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PHOTOSENSITIVE PROTECTION OF FUNCTIONAL GROUPS

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THE recent communication by Barltrop and Schofield[1] makes it desirable for us to publish a preliminary account of some of the results that we have obtained in recent years on photosensitive protection of functional groups.

The readily prepared[2] 2,4-dinitrophenylthio-derivatives of carboxylic acids, on irradiation under nitrogen in ethereal solution (1 - 10 m.molar) in a pyrex flask using a high pressure mercury arc lamp, are reconverted to the corresponding carboxylic acids in high yield. For example, the acetoxy, hexanoyloxy and phenylacetoxy derivatives gave the corresponding acids in 92, 83 and 88% yield respectively with no decarboxylation (titration for carbon dioxide evolution). During photolysis a precipitate appeared which contained 2-amino-4-nitrobenzenesulphonic acid. The latter was also formed by photolysis of 2,4-dinitrophenylsulphenyl chloride along with bis-2,4-dinitrophenyl disulphide. The intramolecular participation of the 2-nitro-group represents an interesting new photochemical rearrangement.

The photolysis of a variety of β-naphthyl esters (I, Ar = $C_{10}H_7$)

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[1] J.A. Barltrop and P. Schofield, Tetrahedron Letters, 697 (1962).

[2] A.J. Havlik and N. Kharasch, J. Amer. Chem. Soc. **78**, 1207 (1956).

was studied to find a photosensitive protecting group for phenols. Aryl esters of simple carboxylic acids are known[3] to rearrange on irradiation to give nuclear-substituted phenols. In agreement, β-naphthyl acetate and benzoate gave little β-naphthol on photolysis. However, esters which can form a stable radical R (see equation below) gave β-naphthol in satisfactory yield (see Table). So far, the best results were obtained with the fluorene-9-carboxylic ester.

$$\underset{\text{(I)}}{\mathrm{ArO - CO - R}} \xrightarrow{h\nu} [\mathrm{ArO - CO - R}]^{*} \longrightarrow \mathrm{ArO\cdot + CO + R\cdot}$$

Table *

(I) R =		Ph	Me	CCl_3	EtO.CS.S	Ph_3C	9-fluorenyl
Irradiation time in hr.	(Pyrex	-	-	-	1.75	-	4
	(Quartz	2	3	3	-	1	-
Yield (%) of β-naphthol	(Crude	8	41	29	33	46	67
	(Pure	4	32	22	24	39	60

* Solutions (4 m.molar) of the esters in ether were irradiated with a 125 w. high pressure mercury arc lamp at 35° under nitrogen.

β-Naphthyl fluorene-9-carboxylate photolysed rapidly in pyrex, carbon monoxide (0.93 mol. by I_2O_5 titration) being produced. On the other hand, the corresponding *p*-cresol derivative was unaffected after prolonged irradiation under these conditions. It was, however, rapidly photolysed in quartz to furnish 60 - 65% of *p*-cresol. Methyl and cholesteryl fluorene-9-carboxylates were stable in both pyrex and quartz. Clearly photolysis is dependent on light absorption by the aryloxy-residue. It is thus possible to cleave aryl esters selectively

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[3] J.D. Anderson and C.B. Reese, Proc. Chem. Soc., 217 (1960); H. Kobsa, J. Org. Chem. 27, 2293 (1962).

leaving their alkyl analogues unchanged. The structure of the esterifying acid, however, determines the ease with which the excited state breaks down by either a one step or two step process.[4] The stability of the radical R determines the nature of the products and governs the extent of radical recombination to furnish either ethers or nuclear substituted phenols.

Further aspects of these reactions are under investigation. The general field of photosensitive protecting groups is also receiving attention.

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[4] See P.D. Bartlett, 'Peroxide Reaction Mechanisms', ed. J.O. Edwards, Interscience, New York, 1962, p. 1.