Reductive Cyclisation of o-Nitrophenyl Benzoate to 2-Phenylbenzoxazole

By D. G. SAUNDERS

(Research Laboratory, Kodak Limited, Wealdstone, Harrow, Middlesex)

Summary Triethyl phosphite has been found to react with o-nitrophenyl benzoate, to give 2-phenylbenzoxazole.

The reduction of nitro-compounds by trialkyl phosphites to give nitrogen heterocycles is well known.1 Recently, Kametani et al. have synthesised benzo[c]naphthyridines, from 3-ethoxycarbonyl-4-(2-nitrophenyl)pyridines, and oxazolo[5,4-b]quinolines from 4-(2-nitrobenzylidene)oxazol-5ones by cyclisation with triethyl phosphite.2

We have now found that the same reagent causes a

similar insertion into the carbonyl group of an o-nitrophenyl ester, leading, in one step, to the formation of a benzoxazole. Thus, o-nitrophenyl benzoate (20.0 mmole) with triethyl phosphite (60.0 mmole) in t-butylbenzene (400 mmole) (N₂ atmosphere, reflux, 2 hr.) gave 2-phenylbenzoxazole (68%). Neither a longer reaction time (7 hr.), nor an excess of triethyl phosphite (90.0 mmole), raised the yield significantly.

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