A New Method for the Conversion of 3-Aroyl-2-cyano-esters into Phosphorylaminofurans: Use of *N*-Phosphorylketenimines

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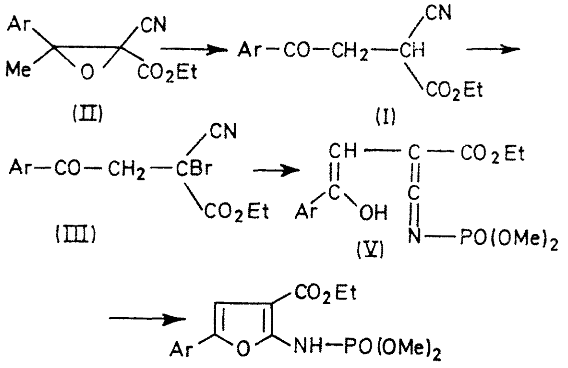
Summary The treatment of 3-aroyl-2-bromo-2-cyano-esters with trimethyl phosphite gives 5-aryl-3-ethoxy-carbonyl-2-phosphorylaminofurans.

THE cyano-esters (I) can be readily prepared from epoxides (II) by thermal rearrangement.[1] The bromination of these cyano-esters (I) by bromine and aqueous Na_2CO_3 gives bromo-esters (III). We have found that treatment of bromo-esters (III) with trimethyl phosphite in anhydrous benzene at room temperature gives furans (IV). The i.r. spectrum (Nujol) of (IVa), recovered in 71% yield, m.p. 96—97° (C_6H_6), shows characteristic bands at ν 3120 (N–H), 1702 (C=O), 1614, and 1518 cm^{-1}; n.m.r. ($CDCl_3$) δ 1·35 (t, *J* 7·0 Hz, 3H, CH_2CH_3), 4·30 (q, *J* 7·0 Hz, 2H, CH_2CH_3 3·88 (d, J_{PH} 12 Hz, 6H, $POCH_3$), 6·77 (s, 1H, CH). (IVb), recovered in 66% yield, had m.p. 154—155°, i.r. (Nujol) ν 3135 (N–H) 1698 (C=O), 1615, and 1592 cm^{-1}; and n.m.r. ($CDCl_3$), δ 1·35 (t, *J* 7·0 Hz, 3H, CH_2CH_3) 4·30 (q, *J* 7·0 Hz, 2H, CH_2CH_3), 1·88 (d, *J* 12 Hz, 6H, $POCH_3$), 6·75 (s, 1H, CH).

It has been recently reported that *N*-phosphorylketenimines were obtained by the reaction of trialkyl phosphite with α-bromo-α-cyano-esters.[2,3] We suggest that the mechanism of the reaction involves an intermediate (V) where the ketenimine and enol groups react rapidly, *via* an intramolecular route.

Satisfactory analyses were obtained on all compounds prepared.



(IV) a; Ar = Ph
b; Ar = *p*-Cl-C_6H_4

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[3] R. D. Partos and A. J. Speziale, *J. Amer. Chem. Soc.*, 1965, **87**, 5068.