180. *The Decomposition of the Nitrites of Some Primary Aliphatic Amines.*

By Donald W. Adamson and J. Kenner.

It has been shown (Jones and Kenner, J., 1933, 363) that the catalytic decomposition of nitroso-β-alkylamino-ketones by alkali results in the transient formation of aliphatic diazo-compounds, and that the subsequent decomposition of the one derived from propylamine yields propylene, *n*- and *iso*-propyl alcohols. In explanation, it was assumed that the aliphatic, like the aromatic, diazo-compounds $RN_2{\cdot}OH$ exist in equilibrium with the corresponding diazonium hydroxides,

$$R{\cdot}N{:}N{\cdot}OH \underset{OH'}{\overset{H^{\cdot}}{\rightleftarrows}} R\overset{+}{N}_2$$

and that decomposition of these gives rise to the products in question. For these products are respectively representative of the three types of change which have been recognised to result from the presence of an anionoid centre in saturated aliphatic compounds:

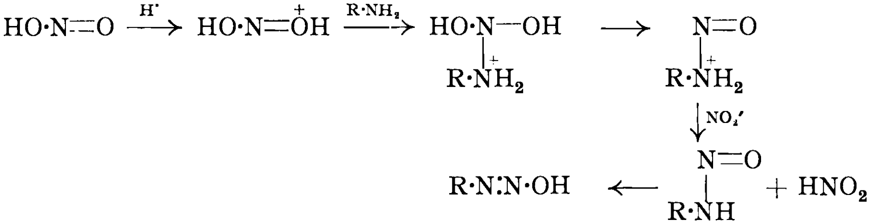
(a) formation of olefins, *e.g.*, from oxonium, ammonium, etc., hydroxides and salts and from alkyl halides;

(b) direct replacement of the anionoid group, *e.g.*, by hydroxyl or alkoxyl;

(c) the Wagner–Meerwein change.

Since, so far as we are aware, their conjunction, as in the above reactions, is unique, it appeared that a systematic study of the decomposition of aliphatic diazonium ions might assist in clearing up the inter-relationships, hitherto somewhat obscure, of the three types. This study is facilitated by the evidence adduced by Jones and Kenner (*loc. cit.*) that the aliphatic diazo-compounds also result from decomposition of the nitrites of aliphatic amines.

In regard to the mechanism of this reaction, Euler observed that methylamine nitrite is stable in 0·05*N*-solution at 40° (*Annalen*, 1904, **330**, 280); Taylor (J., 1928, 1099), confirming this, also showed that, whilst 0·05*N*-methylamine + 0·1*N*-nitrous acid react fairly rapidly at 25°, 0·05*N*-nitrous acid + 0·05*N*-sulphuric acid do not cause decomposition at 25°, though a very slow reaction occurs at 40° (Euler, *loc. cit.*). Taylor's measurements indicated that the velocity of decomposition of the base was proportional to $[\mathrm{MeNH_3{}^{\cdot}}][\mathrm{NO_2{}'}][\mathrm{HNO_2}]$, and a similar result was obtained with dimethylamine (Taylor and Price, J., 1929, 2052). The familiar doctrine that diazotisation involves the salt of an amine rather than the free base is in line with this, but appears highly improbable in view of the lack of co-ordinating power of ammonium ions, and in the light of our knowledge of the behaviour of carbonyl and nitroso-compounds with amines. Since, however, these reactions are assisted by protons (compare, *e.g.*, Conant and Bartlett, *Ind. Eng. Chem.*, 1932, **24**, 467) and $[\mathrm{MeNH_3{}^{\cdot}}]$ is obviously proportional to $[\mathrm{MeNH_2}][\mathrm{H^{\cdot}}]$, we put forward the following detailed representation of the course of the reaction as being essentially more satisfactory, embracing the experimental evidence, and applicable both to primary and to secondary amines in the aliphatic as well as in the aromatic series : *



$$\mathrm{HO{\cdot}N{=}O} \xrightarrow{\mathrm{H}^{\cdot}} \mathrm{HO{\cdot}N{=}\overset{+}{O}H} \xrightarrow{\mathrm{R{\cdot}NH_2}} \begin{array}{c}\mathrm{HO{\cdot}N{-}OH}\\ |{+}\\ \mathrm{R{\cdot}NH_2}\end{array} \longrightarrow \begin{array}{c}\mathrm{N{=}O}\\ |{+}\\ \mathrm{R{\cdot}NH_2}\end{array}$$

$$\downarrow \mathrm{NO_2{}'}$$

$$\mathrm{R{\cdot}N{:}N{\cdot}OH} \longleftarrow \begin{array}{c}\mathrm{N{=}O}\\ |\\ \mathrm{R{\cdot}NH}\end{array} + \mathrm{HNO_2}$$

The decomposition of the nitrites of *n*-propyl- and *n*-butyl-amine was studied carefully by V. Meyer in regard to the nature of the products (*Ber.*, 1876, **9**, 535; 1877, **10**, 130), and Frentzel (*Ber.*, 1883, **16**, 744) and Jeffreys (*Amer. Chem. J.*, 1899, **22**, 37) contributed investigations, obviously less thorough, of the behaviour of *n*-hexylamine and *n*-undecylamine respectively. These appear to be the only researches concerned with normal aliphatic primary amines, although a number of workers have dealt with other aliphatic primary amines (Freund and co-workers, *Ber.*, 1890, **23**, 189, 2865; 1891, **24**, 2150, 3350; 1893, **26**, 2492; Solonina, *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 431, 449; Pauly and Hultenschmidt, *Ber.*, 1903, **36**, 3365; Konowaloff, *Centr.*, 1906, I, 737; Henry, *Compt. rend.*, 1907, **145**, 899, 1248) and aliphatic primary diamines (Demjanow, *Ber.*, 1892, **25**, Ref. 912; 1907, **40**, 2590; Euler, *Ber.*, 1895, **28**, 2952; Bewad, *Ber.*, 1906, **39**, 1233; Neuberg and Rewald, *Biochem. Z.*, 1915, **71**, 162). We now contribute a quantitative study of the decomposition of the nitrites of the amines homologous to those examined by V. Meyer, and the results are summarised in the following table as percentages of original amine represented by each product :

	Amine.					
Product.	*n*-Amyl.	*n*-Hexyl.	*n*-Heptyl.	*n*-Octyl.	*n*-Nonyl.	*n*-Decyl.
Alcohol	50·0	50·5	48·3	46·3	48·5	50·0
Olefin	30·1	28·0	25·4	24·4	24·4	27·4
Nitroso-secondary amine	1·9	2·5	5·3	5·5	9·0	15·3
Primary amine	1·7	1·5	0·8	4·5	1·0	1·1
Primary amine hydrochloride	0·7	1·0	0·5	0·8	0·5	1·4
Total yield, %	84·4	83·5	80·3	81·5	83·4	95·2

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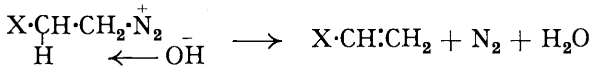
* A similar scheme should also be applicable to the reactions of carbonyl compounds, and there is some indication that this may be so; *e.g.*, Barrett and Lapworth observed that oxime formation was accelerated not only by hydrogen ions but also by hydroxyl ions (J., 1908, **93**, 85; compare Auwers, *Ber.*, 1889, **22**, 603), and Conant and Bartlett (*J. Amer. Chem. Soc.*, 1932, **54**, 2892) observed an increase in the rate of semicarbazone formation with increase in concentration of a sodium acetate–acetic acid buffer solution.

The relatively low total in the first five cases is probably due to incomplete recovery of undecomposed primary amine, as explained in the experimental portion.

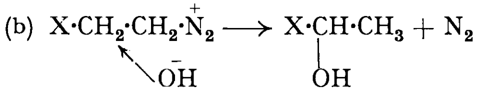
The proportion of secondary alcohol produced is not shown in the table. It diminished rapidly as the series was ascended, for, whereas it constituted perhaps one-third of the total amyl alcohol as against 58% of the alcohol obtained from *n*-propylamine (Henry, *Compt. rend.*, 1907, **145**, 899; compare Jones and Kenner, *loc. cit.*), only about 5% was definitely detected in the octyl alcohol, and none at all in the nonyl and decyl homologues. This is in marked contrast with the approximate constancy in the yield of olefin, which is to be anticipated from familiar theoretical reasoning. In spite, therefore, of the close formal connexion between the Hofmann and the pinacol change (compare Kenner, *Nature*, 1932, **130**, 309) it would seem that at least the controlling factors must be very different. In explanation, the following suggestions are put forward. Olefin formation is regarded as in general a reaction determined primarily by attack of an anion, usually hydroxyl, whilst -onium groups act as predisposing but subsidiary agents (compare Ingold and co-workers, J., 1927, 997; 1928, 3125, 3127; 1929, 2338, 2342, 2357; 1930, 705, 708, 713):



$$\underset{\textstyle H}{X{\cdot}CH}{\cdot}CH_2{\cdot}\overset{+}{N}_2 \;\; \overset{-}{O}H \longrightarrow X{\cdot}CH{:}CH_2 + N_2 + H_2O$$

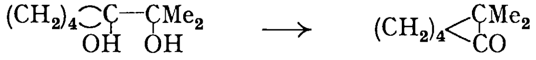
When, however, the tendency of the -onium kation to decompose with liberation of, *e.g.*, water or nitrogen, is pronounced, a change is initiated at the -onium centre which is completed with the aid of an anion, very possibly in the manner of a Walden inversion. The attack by the anion takes place at the carbon atom which is the site of the -onium group or, if the tendency of the oxygen, nitrogen, or other atom of this group to break away is sufficiently strong, alternatively at the adjoining carbon atom:

$$\text{(a)}\ X{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}_2 \xrightarrow{\overset{-}{O}H} X{\cdot}CH_2{\cdot}CH_2{\cdot}OH + N_2$$



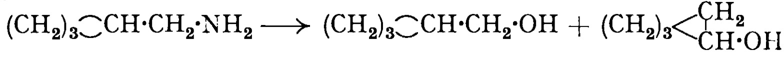
$$\text{(b)}\ X{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}_2 \longrightarrow X{\cdot}\underset{\textstyle OH}{CH}{\cdot}CH_3 + N_2 \qquad \overset{-}{O}H$$

The latter is the case of the Wagner–Meerwein change, and involves migration of an atom or group to the first carbon atom. The importance in this connexion of McKenzie's work on semipinacolinic deamination and its bearing on the possibility that a Walden inversion occurs at the first carbon atom have been referred to previously (Kenyon and Phillips, J., 1930, 415; Kenner, *Nature*, 1932, **130**, 309), and we consider that evidence of a similar change at the second carbon atom is supplied by the modification of ring structure by enlargement or contraction which occurs whenever the carbon atom in question is contained in a saturated ring. Pinacol changes of this type have been observed by Meerwein (*Annalen*, 1910, **376**, 152; 1913, **396**, 200; 1918, **417**, 255; *J. pr. Chem.*, 1922, **104**, 289), and in these the circumstances necessarily involve ring enlargement; *e.g.*,

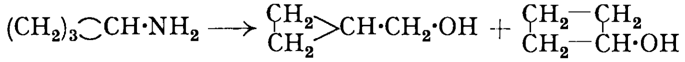


$$(CH_2)_4{>}\underset{\textstyle OH}{C}{-}\underset{\textstyle OH}{CMe_2} \longrightarrow (CH_2)_4{<}\begin{matrix}CMe_2\\ CO\end{matrix}$$

But this has also been observed in other cases. For instance, phenyl*cyclo*hexane results from the action of benzene in presence of aluminium chloride on ω-chloromethyl*cyclo*pentane. The conversion of ω-chloromethyl*cyclo*pentane into *cyclo*hexane by reduction with hydrogen iodide probably also falls in this category, but perhaps the most convincing instances were observed by Demjanow in the action of nitrous acid on amino-derivatives of cyclic hydrocarbons (Demjanow and Luschnikow, *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 26; Demjanow, *Ber.*, 1907, **40**, 4961; compare Kishner, *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 304), *e.g.*,

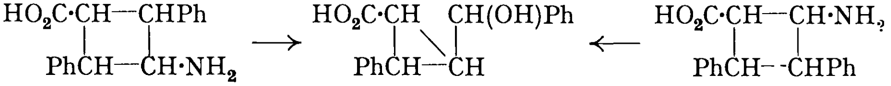


$$(CH_2)_3{>}CH{\cdot}CH_2{\cdot}NH_2 \longrightarrow (CH_2)_3{>}CH{\cdot}CH_2{\cdot}OH + (CH_2)_3{<}\begin{matrix}CH_2\\ CH{\cdot}OH\end{matrix}$$

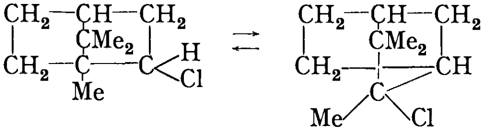


$$(CH_2)_3{>}CH{\cdot}NH_2 \longrightarrow \begin{matrix}CH_2\\ CH_2\end{matrix}{>}CH{\cdot}CH_2{\cdot}OH + \begin{matrix}CH_2{-}CH_2\\ CH_2{-}CH{\cdot}OH\end{matrix}$$

In the following instances, observed by Stoermer and Schenck (*Ber.*, 1927, **60**, 2566), it is clear that the hydroxyl group in the product is not attached to the carbon atom which originally carried the amino-group :



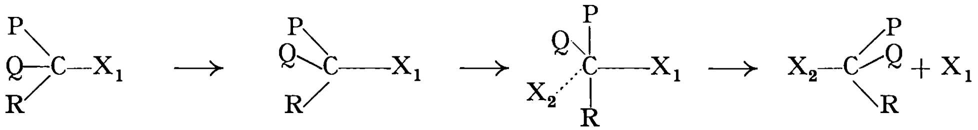
The equilibrium between *iso*bornyl chloride and camphene hydrochloride similarly involves a change in ring structure, rather than migration of hydrogen or methyl :



The same feature characterises the transition from pinene hydrochloride to *iso*bornyl chloride (Meerwein and Emster, *Ber.*, 1922, **55**, 2500). In all these cases the Wagner–Meerwein change has involved migration of an alkyl group in contradistinction to the migration of hydrogen which is observed in all cases in which no ring structure is involved :

$$R{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2 \longrightarrow R{\cdot}CH(OH)Me$$

A possible reason for what thus seems to be a very general phenomenon appears when we consider more closely the course of the Walden inversion, which may be graphically represented in the following manner (compare Meer and Polanyi, *Z. physikal. Chem.*, 1932, **29**, 166 ; Kenner, *Nature, loc. cit.* ; Mills, Presidential Address to Section B, *Brit. Assoc.*, 1932) :

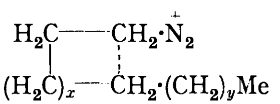


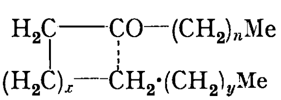
(I). (II.) (III.) (IV.)

As the group X_1 commences to break away from the carbon atom, the mutual repulsions of P, Q, and R will cause an enlargement of the normal tetrahedral angle (II), which will be enhanced with approach of X_2 (III) and ultimately lead to inversion (IV). Similar changes may obviously occur if, as in the Wagner–Meerwein reaction, X_1 is a carbon atom which develops a strong positive polarity, without alteration of its distance from the carbon atom, although in this case actual inversion of configuration may not ensue, since X_2 will displace P, Q, or R. If, of these, P and Q should be participants in a ring structure, their adjustment to the changes involved will be less facile owing to the restriction of their freedom of independent movement ; and this may induce rupture of the ring and consequently determine migration of P or Q, even though R should be displaced in the corresponding open-chain compound.

It is apparent that the conditions under which the Wagner–Meerwein change occurs also permit olefin formation, and accordingly the diazonium hydroxides suffer both types of change. The converse, however, will obviously not apply, so that decomposition of -onium hydroxides normally yields olefins, but not alcohols (compare Ingold and Kuriyan, J., 1933, 991).

The rapid decrease in the proportion of secondary alcohol obtained in our experiments with increase in length of the carbon chain is indicative of a considerably reduced kationoid condition of the carbon atom attached to nitrogen in the diazonium complex. A similar reduction is responsible for the inertia of the higher aliphatic ketones towards the usual reagents and is attributable to an anionic field effect exerted by the carbon chain.





As the length of this is increased to five and more carbon atoms, there will up to a certain point be an increase in the frequency with which one or other of the members in the chain comes into sufficient proximity to the diazonium or carbonyl carbon atom to exert such an influence.

The secondary amines, from which the nitroso-derivatives shown in the table are derived, originate in the same way as these compounds normally do from alkyl halides and primary amines, by interaction of free amines with the kationoid alkyl group of the diazonium hydroxide. The formation of nitrosoamines was also observed by V. Meyer (*loc. cit.*).

The results of a study of the interaction of β-phenylethylamine hydrochloride with silver nitrite were as follows :

Product.	Yield, %.
β-Phenylethyl alcohol	49·1
Styrene	4·8
Nitrosodi-β-phenylethylamine	14·1
β-Phenylethylamine	5·2
β-Phenylethylamine hydrochloride	9·4
	82·6

No secondary alcohol could be detected, and similarly Perkin only observed the formation of primary alcohol from ω-aminoethylpiperonylcarboxylic acid (J., 1890, **57**, 1060). As might be expected, however, secondary as well as primary alcohols and olefin occur in the product from 2-ω-*cyclo*hexylethylamine (Wallach, *Annalen*, 1899, **359**, 312).

The possibility that diazohydrocarbons may be intermediate products in the reactions discussed has been disregarded in view of the classical conversions of the optically active alanine and aspartic acid into active lactic and malic acids respectively by treatment with nitrous acid.

EXPERIMENTAL.

Amines.—These were prepared directly from the corresponding carboxylic acids by Schmidt's hydrazoic acid method (compare *Annalen*, 1931, **490**, 100; Oesterlin, *Z. angew. Chem.*, 1932, **45**, 536), the yields of pure base amounting to 70—75% and of *n*-decylamine to 90% of the theoretical. In each case the boiling point agreed with the data in the literature, and the bases were further characterised by their *picrates*, as shown in the following table :

Base.	M. p. of picrate.	% N, found.	% N, calc.	Base.	M. p. of picrate.	% N, found.	% N, calc.
n-$C_5H_{11}\cdot NH_2$	138—138·5°	17·67	17·72	*n*-$C_8H_{17}\cdot NH_2$	111·5—112·5°	15·85	15·64
n-$C_6H_{13}\cdot NH_2$	126·5	17·03	16·97	*n*-$C_9H_{19}\cdot NH_2$	110·5—111	15·13	15·05
n-$C_7H_{15}\cdot NH_2$	118·5—119	16·27	16·28	*n*-$C_{10}H_{21}\cdot NH_2$	118 —118·5	14·55	14·51

Of the picrates, those of *n*-heptylamine (m. p. 118·5—119·5°; v. Soden and Henle, *Pharm. Ztg.*, 1901, **46**, 1026), *n*-octylamine (m. p. 112—114°; Hoogewerf and van Dorp, *Rec. trav. chim.*, 1887, **6**, 387) and *n*-nonylamine (m. p. 111°; v. Braun and Sobecki, *Ber.*, 1911, **44**, 1470) have been previously described.

In this connexion undecoic acid was prepared by catalytic reduction of undecenoic acid in glacial acetic acid solution more conveniently than in alcohol (compare Fokin, *Z. angew. Chem.*, 1909, **22**, 1499).

Alcohols.—The corresponding primary alcohols as well as secondary octyl alcohol were available by purchase. The remaining secondary alcohols were prepared by reduction of the appropriate methyl ketones with sodium and alcohol (compare Thoms and Mannich, *Ber.*, 1903, **36**, 2544). Of the ketones, methyl octyl ketone was commercially available as " ruteine " (supplied by Messrs. Givaudan, Geneva). In every case the boiling points of the alcohols agreed with the data in the literature. For purposes of identification the respective α-naphthylurethanes were prepared and repeatedly crystallised from light petroleum (b. p. 60—80°). The relevant data are included in the following table :

	α-Naphthylurethane.				α-Naphthylurethane.		
		% N,				% N,	
Alcohol.	M. p.	found.	calc.	Alcohol.	M. p.	found.	calc.
n-$C_5H_{11}\cdot OH$	65·5°	5·46	5·44	*n*-$C_8H_{17}\cdot OH$	66°	4·78	4·68
sec.-$C_5H_{11}\cdot OH$	74·5	5·47	5·44	*sec.*-$C_8H_{17}\cdot OH$	62·5	4·70	4·68
n-$C_6H_{13}\cdot OH$	59	5·23	5·17	*n*-$C_9H_{19}\cdot OH$	65·5	4·57	4·47
sec.-$C_6H_{13}\cdot OH$	60·5	5·27	5·17	*sec.*-$C_9H_{19}\cdot OH$	55·5	4·58	4·47
n-$C_7H_{15}\cdot OH$	59·5	5·16	4·91	*n*-$C_{10}H_{21}\cdot OH$	73	4·34	4·28
sec.-$C_7H_{15}\cdot OH$	54·0	5·14	4·91	*sec.*-$C_{10}H_{21}\cdot OH$	69	4·30	4·28

The α-naphthylurethanes of *n*-heptyl (m. p. 62°) and *n*-octyl alcohols (m. p. 66°) have been previously described (Neuberg and Kansky, *Biochem. Z.*, 1909, **20**, 447).

The depressions of melting point observed in mixtures of the urethane of each primary alcohol with that of its secondary isomeride attested the suitability of these derivatives for our purpose.

Decomposition of the Amines with Nitrous Acid.—Two experiments were performed with each amine and the results showed a concordance which was considered reasonable in view of the procedure involved. A cold neutral solution of the amine in hydrochloric acid (10%) was intimately mixed at the ordinary temperature with silver nitrite (1·2 mols.) and filtered. A diminution in stability of the nitrites with increasing molecular weight was observed, so that in the cases of nonyl- and decyl-amines small amounts of oil had to be removed by shaking the silver salts with ether. The filtrate, with washings of the silver salts, was decomposed by gradually raising its temperature in an oil-bath, and finally distilled until there was only a small residue. This was mixed with water and extracted with ether. The aqueous solution on evaporation yielded a small amount of amine hydrochloride, which was identified by conversion into the picrate. The ethereal extract was added to that derived from the distillate. In the cases of *n*-amyl- and *n*-hexyl-amines, the receiver for the distillate was also connected to four bubblers charged with a solution of bromine in chloroform and cooled in ice. By warming the receiver to 40° and 65° respectively, the olefins were driven over into the bromine. In the other cases, the olefin together with the alcohols was extracted by ether (free from ethyl alcohol) from the aqueous distillate after saturation of the latter with potassium carbonate. The ethereal solution, after being washed with dilute sulphuric acid, combined with that of the distillation residue, and dried over potassium carbonate, was concentrated, and the residue carefully fractionated from an oil-bath through a Widmer column. The lower fractions contained olefin, which was estimated by treatment with a solution of bromine (20%) in chloroform. Finally the olefin dibromide was characterised by distillation and analysis :

Olefin 1 : 2 dibromide.	B. p.	% Br, found.	% Br, calc.	Olefin 1 : 2 dibromide.	B. p.	% Br, found.	% Br, calc.
$C_5H_{10}Br_2$	80°/19 mm.	69·09	69·57	$C_8H_{16}Br_2$	123°/14 mm.	58·56	58·82
$C_6H_{12}Br_2$	95—96°/12 mm.	65·49	65·57	$C_9H_{18}Br_2$.........	133·5°/12 mm.	56·16	55·94
$C_7H_{14}Br_2$	99·5°/10 mm.	61·98	62·01	$C_{10}H_{20}Br_2$	149—150°/15 mm.	53·38	53·33

Of these, the following are described in the literature : $C_5H_{10}Br_2$, b. p. 190—191°/760 mm. (Brochet, *Bull. Soc. chim.*, 1892, **7**, 567); $C_6H_{12}Br_2$, b. p. 98—99°/15 mm. (*idem, ibid.*, p. 569); $C_7H_{14}Br_2$, b. p. 105—107°/15 mm. (Welt, *Ber.*, 1897, **30**, 1495); and $C_{10}H_{20}Br_2$, b. p. 145°/15 mm. (Grosjean, *Ber.*, 1892, **25**, 479).

Fractions of the alcoholic material were collected every 1—2°, and separately treated with α-naphthylcarbimide for comparison with the authentic urethanes already described. There was no difficulty in isolating pure urethanes corresponding to primary alcohols in each case, and those of the secondary amyl, hexyl, and heptyl alcohols were also isolated in the pure condition, m. p. 74·5°, 60·5°, 54°, respectively, but with increasing difficulty. The secondary octyl derivative melted at 57—58° instead of 62·5°, and no indication of secondary alcohols could be obtained in the products from *n*-nonyl- and *n*-decyl-amines. It was not feasible to provide from these results accurate estimates of the relative proportions of primary and secondary alcohols in every case, but it was evident that the amount of secondary alcohol rapidly diminished with increase in molecular weight.

The residue from the fractional distillation usually furnished a further small quantity of primary alcohol when distilled from a smaller flask. The final residue was shown to contain a nitroso-compound by its behaviour towards Liebermann's reagent and towards a solution of cuprous chloride in hydrochloric acid (Jones and Kenner, J., 1932, 711). By evaporation with concentrated hydrochloric acid, a residue of secondary amine hydrochloride was obtained. The amounts obtained from amyl- and hexyl-amines were insufficient for further work. In other cases, the residue was characterised by conversion into a picrate; but these were evidently somewhat impure, since in every case the analytical results were high. The following results were obtained :

Picrate.	M. p.	% N, found.	% N, calc.
Diheptylamine	117—120°	13·5	12·7
Dioctylamine	110—110·5	12·8	11·9
Dinonylamine	106—108	11·7	11·2
Didecylamine	115	11·2	10·6

When the dilute sulphuric acid solution, obtained by washing the ethereal extract of the distillate, was rendered alkaline and again extracted, unchanged primary amine was isolated; it was identified in each case by means of its picrate. A later experiment with *n*-hexylamine, however, indicated that this procedure was unsatisfactory, for a recovery of 8·5%, as against 1·5% recorded in our table of results, was attained by steam distillation of the alkaline solution together with the aqueous potassium carbonate solution from which the alcohols had been separated. The steam distillate was acidified with hydrochloric acid and worked up in the usual manner.

Reaction of β-Phenylethylamine with Nitrous Acid.—As a preliminary α- and β-phenylethyl alcohols were respectively characterised by their *α-naphthylurethanes*, m. p. 106° (Found : N, 4·85) and 117° (Found : N, 4·8. $C_{19}H_{17}O_2N$ requires N, 4·8%).

The decomposition of the amine nitrite was carried out as in the previous cases. The residue from the distillation, on extraction with ether, left a colourless solid, which was soluble in water and identified as β-phenylethylamine hydrochloride, m. p. 216° (Found : Cl, 22·8. Calc. for $C_8H_{11}N,HCl$: Cl, 22·5%). The ethereal extract on distillation yielded phenylethyl alcohol (α-naphthylurethane, m. p. 117°), and a residue, of which a portion was soluble in water and identified as di-β-phenylethylamine hydrochloride, m. p. 266° (Fileti and Piccini, *Gazzetta*, 1879, **9**, 295, give m. p. 265°) (Found : Cl, 13·53. Calc. for $C_{16}H_{19}N,HCl$: Cl, 13·6%). This arose from the decomposition of β-phenylethylamine hydrochloride during distillation. This salt was found to be readily soluble in β-phenylethyl alcohol and so was taken up in the original ethereal extract. The hydrochloride was therefore allocated to β-phenylethylamine hydrochloride in arriving at a final estimate of the various products isolated. The portion of the residue insoluble in water was dissolved in ether and added to that remaining from the fractional distillation of the material isolated from the original aqueous distillate. The last furnished styrene, b. p. 146—147°, identified as dibromide, m. p. 73° (Found : Br, 61·0. Calc. for $C_8H_8Br_2$: Br, 60·6%), and phenylethyl alcohol (α-naphthylurethane, m. p. 117°). No indication of the presence of α-phenylethyl alcohol could be obtained. Nitrosodi-β-phenylethylamine was identified by its behaviour towards Liebermann's reagent and a solution of cuprous chloride in hydrochloric acid, and by its conversion into di-β-phenylethylamine hydrochloride, m. p. 265°, and *picrate*, m. p. 153° (Found : N, 12·4. $C_{22}H_{22}O_7N_4$ requires N, 12·3%).

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