Photochemical Synthesis of Phenanthro[9.10-b]furans

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Summary 2,3,5-Triphenyl- and tetraphenyl-furan react with tetrachloro-1,2-benzoquinone to form adducts which undergo photolysis in propan-2-ol to give excellent yields of the 2-phenyl- and 2,3-diphenyl-phenanthro-[9,10-b] furans respectively.

WE have previously demonstrated that the photolysis of adducts of tetrachloro-1,2-benzoquinone and derivatives of tetraphenylcyclopentadienone gave good yields of phenanthrocyclopentanones. The synthetic use of this reaction is obvious since such a product is not formed by direct photolysis of tetraphenylcyclopentadienone.2

We now report the results obtained from studies with phenylfurans (1a) and (1b). 2,3,5-Triphenyl- and tetraphenylfuran were both treated with tetrachloro-1,2benzoquinone to give adducts (2a)† and (2b), respectively. These adducts were photolysed; under nitrogen as suspensions in propan-2-ol to give excellent yields of the phenanthrofurans (3a) (85%) [τ (CDCl₃) 1·25—1·45 (2H, m), 1.90-2.15 (3H, m), and 2.25-2.65 (9H, m) and (3b) (79%) [1·25—1·65 (2H, m) and 2·35—2·95 (16H, m)].

Subsequently it was demonstrated that the triphenylfuran (1a) did not give phenanthrenoid products on photolysis in cyclohexane-iodine. It did, however, undergo photochemical decomposition. Other workers⁴ have shown that tetraphenylfuran (1b) behaves similarly. This result is in accord with the theoretical predictions^{4,5} that if the sum of free-valence indices (Σ Fr*) of the reacting centres is less than unity then photocyclisation will not take place $(\Sigma \operatorname{Fr}^* = 0.952 \text{ for tetraphenylfuran}^4).$

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$$\bigcap_{Ph} \bigcap_{O} \bigcap_{Ph} \bigcap_{Ph} \bigcap_{O} \bigcap_{Cl} \bigcap_{Cl} \bigcap_{O} \bigcap_{Ph} \bigcap_{(2)} \bigcap_{(3)} \bigcap_{Ph} \bigcap_{(3)} \bigcap_{Ph} \bigcap_{(3)} \bigcap_{Ph} \bigcap_{(3)} \bigcap_{(3)} \bigcap_{Ph} \bigcap_{(3)} \bigcap$$

The method developed by us for these cyclisations has obvious advantages and apparently provides a route by which the electronic effects which prevent cyclisation in the parent molecules are circumvented.

All new compounds gave spectral and analytical data in accord with the proposed structures.

We thank the S.R.C. for a research studentship (to D.T.A.) and the Royal Society for a grant to purchase the photochemical equipment.

(Received, March 29th, 1971; Com. 461.)

- † This adduct was assigned the structure (2a) on the basis of its n.m.r. spectrum which showed, in addition to aryl absorptions. a one-proton singlet at $\tau 4.17$. This absorption is in a position comparable to that reported³ for the 2,5-diphenylfuran-tetrachloro-1,2benzoquinone adduct at + 4.31.
- Photolyses were carried out under nitrogen in an immersion apparatus with a Pyrex filter and a 450 W medium-pressure mercury arc lamp.
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