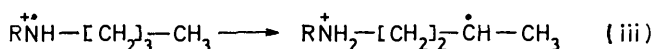
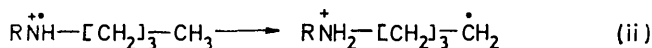
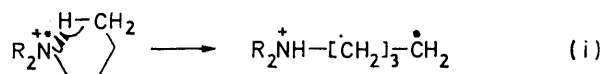


water.⁴ These processes, except for cyclisation, are illustrated in Scheme 1 for an aryldimethylamine *N*-oxide.

A further reaction which we should expect suitably constituted amine radical cations to undergo is intramolecular hydrogen-atom transfer, illustrated for a butyl-substituted member of the series by reaction (i). This possibility was recognised by Ferris *et al.*, but they could not find the products to be expected from such a process from the reaction of butyldimethylamine *N*-oxide with iron(II) ion.³ On the other hand, the corresponding reaction with a secondary amine radical cation [*e.g.* reaction (ii)] is a key step in the Hofmann-Löffler reaction;^{5,6} this process, which involves a six-membered cyclic transition state, occurs in preference to the one involving a five-membered cyclic transition state even though the latter would give the more stable (secondary) radical [reaction (iii)].⁶ We therefore decided to examine the reactions of butyl-substituted *N*-oxides with iron(II) ion in more detail, and here report on both the intramolecular reaction to which we have referred and on subsequent intra- and inter-molecular processes.



RESULTS AND DISCUSSION

We studied first the reaction between tributylamine *N*-oxide (2a) and iron(II) ion under conditions similar to those used by Ferris *et al.* for the reduction of butyldimethylamine *N*-oxide (0.05M-sulphuric acid at reflux temperature),³ seeking products which would be expected from the radicals (4a) and (7a), such as the alcohols (6a) and (9a). However, only tributylamine (64%) and dibutylamine (29%) [the products expected from the one-electron reduction and oxidation, respectively, of the amine radical cation (3a)] were obtained, corresponding to the results obtained by Ferris *et al.* for the *N*-oxide (2b).

The Hofmann-Löffler reaction is normally carried out in much more concentrated solutions of sulphuric acid than in the foregoing experiment. We therefore repeated that experiment with 50% sulphuric acid as the solvent, obtaining, in addition to tributylamine (30%) and dibutylamine (5%), 6% of the primary alcohol (6a) and 39% of the secondary alcohol (9a).

We studied the reactions of two other *N*-oxides under these conditions. The compound (2b) gave 4% of the primary alcohol (6b) and 14% of the secondary alcohol (9b); the lower yields of these products compared

with those of the corresponding products from the *N*-oxide (2a) are no doubt the result, at least in part, of the presence of three butyl groups in (2a), the hydrogen-abstraction reactions consequently competing more successfully with the reduction and oxidation of the amine radical cation (3a) than in the case of (3b). Dimethylpentylamine *N*-oxide gave only one alcoholic product, $\text{Me}_2\text{N}\cdot[\text{CH}_2]_3\text{CH}(\text{OH})\text{Me}$ (72%).

By analogy with the Hofmann-Löffler reaction, we had expected that the *N*-oxides (2a) and (2b) would yield more of the primary alcohols (6a and b) than the secondary alcohols (9a and b). We considered four possible explanations for the opposite behaviour.

(a) The primary alcohols might undergo rearrangement to the secondary alcohols under the reaction conditions. This possibility was ruled out by our finding that both the primary alcohols (6a and b) were stable under the reaction and work-up conditions.

(b) The intramolecular process might occur more readily to give primary carbon radicals, by way of six-membered cyclic transition states as in the Hofmann-Löffler reaction, these yielding secondary alcohols *via* oxidative and rearrangement steps. Of the possible ways in which these might occur, we discounted the radical rearrangement (4) \longrightarrow (7) followed by oxidation, since this would be expected to occur also in the Hofmann-Löffler reaction which involves the same type of primary radical (moreover, no such hydrogen-atom rearrangements have been unambiguously established, at least under moderate conditions⁷). There are two other possibilities. (i) The primary radical might undergo oxidative elimination with iron(III) ion⁸ to give the alkene $\text{R}_2\text{N}\cdot[\text{CH}_2]_2\text{CH}:\text{CH}_2$ ($\text{R} = \text{Bu}$ or Me) as its conjugate acid, the secondary alcohol arising by hydration in the acidic medium. This possibility was eliminated by our finding that when the alkene $\text{Me}_2\text{N}\cdot[\text{CH}_2]_2\text{CH}:\text{CH}_2$ was subjected to the reaction conditions [50% sulphuric acid containing both iron(II) and iron(III) ion at 100° for 16 h], *ca.* 50% was recovered unchanged (whereas none of the alkene was detectable from reaction of the *N*-oxide) and almost as much of the primary alcohol (6b) was formed as the secondary alcohol (9b) (16 and 19%, respectively) (whereas reaction of the *N*-oxide gave over three times as much of the latter). (ii) The primary radical might undergo oxidation by iron(III) ion or by more of the *N*-oxide to the corresponding carbonium ion, followed by, or concerted with, hydride-transfer, leading to the secondary alcohol, in preference to solvolysis to give the primary alcohol; a formal representation is in Scheme 2, sequence (4) \longrightarrow (5) \longrightarrow (8), and evidence consistent with this path is described later.

(c) Reaction of amine radical cation might occur inter- rather than intra-molecularly, reactions giving the radicals (7a and b) being faster than those giving the

⁵ S. Wawzonek and P. J. Thelen, *J. Amer. Chem. Soc.*, 1950, **72**, 2118.

⁶ E. J. Corey and W. R. Hertler, *J. Amer. Chem. Soc.*, 1960, **82**, 1657.

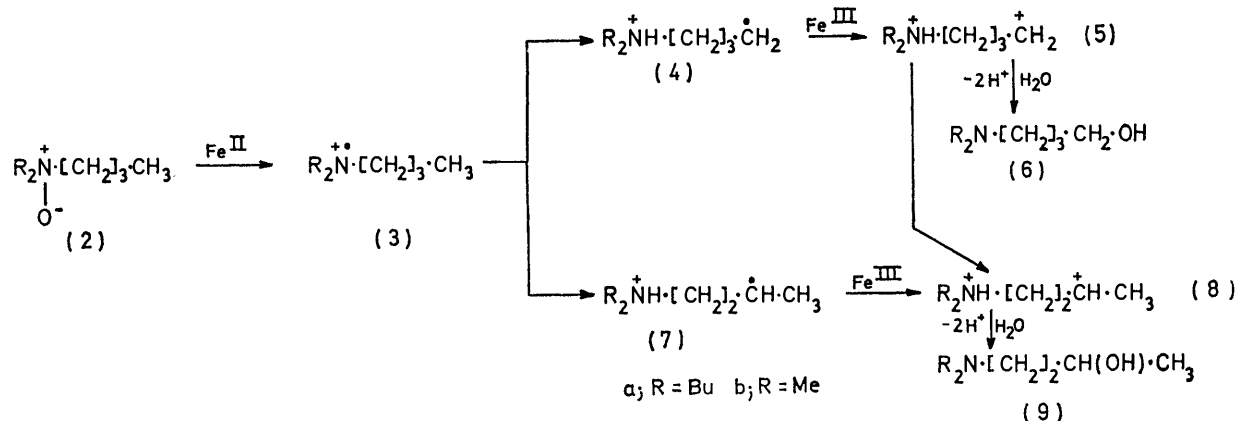
⁷ C. Walling, 'Free Radical Rearrangements,' in 'Molecular Rearrangements,' ed. P. de Mayo, Interscience, 1963, Part 1, ch. 7.

⁸ H. E. De La Mare, J. K. Kochi, and F. F. Rust, *J. Amer. Chem. Soc.*, 1963, **85**, 1437.

radicals (4a and b) because the greater stability of the former is reflected in the relative energies of the transition states.

(d) Reaction of the amine radical cation might occur intramolecularly, as in the Hofmann-Löffler reaction, but with stereochemical control of less significance than in that reaction and outweighed in importance in this case by the greater stability of secondary than of isomeric primary radicals. We sought to distinguish

action conditions). The reactions following formation of the primary carbon radical in the presence of the trap are summarised in Scheme 3; evidently a portion of the bromo-compound (10a) undergoes solvolysis under the reaction conditions to give the alcohol (6a), the rest remaining in solution until, after basification and Hofmann elimination, it yields (12a) and (13a). The Scheme leaves unaccounted for only the 2% yield of the secondary alcohol (9a); since the corresponding alcohol (9b)



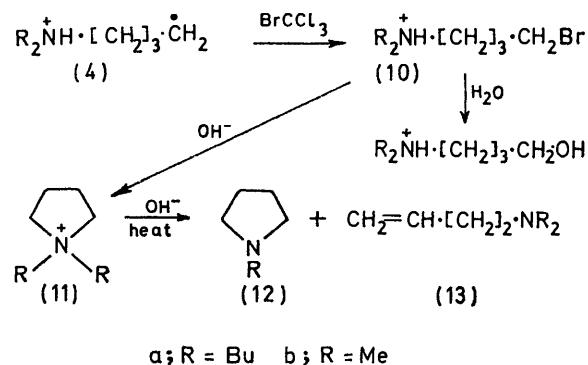
SCHEME 2

between possibilities (b) (ii), (c), and (d) in two ways: first, by trapping the initial carbon radical; secondly, by finding the distribution of deuterium in the alcohols formed from the compound $\text{Me}_2\text{N}^+(\text{O}^-)\cdot[\text{CH}_2]_3\text{CD}_3$.

Trapping Experiments.—Alkyl radicals extract bromine efficiently from bromotrichloromethane.⁹ When this reagent was included in the reaction of the *N*-oxide (2a) with iron(II) ion and the reaction mixture was worked up in the usual way, 2% of the secondary alcohol (9a) and 20% of the primary alcohol (6a) were obtained; when the resulting mixture was treated with base and then, after distillation to dryness, heated at 260° for 2 h (conditions for Hofmann elimination), the pyrrolidine (12a) (15%) and the unsaturated amine (13a) (9%) were obtained. It was found that the cation (10a), as its bromide salt, when submitted to the usual work-up conditions for reaction of the *N*-oxide, gave the primary alcohol (6a) (32%) and, when treated with base and submitted to Hofmann elimination, gave the products (12a) and (13a) in 31 and 16% yields, respectively; and when the hydrobromide of the bromo-amine $\text{Bu}_2\text{N}\cdot[\text{CH}_2]_2\text{-CHBrMe}$ was submitted to the usual work-up conditions, the secondary alcohol (9a) was obtained in 75% yield.

These results are not in accord with the suggestion that the amine radical cation (3a) might yield the radical (7a) more readily than (4a); in particular, if that were the case, we should not have expected an increase in the yield of the primary alcohol in the presence of the trap, or a decrease in that of the secondary alcohol (since the corresponding bromide which would have been formed by reaction of the secondary radical with the trap was shown to give the secondary alcohol efficiently under the re-

from the *N*-oxide (2b) in the presence of the trap was formed in only trace amount (see later), it is likely that (9a) is formed *via* a small amount of the primary radical (4a) which escapes the trap.



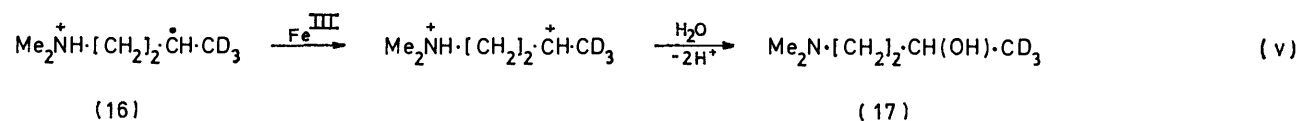
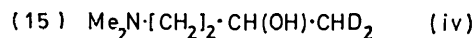
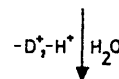
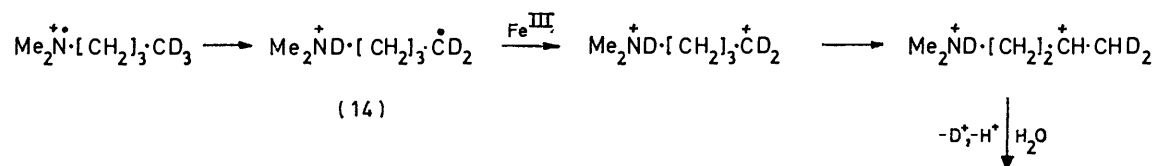
SCHEME 3

The behaviour of the *N*-oxide (2b) in the presence of bromotrichloromethane closely resembled that of (2a) and is interpreted in the same way. Thus, work-up under the usual conditions gave 16% of the primary alcohol (6b) and only a trace (<0.5%) of its secondary isomer (9b), and basification followed by Hofmann elimination gave the unsaturated amine (13b) (5%); the products (6b) and (13b) were also obtained by the corresponding treatment of 4-bromobutyldimethylammonium bromide. The reaction of dimethylpentylamine *N*-oxide in the presence of the trap gave 56% of $\text{Me}_2\text{N}\cdot[\text{CH}_2]_3\text{-CH(OH)Me}$ after normal work-up and 23%

⁹ C. Richardt, K. Herwig, and S. Eichler, *Tetrahedron Letters*, 1969, 421.

of the unsaturated amine $\text{Me}_2\text{N}\cdot[\text{CH}_2]_3\cdot\text{CH}\cdot\text{CH}_2$ after basification and Hofmann elimination. We infer that the secondary radical $\cdot\text{CHMe}\cdot[\text{CH}_2]_3\cdot\text{NHMe}_2^+$ is formed essentially specifically and attribute the much higher yield of the corresponding alcohol in the absence of the trap (72%), compared with the total yields of alcohols from (2a) or (2b), to the fact that formation of the secondary radical from the pentyl-containing compound competes much more effectively with other reactions of the amine radical cation than does formation of the primary radicals from the butylamine derivatives.

Deuterium-label Experiments.—When the *N*-oxide of the deuterium-containing amine $\text{Me}_2\text{N}\cdot[\text{CH}_2]_3\cdot\text{CD}_3$ (94 ± 2 atom % D_3) was treated with iron(II) ion under the same conditions as (2b), the primary alcohol (6b) which was obtained in 2.5% yield contained almost entirely ($92 \pm 3\%$) two deuterium atoms per molecule, as expected for reaction as in Scheme 2. The secondary alcohol (9b) was obtained in 7% yield, $46 \pm 3\%$ of which contained two, and $49 \pm 3\%$ of which contained three, deuterium atoms per molecule. Formation of the dideuterated secondary alcohol is consistent with the occurrence of hydrogen-atom abstraction to give the primary radical followed by oxidation and carbonium-ion rearrangement, as in reaction (iv), but not with reaction by way of the secondary radical. Conversely, formation of the trideuterated secondary alcohol shows that reaction also occurs *via* the secondary radical [reaction (v)].



The lower yields of both the primary and the secondary alcohol from the deuterated amine *N*-oxide than from its protio-analogue are to be expected since, as the result of a primary isotope effect, formation of the radical (14) should compete with other reactions of its precursor less effectively than formation of the radical (4b).

Intra- and Inter-molecular Hydrogen-atom Abstraction.—The results of the trapping experiments show that hydrogen-atom abstraction by the amine radical cation occurs mainly, and probably entirely, to give the primary carbon radical from the butyl-containing *N*-oxides. They show also that the amine radical cation is not scavenged efficiently, if at all, by the trap, since the alcohols from either (2a) or (2b) were formed in significant *total* amount when the trap was present. In contrast, the results of the deuterium-labelling experiments

provide evidence that a significant proportion of the secondary alcohol (9b) *does* arise from the corresponding secondary carbon radical in the absence of the trap. This suggested the possibility that, under the latter conditions, some of the secondary alcohol is formed by intermolecular hydrogen-atom abstraction, and we now describe evidence for this.

We first investigated the possibility that hydrogen-atom abstraction occurs intermolecularly by including tributylamine in equimolar amount with the amine *N*-oxide (2b) for reaction of the latter with iron(II) ion. In addition to the products obtained in the absence of the tributylamine, a 3% yield of the secondary alcohol (9a) was obtained. We infer from this demonstrated intermolecular reaction that such processes are likely to occur during reaction in the absence of tributylamine, involving abstraction from the reduction product (protonated) butyldimethylamine, and from a second molecule of the *N*-oxide (followed in this case by successive one-electron reductions, as well as by conversion of the carbon radical into a hydroxy-function). We now discuss the nature of the species responsible for the intermolecular process.

The trapping experiments have established that hydrogen-atom abstraction by the amine radical cation occurs essentially entirely at the primary carbon atom of the butyl substituent. There are two indications that this is unlikely to occur intermolecularly in significant proportion. First, we should not expect abstraction

from a primary carbon atom to occur more readily than from a secondary carbon atom (see further later). Secondly, the yield (3%) of the secondary alcohol (9a) when tributylamine was included in the reaction of the *N*-oxide (2b) was much smaller than the total yield of alcohols derived from (2b) itself (18%). We sought more direct evidence by including bromotrichloromethane as well as tributylamine in reaction of the *N*-oxide (2b) with iron(II) ion; this resulted in a reduction of the yield of the secondary alcohol (9a) to a trace (<0.05%), although the yield of the primary alcohol (6b) was 15% (*cf.* 16% in the absence of tributylamine). Since the amine radical cation is not scavenged efficiently by the trap, it follows that the main reaction path to the alcohols involves intramolecular hydrogen-atom abstraction, to give the primary radical, and that this, as well as yielding

primary or secondary alcohol by way of oxidation and, in the latter case, rearrangement, can also abstract a hydrogen atom from another molecule.

Further evidence that the intermolecular abstraction is effected by the primary radical was provided by our finding that the butyldimethylamine formed from the *N*-oxide of $\text{Me}_2\text{N}^+\cdot[\text{CH}_2]_3\cdot\text{CD}_3$ contained a smaller proportion of trideuterated material than the reactant ($86 \pm 3\%$, compared with $94 \pm 2\%$), in accord with the formation of the primary radical $\text{Me}_2\text{ND}^+\cdot[\text{CH}_2]_3\cdot\text{CD}_2$, some of which abstracts a hydrogen atom from the methylene group adjacent to CD_3 in either another molecule of the *N*-oxide or a molecule of the conjugate acid of the tertiary amine $\text{Me}_2\text{N}^+\cdot[\text{CH}_2]_3\cdot\text{CD}_3$.

Finally, it is notable that only one alcohol is formed in detectable amount by the intermolecular reaction involving the butylamine derivatives, namely the secondary alcohol derived by abstraction from the methylene group furthest from the nitrogen atom. It is not surprising that the primary alcohol is not formed, since not only would abstraction be expected to occur less readily from primary than from secondary C-H, but also the primary radical, if formed, would be expected to yield the secondary alcohol, as already discussed. On the other hand, we had expected abstraction from the other methylene groups. It is apparent that the abstracting radical is highly selective, presumably because both it and the substrate possess positively charged nitrogen atoms, polar effects serving to make the methylene group furthest from the nitrogen atom in the substrate the most reactive. A precedent for this is that positively charged nitrogen radicals, when abstracting hydrogen from protonated long-chain alcohols or acids, show very high selectivity for reaction at the methylene group furthest from oxygen.¹⁰

In summary, the formation of the amino-alcohols (6) and (9) from the corresponding *N*-oxides is satisfactorily accounted for as follows. An essentially specific δ -hydrogen-atom abstraction occurs intramolecularly within the amine radical cation (3). The resulting primary carbon radical, if not trapped, either undergoes oxidation, followed by solvolysis to yield primary alcohol or rearrangement and solvolysis to yield secondary alcohol, or abstracts hydrogen from another molecule, giving the secondary alcohol; the deuterium-labelling experiments show that the two paths to the secondary alcohol are of similar importance under the conditions used.

¹⁰ N. C. Deno, W. E. Billups, R. Fishbein, C. Pierson, R. Whalen, and J. C. Wyckoff, *J. Amer. Chem. Soc.*, 1971, **93**, 438.

¹¹ R. N. Icke, B. B. Wisegarver, and G. A. Alles, *Org. Synth.*, 1955, Coll. Vol. III, p. 723.

¹² H. C. Brown and W. H. Bonner, *J. Amer. Chem. Soc.*, 1953, **75**, 14.

¹³ R. Willstätter and E. Waser, *Ber.*, 1910, **43**, 1176.

¹⁴ C. D. Lunsford, R. S. Murphey, and E. K. Rose, *J. Org. Chem.*, 1957, **22**, 1225.

¹⁵ E. C. du Feu, F. J. McQuillin, and R. Robinson, *J. Chem. Soc.*, 1937, 53.

¹⁶ R. Lichtenberger and L. Dürr, *Bull. Soc. chim. France*, 1956, 664.

¹⁷ A. W. D. Avison, *J. Appl. Chem.*, 1951, **1**, 469.

EXPERIMENTAL

¹H N.m.r. and mass spectrometry and g.l.c. were performed as described previously;⁴ the stationary phase for g.l.c. was Celite (80–120 mesh) treated with 5% KOH and coated with 20% Apiezon L, 20% Carbowax 20M, or 20% polyethylene glycol 1500.

Materials.—*N*-Oxides were prepared (from the corresponding amines) and estimated as described before⁴ except that tributylamine *N*-oxide was prepared by oxidation of the amine with peracetic acid; its picrate had m.p. 109–111° (lit.,³ 108.5–109.5°).

Tributylamine was available commercially and distilled before use. Butyldimethylamine was prepared by methylating butylamine with formic acid–formaldehyde¹¹ and had b.p. 95–96° (lit.,¹² 94.7–95.2°); its *N*-oxide picrate had m.p. 108–109° (lit.,³ 108–109°). Dimethylpentylamine, prepared likewise, had b.p. 121–122° (lit.,¹³ 122–123°); its *N*-oxide picrate had m.p. 73–74.5° (Found: C, 43.3; H, 5.4; N, 15.7. $\text{C}_{13}\text{H}_{20}\text{N}_4\text{O}_8$ requires C, 43.3; H, 5.6; N, 15.5%). 4-Dibutylaminobutan-1-ol was prepared by the method of Lunsford *et al.*¹⁴ and had b.p. 146–150° at 18 mmHg (lit.,¹⁴ 172–175° at 40 mmHg).

4-Dibutylaminobutan-2-ol, from treatment of dibutylamine hydrochloride with acetone and paraformaldehyde¹⁵ followed by reduction of the ketone with LiAlH_4 , had b.p. 136–137° at 23 mmHg (lit.,¹⁶ 113–123° at 13 mmHg). 4-Dimethylaminobutan-1-ol, prepared by the method of Avison,¹⁷ had b.p. 73–75° at 12 mmHg (lit.,¹⁸ 80–81° at 14 mmHg). 4-Dimethylaminobutan-2-ol, prepared as for the dibutylamino-analogue, had b.p. 54–60° at 15 mmHg (lit.,¹⁹ 50–52° at 13 mmHg). 5-Dimethylaminopentan-1-ol, obtained by reduction of ethyl *NN*-dimethylglutaramate,¹⁷ had b.p. 101–104° at 15 mmHg (lit.,²⁰ 115–116° at 25 mmHg). 5-Dimethylaminopentan-2-ol, prepared from the corresponding ketone²¹ with LiAlH_4 , had b.p. 80–81° at 11 mmHg (lit.,²² 82–86° at 13 mmHg). *N*-Butylpyrrolidine, produced from pyrrolidine and butyl bromide in the presence of sodium carbonate,²³ had b.p. 154–156° (lit.,²⁴ 154–155°). 4-Dimethylaminobut-1-ene, obtained by Hofmann elimination from *NN*-dimethylpyrrolidinium hydroxide, had b.p. 88–90° (lit.,²⁵ 89–92°).

1-Bromo-4-phenoxybutane (23 g) (from 1,4-dibromobutane and phenol²⁶) in ethanol (100 ml) was treated with dimethylamine (40 ml). After 3 days the ethanol was evaporated off and the solution of the residue in 50% HCl was washed with ether and basified (NaOH); the ether extract was dried (MgSO_4) and evaporated, leaving 1-dimethylamino-4-phenoxybutane, b.p. 136–138° at 12 mmHg (lit.,²⁷ 139–140° at 13 mmHg). This compound (5 g) was heated under reflux overnight with 40% HBr (50 ml), and the solution was washed with ether and evaporated to leave 4-dimethylaminobutyl bromide hydrobromide, m.p.

¹⁸ Heilbron and Bunbury, 'Dictionary of Organic Compounds,' 4th edn., Eyre and Spottiswoode, London, 1965.

¹⁹ C. Mannich, *Arch. Pharm.*, 1971, **255**, 261.

²⁰ J. von Braun, *Ber.*, 1916, **49**, 966.

²¹ W. von E. Doering and S. J. Rhoads, *J. Amer. Chem. Soc.*, 1951, **73**, 3082.

²² R. Lukes, Z. Koblicova, and K. Blaha, *Coll. Czech. Chem. Comm.*, 1963, **28**, 2182.

²³ J. W. Bayles and B. Evans, *J. Chem. Soc.*, 1965, 6984.

²⁴ G. H. Coleman, G. Nichols, and T. F. Martens, *Org. Synth.*, Coll. Vol. III, 1955, p. 159.

²⁵ J. von Braun and G. Lemke, *Ber.*, 1922, **55**, 3536.

²⁶ C. S. Marvel and A. L. Tanenbaum, *J. Amer. Chem. Soc.*, 1922, **44**, 2645.

²⁷ J. von Braun, *Annalen*, 1911, **382**, 1.

112—114° (from methanol-ether) (Found: C, 27.8; H, 5.8; N, 5.25. $C_8H_{15}Br_2N$ requires C, 27.6; H, 5.8; N, 5.4%). 1-Dibutylamino-4-phenoxybutane, prepared as for the dimethylamino-analogue, had b.p. 190—193° [τ 2.6—3.2 (5H, m), 6.07 (2H, t), 7.59 (6H, m), and 8.27—9.10 (18H, m)] and was characterised as its *methiodide*, m.p. 99—100° (Found: C, 54.6; H, 8.2; N, 3.2. $C_{19}H_{34}INO$ requires C, 54.4; H, 8.2; N, 3.3%); it was converted, as for the dimethylamino-analogue, into 1-bromo-4-dibutylaminobutane *hydrobromide*, which was obtained as a syrup which did not crystallise [τ 6.50 (2H, t), 6.91 (6H, m), 7.80—8.80 (12H, m), and 9.15 (6H, m)] and gave a mass spectrum consistent with the presence of 1-bromo-4-dibutylaminobutane [m/e 265 (M^+ , 4.7%), 263 (M^+ , 4.7%), 222 (76), 220 (76), 184 (61), 180 (12), 178 (12), 142 (100), 140 (26), 137 (16), 135 (16), 100 (34), 98 (16), 84 (90), 82 (21), 80 (21), 57 (67), and 55 (74)].

2-Bromo-4-dibutylaminobutane *hydrobromide*, produced from the corresponding amino-alcohol with thionyl bromide,²⁸ was also obtained as a syrup [τ 5.80 (1H, m), 6.87 (6H, m), 8.00—8.80 (13H, m), and 8.99 (6H, m)]; m/e 265 (M^+ , 4.5%), 263 (M^+ , 4.5), 222 (75), 220 (75), 184 (12), 154 (30), 152 (10), 143 (11), 142 (100), 141 (11), 140 (96), 100 (30), 98 (23), 86 (42), 84 (23), 82 (32), 81 (10), 80 (32), 70 (10), 69 (11), 67 (11), 57 (28), and 56 (14)].

5-Dimethylaminopent-1-ene, made by distilling a solution of *NN*-dimethylpiperidinium iodide in 5*M*-KOH to dryness and then heating under nitrogen,²⁹ had b.p. 114—116° (lit.,²⁹ 117—118°). *NNN'N'*-Tetramethyloctane-1,8-diamine, obtained from the primary diamine with formic acid-formaldehyde,¹¹ had b.p. 86—87° at 1.5 mmHg; its dihydrochloride had m.p. 243—244.5° (lit.,³⁰ 242—243°).

4,4,4-Trideuteriobutyltrimethylamine.— Perdeuterioacetic acid (Ryvan; 99.5 atom-% [3H_4]) (50 g) in dry bis-(2-methoxyethyl) ether was added to $LiAlH_4$ (30 g) in the same solvent (1 l) and the mixture was stirred for 2 days. Isopentyl alcohol (400 ml) was added and the first 150 ml of the distillate was fractionally distilled; the fraction of b.p. 78—80° (2,2,2-trideuterioethanol) was collected and converted into the bromide (HBr in H_2SO_4 ³¹) and thence, with malonic ester,³¹ into 4,4,4-trideuteriobutyric acid; successive reactions with thionyl chloride, dimethylamine, and $LiAlH_4$ gave 4,4,4-trideuteriobutyltrimethylamine, b.p. 98—100° (lit.,¹² 94.7—95.2° for the protio-analogue), which was shown by contact-shift n.m.r. to be deuteriated only in the C-methyl group, mass spectrometry showing that this group was $94 \pm 2\%$ deuteriated.

²⁸ R. C. Elderfield, C. B. Kremer, S. M. Kupchan, O. Birstein, and G. Cortes, *J. Amer. Chem. Soc.*, 1947, **69**, 1258.

²⁹ J. von Braun, W. Teuffert, and K. Weissbach, *Annalen*, 1929, **472**, 121.

Reactions of N-Oxides.—Concentrated sulphuric acid (12.5 ml) was added to a solution of iron(II) sulphate heptahydrate (2.5 mmol) in water (7.5 ml). The mixture was purged with nitrogen and heated on a boiling water bath; the *N*-oxide (1 mmol) in water (*ca.* 5 ml) was introduced and heating was continued for 16 h in a nitrogen atmosphere. Work-up and analysis were as described previously.⁴

The same procedure was used for reactions in the presence of bromotrichloromethane except that the mixture was stirred. In some of these cases the aqueous solution remaining after normal work-up was basified (NaOH), heated to dryness under nitrogen, and then heated under a slow stream of nitrogen for 2 h at 260°; the effluent nitrogen was passed through 0.5*M*- H_2SO_4 to trap basic products. The residue, after cooling, was dissolved in water and combined with the contents of the trap; after basification, the ether extract was dried ($MgSO_4$), evaporated to small volume, and analysed for the products of Hofmann elimination. In the case of the reaction of tributylamine with iron(II) ion under these conditions, 4-dibutylaminobut-1-ene was isolated by preparative g.l.c. and identified by its n.m.r. [τ 4.2 (1H, m), 4.95 (2H, m), 7.50 (8H, m), and 8.75 (14H, m)] and mass spectra [m/e 183 (M^+ , 6%), 143 (10), 142 (100), 140 (23), 100 (55), 96 (16), 86 (5), 84 (8), 82 (2), 70 (4), 69 (3), 68 (2), 67 (2), 58 (13), 57 (15), 56 (6), and 55 (25)]. Likewise, 4-dimethylaminobut-1-ene was obtained from butyldimethylamine *N*-oxide; m/e 99 (M^+ , 2%), 59 (4), and 58 (100).

The dialkylaminobromoalkane hydrobromides already described were submitted to hydrolytic conditions identical with those for the oxidations (50% H_2SO_4 on a boiling water bath for 16 h under N_2); work-up was as for oxidation mixtures and was followed by Hofmann elimination as already described. 4-Dimethylaminobut-1-ene was hydrated by heating a 0.001*M*-solution in 50% sulphuric acid containing 0.001*M*-iron(II) sulphate heptahydrate and 0.001*M*-iron(III) ammonium sulphate dodecahydrate for 16 h at 100°; work-up as before was followed by analysis for unchanged reactant and the two hydration products, (6b) and (9b). These two products were formed in smaller yield (11 and 13%, respectively) but in the same ratio when reaction was stopped after 3.5 h.

We thank the S.R.C. for a studentship to A. G. R.

[2/2251 Received, 28th September, 1972]

³⁰ V. M. Solov'ev and A. P. Skoldinov, *Zhur. obshchei Khim.*, 1963, **33**, 1821.

³¹ A. I. Vogel, 'Practical Organic Chemistry,' 3rd edn., Longmans, London, 1956.