Photocyclisation of 1,1-Diarylethylenes; the Novel Formation of a Five-membered Ring

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Summary Irradiation of 1-aryl-1-phenylethylenes, in the presence of iodine and oxygen gives five- or six-membered carbocyclic rings by oxidative cyclisation.

Recent reports on the photoreactivity of 1,1-diphenylethylene have pointed out the similarities in the chemistry of benzophenone and 1,1-diphenylethylene excited states.[1] We now report a new example of the photoreactivity of 1-aryl-1-phenylethylenes.

If we accept that the ease of photocyclisation is related to the sum of the free valence indices in the first excited state, ΣF^*, at the two positions which become bonded during the cyclisation,[2] then the 1,1-diarylethylenes (I), (II), and (IIIa,b,c) should cyclise easily since at the positions indicated (●) (Schemes) $\Sigma F^* = 1{\cdot}727$, $1{\cdot}723$, $1{\cdot}669$, $1{\cdot}661$, $1{\cdot}669$ respectively.‡ These compounds are photoreactive but the choice of experimental conditions depends on whether a five- or six-membered ring is to be formed.

(1) Formation of a six-membered ring. When a degassed solution of (I) ($6{\cdot}3 \times 10^{-3}$M) in cyclohexane was irradiated in a quartz vessel using 300 nm light§ for 90 min, a single photoproduct was formed (g.l.c.). Evaporation of the solvent and recrystallisation from ethanol gave (IV), white crystals, m.p. 84 °C,[3] yield 85%. Irradiation of (II) under the same conditions resulted in the quantitative formation of (VI).¶ The photocyclisation of (I) was sensitized by xanthone and Michler's ketone, and oxygen quenched the reaction without oxidative cyclisation to (V). When (I) was irradiated using the standard conditions for the cyclisation of stilbene to phenanthrene[4] (V) was formed in good yield (80%) but the reaction was relatively slow; with Michler's ketone which absorbs all the light, the

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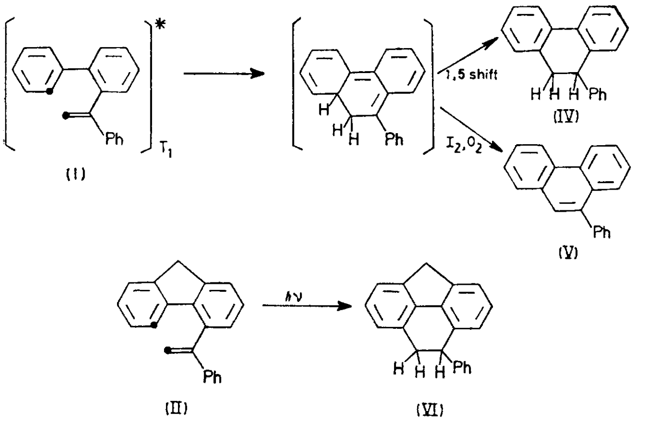
‡ Calculations have been made using the LCAO method and the usual assumption of Huckel theory.

§ All the irradiations have been carried out in a Rayonet Photochemical Reactor at 300 nm (direct irradiations) and 350 nm (sensitized reactions).

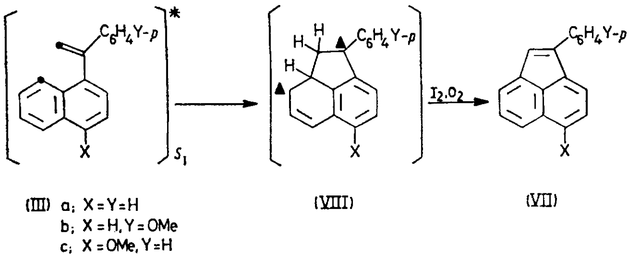
¶ Satisfactory analytical and spectroscopic data have been obtained for all new compounds.

reaction was faster. These results suggest that the triplet state is the reactive state. Irradiation of (I) in degassed $DCCl_3$ gave (IV) without incorporation of deuterium, so a chain reaction[5] has to be rejected and the route in Scheme 1 is proposed.



Scheme 1

(2) Formation of a five-membered ring. The compounds (IIIa,b,c) were not affected by direct irradiation of degassed benzene solutions nor by sensitization with xanthone or benzophenone, but in the presence of O_2, I_2, or $CuBr_2$ they were photocyclised to the acenaphthylenes (VIIa,b,c) (Scheme 2). When a cyclohexane solution of (IIIa) ($6 \cdot 5 \times 10^{-3}$M) and iodine ($1 \cdot 8 \times 10^{-4}$M) was irradiated, with oxygen bubbling, all the olefin had disappeared after 18 h and (VIIa), identified by comparison with an authentic sample,[6] was isolated after recrystallization from ethanol, yield 70%. Comparable yields of the isolated photoproducts were obtained with (IIIb,c). With (IIIc) 1-iodo-2-phenyl-5-methoxyacenaphthylene has been isolated at the beginning of the reaction but analogous derivatives with (IIIa,b) have not been detected and irradiation of (IIIa) in $DCCl_3$ gives (VIIa) without incorporation of deuterium. Xanthone and Michler's ketone do not sensitize the formation of (VIIa) so the singlet state is probably the photoreactive state. In contrast to the corresponding thioketone[7] neither 1,3 migration of hydrogen nor intermolecular protonation by alcohol has succeeded in trapping (VIIIa).



Scheme 2

Although the photochemical formation of six-membered rings from compounds structurally close to (I) and (II) has recently been reported[8] the photochemical formation of five-membered carbocyclic rings is rare.[9]

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