Photosensitive Protective Groups

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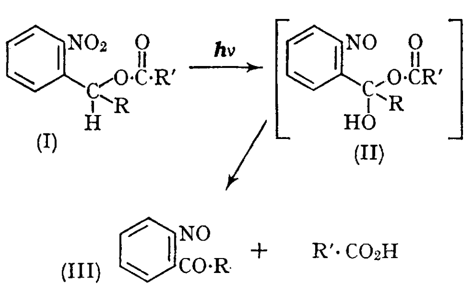
RECENTLY there have been several reports of protecting groups that can be removed by illumination with ultraviolet light.[1] We have attempted to design a photosensitive protecting group which uses in the key deprotection step the general photochemical oxygen-transfer reaction of aromatic nitro-compounds which have a C–H bond in the *ortho*-position.[2] In all cases the product of this reaction may be formulated as that in which the *ortho* C–H function is replaced by C–OH and the nitro-group by NO, followed where appropriate, by a rearrangement to a more stable structure. Thus, an ester of *o*-nitrobenzyl alcohol (I: R=H) would be expected to give on irradiation a primary product (II) which would then decompose into a nitrosobenzene derivative (III) and the corresponding free acid.



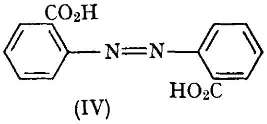
o-Nitrobenzyl benzoate (I: R=H, R'=Ph) gave only a 17% yield of benzoic acid on irradiation since the *o*-nitrosobenzaldehyde (III: R=H) formed in the reaction was further transformed[3] into azobenzene-2,2'-dicarboxylic acid (IV) which acted as an efficient internal light filter. This side reaction was eliminated by the use of α-substituted *o*-nitrobenzyl esters; of the compounds investigated

TABLE

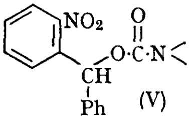
o-Nitrodiphenylmethyl ester of	Irradiation time (hr.)	Solvent	% Yield of free acid
Benzoic acid	$2\frac{1}{2}$	CCl_4 or C_6H_6	90 ± 4 (*a*)
Palmitic acid	3	CCl_4	95 ± 4 (*a*)
Phenylacetic acid	4	CCl_4	87 ± 4 (*a*)
N-Phthalimidoglycine	$3\frac{1}{2}$	C_6H_6	75 (*b*)
N-*o*-Nitrodiphenylmethyloxycarbonyl derivative			
Glycine	3	C_6H_6	94 ± 2 (*a*)
L-Leucine	3	C_6H_6	70 (*b*)(*c*)
L-Leucylglycine	3	C_6H_6	84 (*b*)(*c*)

(*a*) by titration; (*b*) yield of pure acid; (*c*) the photo-product had the correct optical rotation.

the best yields of free acids were obtained from irradiation of *o*-nitrodiphenylmethyl esters (I: R = Ph). Similarly, amines were recovered in good yield from irradiated solutions of *N*-(*o*-nitrodiphenylmethyloxycarbonyl) derivatives (V). These results are shown in the Table.



(IV)



(V)

In all cases a medium pressure mercury arc and Pyrex apparatus were used, and the photo-products were shown to have physical properties identical with those of authentic samples.

Work is at present in hand to assess the stability of these protected derivatives to chemical methods of fission and these results together with further details of the photochemistry of α-substituted *o*-nitrobenzyl compounds will be presented in a future report.

(*Received, October 17th,* 1966; *Com.* 785.)

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[1] J. A. Barltrop and P. Schofield, *J. Chem. Soc.*, 1965, 4758; J. W. Chamberlin, *J. Org. Chem.*, 1966, **31**, 1658; Th. Wieland and C. Lamperstorfer, *Makromol. Chem.*, 1966, **92**, 279; D. H. R. Barton, Y. I. Chow, A. Cox, and G. W. Kirby, *J. Chem. Soc.*, 1965, 3571.

[2] P. De Mayo, *Adv. Org. Chem.*, 1960, **2**, 367.

[3] W. Reid and M. Wilk, *Annalen*, 1954, **590**, 91.