Novel Synthesis of Benzo[*a*]carbazole and Oxazolo[5,4-*b*]quinoline Ring Systems from Aromatic Nitro-compounds with Triethyl Phosphite

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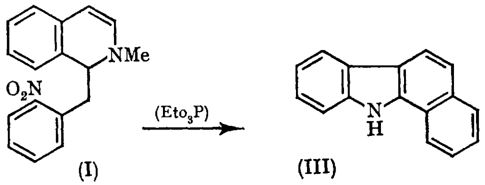
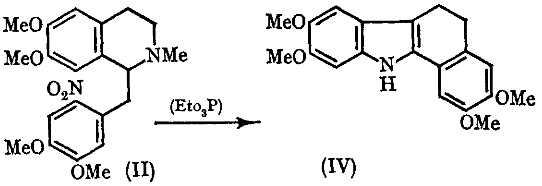
MANY investigations of the reductive cyclisation of nitro-compounds with triethyl phosphite have been carried out. We report some novel cyclisation reactions. 1-(2-Nitrobenzyl)isoquinoline derivatives were converted into benzo[*a*]carbazole derivatives by elimination of N-Me group and 4-(4,5-methylenedioxy-2-nitrobenzylidene)oxazolones into oxazolo[5,4-*b*]quinoline derivatives in which the ring was closed at the nitrogen in a conjugated ϵ-position.

Treatment of 1,2-dihydro-2-methyl-1-(2-nitrobenzyl)isoquinoline (I)[2] (1 mol.) and 6′-nitrolaudanosine[3] (II) (1 mol.) with triethyl phosphite (5 mol.) at 160—165° for 20 hr. in a current of nitrogen afforded the benzo[*a*]carbazole (III), m.p. 226—227° (lit.,[4] m.p. 228°), (37%) *m/e*: 217 (M^+), ν_{max} (KBr) 3430 cm.$^{-1}$, δ (p.p.m.) (in Me_2SO) 7·10—8·65 (10 H, m, aromatic protons), 12·12 (1 H, s, NH proton, disappeared with D_2O), and 5,6-dihydro-2,3,8,9-tetramethoxybenzo[*a*]carbazole (IV), m.p. 202°, (38·5%) *m/e*: 339 (M^+), ν_{max} (KBr) 3400 cm.$^{-1}$, δ (p.p.m.) (in $CDCl_3$) 3·08 (2H, t, *J* 8 c./sec., C(6)-methylene protons), 3·87 (3H, s, OMe), 3·90 (3H, s, OMe), 3·92 (6H, s, 2 OMe), 4·13 (2H, t, *J* 8 c./sec., C(5)-methylene protons), 6·62 (1H, s, NH proton, disappeared with D_2O), 6·74, 6·80, 7·08, and 7·20 (4H, 4 s, aromatic protons).

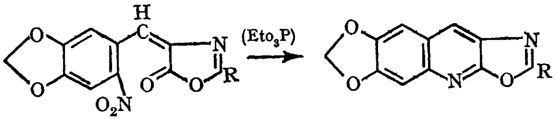
Similar treatment of 2-phenyl- (V; R = Ph) and 2-methyl-4-(2-nitro-4,5-methylenedioxybenzylidene)oxazolone (V; R = Me) afforded 2-phenyl-6,7-methylenedioxyoxazole[5,4-*b*]quinoline (VI; R = Ph), m.p. 270·5°, (57%) *m/e*: 290 (M^+), ν_{max} (KBr) 1635 cm.$^{-1}$, δ (p.p.m.) (in CF_3CO_2H) 6·38 (2H, s, methylenedioxy-protons), 7·64 (2H, s, aromatic protons), 7·81 (3H, br s, aromatic protons), 8·35 (2H, m, aromatic protons), 9·20 (1H, s, C(9)-proton) and 2-methyl-6,7-methylenedioxyoxazolo[5,4-*b*]quinoline (VI; R = Me), m.p. 200—202°, (45%) *m/e*: 228 (M^+), ν_{max} ($CHCl_3$) 1633 cm.$^{-1}$, δ (p.p.m.) (in CF_3CO_2H) 2·91 (3H, s, C(2)-Me protons), 6·32 (2H, s, methylenedioxy-protons), 7·56 (2H, s, aromatic protons), 9·08 (1H, s, C(9)-proton).



(I) (III)



(II) (IV)



(V) (VI)

These reactions might proceed through the nitrene intermediate, but the mechanism of these reactions and application to the other compounds are now under examination.

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