

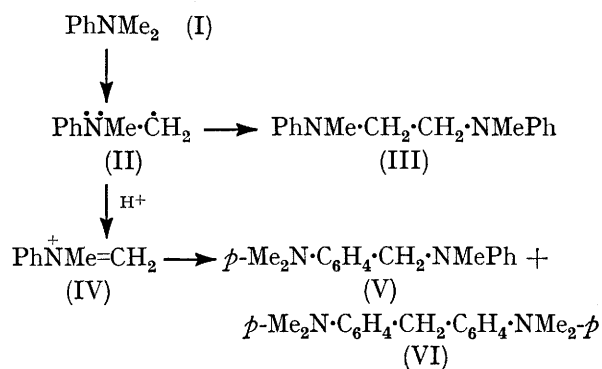
Disproportionation of *N*-Methylanilinomethyl Radicals in the Presence of Acid

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In the presence of acid the *N*-methylanilinomethyl radical undergoes disproportionation in preference to dimerisation, although its lifetime is still then long enough to enable it to react with *N*-phenylmaleimide.

THE action of either γ -rays¹ or *t*-butoxy-radicals² on *NN*-dimethylaniline (I) yields *NN'*-dimethyl-*NN'*-diphenylethylenediamine (III) through dimerisation of the *N*-methylanilinomethyl radical (II). However, γ -radiolysis of (I) in the presence of acid yields *N*-*p*-dimethylaminobenzyl-*N*-methylaniline (V) and bis-(4-dimethylaminophenyl)methane (VI),¹ which must be formed *via* the cation (IV).^{3,4} It has now been shown that acid can effect a similar change from the radical to the ionic mechanism also in the reaction brought about by *t*-butoxy-radicals. When the reaction between *NN*-dimethylaniline and di-*t*-butyl peroxide was carried out as described previously,² except that either acetic or benzoic acid was present, (VI) was the main product.

The radical (II) should be stabilised through orbital overlap of the unpaired electron and the lone pair on the



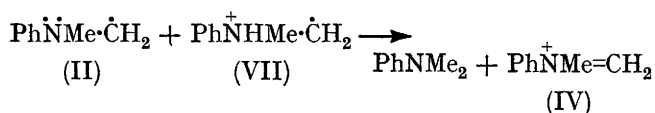
¹ J. M. Fayadh and G. A. Swan, *J. Chem. Soc. (C)*, 1969, 1775.

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

³ J. M. Fayadh, D. W. Jessop, and G. A. Swan, *J. Chem. Soc. (C)*, 1966, 1605.

⁴ J. R. Lindsay Smith, R. O. C. Norman, and W. M. Walker, *J. Chem. Soc. (B)*, 1968, 269.

nitrogen atom, but this stabilisation would be lacking in the protonated radical (VII), although dimerisation there would be discouraged by the cationic charge. It is therefore suggested that whereas in the absence of acid the radicals dimerise, in the presence of acid they undergo disproportionation to give the relatively stable ion (IV).



In support of this it has been found that when di-*t*-butyl peroxide undergoes thermal decomposition in excess of *NN*-dimethylaniline in the presence of benzoic [²H]acid or acetic [²H]acid, the recovered amine is enriched with respect to deuterium in the *N*-methyl groups. The recovered amine was degraded through *p*-nitroso-*NN*-dimethylaniline to dimethylamine, isolated as the hydrochloride; the deuterium enrichment was measured mass spectrometrically from the ratio of the peaks of *m/e* 46 and 45. The results of these experiments, along with appropriate controls, are shown in the Table.

<i>NN</i> -Dimethylaniline (ml.)	Peroxide (g.)	PhCO ₂ D (g.)	MeCO ₂ D (ml.)	<i>t</i> -Butyl alcohol (ml.)	Mol. ratio Base : peroxide : acid	Temp. (°C)	Time (hr.)	Enrichment of D in Me ₂ NH (atom %)
3	0.37	0.45			9.35 : 1 : 1.45	140°	38	0.7 ± 0.2
3	0.56		0.5		6.2 : 1 : 2.2	140	38	1.6 ± 0.3
4.2	1.22		0.98		4 : 1 : 2	140	47	2.3 ± 0.3
2			0.3		3.3 : 0 : 1	148	60	0
2.5			0.6	0.9	1.9 : 0 : 1	140	51	0.2 ± 0.1

As most reactions in which (V) or (VI), rather than (III), were obtained by oxidation of *NN*-dimethylaniline, have either been carried out in the presence of acid (*e.g.* photochemically,⁵ manganese acetate⁶), or have themselves produced acid (*e.g.* cupric chloride,⁴ benzoyl peroxide³), the above findings might have implications in some other cases.

The formation of 1,2,3,4-tetrahydro-1-methylquinoline-*N*-phenyl-3,4-dicarboximide from *NN*-dimethylaniline and *N*-phenylmaleimide, brought about by di-*t*-butyl peroxide⁷ succeeds even in the presence of benzoic acid (as also in the presence of triethylamine); and in the case of the reaction effected by benzoyl peroxide,⁸ benzoic acid is produced. The reaction of the radical (II) with *N*-phenylmaleimide must therefore be rapid compared with its disproportionation.

EXPERIMENTAL

*Reaction of Di-*t*-butyl Peroxide with NN-Dimethylaniline in the Presence of Benzoic Acid or Acetic Acid.*—(a) A mixture of *NN*-dimethylaniline (13 ml.), di-*t*-butyl peroxide (1.46 g.), and benzoic acid (2.4 g.) was heated in a sealed tube for 20 hr. at 140°. Unchanged amine was removed by distillation at 11 mm., and a solution of the residue in chloroform was shaken with sodium hydroxide solution and dried (K₂CO₃). The solvent was removed, and the residue

⁵ C. Pac and H. Sakurai, *Tetrahedron Letters*, 1968, 1865.

⁶ T. Aratani and M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1966, 88, 5479.

chromatographed on alumina. The light petroleum (b.p. 60–80°) eluate, when recrystallised from the same solvent afforded bis-(4-dimethylaminophenyl)methane (VI) (0.8 g.), identical in i.r. spectrum with an authentic sample.

(b) A similar experiment with *NN*-dimethylaniline (4 ml.), di-*t*-butyl peroxide (0.35 ml.), and acetic acid (0.4 ml.) (36 hr. at 145°) yielded the same product (0.2 g.).

*Reaction of Di-*t*-butyl Peroxide with NN-Dimethylaniline in the Presence of Benzoic [²H]Acid or Acetic [²H]Acid.*—(a) Deuterium oxide (5 ml.) was boiled under reflux for 30 min. with benzoic acid (0.5 g.); the mixture was cooled, and the resulting crystals were collected and dried over fresh phosphoric oxide in a vacuum desiccator. A mixture of these crystals (0.45 g.), *NN*-dimethylaniline (3 ml.), and di-*t*-butyl peroxide (0.37 g.) was heated in a sealed tube for 38 hr. at 140°. The product was shaken with a mixture of chloroform and sodium hydroxide solution, and the organic layer was dried (K₂CO₃) and distilled. The distillate of b.p. 80°/11 mm. (2 g.), consisting mainly of *NN*-dimethylaniline, was dissolved in a mixture of concentrated hydrochloric acid (7 ml.) and ice, and stirred, with ice-cooling, while a solution of sodium nitrite (1.2 g.) in water (2 ml.) was added dropwise. After 1 hr. the resulting *p*-nitroso-*NN*-dimethylaniline hydrochloride was collected, washed with ice-cold 2*N*-hydrochloric acid, and then added to sodium hydroxide (4.5 g.) in water (75 ml.).

The mixture was heated in a flask provided with a splash-head and condenser, the lower end of which led into 2*N*-hydrochloric acid (9 ml.), until no more dimethylamine passed over. The acid solution was evaporated to dryness (water-bath/reduced pressure), and the residual dimethylamine hydrochloride was dried by addition of ethanol followed by distillation of the latter. The salt (0.8 g.) was recrystallised three times from ethanol-ether, then dried overnight in a vacuum desiccator (P₂O₅); its i.r. spectrum (KBr) was indistinguishable from that of an authentic sample. It was then introduced through the heated inlet system of an AEI MS 9 mass spectrometer, operating at 10 ev. The deuterium enrichment of the dimethylamine was obtained from an average of 12 measurements of the ratio of the peaks of *m/e* 46 and 45, with the contribution made by ¹²C¹³CH₇N to the 46 peak allowed for. To check that the sample was free from ethanol (which could contribute to the 46 peak) a specimen of dimethylamine hydrochloride was prepared similarly from *NN*-dimethylaniline of normal isotopic composition, and this was examined mass spectrometrically under high resolution; the 46 peak was then resolved into a doublet, the larger component of which represented ¹²C¹³CH₇N (Found: *m/e* 46.0609. Calc.: 46.0612), and the much smaller one C₂H₆DN (46.0641). No peak corresponding to C₂H₆O (46.0419) was observed.

(b) In similar experiments, mixtures of acetic [²H]-

⁷ G. A. Swan, *Chem. Comm.*, 1969, 20.

⁸ R. B. Roy and G. A. Swan, *Chem. Comm.*, 1968, 1446; *J. Chem. Soc. (C)*, 1969, 1886.

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acid, *NN*-dimethylaniline, and di-*t*-butyl peroxide were treated in the same way.

Reaction of Di-t-butyl Peroxide with NN-Dimethylaniline in the Presence of Benzoic Acid and N-Phenylmaleimide.—A mixture of *NN*-dimethylaniline (6.3 ml.), di-*t*-butyl peroxide (0.71 g.), benzoic acid (1.2 g.), and *N*-phenylmaleimide (0.87 g.) was heated in a sealed tube for 36 hr. at 125°. The product was shaken with a mixture of chloroform and *N*-sodium hydroxide. The organic layer was separated and dried (K_2CO_3), and the solvent and unchanged amine were distilled off at 11 mm. The residue was chromatographed on alumina. Elution with benzene–light petroleum (b.p. 60–80°) (1:1) afforded 1,2,3,4-tetrahydro-1-methylquinoline-*N*-phenyl-3,4-dicarboximide,

and further elution with benzene yielded more of the same compound. These products, after recrystallisation from benzene–light petroleum, were identical in i.r. spectrum with an authentic sample⁸ (total yield 0.45 g.).

Reaction of Di-t-butyl Peroxide with NN-Dimethylaniline in the Presence of Triethylamine and N-Phenylmaleimide.—A mixture of *NN*-dimethylaniline (6.3 g.), di-*t*-butyl peroxide (0.73 g.), triethylamine (0.7 ml.), and *N*-phenylmaleimide (0.87 g.) when heated for 20 hr. at 130° afforded the same quinoline (0.15 g.).

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