A Photosensitive Protecting Group for Phosphate Esters

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THE photochemically-excited state of the dianion of 3,5-dinitrophenyl phosphate behaves as the derivative of a strongly acidic phenol.[1] Rapid solvolysis occurs in aqueous solvents, probably by a unimolecular elimination of the phenolate anion to give monomeric metaphosphate.[2]

This mechanism is not possible for the hydrolysis of higher phosphate esters; but the excited 3,5-dinitrophenyl group should also be highly reactive towards nucleophilic attack on carbon. We report the results of some preliminary experiments which support this thesis, and show that the 3,5-dinitrophenyl group is easily removed also from di- and tri-esters of phosphoric acid, on irradiation in aqueous solution at room temperature.

The anion of di-3,5-dinitrophenyl phosphate[3] is quite stable in aqueous solution in the dark. On irradiation with a medium-pressure mercury lamp through a Pyrex filter it was converted directly to orthophosphate, since photolysis of the monoester is faster than that of the diester. In contrast to the reaction of the monoester, the rate increases with pH: the half-life at room temperature being 2½ hr. at pH 7, but only 15 min. in N/100 NaOH.

A convenient medium for the removal of 3,5-dinitrophenyl protecting groups is aqueous pyridine. For example, the photolysis of benzyl 3,5-dinitrophenyl hydrogen phosphate[2] to benzyl phosphate (followed by paper chromatography) was complete after 5 hr. at room temperature in 20% aqueous pyridine. Similarly adenosine monophosphate was synthesised in 40—50% yield (not isolated) from isopropylidene adenosine and di-3,5-dinitrophenyl phosphorochloridate by standard reactions:[4] except that the two 3,5-dinitrophenyl groups were removed from the protected triester by irradiation for 30 min. in 50% pyridine–25% water–25% ethanol.[5]

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[1] A. J. Kirby and A. G. Varvoglis, preceding Communication.

[2] A. J. Kirby and A. G. Varvoglis, *J. Amer. Chem. Soc.*, 1967, **89**, 415.

[3] Prepared by the method of N. S. Corby, G. W. Kenner, and A. R. Todd, *J. Chem. Soc.*, 1952, 1234.

[4] J. Baddiley and A. R. Todd, *J. Chem. Soc.*, 1947, 648.

[5] For previous reports of photosensitive protecting groups, see J. A. Barltrop, P. J. Plant, and P. Schofield, *Chem. Comm.*, 1966, 822, and references therein.