

The Mechanism of Formation of Quinoline Derivatives from *NN*-Dialkylanilines and *N*-Phenylmaleimide in the Presence of Benzoyl Peroxide

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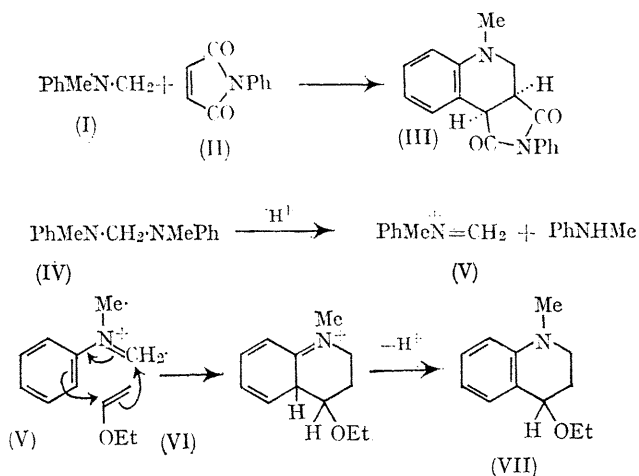
It has been suggested¹ that the formation of 1,2,3,4-tetrahydro-1-methylquinoline-3,4-dicarboxylic-*N*-phenylimide (III) by reaction of benzoyl peroxide with a mixture of *NN*-dimethylaniline and *N*-phenylmaleimide (II) might involve either the radical (I) or the cation (V). Evidence is now presented in favour of the radical mechanism. Thermal decomposition of di-*t*-butyl peroxide in an excess of *NN*-dimethylaniline yields *NN*-dimethyl-*NN'*-diphenylethylenediamine, through dimerisation of the radical (I).² A similar reaction carried out in the presence of (II) yielded (III).

After a solution of *NN'*-dimethyl-*NN'*-diphenylmethylethylenediamine (IV), *N*-phenylmaleimide, and benzoic acid in chloroform had been kept for 2 days the formation of (III) was not detected. The α -diamine would presumably yield

cation (V).³ On the other hand when a solution of (IV) and ethyl vinyl ether (VI) in chloroform was kept for 2 days in the presence of a catalytic amount of benzoic acid it gave a high yield of 4-ethoxy-1,2,3,4-tetrahydro-1-methylquinoline (VII), b.p. 120° (bath temp.)/1 mm.; ν_{\max} (KBr) 1088 (very strong, broad, O-C stretch) and 748 cm.⁻¹ (very strong, *o*-substituted aromatic ring); *M* (mass spectrometric) 191 (C₁₂H₁₇NO), base peak 144 (*N*-methylquinolinium ion, C₁₀H₁₀N); n.m.r. (CDCl₃, 60 MHz): τ 8.82 (t, CH₃-CH₂-, *J* 7 c./sec.), 8.5-7.7 [m, -CH₂-CH₂-CH(OEt)], 7.15 (s, CH₃-N, around 6.8 (m, N-CH₂-CH₂), 6.45 (q, CH₃-CH₂-O, *J* 7 c./sec.), 5.7 [poorly resolved t, -CHOEt-CH₂], 3.6-1.6 (m, aromatic).

Schiff's bases are inert towards typical dienophiles, but react readily with vinyl ethers in the presence of Lewis acids

(e.g. BF₃) the diene system (e.g. >C:C⁺:N:C< in the



conjugate acid) acquiring electrophilic properties and the dienophile acting as the electron donor.⁴ Thus (VII) can be formed from (V) and (VI), but a similar reaction would not be expected with *N*-phenylmaleimide, as this would not act as an electron donor. The reaction with ethyl vinyl ether is therefore regarded as a polar 1,4-cycloaddition and that with *N*-phenylmaleimide as a radical reaction.

Addition of benzoic anhydride to a solution of *NN*-dimethyl-*p*-toluidine-*N*-oxide and (II) in chloroform resulted in the formation of a low yield of 1,2,3,4-tetrahydro-1,6-dimethylquinoline-3,4-dicarboxylic-*N*-phenylimide, which suggests the formation of radical (I) in the system amine oxide + anhydride (cf. ref. 5).

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¹ R. B. Roy and G. A. Swan, *Chem. Comm.*, 1968, 1446.

² H. B. Henbest and R. Patton, *J. Chem. Soc.*, 1960, 3557.

³ H. Böhme, W. Lehnert, and G. Keitzer, *Chem. Ber.*, 1958, **91**, 340; H. Böhme and D. Eichler, *ibid.*, 1967, **100**, 2131.

⁴ L. S. Povarov and B. M. Mikhailov, *Izvest Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1963, 955; L. S. Povarov, *Russ. Chem. Rev.*, 1967, **36**, 656.

⁵ R. B. Roy and G. A. Swan, *Chem. Comm.*, 1966, 427; R. Huisgen, W. Heydkamp, and F. Bayerlein, *Chem. Ber.*, 1960, **93**, 363.