The Reaction of 4-*o*-Nitrophenylpyridine Derivatives with Triethyl Phosphite

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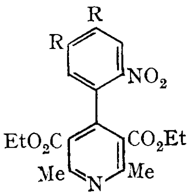
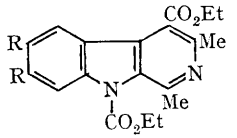
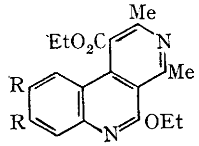
REDUCTIVE cyclisations of aromatic compounds have been studied[1] using triethyl phosphite and it has been postulated that nitrene intermediates are involved in these reactions. Our results suggest that nitrene might be involved in the reduction of the 4-*o*-nitrophenylpyridine derivatives, (I) and (II), with triethyl phosphite.





(I) R=OMe (III)

(II) R=·OCH$_2$O· (IV)



(V; R=OMe)

(VI; R=·OCH$_2$O·)

Thus, heating (I) or (II) (1 mol.), obtained by modified Hantzsch's method,[2] with triethyl phosphite (5 mol.) at 160—170° for 20 hr. in a current of nitrogen resulted in the formation of the β-carboline derivatives (III) (19·4%) m.p. 99—101° [ν_{max} (KBr) 1740 (ester C=O) and 1720 cm.$^{-1}$ (amide C=O), δ (in $CDCl_3$) 1·47 (6H, t, *J* 6·5 c./sec., 2 $-OCH_2CH_3$), 2·67, 2·70 (each 3H, s, CH_4), 3·91, 3·99 (each 3H, s, OCH_3), 4·50 and 4·55 (4H, 2q, *J* 6·5 c./sec., 2 $-OCH_2CH_3$), 7·41 and 7·77 (each 1H, s, aromatic protons)] or (IV) (17%) m.p. 121—123° [ν_{max} (KBr) 1740 (ester C=O) and 1720 cm.$^{-1}$ (amide C=O), δ ($CDCl_3$) 1·48 (6H, t, *J* 6·5 c./sec., 2 $OCH_2{\cdot}CH_3$), 2·66, 2·69 (each 3*H*, s, CH_3), 4·35—4·75 (4H, m, 2 $OCH_2{\cdot}CH_3$), 6·05 (2H, s, $-OCH_2O-$), 7·29 and 7·65 (each 1H, s, aromatic protons)] and benzo[*c*-2,7]naphthyridine derivatives (V) (24·1%) m.p. 116—119°, [ν_{max} (KBr) 1720 cm.$^{-1}$ (ester C=O), δ (in $CDCl_3$) 1·38, 1·51 (each 3H, t, *J* 6·5 c./sec., $-OCH_2CH_3$), 2·62, 3·07 (each 3H, s, OCH_3), 3·91, 3·99 (each 3H, s, OCH_3), 4·49, 4·58 (each 2H, q, *J* 6·5 c./sec., OCH_2CH_3), 7·19, and 7·49 (each 1H, s, aromatic proton) or (VI) (23·5%) m.p. 168—170°, [ν_{max} (KBr) 1720 cm.$^{-1}$ (ester C=O), δ ($CDCl_3$) 1·41, 1·49 (6H, t, $-OCH_2CH_3$), 2·61, 3·06 (each 3H, s, CH_3), 4·48, 4·56 (4H, 2q *J* 6·5 c./sec., OCH_2CH_3) 6·04 (2H, s, $-OCH_2O-$), 7·14 and 7·41 (each 1H, s, aromatic proton).

Since the formation of β-carboline derivatives would be presumably due to the insertion reaction of nitrene,[3] it is of interest that in the first example of this type of reaction the nitrene has been inserted into the carbonyl C(aromatic)–C bond.

The application of this reaction is under examination.

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