Photochemical Cyclization of Diphenylacetylene to Phenanthrene

By WILLIAM TEMPLETON

(*Department of Biochemistry and Chemistry, Medical College of St. Bartholomew's Hospital, Charterhouse Square, London* EC1M 6BQ)

Summary Illumination of a dilute ethanol solution of diphenylacetylene gives phenanthrene in 10% yield.

DIPHENYLACETYLENE has been shown to undergo many polymerization[1] and addition reactions[2] under the influence of light, and its photo-oxidation to benzoic acid has been studied in detail,[3] but no internal photochemical rearrangement of the molecule has hitherto been reported although the oxidative photocyclization of its ethylenic analogue, stilbene, is well known.[4] It now appears that under favourable conditions such a rearrangement does indeed occur.

Illumination of a 10^{-2} M-solution of diphenylacetylene in dry ethanol under nitrogen by a mercury-vapour lamp enclosed in a silica immersion jacket, led to the formation of phenanthrene in 10% yield, together with other products as yet unidentified. When the experiment was repeated with a diphenylacetylene concentration of 6×10^{-2} M, no phenanthrene was detected among the products, which included the two dimers, the trimer, and the tetramer obtained by Büchi and his co-workers[1] by illumination of diphenylacetylene in cyclohexane. Similar results were obtained in methanol solution, while in hexane little change occurred and phenanthrene did not appear to be formed.

The rate of disappearance of diphenylacetylene during illumination in ethanol solution was measured spectrophotometrically (at 297 nm) under various conditions, the initial concentration being 2×10^{-4} M in each case. Filtering the light through Pyrex reduced the rate by a factor of ten, but in the presence of 10^{-3} M-triphenylene, the rate in filtered light was approximately doubled; on the other hand, 10^{-3} M-anthracene caused a 25% reduction of the rate in unfiltered light.

(*Received, August 13th*, 1970; *Com.* 1361.)

[1] G. Büchi, C. W. Perry, and E. W. Robb, *J. Org. Chem.*, 1962, **27**, 4106.
[2] H. E. Zimmerman and L. Craft, *Tetrahedron Letters*, 1964, 2131; D. Bryce-Smith, G. I. Fray, and A. Gilbert, *ibid.*, 1964, 2137; W. H. F. Sasse, P. J. Collin, and G. Sugowdz, *ibid.*, 1965, 3373; 1969, 3843; H. M. Rosenberg and P. Serve, *J. Org. Chem.*, 1968, **33**, 1653.
[3] R. C. Henson, J. L. W. Jones, and E. D. Owen, *J. Chem. Soc.* (*A*), 1967, 116.
[4] E. V. Blackburn and C. J. Timmons, *Quart. Rev.*, 1969, **23**, 482.