, B. E. Foulger, A. Gilbert, and P. J. Twitchett, *Chem. Comm.*, 1971, **794**.