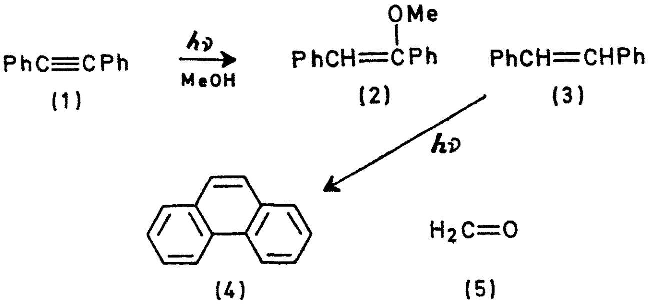
cis-Stilbene as an Intermediate in the Photochemical Cyclization of Diphenylacetylene to Phenanthrene

By T. D. ROBERTS

(*Department of Chemistry, University of Arkansas, Fayetteville, Arkansas* 72701)

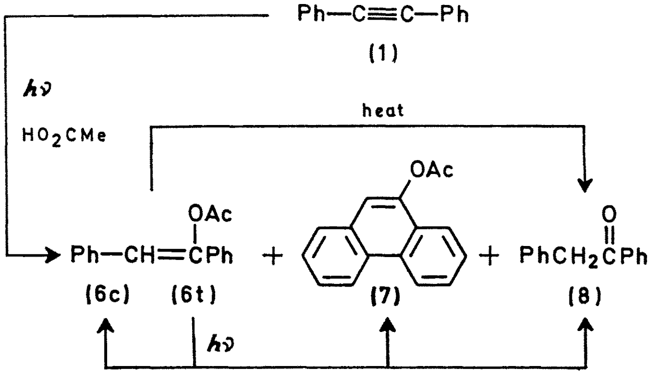
Summary In the photolysis of diphenylacetylene, phenanthrene may be formed *via cis*-stilbene rather than by an internal rearrangement of diphenylacetylene.

It has been suggested that the formation of phenanthrene in 10% yield from diphenylacetylene occurs *via* an internal rearrangement.[1] We suggest an alternative explanation based on new experiments and previous work.[2]

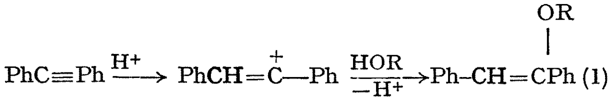


Irradiation of 10^{-2}M-solutions of diphenylacetylene (**1**) in methanol under nitrogen yields *trans*- and *cis*-1,2-diphenylvinyl methyl ether, (**2t** and **c**), *trans*- and *cis*-stilbene (**3t** and **c**), phenanthrene (**4**), and formaldehyde (**5**).[2] Compound (**2**), resulting from addition of methanol, is the major product. The concentrations of (**3c** and **t**) decrease with time while that of (**4**) increases;[2] under these conditions (**4**) may arise entirely from a photoreaction of (**3c**).[3]

When 0·05M-solutions of (**1**) in acetic acid are irradiated† under nitrogen for 70 h and then evaporated under vacuum four major products are isolated by g.l.c.: *cis*- and *trans*-1,2-diphenylvinyl acetate (**6c** and **t**), 9-acetoxyphenanthrene (**7**), and deoxybenzoin (**8**).‡ Addition of acetic acid to yield (**6**) and probably oxidative cyclization of (**6c**) to (**7**) are major pathways. Independent synthesis[4] of (**6t**) and photolysis under identical conditions affords (**6c**), (**7**), and (**8**). Since (**8**) is produced in a dry environment, hydration of (**1**) to (**8**) is not probable but photo-fragmentation of (**6**) to (**8**) is postulated.§ Thermolysis of (**6**) (270°; 9 h; under N_2) gives (**8**) as the only volatile product. Reduction is not a major pathway. Compounds (**3c**), (**3t**), and (**4**) were not detected in g.l.c. analysis and phenanthrene, under identical conditions, does not afford (**7**).



It is possible that the addition of methanol and acetic acid to (**1**) to give (**2**) or (**6**) involves protonation of an excited singlet or vibrationally excited ground state into a vinyl carbonium ion which reacts with the solvent (equation 1).



$$\mathrm{PhC{\equiv}Ph} \xrightarrow{\mathrm{H^+}} \mathrm{PhCH{=}\overset{+}{C}{-}Ph} \xrightarrow[\mathrm{-H^+}]{\mathrm{HOR}} \mathrm{Ph{-}CH{=}\overset{\overset{\textstyle OR}{|}}{C}Ph} \quad (1)$$

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† In a typical run 16 General Electric G25T8 tubes mounted in a circular bank served as the light source for 500-ml solutions.

‡ Compounds (**6t**), (**7**), and (**8**) were shown to be identical with authentic samples. Compound (**6c**), an oil, had the following properties: i.r. 1760 cm^{-1}; n.m.r. ($CDCl_3$) τ 7·8(s, 3H), 3·6(s, 1H), 2·3—2·9(m, 10H); mass spectral parent peak 238; all of which are quite similar to (**6t**). Minor products, whose tentative structures are 1,2-diphenylbutane-1,3-dione and 9-acetoxyphenanthren-10-ol, will be discussed in a forthcoming full paper.

§ Similar observations have been made by A. Yoger, M. Gorodetsky, and Y. Mazur, *J. Amer. Chem. Soc.*, 1964, **86**, 5208.

[1] W. Templeton, *Chem. Comm.*, 1970, 1412.

[2] T. D. Roberts, L. Ardemagni, and H. Shechter, *J. Amer. Chem. Soc.*, 1969, **91**, 6185.

[3] F. R. Stermitz in "Organic Photochemistry," Vol. I, Ed. O. L. Chapman, Marcel Dekker, New York, 1967, p. 248 ff.

[4] R. P. Barnes, S. R. Cooper, V. J. Tulane, and H. Delaney, *J. Org. Chem.*, 1943, **8**, 153.