

834. *Reactions of Organic Peroxides. Part VI.***Reactions with Amines.*

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It has been found that alkaryl hydroperoxides, on treatment with amines, are converted smoothly into the corresponding carbinol by loss of one atom of oxygen. The mechanism of the reaction is uncertain, but it is known that some of the amine is utilised, whilst water is formed in amount corresponding to the oxygen lost by the peroxide. Many amines can be used for this reaction, although in general the speed of reaction follows the order tertiary amines > secondary amines > primary amines; ethylenediamine and 2-hydroxyethylamine, however, react very vigorously.

THE decomposition of di-*tert.*-butyl peroxide in various solvents generally produces a mixture of *tert.*-butanol and acetone; when tri-*n.*-butylamine is the solvent, however, the product is almost entirely *tert.*-butanol (Raley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 1336).

It has now been found that hydroperoxides decompose quite readily when heated with a variety of primary, secondary, or tertiary amines to give almost exclusively the corresponding carbinol. The hydroperoxides studied include those of *isopropylbenzene*, the *diisopropylbenzenes*, *sec.*-butylbenzene, and *isopropyl-naphthalene*. The reaction is usually rapid, the more so with tertiary amines (when it may be complete in 10 minutes) than with secondary or primary amines under similar conditions, but bishydroxyethylamine, piperidine, and piperazine reacted as readily as many tertiary amines, whilst ethylenediamine brought about a very rapid decomposition. On the other hand, aniline reacted extremely slowly under the standard conditions used, but at higher temperatures (140—150°) the decomposition was moderately rapid. Pyridine, quinoline, urea, acetamide, and acetonitrile caused only very slow decomposition even at a higher temperature and the reactions were not taken to completion. Dimethylformamide reacted at an intermediate speed.

At the end of the reactions with $\alpha\alpha$ -dimethylbenzyl hydroperoxide the decomposition products were analysed for $\alpha\alpha$ -dimethylbenzyl alcohol, acetophenone, and α -methylstyrene by study of the infra-red spectra (cf. Part II)†; they showed in almost every case complete conversion of hydroperoxide into carbinol, the product being purer than that obtained by sodium sulphite reduction of the hydroperoxide. At lower temperatures (60—70°) or when the concentrations of amine were small the time required for decomposition increased.

Much of the amine concerned in such reactions was recovered; the quantity consumed bears no apparent stoichiometric relation to the amount of hydroperoxide decomposed.

An attempt was made to determine the fate of the oxygen lost by the hydroperoxide. Very little gas was evolved during the reaction—except a little ethylene when triethylamine was used—or during the subsequent distillation of the products, and the small amount of residue after distillation was insufficient to account for the oxygen lost; the residue does not appear to contain amine oxides. However, water is formed in stoichiometric proportion to the oxygen lost by the hydroperoxide; the hydrogen involved must have been derived from the amine although in what manner is uncertain. It seems possible that the small residues left from these reactions may be polymerised unsaturated amines or amine derivatives, although they are far from being uniform products.

Since this work was completed it has been reported (Horner, *Angew. Chem.*, 1949, **60**, 411, 485) that diacyl peroxides are decomposed by primary, secondary, or tertiary amines. The peroxides are converted into carboxylic acids by abstraction of hydrogen from the amine.

EXPERIMENTAL

The same procedure was adopted for nearly all the amines used. The mixture of hydroperoxide and amine was heated at the bath temperatures given in Table I until the test for

* Part V, *J.*, 1950, 2804.† Part II, *J.*, 1950, 2169.

peroxide was no longer positive; in some cases much peroxide remained after many hours' heating, and the material was not further examined. The solution was then either (a) distilled, to give amine and hydroperoxide-decomposition product, or (b) washed with acid to remove amine and then distilled.

The distillate was analysed by use of the infra-red method mentioned in Part II; generally the residue was not further examined, and it usually consisted of less than 5% of the total products.

α-Dimethylbenzyl Alcohol.—This was obtained as a liquid from the reaction of *αα*-dimethylbenzyl hydroperoxide with many different amines. Two crystallisations from light petroleum yielded a product, m. p. 33–34°, identical with that obtained by synthesis (Part II). Details of the reactions of amines with this hydroperoxide are given in Table I.

TABLE I.

Hydroperoxide, g.	Amine	Wt., g.	Bath temp.	Decomp. time, hr.	Product from peroxide Wt., g.	% Carbinol
20	Triethylamine	50	110–120°	$\frac{1}{2}$	18.5	88
10	"	25	60–70	$9\frac{1}{2}$	9.0	"
5	Triethylamine in <i>iso</i> -propylbenzene	12	110–120	$\frac{1}{2}$	—	"
10	Triethylamine in <i>iso</i> -propylbenzene	2	"	$8\frac{1}{2}$	—	81.5 ^b
		32	"	"	"	"
20	Triethanolamine	50	"	$\frac{1}{2}$	15.9	100
10	Dimethylaniline	20.5	"	$\frac{1}{2}$	9.0	85 ^c
10	Diethylamine	25	110	11–12	9.8	78 ^c
			(internal 63)			
10	Diisopropylamine	25	{ 80–90	2	—	—
			{ 100–110	1	6.5	99.5
10	Bishydroxyethylamine	25	110–120	$\frac{1}{2}$	8.8	94
10	<i>n</i> -Butylamine	25	100–110	$9\frac{1}{2}$	10.0	72 ^c
10	<i>iso</i> Butylamine	25	100–110	16–17	6.5	100
10	Hydroxyethylamine	25	90	$\frac{1}{2}$	5.8	98
10	Aniline	25	140–150	2	6.5	90
2	Ethylenediamine	5	100	$\frac{1}{2}$	—	"
10	Ethylenediamine	27	60–85	3	8.5	80 ^c
10	Piperidine	25	110–120	$\frac{1}{2}$	10.4	87 ^c
2.5	Piperazine in <i>isopropyl</i> -benzene	6	"	$\frac{1}{2}$	—	"
5	Hexamine in <i>isopropyl</i> -benzene	12	"	$\frac{1}{2}$	—	"

^a Not analysed. ^b Together with 13% of acetophenone. ^c The product contained some amine or amine-decomposition product, but no acetophenone or *α*-methylstyrene.

In addition, the mixture from the reaction of the hydroperoxide with the following at 110–120°, or higher, for long periods still contained unreacted peroxide and was therefore not further examined: aniline at 110–120°, pyridine, quinoline, urea, dimethylformamide, acetamide, acetonitrile, and ammonia (passed through a solution in *isopropylbenzene*).

α-Dimethyl-m-isopropylbenzyl Alcohol.—*αα*-Dimethyl-*m-isopropylbenzyl* hydroperoxide (8 g.) was heated at 100–110° for $1\frac{1}{2}$ hr. with triethylamine (25 g.). After removal of the unchanged amine the *carbinol* (6.0 g.) distilled at 119°/15 mm.; the distillate crystallised as it distilled, and had m. p. 36–37° (from light petroleum) (Found: C, 80.65; H, 9.7. C₁₂H₁₈O requires C, 80.9; H, 10.1%).

α-Dimethyl-p-isopropylbenzyl Alcohol.—*αα*-Dimethyl-*p-isopropylbenzyl* hydroperoxide (8 g.) and triethylamine (20 g.) were heated at 110–120° for 1 hr. Distillation gave unchanged amine and a fraction (7.0 g.), b. p. 130–132°/21 mm. Infra-red analysis of the product indicated no substituted acetophenone or methylstyrene homologue. Recrystallisation from petroleum and ethanol-water gave the *carbinol*, m. p. 42.5–43° (Found: C, 80.5; H, 9.8. C₁₂H₁₈O requires C, 80.9; H, 10.1%).

p-Di-(1-hydroxy-1-methylethyl)benzene.—The dihydroperoxide (8 g.) of *p-diisopropylbenzene* and triethylamine (20 g.) were heated at 110–120° for $\frac{3}{4}$ hr. Distillation gave: amine (15 g.); a fraction (1.0 g.), b. p. 90–128°/15 mm., and another (4.5 g.), b. p. 128–160°/15 mm., which slowly crystallised. Recrystallisation of the latter from benzene gave the dihydroxy-compound, m. p. 141–142° (Found: C, 74.2; H, 9.3. Calc. for C₁₂H₁₈O₂: C, 74.2; H, 9.3%). Bogert and Harris (*J. Amer. Chem. Soc.*, 1919, **41**, 1676) report m. p. 142.4–142.9° (corr.) for *p-di-(1-hydroxy-1-methylethyl)benzene*.

1-Methyl-1-β-naphthylethyl Alcohol.—1-Methyl-1-β-naphthylethyl hydroperoxide (10 g.) and

triethylamine (25 g.) were heated for 7 hr. before decomposition was complete. Distillation provided amine; a fraction (4.7 g.), b. p. 160—180°/15—20 mm., which slowly crystallised; and residue (2.8 g.). Recrystallisation of the distillate from light petroleum, followed by aqueous ethanol, provided large crystals, m. p. 62°, of the alcohol (Found: C, 84.1; H, 7.6. Calc. for $C_{13}H_{14}O$: C, 83.9; H, 7.5%).

Heating of the alcohol with fused potassium hydrogen sulphate under reduced pressure led to β -isopropenylnaphthalene, m. p. 54—54.5° (from aqueous ethanol followed by cold methanol) (Found: C, 92.5; H, 7.1. Calc. for $C_{13}H_{12}$: C, 92.8; H, 7.2%).

α -Ethyl- α -methylbenzyl Alcohol.— α -Ethyl- α -methylbenzyl hydroperoxide (5 g.) was heated with triethylamine (12 g.) at 110—120° until the peroxide had decomposed, giving the carbinol, b. p. 53—54°/0.1 mm. (Found: C, 79.4; H, 9.3. Calc. for $C_{10}H_{14}O$: C, 80.0; H, 9.3%). This yielded a phenylurethane, m. p. 89—90°, and α -naphthylurethane, m. p. 129—130.5°, identical with those obtained from the product of sodium sulphite reduction of the hydroperoxide (Part I).

tert.-Butanol.—*tert.*-Butyl hydroperoxide (10 g.) was added gradually to trishydroxyethylamine (25 g.) previously heated to *ca.* 100°. A vigorous reaction followed each addition; after the last, heating was continued for a few minutes, and the low-boiling product (9.0 g.) then distilled off. This contained no acetone (by hydroxylamine determination and infra-red examination) and consisted of *tert.*-butanol (95% of the dried distillate), some water, and a trace of amines.

Detailed Examination of the Products of Reaction of α -Dimethylbenzyl Hydroperoxide.—In the following experiments yields were obtained by analysis; amines were determined by acid titration, water by Fischer's method (Mitchell and Smith, "Aquametry," New York, 1948) and α -dimethylbenzyl alcohol by infra-red analysis. In some cases spectroscopic determination of carbinol gave slightly incorrect results through interference by nitrogenous compounds. Ethylene was measured by absorption analysis (Bone and Wheeler's method) and by study of infra-red spectra.

With triethylamine. (a) Hydroperoxide (24.3 g.) was heated with triethylamine (24.5 g.) at 110° for 20 min.; no peroxide then remained and no gaseous products had been evolved. Distillation gave crude triethylamine (16.7 g.), b. p. 67°, and ethylene (0.023 mole) was evolved. α -Dimethylbenzyl alcohol (18.9 g.), b. p. 82—92°/12 mm., then distilled, leaving a gummy residue (5.9 g.); a mixture of triethylamine and water (2.8 g.) was retained in a cooled trap. The crude amine on refractionation gave pure amine (5.1 g.), b. p. 89° (Found: n_D^{20} 1.400; equiv., 102. NEt_3 has n_D^{20} 1.4032; equiv., 101.2), the remainder being wet triethylamine.

(b) Hydroperoxide (23.6 g.) and amine (23.3 g.), under the same conditions as in (a), gave water (2.6 g.), ethylene (0.024 mole), unchanged amine (15.6 g.), and carbinol (21.6 g.). The residue (3.4 g.) contained 7.1% of nitrogen (Kjeldahl), whilst a small amount of unidentified nitrogenous material always distilled with the carbinol.

With bishydroxyethylamine. Hydroperoxide (20.1 g.) was heated with the amine (52 g.; a large excess) at 90° until a fairly vigorous reaction began, all the peroxide being decomposed in $\frac{1}{2}$ hr.; no gas was evolved. When larger proportions of hydroperoxide were used the reaction was exceptionally violent.

Distillation of the crude product gave the carbinol (12.8 g.), b. p. 89—92°/10 mm., bis-hydroxyethylamine (41.3 g.), b. p. 148—152°/10 mm., and water (2.4 g.). The residue (9.0 g.) contained 10.6% of nitrogen (Kjeldahl) and could not be identified. No morpholine was detected so that it is improbable that the water was derived by dehydration of the amine.

With diisopropylamine. Hydroperoxide (24 g.) and amine (21.8 g.) were heated at 100—110° for 4 hr.; no more peroxide then remained. No gas was evolved, and the crude product,

TABLE 2. (All quantities are in moles.)

Starting materials		Products			
peroxide	amine	carbinol	amine	water	ethylene
0.160	0.243 (triethylamine)	0.139	—	—	0.023
0.155	0.231 "	0.159	0.154	0.143	—
0.132	0.495 (diethanolamine)	0.094	0.365	0.134	—
0.158	0.216 (diisopropylamine)	0.128	0.160	0.129	(+ trace of acetone)

when distilled, gave unchanged diisopropylamine (16.2 g.), b. p. 60°, carbinol (17.4 g.), b. p. 92—93°/14 mm., and water (2.3 g.). Careful refractionation of the diisopropylamine fraction failed to separate the amine from water, but revealed the presence of a small amount of acetone

(semicarbazone, m. p. and mixed m. p. 187°; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 125°). No primary amine or phenol could be detected.

These results are summarised in Table 2.

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