A Novel Formation of Quinoline Derivatives

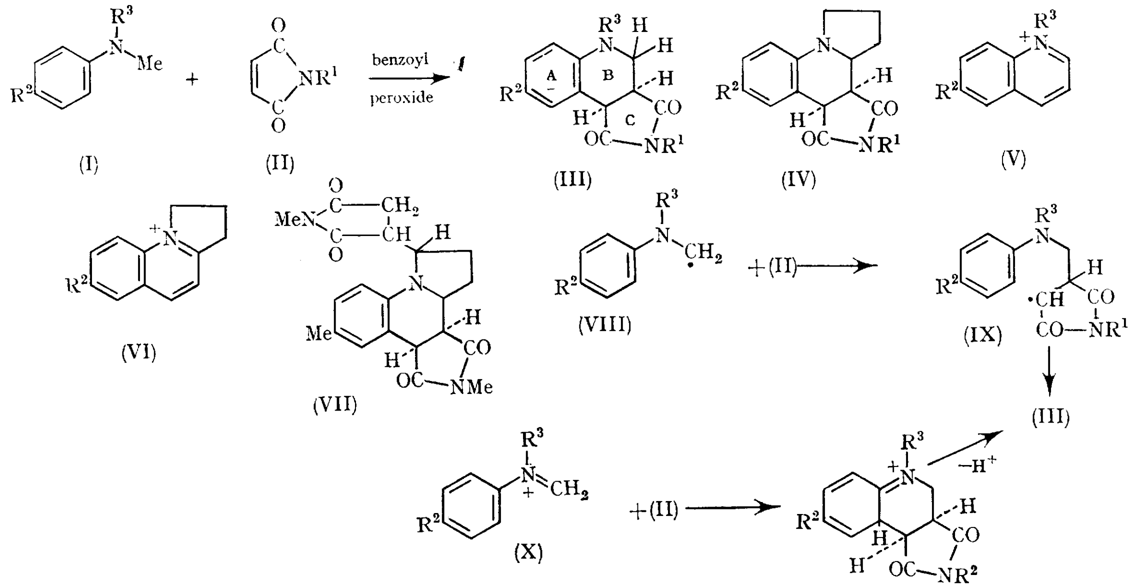
By R. B. ROY and G. A. SWAN*

(*Department of Organic Chemistry, The University of Newcastle upon Tyne, Newcastle upon Tyne* 1)

ADDITION of benzoyl peroxide (1·44 mol.) to a solution of *NN*-dimethylaniline (I; $R^2 = H$, $R^3 = Me$) (4·3 mol.) and *N*-phenylmaleimide (II; $R^1 = Ph$) (1 mol.) in cumene at $-5°$ resulted in the formation of 1,2,3,4-tetrahydro-1-methylquinoline-3,4-dicarboxylic-*N*-phenylimide (III; $R^1 = Ph$, $R^2 = H$, and $R^3 = Me$) [0·59 mol., isolated by elution from alumina with benzene–light petroleum (4 : 1)], m.p. 196° [ν_{max} (KBr) 1775w and 1707s cm.$^{-1}$]. This novel reaction also occurred with *N*-methylmaleimide (II; $R^1 = Me$) instead of (II; $R^1 = Ph$) and chloroform or (in lower yield) acetonitrile as solvent at *ca.* 0°. The following amines reacted similarly to *NN*-dimethylaniline: *NN*-dimethyl-*p*-toluidine (I; $R^2 = R^3 = Me$), *N*-methyldiphenylamine (I; $R^2 = H$, $R^3 = Ph$), and *N*-ethyl-*N*-methyl-*p*-toluidine (I; $R^2 = Me$, $R^3 = Et$) [with *N*-phenylmaleimide the crystalline product isolated, m.p. 112°, was 1-ethyl-1,2,3,4-tetrahydro-6-methylquinoline-3,4-dicarboxylic-*N*-phenylimide (III; $R^1 = Ph$, $R^2 = Me$, and $R^3 = Et$), τ (in $CDCl_3$) 8·9 (3H, t, *J* 7 c./sec., N–CH_2CH_3)]. Similarly *N*-phenylpyrrolidine yielded (IV; $R^1 = Ph$, $R^2 = H$ and (IV; $R^1 = Me$, $R^2 = H$), isolated in two stereoisomeric forms, and *N*-*p*-tolylpyrrolidine gave (IV; $R^1 = Ph$, $R^2 = Me$), and (IV; $R^1 = R^2 = Me$).

The base peak in the mass spectrum of each of the products corresponded to the appropriate quinolinium ion [(V) or (VI)] and the expected molecular ion also occurred. The n.m.r. spectrum of (III; $R^1 = Ph$, $R^2 = R^3 = Me$) in $CDCl_3$ (kindly measured and interpreted by Dr. Keller and Dr. R. J. Stoodley, using a 90 MHz instrument in the laboratory of Spectrospin, A.G. in Zürich) showed an ABX system, with the X proton coupled to another (doublet for the former at τ 5·95) with *J* 10 c./sec., suggesting *cis*-fusion of rings B and C (*cf.* ref. 1). The n.m.r. spectrum of (III; $R^1 = R^2 = R^3 = Me$) in $CDCl_3$ at 60 MHz showed τ 2·75 (1H, s) 3·02 and 3·45 (2H, AB q, $J_{AB} = 8·5$ c./sec.), and 7·05 (R^1), 7·28 (R^3), and 7·75 (R^2) (3H, 3s).

From the reaction of *N*-*p*-tolylpyrrolidine with



N-methylmaleimide a highly insoluble compound, m.p. 325°, was also obtained, for which structure (VII) is suggested on mass spectrometric evidence; $m/e = 381$ ($C_{21}H_{23}H_3O_4$), with strong peaks at 295 [$C_{18}H_{19}N_2O_2$, *cf.* (VI)] and 269 ($C_{16}H_{17}N_2O_2$, *i.e.* loss of the singly attached *N*-methylmaleimide residue).

The formation of the quinoline derivatives might involve the addition of the radical (VIII) to the imide, followed by attack of the resulting radical (IX) in the *ortho*-position and subsequent hydrogen abstraction. The formation of (VII) represents a case where a second molecule of the imide has reacted, but the resulting radical has failed to cyclise for steric reasons. Less probably the reaction could be looked upon as a polar 1,4-cycloaddition[2] of the cation (X) to be the double-bond of the imide, followed by loss of a proton.

Reduction of the above products with lithium aluminium hydride gave the expected compounds, *i.e.* (III) and (IV) with CH_2 in place of each CO.

(*Received, August* 30*th*, 1968; *Com.* 1182.)

---

[1] E. M. Burgess and L. McCullagh, *J. Amer. Chem. Soc.*, **1966**, **88**, 1580.

[2] R. R. Schmidt, *Tetrahedron Letters*, **1968**, 3443.