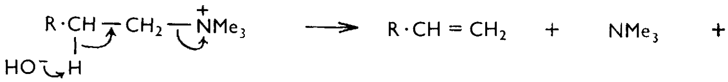
50. *The Thermal Decomposition of Quaternary Ammonium Hydroxides. Part I. Methohydroxides derived from* NN-*Dialkylanilines and Related Compounds.**

By D. A. Archer and H. Booth.

The thermal decomposition of the *N*-methyl methohydroxides of *N*-ethyl-, *N*-propyl-, *N*-butyl-, and *N*-(3-phenylpropyl)-aniline has been studied by product analysis with respect to the two reactions, β-elimination and substitution at *N*-methyl groups. The results, when compared with known results for hydroxides in which the phenyl group is replaced by a methyl group, illustrate the marked inhibitory effect on β-elimination, relative to substitution, of a phenyl group attached to the nitrogen atom.

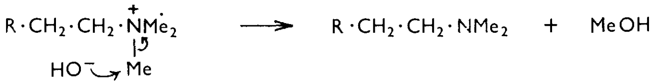
Thermal decomposition of the methohydroxides of *N*-ethyldiphenylamine, *N*-cyclohexyl-*N*-methylaniline, and *N*-phenylpiperidine has also been studied and the results are discussed in terms of electronic and conformational influences. A by-product in the reaction of *N*-ethyldiphenylamine with dimethyl sulphate is shown to be dimethyl *N*-ethyl-*pp*′-iminobisbenzenesulphonate.

Investigations[1] of the thermal decomposition of quaternary ammonium hydroxides (Hofmann degradation) have shown that the primary products are formed by β-elimination or nucleophilic substitution. If the solutions are concentrated, and if at least one hydrogen atom is attached to the β-carbon atom, the principal reaction is probably the concerted bimolecular elimination (1),[1,2] in which attack of hydroxyl ion occurs on a β-hydrogen atom, fission of the C(β)–H bond occurring at approximately (not necessarily exactly) the same time as fission of the N–C(α) bond.



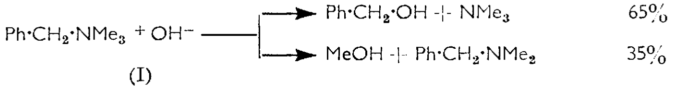
$$\mathrm{R\cdot \underset{HO^{-}\;\;H}{CH}-CH_2-\overset{+}{N}Me_3 \longrightarrow R\cdot CH=CH_2 + NMe_3 + H_2O} \quad . \quad (1)$$

An alternative two-step mechanism (*E*1*cb*), in which the rate-determining step involves the formation of a carbanion by removal of a β-proton, has not yet been demonstrated.[3,4] There is also at present no evidence [4,5] to suggest the occurrence, during *thermal* decomposition of quaternary ammonium hydroxides, of the α′β mechanism of Wittig and Polster.[6]



$$\mathrm{R\cdot CH_2\cdot CH_2\cdot \underset{HO^{-}\;\;Me}{\overset{+}{N}Me_2} \longrightarrow R\cdot CH_2\cdot CH_2\cdot NMe_2 + MeOH} \quad . \quad . \quad . \quad . \quad (2)$$

The nucleophilic substitution (2), which is itself usually of second order, involves attack of hydroxyl ion on an α-carbon atom, leading to the formation of an alcohol; this alcohol is normally methanol if at least one *N*-methyl group is available, although allyl and benzyl groups are also split off with ease.



$$\mathrm{Ph\cdot CH_2\cdot \overset{+}{N}Me_3 + OH^-} \begin{cases} \longrightarrow \mathrm{Ph\cdot CH_2\cdot OH + NMe_3} & 65\% \\ \longrightarrow \mathrm{MeOH + Ph\cdot CH_2\cdot NMe_2} & 35\% \end{cases}$$

(I)

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* For a preliminary report see Archer and Booth, *Chem. and Ind.*, 1962, 894.

[1] Reviewed by Cope and Trumbull, *Org. Reactions*, 1960, **11**, 317.

[2] Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, Chapter VIII.

[3] Doering and Meislich, *J. Amer. Chem. Soc.*, 1952, **74**, 2099.

[4] Shiner and Smith, *J. Amer. Chem. Soc.*, 1958, **80**, 4095.

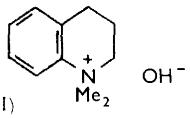
[5] Weygand, Daniel, and Simon, *Chem. Ber.*, 1958, **91**, 1691; Franzen, *Chem.-Ztg.*, 1958, **82**, 832; Cope, Le Bel, Moore, and Moore, *J. Amer. Chem. Soc.*, 1961, **83**, 3861; Ayrey, Buncel, and Bourns, *Proc. Chem. Soc.*, 1961, 458.

[6] Wittig and Polster, *Annalen*, 1958, **612**, 102.

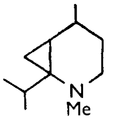
Substitution may compete successfully with elimination during decomposition in the presence of carbon dioxide, which reduces the nucleophilic power of the attacking anion.[2,7] Elimination is favoured by high temperatures when dilute solutions of quaternary hydroxides are decomposed.[2] However, for dry or syrupy quaternary hydroxides, where elimination appears in any case to be strongly favoured,[7] it is unlikely that an increase in temperature above the temperature at which decomposition is noticeably vigorous will affect greatly the proportions of elimination and substitution. A hydroxide, *e.g.*, (I), in which no β-hydrogen is available, represents an extreme case in which decomposition occurs solely by substitution.[8]

The effect of α- and β-alkyl groups on the elimination has been thoroughly investigated.[7,9-14] The inhibiting influence of a β-alkyl group is due probably to its inductive (electron-repelling) effect, but steric effects may also operate when the group is particularly bulky.[11,14-16]

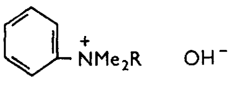
A particularly interesting case is 1,2,3,4-tetrahydro-1-methylquinoline methohydroxide (II), distillation of which was reported to yield 1,2,3,4-tetrahydro-1-methylquinoline as the only basic product.[17] This is evidently due to the presence in the salt (II) of structural features which prevent β-elimination. The purpose of this investigation was to determine the nature of these features by examination of the behaviour on thermal decomposition of structurally related quaternary hydroxides. During the investigation, it was shown (see Part II) that about 5% of β-elimination does occur when the hydroxide (II) is decomposed under reflux conditions at 160°.



(II)



(III)



(IV)

The presence of an aromatic ring or other electron-rich group directly attached to the quaternary nitrogen atom may inhibit the elimination. Thus, whilst pyrolysis of 1,1-dimethylpiperidinium hydroxide gives an 82% yield of the product of β-elimination,[7] similar treatment of 1-methyl-1-phenylpiperidinium hydroxide leads to 1-phenylpiperidine in almost 100% yield[18] (but see below). In a second example, the methiodide of 1-isopropyl-2,5-dimethyl-2-azabicyclo[4,1,0]heptane (III) has been converted by aqueous sodium hydroxide into the saturated tertiary base and methanol.[19] As explanation, Burrows and Eastman[19] suggested that an electron-rich group joined to the quaternary centre diffuses the positive charge to such an extent that the acidity of the β-hydrogen atom is reduced below the level required for β-elimination. The inhibitory effect on elimination of an N-attached aromatic ring has now been confirmed by quantitative analysis of the products from quaternary hydroxides structurally related to (II).

Thermal decompositions were performed by heating syrupy quaternary hydroxides until decomposition was noticeably vigorous; this occurred at between 110° and 140°. The temperature was then increased by about 20° and maintained at the higher point for

[7] von Braun, Teuffert, and Weissbach, *Annalen*, 1929, **472**, 121.
[8] Hughes and Ingold, *J.*, 1933, 69.
[9] von Braun, *Annalen*, 1911, **382**, 1.
[10] Ingold and Vass, *J.*, 1928, 3125.
[11] Smith and Frank, *J. Amer. Chem. Soc.*, 1952, **74**, 509.
[12] von Braun and Anton, *Ber.*, 1931, **64**, 2865.
[13] Cope, Le Bel, Lee, and Moore, *J. Amer. Chem. Soc.*, 1957, **79**, 4720.
[14] Cope and Ross, *J. Amer. Chem. Soc.*, 1961, **83**, 3854.
[15] Brown and Moritani, *J. Amer. Chem. Soc.*, 1956, **78**, 2190; Banthorpe and Hughes, *Bull. Soc. chim. France*, 1960, 1373.
[16] Banthorpe, Hughes, and Ingold, *J.*, 1960, 4054.
[17] Feer and Koenigs, *Ber.*, 1885, **18**, 2388; Knorr, *Ber.*, 1899, **32**, 734.
[18] von Braun, *Ber.*, 1907, **40**, 3914.
[19] Burrows and Eastman, *J. Amer. Chem. Soc.*, 1957, **79**, 3756.

2—4 hr. All experiments were carried out at least twice and the results for product composition were consistent to ±2%.

Thermal decomposition of ethyldimethylanilinium hydroxide (IV; R = Et) gave as the basic fraction a mixture containing 72% of *NN*-dimethylaniline (elimination) and 28% of *N*-ethyl-*N*-methylaniline (substitution). This mixture, as with most mixtures isolated, was analysed by refractive-index measurements and the result was checked by gas chromatography; the quoted figures (Table 1) are those obtained by the use of refractive indices, as this method was considered to be the more accurate. As expected, replacement of a β-hydrogen atom by a methyl group reduced considerably the tendency for β-elimination. Thus, decomposition of the hydroxide (IV; R = Pr), which resembles tetrahydro-1-methylquinoline methohydroxide (II) in structure, gives 15% of dimethylaniline and 85% of methylpropylaniline. The expectation that further lengthening of the n-alkyl group R in (IV) would hardly affect the proportions of elimination and substitution was realised when the basic mixture from the decomposition of the butyl compound (IV; R = Bu) was found to contain 10% of dimethylaniline and 90% of butylmethylaniline. Finally, an attempt was made to simulate the presence of an electron-rich group at the 4-position of compound (II) by studying the thermal decomposition of dimethyl-3-phenylpropylanilinium hydroxide (IV; R = $Ph\cdot[CH_2]_3$). Product analysis showed that the replacement of the γ-hydrogen by phenyl slightly favoured elimination, possibly as a result of the relayed inductive (electron-attracting) effect of the phenyl substituent. In Table 1, the results just described are compared with the known results for hydroxides in which the phenyl group is replaced by a methyl group. The decomposition of *NNN*-trimethyl-3-phenylpropylammonium hydroxide was repeated since the results of published work [20–22] were at variance.

TABLE 1.

Composition (mol. %) of product from the thermal decomposition of $RR'NMe_2^+OH^-$.

R in $RR'NMe_2^+OH^-$	R′ = Me		R′ = Ph	
	Composition (mol. %) of product		Composition (mol. %) of product	
	Olefin (elimn.)	$R\cdot NMe_2$ (substn.)	$Ph\cdot NMe_2$ (elimn.)	Ph·NMeR (substn.)
Et	100,* 95—100 †	0,* 0—5 †	72	28
Pr	90 †‡	10 †	15	85
Bu	81 †§¶	19 †§	10	90
$Ph[CH_2]_3$	91 **††	9 **††	21	79

* Collie and Schryver, *J.*, 1890, **57**, 767. † Calc. from the mean yields of ref. 10. ‡ Ref. 11 gives yield of olefin as 83%. § Ref. 7 gives 77% of olefin and 10% of $R\cdot NMe_2$. ¶ Ref. 11 gives 86% olefin. ** This paper; ref. 20 gives 28% of olefin and 70% of $R\cdot NMe_2$. †† Ref. 21 gives 73% of olefin; ref. 22 gives 96%.

It is clear that a phenyl group attached to the nitrogen atom inhibits β-elimination relative to substitution at *N*-methyl groups. The effect of an additional *N*-attached aromatic group was estimated by studying the thermal decomposition of ethylmethyldiphenylammonium hydroxide. The basic product was a mixture estimated by refractive-index analysis to contain 68% of *N*-methyl- and 32% of *N*-ethyl-diphenylamine. A check on the results was obtained by measuring the intensities of selected peaks in the infrared spectrum of the mixture, as compared with the spectra of artifically prepared mixtures. Now, if it is assumed that the rate of substitution at *N*-methyl groups is independent of other groups in the molecule (cf. ref. 16), and that the second phenyl group has no inhibitory effect on elimination, then the replacement in compound (IV; R = Et) of methyl by phenyl should cause the proportion of elimination (Ph_2NMe) to

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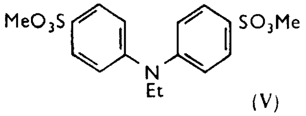
[20] von Braun, *Annalen*, 1911, **382**, 47.
[21] Weinstock, *J. Org. Chem.*, 1956, **21**, 540.
[22] Cope and Bumgardner, *J. Amer. Chem. Soc.*, 1957, **79**, 960.

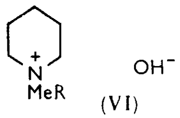
increase to 86%. Since the proportion of elimination was found to be 68%, it may be concluded that a second nitrogen-attached phenyl group further depresses β-elimination.

The preparation of *N*-ethyl-*N*-methyldiphenylammonium hydroxide involved heating *N*-ethyldiphenylamine with dimethyl sulphate in benzene. A by-product of the methylation was a white solid, m. p. 126°, easily isolated because of its insolubility in ether and water. Elemental analysis and methoxyl and *N*-ethyl determinations suggested that the compound was a dimethyl *N*-ethyliminobisbenzenedisulphonate. Presence of the sulphonate groups was confirmed by the strong bands at 1170 and 1350 cm.$^{-1}$ in the infra-red spectrum, which also showed a band at 825 cm.$^{-1}$ suggestive of a 1,4-disubstituted benzene structure. Structure (V) was conclusively proved by the nuclear magnetic resonance spectrum. In particular, the aromatic substitution pattern was proved by the presence of an AB quartet, centred on 2·40 τ, with $\tau_A = 2{\cdot}09$ and $\tau_B = 2{\cdot}71$, and coupling constant $J_{AB} = 8{\cdot}7$ c./sec., a value characteristic of interaction between *ortho*-protons in an aromatic ring.

A structural feature of the hydroxide (II) which is absent from the model compounds hitherto examined is the reduced heterocyclic ring, the stereochemistry of which may affect the ease of β-elimination. The most stable conformation of the ring in 1,1-dimethylpiperidinium hydroxide (VI; R = Me) is probably a chair conformation (cf. piperidine [23,24] and 1-methylpiperidine [24]), in which the stereochemical condition for easy β-elimination, *trans*-coplanarity of the four centres $^{+}$N–C(α)–C(β)–H,[25] is satisfied for an equatorial β-hydrogen atom. On this basis, the observation that the decomposition of *N*-alkyl-*N*-methylpiperidinium hydroxide (VI; R = *e.g.*, butyl or hexyl) causes a β-hydrogen atom of the ring to be eliminated as readily as one in the *N*-alkyl group [26] is intelligible; for it is reasonable to assume that, at the temperature of decomposition, the rate of chair–chair inversion,[27] which allows all β-hydrogen atoms to assume an equatorial direction, is much faster than any β-elimination or substitution. The pentamethylene portion of (VI; R = Me) may therefore be considered to be roughly equivalent to two butyl groups, and it is therefore understandable that von Braun *et al.*[7] reported the isolation of *NN*-dimethylpent-4-enylamine (82%) and "hardly any" 1-methylpiperidine on thermal decomposition of the hydroxide (VI; R = Me). The decomposition of 1-methyl-1-phenylpiperidinium hydroxide (VI; R = Ph) which, like 1-phenylpiperidine,[28] probably has a chair configuration, is expected to give a much lower proportion of β-elimination than that given by the hydroxide (VI; R = Me). However, the complete absence of elimination, reported by von Braun,[18] was so unexpected that we have repeated the experiment. The isolated base was a mixture of 1-phenylpiperidine and the expected elimination product, *N*-methyl-*N*-pent-4-enylaniline. When the mixture was hydrogenated over palladised charcoal in methanol, the volume of hydrogen absorbed corresponded to a mixture of about 25% of unsaturated amine and 75% of 1-phenylpiperidine; a more accurate estimation, based on refractive-index measurements, gave 22% of unsaturated amine (elimination) and 78% of 1-phenylpiperidine (substitution).



(V)



(VI)

Finally, the Hofmann degradation of *N*-cyclohexyl-*N*-methylaniline was investigated. The acid-soluble portion of the product was the expected mixture of *NN*-dimethylaniline

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[23] Barton and Cookson, *Quart. Rev.*, 1956, **10**, 73.

[24] Aroney and Le Fèvre, *J.*, 1958, 3002.

[25] McKenna, *Chem. and Ind.*, 1954, 406.

[26] von Braun, *Ber.*, 1931, **64**, 2610.

[27] Cf. Jensen, Noyce, Sederholm, and Berlin, *J. Amer. Chem. Soc.*, 1960, **82**, 1256; Harris and Sheppard, *Proc. Chem. Soc.*, 1961, 418.

[28] Aroney and Le Fèvre, *J.*, 1960, 2161.

and *N*-cyclohexyl-*N*-methylaniline. Measurements of band intensities in the infrared spectrum of this mixture, and of artificially prepared mixtures, indicated that the basic product contained 28—30% of *NN*-dimethylaniline (elimination) and 70—72% of *N*-cyclohexyl-*N*-methylaniline (substitution). The thermal decomposition of *NNN*-trimethylcyclohexylammonium hydroxide has been reported [29] to give 62% of cyclohexene and 15% of *NN*-dimethylcyclohexylamine, *i.e.*, ~80% of elimination and 20% of substitution. The lower proportion of elimination in the decomposition of the methohydroxide of *N*-cyclohexyl-*N*-methylaniline may be due to (*a*) the presence of the *N*-phenyl substituent, and (*b*) the preference of the molecule for a conformation in which the bulky NMe_2Ph group is equatorial and none of the β-hydrogen atoms is ideally placed for β-elimination.

EXPERIMENTAL

In examination of products by gas chromatography the carrier gas was nitrogen and the material eluted was detected with a conductivity cell. Unless otherwise stated, the standard 2-m. Perkin-Elmer column, packed with Celite coated with Apiezon grease, was operated at 193° and atmospheric pressure. Samples of 1—5 μl. were used. Analytical figures were obtained by cutting out and weighing the portions of paper underneath the peaks.

Analytical figures based on refractive-index measurements were obtained from curves of refractive index of prepared mixtures plotted against composition. *NN*-Dimethylaniline has n_D^{23} 1·5568.

Infrared spectra were determined on a Unicam S.P. 100 spectrophotometer.

N-*Ethyl*-N-*methylaniline*.—*N*-Methylaniline (21·4 g.), ethyl iodide (34·3 g.), sodium carbonate (13 g.), ethanol (200 ml.), and water (100 ml.) were heated under reflux for 24 hr. After ethanol had been removed by distillation, the residue was extracted with ether. Fractional distillation of the dried ($MgSO_4$) ethereal extracts gave *N*-ethyl-*N*-methylaniline (25 g., 93%), b. p. 94—96°/14 mm. (lit.,[30] 201°), n_D^{23} 1·5475. Examination of the base by gas chromatography gave a curve showing one peak, of retention time 7 min. 30 sec. (Mono- and di-methylaniline both gave a retention time of 6 min.) The picrate had m. p. 134—135° (lit.,[31] 134—135°) and the hydrochloride m. p. 114° (lit.,[32] 114°).

Hofman Degradation of N-*Ethyl*-N-*methylaniline*.—A mixture of the above base (5 g.) and methyl iodide (5 ml.) was allowed to remain in the dark for 3 days. The crude methiodide was isolated by addition of dry ether and filtration. Crystallisation from dry ethanol–ether gave *N*-ethyl-*NN*-dimethylanilinium iodide (3 g.) as needles, m. p. 136° (lit.,[30,33,34] 126°, 136°, and 134°) (Found: C, 43·3; H, 5·7; N, 5·0. Calc. for $C_{10}H_{16}IN$: C, 43·3; H, 5·7; N, 5·0%). This salt, which was similarly prepared from dimethylaniline and ethyl iodide, produced no turbidity when treated with aqueous sodium carbonate, demonstrating the absence of hydriodide. The syrupy methohydroxide, prepared in the usual way (silver oxide) from the above methiodide (10 g.), was heated under reflux to 110°, where decomposition became vigorous. The temperature was then increased to 130° and maintained at 130° for 2 hr. The cooled solution was extracted with ether and evaporation of the dried (KOH) extracts gave an oil (4·2 g.), n_D^{23} 1·5545. Total distillation of the oil gave a distillate of n_D^{23} 1·5547, corresponding to ethylmethyl- 28 mol. % and dimethyl-aniline 72 mol. %. Examination of the distillate by gas chromatography showed that only the two amines mentioned were present; quantitative analysis gave 28 mol. % of ethylmethyl- and 72 mol. % of dimethyl-aniline.

N-*Methyl*-N-*propylaniline*.—By the method described above, *N*-methylaniline (21·4 g.) was converted by propyl bromide (27 g.) in the presence of sodium carbonate into *N*-methyl-*N*-propylaniline (21 g., 70%), b. p. 99—101°/14 mm. (lit.,[32,35] 212°, 95—98°/10 mm., respectively), n_D^{23} 1·5385. The base gave only one peak when examined by gas chromatography. The picrate had m. p. 106—107° (lit.,[31] 106—107°) and the hydrochloride m. p. 106° (lit.,[32] 106°).

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[29] Cope, Pike, and Spencer, *J. Amer. Chem. Soc.*, 1953, **75**, 3212; cf. Skita and Rolfes, *Ber.*, 1920, **53**, 1250; Menzies and Robinson, *J.*, 1924, **125**, 2165.

[30] Claus and Howitz, *Ber.*, 1884, **17**, 1325.

[31] Singh, *J.*, 1916, **109**, 790.

[32] Claus and Hirzel, *Ber.*, 1886, **19**, 2789.

[33] Willstätter and Utzinger, *Annalen*, 1911, **382**, 149.

[34] Guaisnet-Pilaud, *Ann. Chim.* (*France*), 1935, **4**, 365.

[35] Bent, Dessloch, Duennebier, Fassett, Glass, James, Julian, Ruby, Snell, Sterner, Thirtle, Vittum, and Weissberger, *J. Amer. Chem. Soc.*, 1951, **73**, 3100.

Hofmann Degradation of N-*Methyl*-N-*propylaniline*.—Jones's method [36] was used. The above base was converted by methyl iodide into *NN*-dimethyl-*N*-propylanilinium iodide, deliquescent prisms, m. p. 69° (lit.,[36] 68·5°). The derived syrupy methohydroxide was heated under reflux to 120°, where decomposition was vigorous, and then to 140° for 2 hr. The product recovered by ether-extraction and total distillation was an oil, of n_D^{23} 1·5425, corresponding to *N*-methyl-*N*-propyl-(85 mol.%) and *NN*-dimethyl-aniline (15 mol. %). Gas chromatography indicated the presence of two components only: *N*-methyl-*N*-propyl- (83 mol. %) and *NN*-dimethyl-aniline (17 mol. %).

N-*Butyl*-N-*methylaniline*.—*N*-Methylaniline (21·4 g.) was converted by n-butyl bromide (30 g.), in the presence of sodium carbonate, into *N*-butyl-*N*-methylaniline (26 g., 78%), b. p. 114—116°/13 mm. (lit.,[35] 114—116°/12 mm.), n_D^{23} 1·5310. The base gave only one peak when examined by gas chromatography. The picrate had m. p. 90° (lit.,[37, 38] 90° and 86°).

Hofmann Degradation of N-*Butyl*-N-*methylaniline*.—A mixture of *N*-butyl-*N*-methylaniline and an excess of methyl iodide was allowed to remain in the dark in a stoppered flask for 3 days. The *methiodide* was isolated by addition of dry ether and filtration. Recrystallisation from dry ethanol–dry ether gave needles, m. p. 97—97·5° (Found: C, 46·9; H, 7·0; N, 4·9. $C_{12}H_{20}IN$ requires C, 47·2; H, 6·6; N, 4·6%). The syrupy methohydroxide, prepared in the usual way from the above salt, was decomposed at 130° (vigorous decomposition) and then at 150° for 3 hr. Ether-extraction of the cooled solution, followed by removal of ether and total distillation of the residue, gave an oil, n_D^{23} 1·5330, corresponding to *N*-butyl-*N*-methyl- 90 mol. % and *NN*-dimethyl-aniline 10 mol. %. Gas chromatography indicated two components, *N*-butyl-*N*-methyl- (92 mol. %) and *NN*-dimethyl-aniline (8 mol. %).

N-*Methyl*-N-3-*phenylpropylaniline*.—1-Bromo-3-phenylpropane, prepared in 90% yield by heating 3-phenylpropan-1-ol with 48% w/v hydrobromic acid, had b. p. 108—110°/14 mm. (lit.,[21] 108—109°/10 mm.). A mixture of the bromo-compound (20 g.) and *N*-methylaniline (25 g.) was heated on a steam-bath for 48 hr. The cooled mixture was dissolved in 10% hydrochloric acid (100 ml.), and the resulting solution shaken several times with ether, the ethereal extracts being discarded. The aqueous solution was basified and the liberated amines were extracted into ether. Distillation of the dried (KOH) ethereal extracts gave N-*methyl*-N-3-*phenylpropylaniline* (21 g., 93%), b. p. 182—184°/14 mm., n_D^{23} 1·5833 (Found: C, 85·2; H, 8·2; N, 6·5. $C_{16}H_{19}N$ requires C, 85·3; H, 8·4; N, 6·2%), $\lambda_{max.}$ 258 and 305 mμ (ε 15,400 and 2440, respectively, in EtOH). The *picrate* had m. p. 133—134° (Found: C, 58·0; H, 4·7; N, 12·4. $C_{22}H_{22}N_4O_7$ requires C, 58·1; H, 4·8; N, 12·3%). The methiodide was an oil but the *methyl methosulphate*, prepared by treating the base with dimethyl sulphate in the cold, had m. p. 155° (Found: C, 61·6; H, 7·15; N, 3·9. $C_{18}H_{25}NO_4S$ requires C, 61·5; H, 7·1; N, 4·0%).

Hofmann Degradation of N-*Methyl*-N-3-*phenylpropylaniline*.—A solution of the above methyl methosulphate (10 g.) in water (50 ml.) was treated with sodium hydroxide (2 g.) in water (10 ml.) and the mixture was evaporated at 40°, under reduced pressure, to remove water. The resulting syrup was decomposed at 150° in 4 hr. and the cooled solution was then diluted with water (10 ml.) and extracted several times with ether. Basic material was removed from the ether by shaking the solution with 15% hydrochloric acid. Distillation of the dried ($MgSO_4$) ether gave a mixture of phenylpropenes (0·4 g.), n_D^{23} 1·5460, for which gas chromatography demonstrated two components, probably *trans*- and *cis*-1-phenylpropene (cf. refs. 21, 22), in the ratio of about 10 : 1. The infrared spectrum (liquid film) had max. at 1660, 965, 768, 735, and 693 cm.$^{-1}$.

The basic fraction (5 g.) was recovered from the acid extracts by addition of sodium hydroxide solution and ether-extraction. The usual working-up gave an oil, n_D^{23} 1·5800, corresponding to 79 mol. % of *N*-methyl-*N*-3-phenylpropylaniline and 21 mol. % of *NN*-dimethylaniline. Fractional distillation of the oil gave successively dimethylaniline (picrate, m. p. and mixed m. p. 163°) and *N*-methyl-*N*-3-phenylpropylaniline (picrate, m. p. and mixed m. p. 133—134°). The two bases were also separated and identified by gas chromatography, on a 1-m. column, operated at 220°, packed with a support derived from " Tide " (method D of ref. 39) and coated with 10% Apiezon " M." No other products were detected.

[36] Jones, *J.*, 1903, **83**, 1400.
[37] Reilly and Hickinbottom, *J.*, 1920, **117**, 130.
[38] Chow and Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 1095.
[39] Decora and Dinneen, *Analyt. Chem.*, 1960, **32**, 164.

Identical results were secured for the composition of the basic fraction when the methohydroxide was initially obtained from the oily methiodide by treatment with silver oxide.

Hofmann Degradation of NN-*Dimethyl-3-phenylpropylamine*.—*NNN*-Trimethyl-3-phenylpropylammonium bromide, m. p. 151—152°, was prepared by Weinstock's method.[21] The derived syrupy methohydroxide [from the above salt (10 g.)] was decomposed at 150° for 4 hr. The product was separated into neutral and basic fractions by using ether and 10% hydrochloric acid. The neutral fraction (3·585) of mixed phenylpropenes had n_D^{22} 1·5470 and its behaviour on gas chromatography was identical with that of the mixture of phenylpropenes obtained in the preceding degradation. The basic fraction (0·497 g.) was totally distilled at 15 mm. and had n_D^{22} 1·4980. The picrate had m. p. 99° (lit.,[40,41] 99° and 103°). Quantitative formation of the methobromide, m. p. and mixed m. p. 151—152°, showed that the basic fraction was entirely *NN*-dimethyl-3-phenylpropylamine.

N-*Methyldiphenylamine* (cf. ref. 42).—A mixture of diphenylamine (33·8 g.) and dry dimethyl sulphate (37·8 g.) was heated to 50° on a water-bath and treated during 0·5 hr. with a solution of sodium carbonate (35 g.) in water (200 ml.). The solution was heated at 50° for a further 3 hr., cooled, and extracted several times with benzene. The combined benzene extracts (300 ml.) were allowed to remain overnight in contact with concentrated hydrochloric acid (50 ml.). Diphenylamine hydrochloride was removed by filtration, the filtrate basified, and the organic layer separated, dried (KOH), and distilled. The crude *N*-methyldiphenylamine thus secured in 80% yield showed appreciable absorption, at 3360 cm.$^{-1}$ (NH stretching), in the infrared region and complete removal of diphenylamine was only achieved after distillation over sodamide. Pure *N*-methyldiphenylamine had b. p. 153—158°/14 mm. (lit.,[42] 145—145·5°/10 mm.), n_D^{26} 1·6195, $\lambda_{\text{max.}}$ 206, 245, and 292 mμ (ε 29,700, 9200, and 11,300, respectively, in EtOH), $\lambda_{\text{max.}}$ 250, 256, 259, and 266 mμ (ε 596, 715, 605, and 394, respectively; in concentrated hydrochloric acid). The infrared spectrum (in CCl_4) differed from that of *N*-ethyldiphenylamine (see below) in having max. at 2815, 1347, and 1097 cm.$^{-1}$ (ε 29, 250, and 50, respectively). The chloroplatinate had m. p. 207—209° (decomp.) (lit.,[42] 207—209°). The methiodide, prepared by the method of Gibson and Vining,[42] had m. p. 170—170·5° (lit.,[42–44] 163°, 163°, and 158°, respectively) (Found: C, 51·3; H, 4·9; N, 4·3. Calc. for $C_{14}H_{16}IN$: C, 51·6; H, 4·9; N, 4·3%), $\lambda_{\text{max.}}$ 250, 256, 260, and 267 mμ (ε 512, 500, 430, and 315, respectively, in EtOH). The methiodide gave no turbidity with aqueous sodium carbonate, demonstrating the absence of hydriodide.

N-*Ethyldiphenylamine* (cf. ref. 42).—Diethyl sulphate was dried (Na_2CO_3) and distilled (b. p. 89—92°/13 mm.). A mixture of diphenylamine (33·8 g.) and diethyl sulphate (46·2 g.) was heated on the water-bath for 48 hr. Sodium carbonate solution was then added and the mixture was heated for a further 24 hr. at 100°. The cooled solution was treated as described above for *N*-methyldiphenylamine. After distillation from sodamide, pure *N*-ethyldiphenylamine had b. p. 153—154°/14 mm. (lit.,[42] 149·5—150°/10 mm.), n_D^{26} 1·6065, $\lambda_{\text{max.}}$ 249 and 293 mμ (ε 8380 and 11,400, respectively, in EtOH), $\lambda_{\text{max.}}$ 250, 256, 260, and 267 mμ (ε 256, 334, 286, and 132, respectively, in concentrated hydrochloric acid). The infrared spectrum (in CCl_4) differed from that of *N*-methyldiphenylamine in having max. at 1460, 1374, and 1352 (ε 41, 170, and 97, respectively). The hexachloroplatinate had m. p. 166° (decomp.) (lit.,[42] 166—169°).

Methylation of N-*Ethyldiphenylamine*.—Pure *N*-ethyldiphenylamine (10 g.) was heated on a water-bath with dry dimethyl sulphate (20 g.) and dry benzene (50 ml.) for 7 days. The cooled solution was poured into dry ether (200 ml.), a blue gum separating. The ethereal solution was decanted, and the gum was washed with several portions of dry ether (5 × 50 ml.). At 0° the combined ethereal washings deposited pale blue crystals (see below). The blue gum was dissolved in boiling water (30 ml.), the solution filtered, and treated with a cold saturated solution of potassium iodide (20 g.). The crystals which separated were filtered off, washed with ether, and reprecipitated with dry ether from a solution in dry chloroform. Finally, crystallisation from ethanol–ether gave N-*ethyl*-N-*methyldiphenylammonium iodide* (2 g.) as needles, m. p. 141—142° (Found: C, 53·1; H, 5·4; N, 4·4. $C_{15}H_{18}IN$ requires C, 53·1; H, 5·3; N, 4·1%), $\lambda_{\text{max.}}$ 250, 256, 261, and 267 mμ (ε 562, 540, 456, and 324, respectively, in EtOH). The methiodide

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[40] Senfter and Tafel, *Ber.*, 1894, **27**, 2309.

[41] Mannich and Heilner, *Ber.*, 1922, **55**, 361.

[42] Gibson and Vining, *J.*, 1923, **123**, 831.

[43] Gadomska and Decker, *Ber.*, 1903, **36**, 2487.

[44] Hughes and Whittingham, *J.*, 1960, 806.

gave no turbidity when treated with aqueous sodium carbonate. The yield was not improved by carrying out the quaternisation in nitromethane or in the absence of solvent.

Recrystallisation of the pale blue crystals from ethanol gave colourless prisms, m. p. 126°, of *dimethyl* N-*ethyliminobis*-pp′-*benzenesulphonate* (Found: C, 50·2; H, 5·1; N, 3·5; S, 16·5; OMe, 19·5; *N*-Et, 7·6. $C_{16}H_{19}NO_6S_2$ requires C, 49·9; H, 5·0; N, 3·6; S, 16·6; OMe, 16·1; *N*-Et, 7·5%), $\lambda_{max.}$ 221, 240, 267, and 338 mμ (ε 16,200, 8440, 13,300, and 22,800, respectively, in EtOH). The infrared spectrum (KBr disc) had many peaks, including those at 1350, 1170, and 825 cm.$^{-1}$. The nuclear magnetic resonance spectrum was determined on an A.E.I. spectrometer with a 60 Mc. oscillator. Tetramethylsilane was used as the internal reference. In methylene dichloride, the following characteristics were observed: (*a*) a triplet (area 3 protons) at 8·67 (*J* 6·7 c./sec.), due to methyl protons of the *N*-ethyl group; (*b*) a singlet (area 6) at 6·18, due to methyl protons of the ester groups; (*c*) a quartet at 6·01 (*J* 6·7 c./sec.), partly obscured by the previous peak, due to methylene protons of the *N*-ethyl group; (*d*) an AB quartet (area 8) (see p. 325).

Hofmann Degradation of N-*Ethyldiphenylamine*.—The syrupy methohydroxide, prepared from the preceding methiodide (5 g.), was decomposed under reflux at 125° (vigorous decomposition) and then for 3 hr. at 150°. The resulting solution was shaken several times with ether and the combined extracts were dried (KOH) and totally distilled. The distillate had n_D^{26} 1·6150, corresponding to a mixture of *N*-ethyl- 31·6 mol. % and *N*-methyl-diphenylamine 68·4 mol. %. The infrared spectrum (in CCl_4) of the mixture showed max. at 2815, 1460 (infl.), 1374, 1346, and 1098 cm.$^{-1}$ (ε 25, 35, 70, 210, and 42, respectively). A prepared mixture of 33·8 mol. % of *N*-ethyl- and 66·2 mol. % of *N*-methyl-diphenylamine had max. at 2813, 1461 (infl.), 1375, 1347, and 1097 cm.$^{-1}$ (ε 24, 33, 70, 200, and 40, respectively). The two infrared curves were practically superimposable.

Hofmann Degradation of 1-*Phenylpiperidine*.—1-Phenylpiperidine was prepared in almost theoretical yield by Brotherton and Bunnett's method.[45] The base had n_D^{21} 1·5622 and gave a picrate, m. p. 148° (lit.,[18] 148°), and methiodide, m. p. 146° (lit.,[18] 146°). The methohydroxide from the methiodide (9·8 g.) was decomposed at about 160° and the products were isolated by ether-extraction of the cooled solution. After removal of ether from the dried (KOH) ethereal extracts, the residue was totally distilled. The distillate had n_D^{21} 1·5524 and an infrared band at 1630 cm.$^{-1}$ (C=C), absent from the spectrum of 1-phenylpiperidine. The distillate (2·5 g.), in methanol (50 ml.) containing sufficient 12N-hydrochloric acid to form an acid solution, was hydrogenated at room temperature and pressure over 10% palladised charcoal (0·3 g.) (absorption 105 ml. at 23°/760 mm.). Isolation in the usual way gave, after total distillation, a liquid of n_D^{21} 1·5535, corresponding to a mixture of 22% of *N*-methyl-*N*-pentylaniline and 78% of 1-phenyl-piperidine. *N*-Methyl-*N*-pentylaniline was synthesised by heating on the water-bath for 5 days a mixture of pentyl bromide and an excess of *N*-methylaniline. The cooled solution was successively acidified, washed with ether, basified, and extracted with ether. Fractional distillation of the dried (KOH) ethereal extracts gave *N*-methyl-*N*-pentylaniline, n_D^{21} 1·5282 [picrate, m. p. 81—83° (lit.,[46] 97·5°) (Found: C, 53·3; H, 5·1; N, 14·2. Calc. for $C_{18}H_{22}N_4O_7$: C, 53·2; H, 5·4; N, 13·8%)].

N-*Cyclohexyl*-N-*methylaniline*.—A mixture of bromocyclohexane (15 g.) and *N*-methylaniline (40 g.) was heated on a water-bath for 72 hr. The resulting solution was treated with 10% hydrochloric acid (200 ml.) and extracted with ether (4 × 100 ml.). Basification of the acid extracts, followed by ether-extraction and fractional distillation of the dried (KOH) extracts, gave N-*cyclohexyl*-N-*methylaniline* (15 g.), b. p. 150—152°/14 mm., n_D^{25} 1·5575 (Found: C, 82·5; H, 10·45; N, 7·5. $C_{13}H_{19}N$ requires C, 82·5; H, 10·05; N, 7·4%), $\lambda_{max.}$ 256 and 303 mμ (ε 14,300 and 1760 in ethanol), $\lambda_{max.}$ 249, 255, 258, 261, and 265 mμ (ε 181, 222, 180, 178, and 121. respectively, in 12N-hydrochloric acid). The infrared spectrum (in CCl_4) differed from that of *NN*-dimethylaniline in having max. at 898, 1106, 1303, and 1397 cm.$^{-1}$ (ε 37, 110, 98, and 64, respectively). The *picrate* had m. p. 96—97° (Found: C, 54·5; H, 5·15; N, 13·2. $C_{19}H_{22}N_4O_7$ requires C, 54·3; H, 5·3; N, 13·3%). The *methiodide* had m. p. 163·5—164·5° (Found: C, 50·8; H, 6·7; N, 4·1. $C_{14}H_{22}IN$ requires C, 50·75; H, 6·7; N, 42%), $\lambda_{max.}$ 209, 219, 251, 253, 255, 259, and 265 mμ (ε 13,800, 13,800, 250, 250, 263, 238, and 175, respectively, in EtOH).

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[45] Brotherton and Bunnett, *Chem. and Ind.*, 1957, 80.

[46] Meisenheimer and Link, *Annalen*, 1930, **479**, 211.

Hofmann Degradation of N-*Cyclohexyl*-N-*methylaniline*.—The methohydroxide, prepared in the usual way from the above methiodide (2·5 g.), was decomposed at 140—160° for 4 hr. The product (1·30 g.) which was recovered by ether-extraction and total distillation of the extracts had n_D^{22} 1·5575. The infrared spectrum (in CCl_4) included max. at 898, 1106, 1303, and 1397 cm.$^{-1}$ (ε 30, 86, 77, and 53, respectively). A prepared mixture of 73 mol. % of *N*-cyclohexyl-*N*-methyl- and 27 mol. % of *NN*-dimethyl-aniline had max. at 898, 1106, 1303, and 1397 cm.$^{-1}$ (ε 30, 88, 79, and 55, respectively). The infrared curve of this mixture was almost superimposable on that of the degradation product.

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