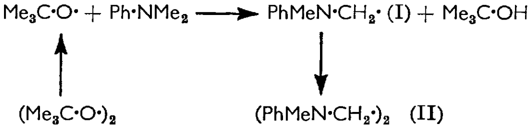
712. *Amine Oxidation. Part VI.* The Formation of Tetra-N-substituted 1,2-Diamines from Tertiary Amines.*

By H. B. HENBEST and R. PATTON.

Some tertiary amines are converted by reaction with t-butoxy-radicals into tetra-*N*-substituted 1,2-diamines. The best yields (up to 50%) have been obtained in the dimethylaniline series.

TRIALKYLAMINES containing *N*-ethyl groups are often dehydrogenated to vinylamines on reaction with halogenated *p*-benzoquinones [1] or with benzoyl peroxide.[2] The formation of the (usually unstable) vinylamines can be detected by reaction with halogenated quinones, blue or purple dialkylaminovinylquinones being formed.[1] If either of the above oxidising agents abstracts a hydrogen atom from the amine in the initial stages of the dehydrogenation, radicals $R_2N{\cdot}CR_2{\cdot}$ will be produced. In order to obtain some information regarding the chemical properties of such radicals, their formation by a relatively unambiguous method was attempted.



$$\begin{tikzcd} \mathrm{Me_3C{\cdot}O{\cdot}} + \mathrm{Ph{\cdot}NMe_2} \arrow[r] & \mathrm{PhMeN{\cdot}CH_2{\cdot}}\ (\mathrm{I}) + \mathrm{Me_3C{\cdot}OH} \arrow[d] \\ (\mathrm{Me_3C{\cdot}O{\cdot}})_2 \arrow[u] & (\mathrm{PhMeN{\cdot}CH_2{\cdot}})_2\ (\mathrm{II}) \end{tikzcd}$$

t-Butoxy-radicals, formed by homolysis of the peroxide, remove hydrogen from many organic molecules, giving t-butyl alcohol and an organic radical.[3] Tertiary amines should therefore give radicals $R_2N{\cdot}CR_2{\cdot}$, provided that the nitrogen promotes selective attack at an adjacent CH group. In a kinetic study of the thermal decomposition of di-t-butyl peroxide, Raley, Rust, and Vaughan [4] showed that the peroxide decomposed by a first-order process at similar rates in the gas phase and in solvents, including one amine (tri-n-butylamine). Urry and Juveland [5] have shown that terminal olefins add to the radicals produced by decomposition of the peroxide in primary and secondary amines. They also found that the decomposition of the peroxide in 1-methylpiperidine in the presence of oct-1-ene gave 1-methyl-2-n-octylpiperidine. More recently, Swan, Timmons, and Wright [6] obtained *meso*- and racemic 2,3-bisdiethylaminobutane on γ-ray irradiation of triethylamine, and Huang [7] obtained αβ-bisdibenzylaminobibenzyl in 4% yield on decomposition

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* Part V, Henbest and Slade, *J.*, 1960, 1588.

[1] Buckley, Dunstan, and Henbest, *J.*, 1957, 4880.

[2] Buckley, Dunstan, and Henbest, *J.*, 1957, 4901.

[3] Cf. Gray and Williams, *Chem. Rev.*, 1959, **59**, 278.

[4] Raley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 1336.

[5] Urry and Juveland, *J. Amer. Chem. Soc.*, 1958, **80**, 3322.

[6] Swan, Timmons, and Wright, *J.*, 1959, 9.

[7] Huang, *J.*, 1959, 1816.

of di-t-butyl peroxide in tribenzylamine. Both of these reactions were interpreted as proceeding by the formation and dimerisation of $R_2N{\cdot}CR_2{\cdot}$ radicals.

In our experiments,[8] t-butyl peroxide was decomposed thermally in an excess of dimethylaniline in various molecular ratios. From the experiments in which 1 : 5 and 1 : 10 ratios of peroxide to amine were used, t-butyl alcohol was obtained in 92 and 100% yield respectively, showing that the alkoxyl radicals abstract hydrogen from the amine rather than decompose to acetone and methyl radicals. Removal of unchanged dimethylaniline by distillation, followed by chromatography of the residue, gave the substituted ethylenediamine (II), and two other crystalline products. The formation of the diamine (II) indicates that the reaction between the t-butoxy-radicals and dimethylaniline generates *N*-methylanilinomethyl radicals (I) that dimerise. The best yield (50%) of diamine (II) was obtained from reaction between the peroxide and amine in the ratio 1 : 10.

The results are similar to those reported earlier for toluene which gives bibenzyl as the main product on reaction with various radicals [9] including t-butoxy. The product (1,2,3-triphenylpropane) derived from dehydrogenative coupling of bibenzyl and toluene was also detected in one investigation.[10]

Decomposition of di-t-butyl peroxide in dimethyl-*p*-toluidine (ratio 1 : 5) gave the 1,2-diamine related to (II) in the same yield (29%) as that obtained for the diamine (II) from dimethylaniline.

Other reactions, apart from hydrogen-abstraction and dimerisation, can take place when t-butyl peroxide is decomposed in other amines. *N*-Methyldiphenylamine gave t-butyl alcohol and diphenylamine. t-Butyl methyl ether was not formed, showing that the *N*-methyl group in the initial amine is not removed by combination with a t-butoxy-radical. This reaction is being studied further.

Decomposition of the peroxide in 1-dimethylaminonaphthalene gave intractable material; a similar result was obtained when this amine was oxidised with manganese dioxide (following paper).

EXPERIMENTAL

M. p.s were determined on a Kofler hot stage. Light petroleum refers to the fraction of b. p. 40—60°. P. Spence alumina (Grade H) was used for chromatography.

Oxidation of Dimethylaniline.—The amine (in the amounts specified below) and the peroxide (1·462 g.) were heated together in a sealed tube in the dark at 140° for 44 hr. Most of the unchanged amine was removed by distillation at 20 mm., and the residue was adsorbed on alumina (100 g.). Elution with benzene–light petroleum (1 : 4) gave *NN'*-dimethyl-*NN'*-diphenylethylenediamine (II), m. p. and mixed m. p. 48·5° (after crystallisation from light petroleum). Elution with benzene–light petroleum (1 : 1) gave a compound [? N-*methyl*-N-(2-N-*methylanilino*-1-N-*methylanilinomethylethyl*)*aniline*], m. p. 91° (from light petroleum) or m. p. 101° (from light petroleum–ethanol) (Found: C, 80·2; H, 8·45. $C_{24}H_{29}N_3$ requires C, 80·2; H, 8·15%). Elution with benzene–light petroleum (4 : 1) gave another compound, m. p. 163° (from benzene–light petroleum) (Found: C, 80·5; H, 8·4%). Evidence for the structures of these compounds will be presented later.

$NPhMe_2$ (g.)	Amine : Peroxide (mol.)	Diamine (II) (%)	Bu^tOH (%)	$NPhMe_2$ recovd. (%)
3·03	2·5	26	Not determined	
6·06	5	29	92	80
12·12	10	50	100	84
24·24	20	44	Not determined	

t-Butyl alcohol was estimated on a sample of the total reaction mixture by vapour-phase chromatography over silicone–Celite at 60° with methanol as internal standard. Dimethylaniline was estimated similarly at 180° with *m*-xylene as standard.

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[8] Cf. Henbest and Patton, *Proc. Chem. Soc.*, 1959, 225.

[9] Wilen and Eliel, *J. Amer. Chem. Soc.*, 1958, **80**, 3309, and references there given.

[10] Farmer and Moore, *J.*, 1951, 131.

*Oxidation of Dimethyl-*p*-toluidine.*—The amine (3·426 g., 5 mol.) and the peroxide (0·718 g., 1 mol.) were heated in a sealed tube at 166° for 24 hr. Lower-boiling products including unchanged amine were distilled at 0·1 mm., and then the diamine (0·368 g.) was collected at 142°/0·03 mm., leaving only a trace of residue. Crystallisation from pentane gave *NN'*-dimethyl-*NN'*-di-*p*-tolylethylenediamine (0·37 g., 29%), m. p. and mixed m. p. 81·5°, the authentic sample being prepared from *N*-methyl-*p*-toluidine and ethylene dibromide.[11]

Oxidation of N-*Methyldiphenylamine.*—The amine (1·696 g., 5 mol.) and the peroxide (0·2736 g., 1 mol.) were heated in a sealed tube at 140° for 39 hr. The product (1·91 g.) was adsorbed on alumina (140 g.). Elution with benzene–light petroleum (3 : 7) gave unchanged amine (1·263 g.), n_D^{24} 1·6180. Elution with benzene–light petroleum (9 : 1) gave diphenylamine (0·55 g.), m. p. and mixed m. p. 52°. (In a control experiment *N*-methyldiphenylamine was eluted unchanged from alumina.) The yield of diphenylamine is 43% or 86% depending whether 1 mol. of the peroxide gives 2 or 1 mol. of the secondary amine.

In another experiment, t-butyl alcohol (58%) was obtained by distillation of the reaction mixture. Infrared analysis showed the absence of t-butyl methyl ether (b. p. 55°) in the distillate.

Oxidation of NN-*Dimethyl-α-naphthylamine.*—The reaction was carried out as in the preceding experiment between the amine (17·21 g., 5 mol.) and the peroxide (2·99 g., 1 mol.). Unchanged amine was removed at 138°/9 mm., and the residue (2 g.) was chromatographed on alumina (120 g.). Viscous materials were eluted with mixtures of benzene and ether. No crystalline products were obtained.

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[11] Fröhlich, *Ber.*, 1907, **40**, 763.