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 demonstrated¹ 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%) [7 (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 ($\Sigma \operatorname{Fr}^*$) of the reacting centres is less than unity then photocyclisation will not take place $(\Sigma \operatorname{Fr}^* = 0.952 \text{ for tetraphenylfuran}^4).$



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.

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† 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 τ 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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