168. *The Chemical Effects of γ-Radiation on Organic Systems. Part IV.*[1] *The Action of Radiation on Diethylamine, Trimethylamine, Benzylamine, Phenethylamine,* 1-*Methylpiperidine,* N-*Methyldiethylamine, and* t-*Butylamine.*

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Products formed by γ-radiolysis of the amines named in the title have been isolated, characterised, and identified by comparison with authentic samples. A number of these were new compounds and have therefore also been synthesised chemically. Except for phenethylamine and t-butylamine, the changes appear to involve loss of hydrogen from a carbon atom α to the nitrogen atom and combination of the resulting radicals. In the cases of 1-methylpiperidine and *N*-methyldiethylamine attack is possible at either the methyl or the methylene group, resulting in the formation of the mixed coupling product, as well as of the two dimers. In some cases, radiolysis also causes fission of a C–N or N–H bond, leading to bibenzyl from benzylamine, and *NN*-diethylaniline from a mixture of diethylamine and bromobenzene. When dimerisation yields a symmetrical product containing two asymmetric carbon atoms, the *meso*-form was obtained, accompanied in some cases by the racemic form. The yield of irradiation products from t-butylamine was much lower than from any other amine investigated: here, loss of hydrogen from the amino- and methyl groups occurred.

Previous work [1] has shown that γ-radiolysis of triethylamine gives approximately equal amounts of *meso*- and racemic *NNN'N'*-tetraethylbutane-2,3-diamine, supposedly by dimerisation of the radical $CH_3\cdot\dot{C}H\cdot NEt_2$ although the reaction is formally analogous to the formation of ethylene glycol from methanol, which Schuler [2] believes may go through an ion-molecule reaction. We have therefore studied the γ-radiolysis of a number of primary, secondary, and tertiary amines, most of which have at least one methylene or methyl group (and in some cases both) adjacent to the nitrogen atom. The work is essentially qualitative and, except where otherwise stated, the *G* values given in this paper are based on yields of pure, crystalline products isolated: in general, therefore, the true *G* values will be higher than the values given. The experimental section describes, however, trial separations, carried out on mixtures of known composition, which afford some idea of the magnitude of the deficiencies. It is possible that the use of gas chromatography might reveal the presence of other products and give higher recoveries; but we are at present unable to pursue this.

Irradiation of diethylamine gave a mixture of *meso*- and racemic *NN'*-diethylbutane-2,3-diamine (II) which in contrast to the isomeric forms of *NNN'N'*-tetraethylbutane-2,3-diamine, could not be separated by partition chromatography, with an aqueous phosphate buffer on kieselguhr as stationary phase and ether as mobile phase. The racemic form was therefore isolated as the crystalline dihydrochloride (*G* 0·78), the corresponding *meso*-salt being gummy; and the *meso*-form was isolated as the sparingly soluble dipicrate (*G* 0·77).

The formation of these products might be explained if radiolysis of diethylamine yielded the radical (I), which could dimerise:

$$CH_3\cdot CH_2\cdot NHEt \xrightarrow{\sim\sim} CH_3\cdot\dot{C}H\cdot NHEt \ (I) + H\cdot$$

$$2CH_3\cdot\dot{C}H\cdot NHEt \longrightarrow (EtHN\cdot CHMe\cdot)_2 \ (II)$$

[1] Part III, Swan, Timmons, and Wright, *J.*, 1959, 9.
[2] Schuler, *J. Chem. Phys.*, 1957, **26**, 425.

One might then expect disproportionation of the radicals to give *N*-ethylidene-ethylamine (III):

$$2CH_3\cdot\dot{C}H\cdot NHEt \longrightarrow Me\cdot CH{:}NEt\ (III) + NHEt_2$$

If this compound (b. p. 48°) [3] had been formed, it would have been lost during the working up. If fission of the N–H bond occurred, the formation of tetraethylhydrazine (IV) might be possible:

$$Et_2N{-}H \longrightarrow Et_2N\cdot + H\cdot$$
$$2Et_2N\cdot \longrightarrow Et_2N\cdot NEt_2\ (IV)$$

However, we failed to detect its presence in the irradiated amine; but the isolated, crystalline compounds accounted for only approximately 77% of the distillable product which was less volatile than diethylamine. A small amount of undistillable material was also formed.

We also irradiated an equimolecular mixture of diethylamine and bromobenzene. Diethylamine hydrobromide crystallised [*G*(HBr) 9·6] and unchanged diethylamine was removed by fractional distillation. From the non-basic fraction of the product, biphenyl (*G* 0·47) was isolated. The residual basic fraction was subjected to partition chromatography and the following were isolated and characterised as their picrates: *NN*-diethylaniline (*G* 0·23; eluted at pH 5), *N*-ethyl-α-methylbenzylamine [4] (V) (*G* 0·11; retained at pH 5, but eluted at pH 6·5), and *meso-NN'*-diethylbutane-2,3-diamine (II) (*G* 0·12; retained at pH 6·5, but eluted at pH 7·5). The yields of these isolated compounds account for only approximately 32% of the distillable, basic product less volatile than diethylamine; and there was also some involatile residue. A synthetic sample of tetraethylhydrazine was eluted at pH 5; but the presence of this compound in the irradiated material could not be established; it is, however, very volatile and if formed in only low yield might have been lost during the distillation of the unchanged diethylamine; also the picrate, which we used for its isolation, is rather soluble in solvents in which picric acid is also soluble. The picrate of the amine (V) is also rather soluble, so the corresponding *G* value may be low. The failure to detect racemic *NN'*-diethylbutane-2,3-diamine in this case is, however, surprising.

Formation of the amine (V) can be attributed to combination of the radical (I) with a phenyl radical (generated by radiolysis of bromobenzene):

$$CH_3\cdot\dot{C}H\cdot NHEt\ (I) + Ph\cdot \longrightarrow Ph\cdot CHMe\cdot NHEt\ (V)$$

NN-Diethylaniline is presumably formed by interaction of a phenyl radical with the radical $Et_2N\cdot$:

$$Ph\cdot + Et_2N\cdot \longrightarrow PhNEt_2$$

But it is not clear whether the latter radical results from direct radiolysis:

$$Et_2N{-}H \longrightarrow Et_2N\cdot + H\cdot$$

or is formed by hydrogen-abstraction by one of the radicals formed by radiolysis of the bromobenzene, *e.g.*:

$$Et_2N{-}H + Br\cdot \longrightarrow Et_2N\cdot + HBr$$

The absence of tetraethylhydrazine might be due to the greater tendency for the radical $Et_2N\cdot$ to react with a phenyl radical than to dimerise.

meso- and Racemic *NN'*-diethylbutane-2,3-diamine (II) were synthesised by reduction, with lithium aluminium hydride, of the corresponding forms of *NN'*-diacetylbutane-2,3-diamine. Of a number of methods investigated for the separation of these stereoisomeric bases, that mentioned above was found to be best.

[3] Henry, *Bull. Acad. roy. Belg.*, 1904, **6**, 741.
[4] Parrack, Swan, and Wright, *J.*, 1962, 911.

Although tetraethylhydrazine had been prepared by Westphal and Eucken,[5] we obtained it in two different ways, the first of which we consider to be superior in simplicity and yield to that of the German authors. 1,2-Dibenzoylhydrazine, on treatment with ethyl sulphate and sodium hydroxide, yielded 1,2-dibenzoyl-1,2-diethylhydrazine, which was hydrolysed by hydrochloric acid to 1,2-diethylhydrazine (subsequently Ried and Wisselborg [6] described a similar synthesis of this compound). The 1,2-diacetyl derivative of the latter product, on reduction with lithium aluminium hydride, yielded tetraethylhydrazine (IV). Renaud and Leconte [7] failed to obtain 1,2-diethylhydrazine by catalytic hydrogenation of *NN'*-diethylidenehydrazine; we, however, succeeded in doing so (cf. Langley, Lythgoe, and Rayner [8]). 1,2-Diacetyl-1,2-diethylhydrazine, obtained by acetylation of 1,2-diethylhydrazine prepared by either method, gave carbon values approximately 1% lower than required by theory.

Irradiation of trimethylamine at −78° yielded a liquid, b. p. 70—125°, which contained *NNN'N'*-tetramethylethylenediamine (VI) (*G* 2·5) and *NNN'N'*-tetramethylmethylenediamine (VIII) (*G* 1·22). The first of these products was isolated as the dipicrate, and the ethanolic mother-liquor yielded dimethylamine picrate, formed by decomposition of *NNN'N'*-tetramethylmethylenediamine. Treatment of the mixture of bases with hydrochloric acid yielded formaldehyde and the hydrochlorides of *NNN'N'*-tetramethylethylenediamine and dimethylamine, identified by conversion into picrates. The *G* value for *NNN'N'*-tetramethylmethylenediamine is based on a formaldehyde estimation, rather than on the yield of dimethylamine picrate, as the losses involved in the isolation of the latter are considerable. There was very little product boiling above 125°. In one experiment we isolated a picrate, separated from dimethylamine picrate by fractional crystallisation, which appeared to be tetramethylhydrazine monopicrate; but in subsequent experiments (at either −78° or −3°) we were unable to find this. Irradiation in the presence of air resulted also in the formation of *NN*-dimethylformamide.

The products identified could be explained if, on radiolysis, trimethylamine breaks down in two ways:

$$Me_2N{\cdot}CH_3 \longrightarrow Me_2N{\cdot}CH_2{\cdot} + H{\cdot}$$

$$Me_2N{\cdot}CH_3 \longrightarrow Me_2N{\cdot} + CH_3{\cdot}$$

The products might then result by radical combination:

$$2Me_2N{\cdot}CH_2{\cdot} \longrightarrow Me_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2 \quad (VI)$$

$$2Me_2N{\cdot} \longrightarrow Me_2N{\cdot}NMe_2 \quad (VII)$$

$$Me_2N{\cdot}CH_2{\cdot} + Me_2N{\cdot} \longrightarrow Me_2N{\cdot}CH_2{\cdot}NMe_2 \quad (VIII)$$

In contrast to other amines which we have so far studied, here the fission of a C–N bond appears to play an important part in the radiolysis. Evidence of such a fission, to a minor extent, has been obtained in the radiolysis of a mixture of triethylamine and bromobenzene.[1] The larger number of C–N bonds in relation to the number of C–H bonds may be favourable to C–N bond fission in the case of trimethylamine. Trimethylamine is the only amine which we have irradiated at temperatures other than room temperature and this fact may be significant. It is hoped to study the radiolysis of other amines at low temperatures. On the other hand, Watson [9] obtained tetramethylhydrazine by photolysis or pyrolysis of tetramethyltetrazine, presumably by dimerisation of $Me_2N{\cdot}$ radicals. Disproportionation also resulted in the formation of dimethylamine and *N*-methylmethyleneimine, isolated as a trimer (b. p. 63—66°/25 mm.):

$$Me_2N{\cdot} \longrightarrow Me_2NH + MeN{:}CH_2$$

[5] Westphal and Eucken, *Ber.*, 1943, **76**, 1137.
[6] Ried and Wisselborg, *Annalen*, 1958, **611**, 71.
[7] Renaud and Leconte, *Canad. J. Chem.*, 1954, **32**, 545.
[8] Langley, Lythgoe, and Rayner, *J.*, 1952, 4191.
[9] Watson, *J.*, 1956, 3677.

The formation of a small amount of tetramethylmethylenediamine (VIII), however, remained unexplained. We did not detect the imine trimer in our irradiated trimethylamine. If dimethylamine had been formed, it would have been lost during the working-up.

Irradiation of benzylamine, earlier reported to yield *meso*-stilbenediamine [1] (IX), has now been investigated in greater detail. When the unchanged base (b. p. <187°), removed by fractional distillation from irradiated benzylamine, was treated with dilute hydrochloric acid, benzaldehyde was obtained. Treatment of the residue (b. p. >187°) from the distillation with dilute hydrochloric acid yielded *meso*-stilbenediamine dihydrochloride, which was filtered off, and the filtrate was then extracted with ether. The latter extract contained bibenzyl (X) (*G* 0·11) and a dark yellow oil, showing strong absorption at 220 and 320 mμ. The bases present in the acidic layer were subjected to partition chromatography, yielding unchanged benzylamine (retained at pH 7·5), a little *meso*-stilbenediamine (retained at pH 6·5, but eluted at pH 7·5), and *N*-benzylidenebenzylamine (XII) (*G* 0·11; eluted at pH 5). The latter, like a synthetic sample,[10] on treatment with picric acid yielded benzylamine picrate and benzaldehyde. The *G* value for the formation of *meso*-stilbenediamine was 2·76.

meso-Stilbenediamine was synthesised by Darapsky and Spannagel's method; [11] but, in agreement with other workers,[12] we found that the racemic form prepared by Feist's method [13,14] always contained some of the *meso*-isomer. Lifschitz and Bos's preparation [15] of the pure racemic form is long and we found it more convenient to separate it from the impure material, obtained by Feist's method, by conversion into a mixture of nickel(II) chloride complexes.[16,17] The purple, racemic complex was readily separable from the yellow *meso*-complex by fractional crystallisation from ethanol, and the free stilbenediamines were obtained by decomposition of the complexes with hydrogen sulphide. We were unable to detect the presence of racemic stilbenediamine in the irradiated benzylamine, even when using these nickel complexes; the isolated diamine appeared to be the pure *meso*-form.

The formation of the observed products could be explained if the action of γ-radiation on benzylamine causes fission of the molecule in two ways:

$$Ph{\cdot}CH_2{\cdot}NH_2 \longrightarrow Ph{\cdot}\dot{C}H{\cdot}NH_2 + H{\cdot}$$
$$Ph{\cdot}CH_2{\cdot}NH_2 \longrightarrow Ph{\cdot}CH_2{\cdot} + NH_2{\cdot}$$

Dimerisation of the respective radicals would then yield stilbenediamine and bibenzyl:

$$2Ph{\cdot}\dot{C}H{\cdot}NH_2 \longrightarrow \begin{matrix} Ph{-}CH{-}NH_2 \\ | \\ Ph{-}CH{-}NH_2 \end{matrix} \quad (IX)$$
$$2Ph{\cdot}CH_2{\cdot} \longrightarrow Ph{\cdot}CH_2{\cdot}CH_2{\cdot}Ph \quad (X)$$

The formation of benzaldehyde by treatment of the recovered benzylamine with hydrochloric acid suggests that benzaldimine (XI) (*G* 0·94) had been produced by irradiation. This might arise by disproportionation:

$$2Ph{\cdot}\dot{C}H{\cdot}NH_2 \longrightarrow Ph{\cdot}CH_2{\cdot}NH_2 + Ph{\cdot}CH{:}NH \quad (XI)$$

The benzylidenebenzylamine (XII) may have been formed by reaction of part of the

[10] Mason and Winder, *J.*, 1894, **65**, 191.
[11] Darapsky and Spannagel, *J. prakt. Chem.*, 1915, **92**, 272.
[12] McRae and Townshend, *Canad. J. Res.*, 1934, **11**, 628.
[13] Feist, *Ber.*, 1894, **27**, 214.
[14] Pfeiffer, Hesse, Pfitzner, Scholl, and Thielert, *J. prakt. Chem.*, 1937, **149**, 217.
[15] Lifschitz and Bos, *Rec. Trav. chim.*, 1940, **59**, 173.
[16] Lifschitz, Bos, and Dijkema, *Z. anorg. Chem.*, 1939, **242**, 97.
[17] Lifschitz and Bos, *Rec. Trav. chim.*, 1940, **59**, 407.

benzaldimine with benzylamine, during the irradiation or in the working-up (probably during the distillation of the excess of benzylamine):

$$Ph{\cdot}CH{:}NH + Ph{\cdot}CH_2{\cdot}NH_2 \longrightarrow NH_3 + Ph{\cdot}CH{:}N{\cdot}CH_2Ph \quad (XII)$$

If it is not, in fact, an irradiation product, then the G value for the formation of benzaldimine should be 1·05. Bamford,[18] however, postulated the formation of analogous compounds as intermediates in the photolysis of aliphatic primary amines to account for the formation of polymeric products. Such compounds are also formed by the action of t-butyl hydroperoxide on amines.[19] The compound which yields benzaldehyde from the recovered benzylamine (b. p. <187°) must be benzaldimine rather than *N*-benzylidenebenzylamine, as the latter has b. p. 200°/15 mm.

On the above basis and by analogy with benzyl alcohol [20] (which yields 1,2-diphenylethanol among its irradiation products), the formation of 1,2-diphenylethylamine (XIII) might be expected:

$$Ph{\cdot}CH_2{\cdot} + Ph{\cdot}\dot{C}H{\cdot}NH_2 \longrightarrow Ph{\cdot}CH_2{\cdot}CHPh{\cdot}NH_2 \quad (XIII)$$

but this compound was not detected.

The annexed Table shows the analogy between the irradiation products of benzylamine and benzyl alcohol, although it must be remembered that in the latter case the yields were determined by the isotope dilution method, whereas in the former they are based on weights of products isolated.

G Values of products formed by irradiation of benzylamine and benzyl alcohol.

Benzylamine (dose 9·88 × 10^{20} ev/ml.)		Benzyl alcohol (dose 4·98 × 10^{20} ev/ml.)	
Bibenzyl	0·11	Bibenzyl	0·29
Benzaldimine	1·05	Benzaldehyde	1·32
meso-Stilbenediamine	2·76	*meso*-Hydrobenzoin	0·20
		Racemic hydrobenzoin	0·22
		1,2-Diphenylethanol	0·68

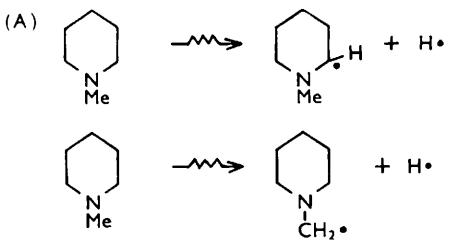
The above results suggest that in the case of benzyl alcohol the probability of fission of a C–H bond is approximately twice that of a C–O bond, but as there are twice as many of the former this implies equal ease of fission. The results from benzylamine, however, suggest that the fission of a C–H bond occurs more readily and that of a C–N bond is very much less frequent. It could, however, be that we failed to isolate some products formed from benzyl radicals (*e.g.*, dibenzylamine, nuclear benzylation products of benzylamine, or 1,2-diphenylethylamine).

Irradiation of phenethylamine led to a basic gum, which could not be distilled and failed to give crystalline salts. Considerable amounts of a non-basic gum were also formed. The latter failed to give a precipitate with 2,4-dinitrophenylhydrazine but gave a positive test with Ehrlich's reagent and when it was chromatographed on alumina it gave a series of gums, together with a very small amount of *meso*-2,3-diphenylbutane.[21]

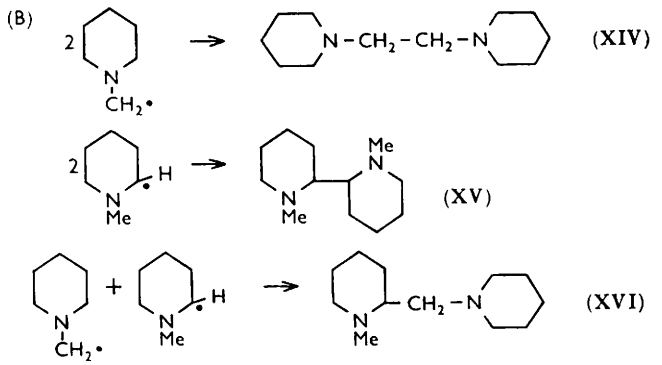
When 1-methylpiperidine was irradiated, the unchanged base recovered by distillation (b. p. <107°) contained piperidine (G 0·18), as shown by the formation of 1-benzoylpiperidine by refluxing it with benzoic anhydride. The residue (b. p. >107°) contained 1,2-dipiperidinoethane (XIV) (G 0·37), *meso*-1,1′-dimethyl-2,2′-bipiperidyl (XV) (G 0·75), and 1-methyl-2-(piperidinomethyl)piperidine (XVI) (G 0·39), together with a black gum of high boiling point. The first of these bases was isolated as the crystalline dihydrochloride, the second from the mother-liquor as dihydrobromide and from the remaining material, the third base as dipicrate. The yields of these three crystalline compounds account for 77% of the distillable material of b. p. >107°.

[18] Bamford, *J.*, 1939, 17.
[19] de la Mare, *J. Org. Chem.*, 1960, **25**, 2114.
[20] Swan and Wright, *J.*, 1958, 4673.
[21] Ley and Rinki, *Ber.*, 1923, **56**, 771.

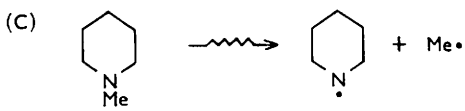
The formation of the above compounds could be explained if radiolysis of 1-methylpiperidine gives two organic radicals (see A):



The three major products could then arise by radical couplings (B):



The production of piperidine in low yield suggests that, to a smaller extent, fission (C) into methyl and piperidino-radicals also occurs.



Leonard and Hauck [22] have shown that dehydrogenation of 1-methylpiperidine by mercuric acetate gives Δ^2-tetrahydro-1,1′-dimethylanabasine, by dimerisation of the intermediate 1,2,3,4-tetrahydro-1-methylpyridine, but we did not prove the presence of this compound in the irradiated 1-methylpiperidine.

meso-1,1′-Dimethyl-2,2′-bipiperidyl (XV) was synthesised by hydrogenation of 2,2′-bipyridyl dimethochloride in the presence of Adams catalyst and also by methylation (with formaldehyde and formic acid) of 2,2′-bipiperidyl, obtained by hydrogenation of 2,2′-bipyridyl. The products obtained by both syntheses and from the irradiation were identical, as were the corresponding crystalline derivatives. This material is therefore assumed to be the more stable *meso*-isomer. Attempts to prepare complexes with various metallic salts gave only coloured solutions.[17,23,24] We therefore investigated other possible methods for separation of *meso*- and racemic forms, making use of compounds of which we already had pure samples of both isomers, hoping thus to find a way of isolating racemic 1,1′-dimethyl-2,2′-bipiperidyl. Attempts to separate the *meso*- and the racemic form of stilbenediamine, *NN*′-diethylbutane-2,3-diamine, and *NNN*′*N*′-tetraethylbutane-2,3-diamine by electrophoresis of their salts on untreated paper or on paper impregnated

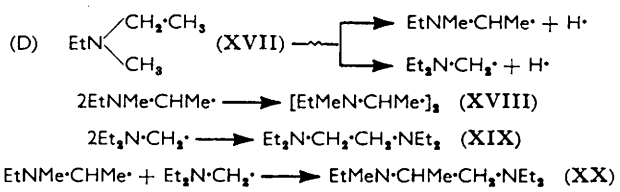
[22] Leonard and Hauck, *J. Amer. Chem. Soc.*, 1957, **79**, 5279.
[23] Morgan and Burstall, *J.*, 1930, 2594; 1931, 2213.
[24] Basolo, Chen, and Murmann, *J. Amer. Chem. Soc.*, 1954, **76**, 956.

with buffer solutions [25] or metallic salts which might be expected to form complexes, or by paper chromatography of these salts with various solvents (cf. ref. 26), gave little or no separation of isomers. The behaviour of these pairs of isomers in potentiometric or complexometric titrations was too similar to be helpful.

We also dehydrogenated *meso*-1,1′-dimethyl-2,2′-bipiperidyl with mercuric acetate (cf. ref. 22), hoping to obtain racemic 1,1′-dimethyl-2,2′-bipiperidyl by hydrogenation of the resulting base (cf. ref. 27). However, the latter resisted hydrogenation.

1-Methyl-2-(piperidinomethyl)piperidine was synthesised by treating ethyl 1-methylpiperidine-2-carboxylate with piperidine and reducing the resulting amide with lithium aluminium hydride.

Irradiation of *N*-methyldiethylamine (XVII) yielded *NNN′N′*-tetraethylethylenediamine (XIX), *meso*-*NN′*-diethyl-*NN′*-dimethylbutane-2,3-diamine (XVIII) (*G* 0·50), and *NN*-diethyl-2-ethylmethylaminopropylamine (XX). The *meso*-compound was isolated as the crystalline dihydrochloride, and the other two bases by fractional crystallisation of their picrates. These products might result if radiolysis and coupling occurred as in (D).



meso- and Racemic forms of the base (XVIII) were synthesised by methylation of the corresponding forms of *NN′*-diethylbutane-2,3-diamine (II) with formaldehyde and formic acid. With a view to the synthesis of base (XX), ethyl α-bromopropionate was treated with *N*-methylethylamine, and the resulting ethyl α-ethylmethylaminopropionate was heated with diethylamine, but even after 6 hours at 250° the bulk of it was recovered unchanged. However, α-bromo-*NN*-diethylpropionamide reacted readily with *N*-methylethylamine and the product was reduced by lithium aluminium hydride to *NN*-diethyl-2-ethylmethylaminopropylamine (XX).

Irradiation of t-butylamine yielded a liquid, b. p. 60—100° (bath)/14 mm., and a brown tar. The former gave a mixture of picrates A, B, and C (in order of decreasing solubility). The yield of liquid base was much the lowest in our series, and the recovery of crystalline compounds was also the poorest (18%). We had, therefore, only very small amounts of picrates at our disposal.

Picrate A proved to be the monopicrate of di-*NN′*-t-butylformamidine, $Bu^tN{:}CH{\cdot}NHBu^t$, identical with a specimen prepared by interaction [28] of t-butylamine and bromoform. Treatment of its hydrochloride with zinc and sodium hydroxide yielded t-butylamine, isolated as the hydrochloride. Attempts to synthesise 1,2-di-t-butylhydrazine failed. t-Butylamine was obtained by reduction of 1,1,1′,1′-tetramethylazoethane [29] with zinc and sodium hydroxide and also by alkaline dithionite at 0°. Attempts to hydrogenate the azoethane catalytically failed.[30] Klages *et al.*[31] found that the action of methylmagnesium bromide on acetone azine yielded only mono-t-butylhydrazine, because of precipitation of the mono-complex, and we also failed to obtain di-t-butylhydrazine by this reaction or by using methylmagnesium iodide.

Picrate B was the dipicrate of 1,1-dimethyl-2-t-butylaminoethylamine (XXII). The

[25] Honegger and Honegger, *Nature*, 1959, **184**, 550.
[26] Dalgliesh, *J.*, 1952, 3940.
[27] McKenna and Tulley, *J.*, 1960, 945.
[28] Cf. Davis and Yelland, *J. Amer. Chem. Soc.*, 1937, **59**, 1998.
[29] Farenhorst and Kooyman, *Rec. Trav. chim.*, 1953, **72**, 993.
[30] Beringer, Farr, and Sands, *J. Amer. Chem. Soc.*, 1953, **75**, 3984.
[31] Klages, Nober, Kircher, and Bok, *Annalen*, 1941, **547**, 1.

base was synthesised by reduction of *N*-(2-methyl-2-nitropropyl)-t-butylamine, obtained by Mannich condensation of 2-nitropropane, t-butylamine, and formaldehyde.

Picrate C was the dipicrate of 2,5-dimethylhexane-2,5-diamine (XXI). Konowalow [32] prepared this compound and reported m. p. 293°, but we found the nitration of 2,5-dimethylhexane to be very troublesome. We therefore attempted to prepare it by a number of methods. Attempts to bring about reaction of 2,5-dichloro- or 2,5-dibromo-2,5-dimethylhexane with lithium, n-butyl-lithium, or sodium nitrite [33] failed. Reaction of the sodio-derivative of 2-nitropropane with ethylene dibromide yielded only 2,3-dimethyl-2,3-dinitropropane.[34] Following Linstead, Shepard, and Weedon's general direction,[35] we electrolysed a methanolic solution of β-benzamido-β-methylbutyric acid, with the hope of obtaining *NN'*-dibenzoyl-2,5-dimethylhexane-2,5-diamine. On two occasions we isolated very small amounts of a crystalline compound believed to be this amide, but in many other attempts we obtained only gums. Hydrolysis of this amide with hydrochloric acid yielded a base, the picrate of which was not obtained pure (on account of the amount available). Finally we obtained an extremely small amount of the base (XXI) by heating 2,5-dibromo-2,5-dimethylhexane with ammonium hydroxide under pressure. This diamine is also stated [36] to be formed by the action of Fenton's reagent on t-butylamine.

The yields isolated correspond to the following *G* values: *NN'*-di-t-butylformamidine (0·026), (XXII) (0·025), and (XXI) (0·008). These contrast sharply with the much higher yields of products from amines with a α-hydrogen atom.

The formation of the second and the third of these bases might be explained if radiolysis of t-butylamine gives two different organic radicals, which can dimerise or couple (scheme E). Formation of radicals corresponding to the second type has recently been suggested in irradiated amides.[37]

$$\text{(E)}\quad \text{Bu}^t\text{NH}_2 \rightsquigarrow \begin{cases} \longrightarrow \text{Bu}^t\text{NH}\cdot + \text{H}\cdot \\ \longrightarrow \text{NH}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot + \text{H} \end{cases}$$

$$2\text{NH}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot \longrightarrow [\text{NH}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot]_2 \quad \text{(XXI)}$$

$$\text{Bu}^t\text{NH}\cdot + \cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NH}_2 \longrightarrow \text{Bu}^t\text{NH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NH}_2 \quad \text{(XXII)}$$

The position regarding the *NN'*-di-t-butylformamidine is not absolutely certain. The original t-butylamine was carefully fractionated and its mass spectrum (kindly determined by Mr. P. Kelly, M.Sc.) was indistinguishable from that already recorded for the pure compound in the American Petroleum Institute's "Catalogue of Mass Spectral Data." We are convinced that the formamidine could not have been present in the original t-butylamine; but it is more difficult to be sure that t-butyl isocyanate might not have been there, although this would be expected to react with t-butylamine during purification. If the *NN'*-di-t-butylformamidine is indeed a true irradiation product, its formation implies the radiolytic loss of a methyl group to give a fragment which supplies the central carbon atom of the formamidine. The radiolytic loss of a methyl group from t-butyl alcohol is known.[38]

Since our publications on the radiation-induced dimerisation of triethylamine [1] and benzyl alcohol [20] Henbest and Patton [39] have achieved a similar dimerisation of *NN*-dimethylaniline and dimethyl-*p*-toluidine, induced by t-butoxy-radicals generated by thermal decomposition of t-butyl peroxide, and similar reactions have been carried out on tribenzylamine by Huang [40] and on primary and secondary alcohols by Schwetlich,

[32] Konowalow, *Ber.*, 1895, **28**, 1854; *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 109.
[33] Cf. Stille and Vessel, *J. Org. Chem.*, 1960, **25**, 478.
[34] Cf. van Tamelan and Zyl, *J. Amer. Chem. Soc.*, 1949, **71**, 835.
[35] Linstead, Shepard, and Weedon, *J.*, 1951, 2854.
[36] Coffmann, Jenne, and Lipscomb, *J. Amer. Chem. Soc.*, 1958, **80**, 2864.
[37] Burrill, *J. Amer. Chem. Soc.*, 1961, **83**, 574.
[38] McDonell and Newton, *J. Amer. Chem. Soc.*, 1954, **76**, 4651.
[39] Henbest and Patton, *J.*, 1960, 3557.
[40] Huang, *J.*, 1959, 1816.

Geyer, and Hartmann.[41] The addition of amines to olefins, induced by t-butyl peroxide,[42] is considered to be a chain reaction in which the t-butoxy-radical attacks a hydrogen atom attached to an α-carbon atom of the amine, and the resulting radical derived from the amine may then attack the olefinic double bond. This reaction has a number of interesting features, one of which is the formation of **1 : 1** addition products in relatively high yield, even without the amine in excess; and this has been explained as due to chain termination by disproportionation of the radicals derived from the amine. Primary amines reacted satisfactorily but, of the secondary amines investigated, only piperidine and pyrrolidine gave satisfactory yields (perhaps because of steric and statistical effects). 1-Methylpiperidine was the only tertiary base of satisfactory behaviour and was apparently attacked only at the *N*-methylene groups, in contrast to our finding of radiolytic attack also at the methyl group. However, the yield obtained was lower than with piperidine, and it is possible that products of attack at the methyl group were not isolated. Benzoyl peroxide could not effectively replace t-butyl peroxide. As triethylamine and diethylamine gave with oct-1-ene yields too small for isolation and identification, we intend to investigate the irradiation of amine–olefin mixtures, in particular to see whether radiation might succeed in cases where t-butoxy-radicals failed for steric reasons.

Experimental

General Directions.—Arrangements for the irradiations and dosimetry were as described in Part I.[43] Except in the case of trimethylamine all irradiations were carried out at room temperature. Ultraviolet spectra were measured for ethanolic solutions by using a Unicam spectrophotometer. For unknown irradiation products, the extinction coefficients were calculated by using the molecular weight of the irradiated compound. Partition chromatography was carried out as described in Part III,[1] a weight ratio of Supercel : base of 40 : 1 being used. Except where otherwise stated, ethereal and similar extracts were dried with sodium sulphate and evaporations of aqueous and acetic acid solutions were under reduced pressure from a water-bath. For all crystalline compounds, identity claimed was established by mixed m. p. (capillary tube) and infrared spectra. Picrates were prepared in ethanolic solution, only slightly more than the expected theoretical amount of picric acid being used. Except where otherwise stated, the amines irradiated were commercial samples which had been purified by fractional distillation.

Irradiation of Diethylamine.—Diethylamine (275 ml.) was irradiated for 348 hr. (total dose $3{\cdot}51 \times 10^{23}$ ev) and unchanged material was removed by fractional distillation. The residue (2·01 g.), on redistillation, yielded a pale yellow liquid (1·70 g.), b. p. 60—110° (bath)/15 mm., consisting mainly of *meso*- and racemic *NN'*-diethylbutane-2,3-diamine (II). A solution of this mixture (0·27 g.) in benzene was saturated with dry hydrogen chloride, giving a gum which crystallised from ethanol as plates, m. p. 276° (0·16 g.), identical with racemic NN'-*diethylbutane*-2,3-*diamine dihydrochloride* (see below) (Found: C, 44·6; H, 10·2; N, 13·1. $C_8H_{20}N_2,2HCl$ requires C, 44·4; H, 10·1; N, 12·9%). The corresponding base yielded a *picrate*, m. p. 160°, identical with racemic *NN'*-diethylbutane-2,3-diamine dipicrate (Found: C, 40·1; H, 4·3; N, 18·9. $C_8H_{20}N_2,2C_6H_3N_3O_7$ requires C, 40·0; H, 4·3; N, 18·6%).

The gum left on evaporation of the ethanolic mother-liquor was basified with 40% sodium hydroxide solution and extracted with ether. Removal of ether from the dried extract yielded a yellow oil (0·12 g.), which gave a picrate, separating from ethanol–ethyl acetate (2 : 1) as plates, m. p. 214° (decomp.) (0·43 g.), identical with meso-NN'-*diethylbutane*-2,3-*diamine dipicrate* (see below) (Found: C, 40·3; H, 4·5; N, 18·8%).

Irradiation of a Mixture of Diethylamine and Bromobenzene.—An equimolecular mixture (275 ml.) of diethylamine and bromobenzene was irradiated for 406 hr. (total dose $3{\cdot}7 \times 10^{23}$ ev), then diluted with ether (200 ml.). The precipitated diethylamine hydrobromide (9·06 g.) was collected and when recrystallised from ethanol–ether had m. p. 213° (Found: C, 31·4; H, 7·4. Calc. for $C_4H_{11}N,HBr$: C, 31·2; H, 7·8%). The ether and unchanged diethylamine were removed by fractional distillation and the residue was acidified with 5N-hydrochloric

[41] Schwetlich, Geyer, and Hartmann, *Angew. Chem.*, 1960, **72**, 779.
[42] Urry and Juveland, *J. Amer. Chem. Soc.*, 1958, **80**, 3322.
[43] Swan and Timmons, *J.*, 1958, 4669.

acid and extracted with ether. The ethereal extracts, when washed with water and dried, yielded the neutral fraction (A). Basification, with 40% sodium hydroxide solution, of the acidic layer, followed by re-extraction with ether yielded the basic fraction (B).

The ether and unchanged bromobenzene were removed from material A by fractional distillation and the residue (3·74 g.) was chromatographed on alumina (110 g.). Elution with light petroleum (b. p. 40—60°) (250 ml.) yielded a mixture of crystals, m. p. 61° (0·45 g.), and an oil (0·19 g.) which probably contained bromobiphenyl. The crystals, when recrystallised from aqueous methanol, had m. p. 69° ($\lambda_{max.}$ 250 mμ, ε 15,650), identical with biphenyl; and when nitrated yielded crystals, m. p. 115° (from ethanol), identical with 4-nitrobiphenyl (Found: C, 72·2; H, 4·6. Calc. for $C_{12}H_9NO_2$: C, 72·5; H, 4·5%). Elution of the chromatogram with benzene or benzene–chloroform yielded only gums, which failed to yield 2,4-dinitrophenylhydrazones and had $\lambda_{max.}$ 260 mμ (ε 870—9750). Elution with methanol yielded a small amount of impure solid, m. p. 162—168°, perhaps a terphenyl or tetraphenyl.

Evaporation of material B yielded a residue (1·55 g.) which was subjected to partition chromatography at pH 6·5. The bases eluted (0·69 g.) were re-chromatographed at pH 5, fraction (i) being eluted and (ii) retained; and the bases retained at pH 6·5, were recovered (0·59 g.) by basification and extraction with ether and were then re-chromatographed at pH 7·5, fraction (iii) being eluted and (iv) retained.

Fraction (i) on distillation yielded the following (bath-temp./15 mm.): (*a*) b. p. 80—100° (0·23 g.), (*b*) b. p. 120—160° (0·07 g.), (*c*) b. p. 160—180° (0·05 g.), and (*d*) residue (0·15 g.). The infrared and ultraviolet spectra of (*a*) ($\lambda_{max.}$ 215, 260, and 300 mμ; ε 7110, 12,500, and 2420) resembled those of *NN*-diethylaniline, although the base was impure (Found: C, 76·0; H, 10·45. Calc. for $C_{10}H_{15}N$: C, 80·5; H, 10·1%). However it (0·1 g.) yielded a picrate (0·2 g.), needles, m. p. 139° (from ethanol), identical with diethylanilir.e picrate (Found: C, 50·2; H, 4·6. Calc. for $C_{10}H_{15}N,C_6H_3N_3O_7$: C, 50·8; H, 4·65%). Both spectra of fraction (*b*) also resembled those of diethylaniline (Found: C, 73·3; H, 9·6%), although the picrate was gummy and chromatography on alumina gave fractions, affording gummy hydrochlorides. Gummy picrates and hydrochlorides were also obtained from fraction (*c*) ($\lambda_{max.}$ 215 and 260 mμ; ε 3920 and 223) (Found: C, 79·7; H, 11·7%). Fraction (ii) on distillation yielded the following (bath-temp./15 mm.): (*a'*) b. p. 70—90° (0·11 g.), (*b'*) b. p. 120—140° (0·05 g.), (*c'*) residue (0·03 g.). Although the ultraviolet spectrum of (*a'*) ($\lambda_{max.}$ 215 and 250 mμ; (ε 4560 and 727) resembled that of benzylamine ($\lambda_{max.}$ 220 and 260 mμ; ε 3162 and 168), its infrared spectrum suggested a secondary amine (Found: C, 78·2; H, 9·95. Calc. for $C_{10}H_{15}N$: C, 80·6; H, 10·05%). This material (0·07 g.) yielded a picrate (0·12 g.), cubic crystals, m. p. 168° (from ethanol), identical with *N*-ethyl-α-methylbenzylamine picrate[4] (Found: C, 50·5; H, 4·6. Calc. for $C_{10}H_{15}N,C_6H_3N_3O_7$: C, 50·8; H, 4·65%). No crystalline picrate or hydrochloride was obtained from fraction (*b'*) (Found: C, 76·1; H, 7·65%). Fraction (iii) on distillation yielded the following (bath-temp./15 mm.): (*a''*) b. p. 60—100° (0·17 g.), (*b''*) 100—140° (0·10 g.), (*c''*) b. p. 140—190° (0·07 g.), (*d''*) residue (0·07 g.). The spectrum of (*a''*) showed $\lambda_{max.}$ 220 and 260 mμ (ε 6650 and 775) (Found: C, 70·3; H, 13·1. Calc. for $C_8H_{20}N_2$: C, 66·65; H, 13·9%) and this material (0·05 g.) yielded a picrate (0·13 g.) which, when recrystallised from ethanol, formed plates, m. p. 210—215° (decomp.) (0·12 g.), identical with *meso-NN'*-diethylbutane-2,3-diamine dipicrate (Found: C, 40·3; H, 4·6%). Only a gummy hydrochloride was obtained from fractions (*a''*) and (*b''*) ($\lambda_{max.}$ 215 and 260 mμ; ε 1982 and 316) (Found: C, 69·8; H, 12·1%). The latter (0·015 g.) yielded *meso-NN'*-diethylbutane-2,3-diamine dipicrate, m. p. 212—215° (decomp.) (0·011 g.) (Found: C, 40·1; H, 4·7%). No crystalline derivatives were obtained from fraction (*c''*) ($\lambda_{max.}$ 220 and 260 mμ; ε 2650 and 740) (Found: C, 72·6; H, 11·3%). Fraction (iv) on distillation yielded three fractions (bath-temp./15 mm.): b. p. 60—80° (0·05 g.), b. p. 100—120° (0·03 g.), b. p. 140—160° (0·004 g.). The spectrum of the first showed $\lambda_{max.}$ 215 and 255 mμ (ε 3840 and 685) (Found: C, 65·5; H, 15·4%), and that of the second $\lambda_{max.}$ 215 and 255 mμ (ε 2840 and 371) (Found: C, 67·5; H, 13·2%). No crystalline derivatives were obtained from any of these fractions.

meso- *and Racemic* NN'-*Diethylbutane*-2,3-*diamine* (II).—A mixture (46 g.) of *meso*- and racemic *NN'*-diacetylbutane-2,3-diamine, obtained by acetylation of the reduction product (28 g.) of dimethylglyoxime,[44] was fractionally crystallised from acetone; it yielded the *meso*-diamide (21·2 g.), m. p. 281°, and the more soluble racemic diamide (18·8 g.), m. p. 179°. A warm solution of the latter (5 g.) in tetrahydrofuran (250 ml.) was added with stirring, during

[44] Dickey, Fickett, and Lucas, *J. Amer. Chem. Soc.*, 1952, **74**, 944.

30 min., to lithium aluminium hydride (2 g.) in tetrahydrofuran (75 ml.), and the mixture was refluxed for 2½ hr., cooled in ice, and treated with ethyl acetate (20 ml.), followed by 6N-hydrochloric acid (100 ml.). The ethereal layer was removed and the aqueous layer was extracted with ether, then evaporated to a syrup. A concentrated, aqueous solution of the latter was dropped gradually into hot, concentrated potassium hydroxide solution, and the mixture was distilled. The distillate was cooled in ice and saturated with potassium hydroxide, and the organic layer was dried (KOH) and distilled, yielding the racemic diamine (1·26 g.), b. p. 60—80° (bath)/12 mm., the dipicrate of which separated from dimethylformamide–ethanol as plates, m. p. 160° (decomp.) (Found: C, 39·95; H, 4·25%). A solution of the diamine in benzene, when treated with dry hydrogen chloride, yielded a gum which crystallised from ethanol, affording the racemic dihydrochloride as plates, m. p. 276° (Found: C, 44·7; H, 10·4; N, 13·2%). The racemic NN′-*dibenzoyl derivative* separated from ethanol as cubes, m. p. 104° (Found: C, 74·8; H, 8·4; N, 7·4. $C_{32}H_{28}N_2O_2$ requires C, 75·0; H, 8·0; N, 8·0%), and was obtained from the base by treatment with benzoyl chloride in pyridine.

Reduction of the *meso*-diamide (5 g.) by lithium aluminium hydride (2·2 g.) in tetrahydrofuran (250 ml.), by the Soxhlet method, yielded the meso-diamine (1·22 g.), b. p. 50—70° (bath)/12 mm., the dipicrate of which separated from dimethylformamide–ethanol as plates, m. p. 214° (decomp.) (Found: C, 40·3; H, 4·6%), and the hydrochloride of which was a gum. The meso-NN′-*dibenzoyl* derivative separated from ethanol–ether (1 : 8) as cubic crystals, m. p. 150° (Found: C, 75·0; H, 8·6; N, 7·6%).

Attempts to Separate a Mixture of meso- *and Racemic* NN′-*Diethylbutane*-2,3-*diamine*.—(*a*) Treatment of the racemic base (0·1 g.) with a 20% solution of carbonyl chloride in benzene (0·5 g.) yielded the dihydrochloride, m. p. 276° (0·05 g.) (Found: C, 44·8; H, 10·3; N, 13·3%), suggesting that reaction had occurred; but evaporation of the benzene mother-liquor yielded only a gum. The *meso*-base gum gave a similar result (cf. Boon [45]). (*b*) Both the *meso*- and the racemic dihydrochloride afforded blue complexes with cobalt(II), but these could not be separated by fractional crystallisation. (*c*) Separation of a mixture of the *meso*- (0·2 g.) and the racemic (0·2 g.) base, as described in the case of the corresponding mixtures obtained from the irradiation of diethylamine, gave the *meso*-dipicrate, m. p. 214° (0·79 g., 77% recovery), and the racemic dihydrochloridc, m. p. 276° (0·23 g., 74% recovery).

1,2-*Diethylhydrazine*.—*NN′*-Diethylidenehydrazine [46] was hydrogenated in ethanolic solution containing concentrated hydrochloric acid in the presence of Adams catalyst at 4 atm. The hydrochloride was obtained in 30% yield by evaporation of the solution.

1,2-*Diacetyl*-1,2-*diethylhydrazine*.—A mixture of 1,2-diethylhydrazine dihydrochloride (3·5 g.) and acetic anhydride (30 ml.) was refluxed for 2½ hr., poured into water (200 ml.), basified with sodium carbonate, and extracted with chloroform. Removal of the chloroform from the dried (K_2CO_3) extract yielded the *product* (2·25 g.), b. p. 140—160° (bath)/14 mm. (Found: C, 54·4; H, 9·1. $C_8H_{16}N_2O_2$ requires C, 55·8; H, 9·3%).

Tetraethylhydrazine (IV).—A solution of the above compound (2·25 g.) in ether (7 ml.) was added gradually to an ice-cold solution of lithium aluminium hydride (0·55 g.) in ether (12 ml.). The mixture was refluxed for 50 min., then treated with water (8 ml.), and the ether was removed through a fractionating column. The residue was distilled after addition of sodium hydroxide (4 g.) in water (5 ml.). The distillate up to 100° was cooled and saturated with potassium hydroxide. The resulting oil was separated and the aqueous layer was extracted with ether (7 ml.). The combined organic layers were dried (K_2CO_3) and fractionated, yielding the base as an oil (1·28 g.), b. p. 40—50° (bath)/17 mm., which afforded a *monopicrate*, separating from a small volume of ethanol as needles, m. p. 134° (Found: C, 45·2; H, 6·4. $C_8H_{20}N_2,C_6H_3N_3O_7$ requires C, 45·0; H, 6·2%).

Irradiation of Trimethylamine.—Trimethylamine (275 ml.) was irradiated at −78° for 322 hr. (total dose $2·41 \times 10^{23}$ ev) and unchanged material was then removed by fractional distillation. The residue (2·52 g.) on distillation yielded a mixture of bases (2·22 g.), b. p. 70—125°. The above operations were carried out under dry nitrogen.

Treatment of the mixture of bases (0·2 g.) with ethanolic picric acid (0·92 g.) gave a precipitate (0·55 g.) which, when recrystallised from dimethylformamide–ethanol, yielded needles, m. p. 263° (decomp.) (0·52 g.), identical with *NNN′N′*-tetramethylethylenediamine dipicrate (Found: C, 37·5; H, 3·9; N, 19·4. Calc. for $C_6H_{16}N_2,2C_6H_3N_3O_7$: C, 37·7; H, 3·8;

[45] Boon, *J.*, 1947, 307.
[46] Mailhe, *Bull. Soc. chim. France*, 1920, **22**, 541.

N, 19·6%). Concentration of the ethanolic mother-liquor gave needles, m. p. 155° (0·18 g.), of dimethylamine picrate.

An aqueous solution of the mixture of bases (0·2 g.) was dropped into 20% hydrochloric acid (7 ml.), and the mixture was distilled into a receiver containing water (10 ml.), followed by an absorption train of three cooled traps, each containing water. When most of the water had distilled, the residue was evaporated to dryness and the residual gum crystallised from ethanol, affording a solid (0·18 g.) which separated from aqueous ethanol as plates, m. p. 300° (decomp.) (0·17 g.), identical with *NNN'N'*-tetramethylethylenediamine dihydrochloride (Found: C, 38·2; H, 9·3; N, 14·8. Calc. for $C_6H_{16}N_2,2HCl$: C, 38·2; H, 9·5; N, 14·8%). The ethanolic mother-liquor was evaporated to dryness and the residue was treated with 40% sodium hydroxide solution and extracted with ether. The dried, ethereal extract was treated with ethanolic picric acid (0·4 g.) and evaporated to dryness. The resulting gum crystallised from ethanol–ether. Crystallisation of the product from ethanol–ether then afforded a compound, m. p. 156° (0·16 g.), identical with dimethylamine picrate. The amount of formaldehyde present in the water distilled off and determined by Johnson and Scholes's method [47] was $0·44 \times 10^{-3}$ mole (corresponding to 0·045 g. of *NNN'N'*-tetramethylmethylenediamine).

The product from trimethylamine, which had been irradiated in the presence of air, was fractionated, yielding, apart from the above bases, a product, b. p. 155° the infrared spectrum of which was identical with that of *NN*-dimethylformamide (Found: C, 49·0; H, 9·45. Calc. for C_3H_7NO: C, 49·3; H, 9·6%).

Tetramethylhydrazine (VII).—This was prepared by Beltrami and Bissel's method [48] and afforded a gummy hydrochloride, but a *monopicrate* separating from ethanol as needles, m. p. 212° (Found: C, 37·9; H, 4·7; N, 22·2. $C_4H_{12}N_2,C_6H_3N_3O_7$ requires C, 37·9; H, 4·7; N, 22%).

NNN'N'-*Tetramethylethylenediamine* (VI).—This was prepared by Freund and Michael's method.[49] The dipicrate separated from dimethylformamide–ethanol as needles, m. p. 263° (decomp.), in agreement with the value given by Hanhart and Ingold [50] rather than that (252°) given by Knorr [51] (Found: C, 37·6; H, 3·8; N, 19·6. Calc. for $C_6H_{16}N_2,2C_6H_3N_3O_7$: C, 37·7; H, 3·8; N, 19·6%).

NNN'N'-*Tetramethylmethylenediamine* (VIII).—This was prepared by Jones and Whalen's method.[52] When treated with ethanolic picric acid, it yielded formaldehyde and dimethylamine picrate, needles, m. p. 156° (from ethanol–ether) (Found: C, 34·7; H, 3·5; N, 19·6. Calc. for $C_2H_7N,C_6H_3N_3O_7$: C, 35·0; H, 3·65; N, 20·4%) (cf. ref. 53).

Separation of a Mixture of NNN'N'-*Tetramethylethylenediamine* (VI), *Tetramethylhydrazine* (VII), *and* NNN'N'-*Tetramethylmethylenediamine* (VIII).—A mixture of 0·1 g. of each of the three bases when treated with hydrochloric acid, as for the irradiation product of trimethylamine, yielded *NNN'N'*-tetramethylethylenediamine dihydrochloride, m. p. 300° (decomp.) (0·14 g., 86% recovery), tetramethylhydrazine monopicrate, m. p. 212° (0·28 g., 78% recovery), dimethylamine picrate, m. p. 155° (0·10 g., 41% yield), and formaldehyde ($0·855 \times 10^{-3}$ mole, corresponding to 0·087 g. of tetramethylmethylenediamine, 87% yield).

Irradiation of Benzylamine.—Benzylamine (275 ml.) was irradiated for 330 hr. (total dose $2·69 \times 10^{23}$ ev), then fractionated to give material A, b. p. <187° (265 ml.), and B, a brown, oily residue.

Material A consisted mainly of unchanged benzylamine. A portion (25 ml.) was treated with 5N-hydrochloric acid and the mixture was extracted with ether. The dried extract, on evaporation, yielded an oil (0·062 g.) which gave benzaldehyde 2,4-dinitrophenylhydrazone (0·16 g.), needles, m. p. 234° (from ethyl acetate–chloroform) (Found: C, 54·3; H, 3·3. Calc. for $C_{13}H_{10}N_4O_4$: C, 54·5; H, 3·5%).

Residue B was treated with 5N-hydrochloric acid and the resulting grey precipitate was collected, washed with 5N-hydrochloric acid, and recrystallised from aqueous ethanol, giving colourless plates, m. p. 252—253° (3·40 g.), of *meso*-stilbenediamine dihydrochloride (Found: C, 58·6; H, 6·0. Calc. for $C_{14}H_{16}N_2,2HCl$: C, 59·0; H, 6·3%). The latter, when decomposed

[47] Johnson and Scholes, *Analyst*, 1954, **79**, 217.
[48] Beltrami and Bissel, *J. Amer. Chem. Soc.*, 1956, **78**, 2467.
[49] Freund and Michael, *Ber.*, 1897, **30**, 1385.
[50] Hanhart and Ingold, *J.*, 1927, 997.
[51] Knorr, *Ber.*, 1904, **37**, 3507.
[52] Jones and Whalen, *J. Amer. Chem. Soc.*, 1925, **47**, 1351.
[53] Henry, *Bull. Acad. roy. Belg.*, 1894, **28**, 368; Snow and Stones, *J.*, 1923, **123**, 1509.

with sodium hydroxide solution, gave the base, isolated by ether and crystallised from light petroleum (b. p. 80—100°) as needles, m. p. 117°, identical with *meso*-stilbenediamine (IX) (Found: C, 78·75; H, 7·9; N, 13·0. Calc. for $C_{14}H_{16}N_2$: C, 79·2; H, 7·6; N, 13·2%) ($\lambda_{max.}$ 226, 255, 260, 264, and 346 mμ; ε 10,870, 500, 620, 462, and 42). This afforded a picrate, m. p. and mixed m. p. 240° (decomp.) (Found: C, 46·8; H, 3·6; N, 17·05. Calc. for $C_{14}H_{16}N_2,2C_6H_3N_3O_7$: C, 46·5; H, 3·3; N, 16·7%). With nickel chloride the dihydrochloride yielded only the yellow *meso*-complex.

The acidic solution, from which the diamine dihydrochloride had been filtered, was extracted with ether. The extract was shaken with 40% sodium hydrogen sulphite solution, and the aqueous layer was refluxed with concentrated hydrochloric acid, then distilled in steam. The distillate (170 ml.) was extracted with ether; the residue from the evaporated extract yielded benzaldehyde 2,4-dinitrophenylhydrazone, needles, m. p. 234—235° (1·03 g.) (from ethyl acetate–chloroform) (Found: C, 54·25; H, 3·4%). The ethereal extract which had been treated with sodium hydrogen sulphite was evaporated and the residue (0·49 g.) was chromatographed on alumina (13 g.). Light petroleum (b. p. 40—60°) (200 ml.) eluted a fraction (0·07 g.) which, when distilled, yielded a colourless solid, m. p. 51°, the ultraviolet spectrum of which ($\lambda_{max.}$ 220 and 260 mμ; ε 15,620 and 540) resembled that of bibenzyl (X); on nitration [54] this solid yielded 2,2′,4,4′-tetranitrobibenzyl, separating from acetic acid as needles, m. p. 168° (Found: C, 46·1; H, 4·3; N, 15·9. Calc. for $C_{14}H_{16}N_4O_8$: C, 45·6; H, 4·35; N, 15·2%). Subsequent eluates from the chromatogram yielded oils or gums with strong absorption around 220 and 320 mμ.

The acidic solution, which had been extracted with ether after removal of the diamine dihydrochloride, was basified and extracted with ether. Removal of ether from the dried extract gave a brown oil (0·58 g.), which was subjected to partition chromatography at pH 6·5. The eluted material was re-chromatographed at pH 5, fraction (i) (0·21 g.) being eluted and (ii) (0·003 g.) retained. The material retained at pH 6·5 was re-chromatographed at pH 7·5, fraction (iii) (0·08 g.) being eluted and (iv) (0·22 g.) retained.

Fraction (i) on distillation yielded the following (bath-temp./15 mm.): (*a*) b. p. 120—140° (0·03 g.), (*b*) b. p. 180—220° (0·09 g.), and (*c*) b. p. 270—310° (0·07 g.). Fraction (*a*) probably consisted of a mixture of *N*-benzylidenebenzylamine (XII) with a little benzylamine ($\lambda_{max.}$ 215 and 250 mμ; ε 1650 and 774) (Found: C, 83·1; H, 7·85%), and when treated with picric acid it yielded benzaldehyde and benzylamine picrate, m. p. 200° (Found: C, 46·3; H, 3·8. Calc. for $C_7H_9N,C_6H_3N_3O_7$: C, 46·5; H, 3·6%). Fraction (*b*) appeared to be almost pure *N*-benzylidenebenzylamine ($\lambda_{max.}$ 210 and 245 mμ; ε 6500 and 2090) (Found: C, 86·5; H, 6·75. Calc. for $C_{14}H_{13}N$: C, 86·2; H, 6·7%), and its infrared spectrum was nearly identical with that of the latter. When treated with picric acid or hydrochloric acid it yielded benzaldehyde and products which were identical with the picrate (Found: C, 47·1; H, 3·6%) and hydrochloride, respectively, of benzylamine. In these salts, the strong absorption at 1645 cm.$^{-1}$ of *N*-benzylidenebenzylamine is missing. Fraction (*c*) possibly contained dibenzylamine, or some related compound, although it failed to give crystalline derivatives (Found: C, 85·1; H, 7·55. Calc. for $C_{14}H_{15}N$: C, 85·2; H, 7·65%). It lacked strong absorption at 1645 cm.$^{-1}$ ($\lambda_{max.}$ 210 and 255 mμ; log ε 10,200 and 2450).

Fraction (ii) yielded benzylamine picrate, m. p. 200°.

Fraction (iii), when kept with light petroleum (b. p. 40—60°) in a refrigerator, afforded needles which, when recrystallised from light petroleum (b. p. 80—100°), had m. p. 117°, identical with *meso*-stilbenediamine (Found: C, 78·95; H, 7·4; N, 13·6%). This afforded only the yellow nickel chloride complex.

Fraction (iv) appeared to consist mainly of benzylamine (Found: C, 78·4; H, 8·4. Calc. for C_7H_9N: C, 78·5; H, 8·45%). Its ultraviolet ($\lambda_{max.}$ 220 and 260 mμ; ε 2870 and 640) and infrared spectra were very similar to those of benzylamine ($\lambda_{max.}$ 220 and 260 mμ; ε 3230 and 168), and its picrate, needles, m. p. 200—201°, was identical with benzylamine picrate.

N-*Benzylidenebenzylamine* (XII).—This was prepared by Mason and Winder's method,[10] had b. p. 200°/15 mm., and with ethanolic picric acid yielded benzaldehyde and benzylamine picrate, m. p. 200° (Found: C, 46·6; H, 3·8%). Treatment with hydrochloric acid likewise gave benzaldehyde and benzylamine hydrochloride.

meso- *and Racemic Stilbenediamine* (IX).—*meso*-Stilbenediamine, prepared by Darapsky and Spannagel's method,[11] was converted into the nickel(II) chloride complex as described

[54] von Braun and Rawicz, *Ber.*, 1916, **49**, 799.

by Lifschitz, Bos, and Dijkema,[16] only the yellow complex being obtained. A solution of this complex (0·52 g.) in ethanol (15 ml.) was treated with 20% sodium hydroxide solution (15 ml.), then saturated with hydrogen sulphide and centrifuged. The clear liquid was extracted with ether, and the residue from the dried extract separated from light petroleum (b. p. 100—120°) as pale yellow needles, m. p. 118° (0·39 g.), of *meso*-stilbenediamine, affording a picrate, m. p. 240° (decomp.).

Feist's method [13] for the preparation of the racemic diamine gave a product, m. p. 68—72°, which was converted into its hydrochloride. The latter (0·6 g.) when treated [15] with nickel chloride gave a complex which separated from ethanol as purple rhombs (0·43 g.). Concentration of the mother-liquor yielded yellow cubes (0·09 g.) which, when decomposed by hydrogen sulphide, afforded a base, m. p. 118°, identical with *meso*-stilbenediamine and giving the same picrate, m. p. 240° (decomp.), as the latter. Decomposition of the purple complex yielded the racemic diamine, separating from light petroleum (b. p. 80—100°) as cream needles, m. p. 83° (0·3 g.), which afforded a picrate, plates, m. p. 220° (decomp.) (from ethanol), and a hydrochloride, colourless plates, m. p. 247° (from aqueous ethanol).

Separation of meso- *and Racemic Stilbenediamine.*—A mixture of the *meso*- and racemic diamine dihydrochlorides (0·6 g. of each) was converted into the mixed nickel chloride complexes, which were dissolved in hot ethanol to give a green solution which, on cooling, deposited the purple racemic complex. The latter was filtered off. The yellow filtrate, when concentrated, gave cubes of the yellow *meso*-complex. The two complexes were recrystallised from ethanol and decomposed with hydrogen sulphide, and the resulting bases were recrystallised from light petroleum (b. p. 100—120° for the *meso*- and 80—100° for the racemic base), affording the *meso*- (m. p. 118°; 0·41 g., 92% recovery) and the racemic (m. p. 83°; 0·43 g., 96% recovery) diamine.

Irradiation of Phenethylamine.—Phenethylamine (275 ml.) was irradiated for 216 hr. (total dose $1·73 \times 10^{23}$ ev). The unchanged base was removed by fractional distillation and the residue was acidified with hydrochloric acid and extracted first with ether (A), then with chloroform (B). The aqueous layer was basified with 40% sodium hydroxide solution and extracted with ether (C). The three extracts were washed with water, dried, and evaporated. Residue A (0·2 g.) was chromatographed on alumina, but only gums were obtained. Residue B (1·18 g.) was chromatographed on alumina (38 g.); elution with benzene, chloroform, or mixtures yielded gums. The gums eluted by chloroform–methanol (9 : 1) and finally methanol were combined, dissolved in ether, and washed with dilute hydrochloric acid. The residue from the dried, ethereal extract was a solid which when recrystallised from methanol–chloroform weighed 2 mg. and had m. p. 126—127° and $\lambda_{max.}$ 220 and 260 mμ (ε 3978 and 1850), identical with the values for *meso*-2,3-diphenylbutane.[21] The gums from both chromatograms had $\lambda_{max.}$ 215 and 260 mμ (ε *ca.* 5500 and 4500). Attempts to distil residue C (2·73 g.) under reduced pressure led to decomposition.

Irradiation of 1-*Methylpiperidine.*—Commercial 1-methylpiperidine (350 ml.) was refluxed for 3 hr. with benzoic anhydride (7 g.) and then fractionated, the infrared spectrum of the purified base indicating the absence of secondary amine. The purified base (275 ml.) was irradiated for 386 hr. (total dose $3·56 \times 10^{23}$ ev), then the unchanged base was removed by fractional distillation (b. p. $<107°$). The distillate contained piperidine, as shown by refluxing it for 3 hr. with benzoic anhydride (7 g.), followed by fractional distillation. The residue (b. p. $>107°$) from the latter was dissolved in ether and shaken first with 10% hydrochloric acid (5×25 ml.), then with 30% sodium hydroxide solution (5×25 ml.), and finally with water. Distillation of the dried, ethereal extract yielded a liquid (0·21 g.), b. p. 150—160° (bath)/15 mm., the infrared spectrum of which was identical with that of 1-benzoylpiperidine (Found: C, 76·2; H, 8·1; N, 7·7. Calc. for $C_{12}H_{15}NO$: C, 76·2; H, 7·9; N, 7·45%).

The residue, from which the unchanged 1-methylpiperidine (containing piperidine) had been removed after the irradiation, was distilled, giving a brown oil (2·27 g.), b. p. 70—80°/13 mm., and a black, gummy residue (1·63 g.). An ethanolic solution of the brown oil (1 g.) was saturated with dry hydrogen chloride, then evaporated to give a gum which crystallised from ethanol to yield a colourless solid (0·18 g.). Concentration of the mother-liquor yielded a further crop of the latter (0·11 g.). The combined precipitates recrystallised from aqueous ethanol as plates (0·26 g.), m. p. 256° (sealed capillary), identical with 1,2-*dipiperidinoethane dihydrochloride* (see below) (Found: C, 53·5; H, 9·7; N, 10·2. $C_{12}H_{24}N_2,2HCl$ requires C, 53·6; H, 9·7; N, 10·4%).

The above ethanolic mother-liquor was evaporated to a gum, which was then treated with 30% sodium hydroxide solution and extracted with ether. An ethanolic solution of the oil (0·74 g.) left by evaporation of the ethereal extract was saturated with dry hydrogen bromide and then evaporated to a gum, which crystallised from ethanol, yielding a solid (0·59 g.). Concentration of the mother-liquor and dilution with ether gave further solid (0·13 g.). The combined solid recrystallised from aqueous ethanol as plates, m. p. 261° (0·70 g.), identical with meso-1,1′-*dimethyl*-2,2′-*bipiperidyl dihydrobromide* (Found: C, 40·0; H, 7·1; N, 7·7. $C_{12}H_{24}N_2$,2HBr requires C, 40·2; H, 7·3; N, 7·8%).

Evaporation of the mother-liquor from which the *meso*-dihydrobromide had been obtained gave a gum (0·59 g.), which was basified with 30% sodium hydroxide solution and extracted with ether. The oil (0·31 g.) left on evaporation of the ethereal extract was distilled, yielding a pale yellow oil (0·29 g.), b. p. 125—135° (bath)/13 mm., consisting of almost pure 1-*methyl*-2-(*piperidinomethyl*)*piperidine* (XVI) (Found: C, 73·2; H, 12·1; N, 14·8. $C_{12}H_{24}N_2$ requires C, 73·5; H, 12·2; N, 14·3%). The infrared spectrum of the oil was almost identical with that of the latter compound and was different from that of 1,2-dipiperidinoethane and *meso*-1,1′-dimethyl-2,2′-bipiperidyl. It had peaks of low intensity at 1595 and 1653 cm.$^{-1}$ which were lacking in the spectrum of 1-methyl-2-(piperidinomethyl)piperidine. The oil (0·07 g.) when treated with ethanolic picric acid (0·16 g.) gave a solid (0·20 g.) which recrystallised from dimethylformamide–ethanol as plates, m. p. 206—207° (decomp.) (0·16 g.), identical with 1-*methyl*-2-(*piperidinomethyl*)*piperidine dipicrate* (see below) (Found: C, 44·2; H, 4·8; N, 17·4. $C_{12}H_{24}N_2$,2$C_6H_3N_3O_7$ requires C, 44·1; H, 4·6; N, 17·2%).

1,2-*Dipiperidinoethane* (XIV).—This was prepared by Bruhl and Warschau's method [55] and had b. p. 263°/756 mm., 132°/14 mm. The dihydrochloride separated from aqueous ethanol as plates, m. p. 255° (sealed capillary) (Found: C, 53·4; H, 9·9; N, 10·3%). The dipicrate [56] separated from dimethylformamide–ethanol as needles, m. p. 225°.

meso-1,1′-*Dimethyl*-2,2′-*bipiperidyl* (XV).—(1) 2,2′-Bipyridyl dimethiodide [57] (3·25 g.) was refluxed and stirred in 50% aqueous methanol (150 ml.) with freshly prepared silver chloride (4 g.) for 4 hr. and the mixture was then filtered. The filtrate was treated with concentrated hydrochloric acid (5 ml.) and filtered through Supercel. Evaporation of the filtrate yielded a solid which crystallised from methanol–ether as colourless needles (1·85 g.) of 2,2′-*bipyridyl dimethochloride*, which sublimed at 260° without melting (Found: C, 52·3; H, 6·0; N, 9·5. $C_{12}H_{14}N_2Cl_2,H_2O$ requires C, 52·5; H, 5·8; N, 10·2%). A solution of this (1·6 g.) in acetic acid (50 ml.) was hydrogenated for 24 hr. at 90 atm. in the presence of Adams catalyst (0·15 g.). The catalyst was filtered off, the filtrate was evaporated, and the residue was treated with 40% sodium hydroxide solution (25 ml.) and extracted with ether. Distillation of the dried, ethereal extract yielded meso-1,1′-*dimethyl*-2,2′-*bipiperidyl* (XV) (1·25 g.), b. p. 130—145° (bath)/15 mm. (Found: C, 73·4; H, 12·6; N, 14·1. $C_{12}H_{24}N_2$ requires C, 73·5; H, 12·3; N, 14·3%). The *dipicrate* separated from dimethylformamide–ethanol as needles, m. p. 226° (Found: C, 44·1; H, 4·7; N, 17·4. $C_{12}H_{24}N_2$,2$C_6H_3N_3O_7$ requires C, 44·1; H, 4·6; N, 17·2%). Refluxing the base in methanol with excess of methyl iodide for 6 hr. yielded the *monomethiodide*, cubes, m. p. 155° (from methanol–ether) (Found: C, 44·8; H, 7·8. $C_{13}H_{27}IN_2$ requires C, 46·0; H, 8·0%); but reaction in a sealed tube for 3 hr. at 100° gave the *dimethiodide*, plates, m. p. 272° (from methanol–ether) (Found: C, 35·3; H, 6·8; N, 5·4. $C_{14}H_{30}I_2N_2$ requires C, 35·0; H, 6·3; N, 5·8%). The *dihydrochloride* separated from ethanol–ether as plates, m. p. 260° (Found: C, 53·2; H, 9·5; N, 10·1. $C_{12}H_{24}N_2$,2HCl requires C, 53·5; H, 9·7; N, 10·4%). The dihydrobromide separated from aqueous ethanol as plates, m. p. 261° (Found: C, 39·7; H, 7·4; N, 7·7%). There was no evidence of the presence of an isomer in the mother-liquors from which any of the above derivatives had been obtained.

(2) A solution of 2,2′-bipyridyl (0·42 g.) in acetic acid (30 ml.) absorbed 6 mol. of hydrogen during 96 hr. in the presence of Adams catalyst (0·2 g.). Concentrated hydrochloric acid (10 ml.) was added to the filtered solution, which was then evaporated to dryness and the residue was basified with sodium hydroxide and extracted with ether. Distillation of the extract yielded an oil (0·42 g.), b. p. 110—120° (bath)/13 mm., the ultraviolet spectrum of which indicated complete reduction. This 2,2′-bipiperidyl was heated with 90% formic acid (3 ml.) and 40% aqueous formaldehyde (3·5 ml.) in a sealed tube for 14 hr. at 130°. The

[55] Bruhl and Warschau, *Ber.*, 1871, **4**, 738.
[56] Knorr, Hörlein, and Roth, *Ber.*, 1905, **38**, 3136.
[57] Blau, *Monatsh.*, 1889, **10**, 382.

product was acidified with concentrated hydrochloric acid (5 ml.) and evaporated to dryness. The residue was basified with 40% sodium hydroxide solution and extracted with ether. Distillation of the extract yielded *meso*-1,1′-dimethyl-2,2′-bipiperidyl (0·46 g.), b. p. 130—150° (bath)/15 mm. (Found: C, 73·6; H, 12·7, N, 14·0%), identical in infrared spectrum with the base obtained by method (1) and yielding the same picrate, hydrochloride, hydriodide, and methiodide. Again, no indication was obtained of the presence of an isomer.

1-*Methyl*-2-(*piperidinomethyl*)*piperidine* (XVI).—Ethyl piperidine-2-carboxylate [58] (4·2 g.) was heated in a sealed tube for 6 hr. at 250° with piperidine (4·2 g.). The product was distilled up to 130°/22 mm. and the residue was treated with ether, giving a solid (0·41 g.) which recrystallised from ethanol–ether as plates, m. p. 215° (Found: C, 57·4; H, 10·0. $C_{11}H_{24}N_2O_3$ requires C, 57·2; H, 10·0%). A further crop (0·09 g.) of this *piperidine carbonate* was filtered off after concentration of the ethereal mother-liquor, and the filtrate was then distilled, yielding 1-(*piperidine*-2-*carbonyl*)*piperidine* (1·96 g.), b. p. 125—130° (bath)/0·03 mm., 185—190° (bath)/15 mm. (Found: C, 68·6; H, 10·6; N, 12·9. $C_{12}H_{22}N_2O$ requires C 68·5; H, 10·5; N, 13·3%), which showed strong absorption at 1637 cm.$^{-1}$.

A solution of this amide (1·1 g.) in ether (7 ml.) was added with stirring to lithium aluminium hydride (0·5 g.) in ether (60 ml.) and the mixture was stirred for 2 hr. at 20°, then for 1 hr. under reflux. Ethyl acetate (15 ml.) was added to the cooled solution, followed by 20% hydrochloric acid (20 ml.). The ethereal layer was separated and the aqueous layer was extracted with ether (2 × 20 ml.), then evaporated to dryness. The residue was basified with 40% sodium hydroxide solution and extracted with ether. Distillation of the ethereal extract yielded the base as a liquid (0·81 g.), b. p. 130—140° (bath)/17 mm., which afforded a dipicrate, separating from dimethylformamide–ethanol as plates, m. p. 207—208° (decomp.) (Found: C, 44·3; H, 4·7; N, 17·0%). The hydrochloride and hydrobromide were soluble in ethanol and failed to crystallise.

Separation of a Mixture of 1,2-*Dipiperidinoethane* (XIV), meso-1,1′-*Dimethyl*-2,2′-*bipiperidyl* (XV), *and* 1-*Methyl*-2-(*piperidinomethyl*)*piperidine* (XVI).—A mixture of 0·2 g. of each of the three bases, when separated as described for the irradiation products of 1-methylpiperidine, yielded 1,2-dipiperidinoethane dihydrochloride, m. p. 254° (sealed capillary) (0·22 g., 80% recovery), *meso*-1,1′-dimethyl-2,2′-bipiperidyl dihydrobromide, m. p. 261° (0·30 g., 83% recovery), and 1-methyl-2-(piperidinomethyl)piperidine dipicrate, m. p. 206° (0·48 g., 72% recovery).

Irradiation of N-*Methyldiethylamine*.—The base, prepared by Robinson and Robinson's method,[59] was refluxed with sodium, then fractionated. Gas-chromatography showed the high purity of the product. This base (275 ml.) was irradiated for 358 hr. (total dose 2·84 × 10^{23} ev) and the unchanged base was removed by fractionation, leaving a yellow residue (3·03 g.) which, on distillation, afforded a mixture of bases (2·71 g.), b. p. 60—80° (bath)/14 mm. A solution of this mixture (1·5 g.) in ethanol (15 ml.) was saturated with hydrogen chloride, then evaporated to a gum which crystallised from ethanol–ether, affording a solid (0·34 g.) which recrystallised from ethanol–ether as plates, m. p. 239° (0·32 g.), identical with meso-NN′-*diethyl*-NN′-*dimethylbutane*-2,3-*diamine* (XVIII) *dihydrochloride* (Found: C, 48·7; H, 10·9; N, 11·9. $C_{10}H_{24}N_2$,2HCl requires C, 49·0; H, 10·6; N, 11·4%). This hydrochloride was converted into a picrate, m. p. 203° (decomp.), identical with authentic material.

Evaporation of the original ethanolic mother-liquor gave a gummy mixture of hydrochlorides, from which the bases were recovered and then converted into picrates. Fractional crystallisation from acetone–ethanol afforded a less soluble picrate, m. p. 242—243° (decomp.), identical with *NNN′N′*-tetraethylethylenediamine dipicrate (Found: C, 41·65; H, 4·7. Calc. for $C_{10}H_{24}N_2$,$2C_6H_3N_3O_7$: C, 41·9; H, 4·8%). Concentration of the mother-liquor afforded a more soluble picrate which, although it was subsequently recrystallised many times from acetone–ethanol, was probably not quite pure and had then m. p. 160—169° (Found: C, 42·3; H, 4·5%). The infrared spectrum of the latter was, however, indistinguishable from that of *NN*-diethyl-2-ethylmethylaminopropylamine dipicrate and a mixture melted at 162—167°.

NNN′N′-*Tetraethylethylenediamine* (XIX).—This was prepared by Hofmann's method [60] and had b. p. 186°/758 mm., 70—75° (bath)/14 mm. The *dipicrate* separated from dimethylformamide–ethanol as needles, m. p. 242° (decomp.) (Found: C, 42·1; H, 5·0; N, 18·3.

[58] Hess and Leibbrandt, *Ber.*, 1917, **50**, 385.
[59] Robinson and Robinson, *J.*, 1923, **123**, 538.
[60] Hofmann, *Jahresber. Fortschr. Chem.*, 1861, 520.

Calc. for $C_{10}H_{24}N_2,2C_6H_3N_3O_7$: C, 41·9; H, 4·8; N, 17·8%). The *diperchlorate* separated from ethanol–ether as needles, m. p. 167° (Found: C, 32·5; H, 7·4; N, 8·1. $C_{10}H_{24}N_2,2HClO_4$ requires C, 32·2; H, 7·0; N, 7·5%).

meso-NN′-*Diethyl*-NN′-*dimethylbutane*-2,3-*diamine* (XVIII).—A mixture of *meso-NN′*-diethylbutane-2,3-diamine (II) (1·2 g.), formic acid (1 ml.), and 40% aqueous formaldehyde (0·5 ml.) was heated in a sealed tube for 4 hr. at 100°, then acidified with 20% hydrochloric acid (7 ml.) and evaporated to dryness. The residue was basified with 40% sodium hydroxide solution and extracted with ether. Distillation of the dried extract gave the base (1·05 g.), b. p. 70—80° (bath)/15 mm. The dihydrochloride separated from aqueous ethanol as plates, m. p. 240° (Found: C, 48·6; H, 10·8; N, 11·2%). The *dipicrate* separated from dimethylformamide–ethanol as needles, m. p. 203° (decomp.) (Found: C, 41·8; H, 4·9; N, 18·5. $C_{10}H_{24}N_2,2C_6H_3N_3O_7$ requires C, 41·9; H, 4·8; N, 17·8%). The *diperchlorate* separated from ethanol as needles, m. p. 159° (Found: C, 31·9; H, 7·0; N, 8·0. $C_{10}H_{24}N_2,2HClO_4$ requires C, 32·2; H, 7·0; N, 7·5%).

Racemic NN′-*Diethyl*-NN′-*dimethylbutane*-2,3-*diamine* (XVIII).—Methylation, as above, of racemic *NN′*-diethylbutane-2,3-diamine (II) (1·2 g.) afforded the base (1·14 g.), b. p. 65—80° (bath)/14 mm., the hydrochloride and perchlorate of which failed to crystallise. The *dipicrate* separated from dimethylformamide–ethanol as cubes, m. p. 168° (decomp.) (Found: C, 41·5; H, 4·9; N, 18·3%).

Ethyl α-Ethylmethylaminopropionate.—A solution of ethyl α-bromopropionate (8 g.) in benzene (12 ml.) was slowly added to a stirred and cooled solution of *N*-methylethylamine [61] (5 g.) in benzene (15 ml.). The mixture was kept below 0° for 30 min., then at room temperature for 9 hr., during which the oil which had separated after 1 hr. crystallised. It was then shaken with 25% hydrochloric acid, and the aqueous layer was cooled in ice and treated with ether (30 ml.), followed by potassium carbonate until a porridge-like mass had formed. The ether was decanted and the residue shaken vigorously with successive portions of ether. The combined ethereal extracts were dried (K_2CO_3) and distilled, yielding the *ester* (4·62 g.), b. p. 169—170° (Found: C, 60·0; H, 10·8; N, 9·2. $C_8H_{17}NO_2$ requires C, 60·4; H, 10·7; N, 8·8%).

NN-*Diethyl-α-bromopropionamide*.—An ethereal solution of diethylamine (6·7 ml.) was added gradually with shaking to one of α-bromopropionyl chloride (5·6 g.). The mixture was kept overnight in a refrigerator, shaken with dilute hydrochloric acid, and extracted with ether. The extract afforded the *amide* (5·3 g.), b. p. 128°/16 mm. (Found: C, 39·95; H, 6·6. $C_7H_{14}BrNO$ requires C, 40·4; H, 6·75%).

NN-*Diethyl-α-ethylmethylaminopropionamide*.—A solution of the above bromo-amide (1·5 g.) and *N*-methylethylamine [61] (1·45 g.) in benzene (12 ml.) was heated in a sealed tube for 17 hr. at 100°, then shaken with dilute hydrochloric acid. The acidic layer was extracted with ether, basified with 40% sodium hydroxide solution, and re-extracted with ether. The latter extract was dried (K_2CO_3) and distilled, giving the *product* (1·25 g.), b. p. 125—135° (bath)/15 mm. (Found: C, 63·7; H, 11·65. $C_{10}H_{22}N_2O$ requires C, 64·5; H, 11·8%).

NN-*Diethyl*-2-*ethylmethylaminopropylamine* (XX).—Reduction of the above amide (1·25 g.) by lithium aluminium hydride (0·7 g.) in ether yielded the *diamine* as a colourless liquid (1 g.), b. p. 85—125° (bath)/15 mm. (Found: C, 69·6; H, 14·05. $C_{10}H_{24}N_2$ requires C, 69·75; H, 13·95%). The *dipicrate* separated from acetone–methanol as needles, m. p. 165—168° (Found: C, 42·3; H, 5·2. $C_{10}H_{24}N_2,2C_6H_3N_3O_7$ requires C, 41·9; H, 4·75%).

Irradiation of t-Butylamine.—t-Butylamine (275 ml.) was irradiated for 351 hr. (total dose $3·36 \times 10^{23}$ ev) and the unchanged base was then removed by fractionation. The residue of b. p. >50° (0·93 g.), on distillation, afforded a pale yellow, mobile liquid (0·26 g.), b. p. 60—100° (bath)/14 mm. and a brown tar (0·46 g.). When the liquid was treated with an ethanolic solution of picric acid (0·84 g.) and set aside it yielded a mixture of picrates (0·31 g.) which, on fractional crystallisation from ethanol, afforded picrates A, yellow needles, m. p. 197° (54 mg.), B, orange cubes, m. p. 237° (89 mg.), and C, yellow prisms, decomp. 250° (29 mg.).

The most soluble picrate A was depressed in m. p. on admixture with t-butylamine picrate and the infrared spectra of these two picrates were different; it was identical with NN′-*di-t-butylformamidine monopicrate* (see below) (Found: C, 46·7; H, 6·0; N, 17·85, 18·6. $C_9H_{20}N_2,C_6H_3N_3O_7$ requires C, 46·75; H, 5·95; N, 18·2%). The picrate (40 mg.) in 50% aqueous acetone solution was passed through a column of Dowex 1 hydrochloride, being converted into a *hydrochloride*, separating from ethanol–ether as plates (9 mg.), m. p. 263°

[61] Meisenheimer, *Annalen*, 1922, **428**, 256.

(Found: C, 56·5; H, 11·7; N, 15·2. $C_9H_{20}N_2$,HCl requires C, 56·1; H, 10·9; N, 14·55%). The infrared spectrum of this hydrochloride had strong peaks at 1684 and 1075 cm.$^{-1}$, unlike that of t-butylamine hydrochloride. The hydrochloride (14 mg.) was shaken for 24 hr. at 0° with zinc dust and 8% sodium hydroxide solution (5 ml.). The filtered solution was steam-distilled into dilute hydrochloric acid and the distillate was evaporated to dryness, giving t-butylamine hydrochloride which separated from ethanol–ether as plates (7 mg.), m. p. 310° (Found: C, 43·5; H, 10·9; N, 13·0. Calc. for $C_4H_{11}N$,HCl: C, 43·8; H, 10·9; N, 12·8%).

Picrate B was 1,1-*dimethyl*-2-*t*-*butylaminoethylamine dipicrate* (Found: C, 40·4; H, 4·3; N, 19·6. $C_8H_{20}N_2$,$2C_6H_3N_3O_7$ requires C, 39·9; H, 4·3; N, 18·6%). It was converted into a hydrochloride, by using Dowex 1 hydrochloride, but attempts to benzoylate this gave an oil.

The least soluble picrate C (29 mg.) was boiled with acetone to remove traces of other picrates, then recrystallised from dimethylformamide–ethanol, affording orange needles (21 mg.), decomp. 250°, identical with 2,5-dimethylhexane-2,5-diamine dipicrate (Found: C, 40·15; H, 4·5; H, 20·15. Calc. for $C_8H_{20}N_2$,$2C_6H_3N_3O_7$: C, 39·9; H, 4·3; N, 18·6%). A solution of this picrate (15 mg.) in 50% aqueous acetone was passed through a column of Dowex 1 hydrochloride; the resulting hydrochloride sintered at 280° but did not melt below 360° (Found: C, 44·7; H, 10·6; N, 13·5. $C_8H_{20}N_2$,2HCl requires C, 44·25; H, 10·15; N, 12·9%).

Reduction of 1,1,1′,1′-*Tetramethylazoethane*.—The azo-compound [29] (3 g.) was stirred for 24 hr. at 0°, then for 16 hr. at room temperature, with 8% sodium hydroxide solution (300 ml.) and zinc dust (15 g.). The solution was filtered and distilled in steam, the distillate being collected in dilute hydrochloric acid. Evaporation of the distillate yielded a gum (3·9 g.) which crystallised from ethanol–ether as plates, m. p. 310°, identical with t-butylamine hydrochloride (Found: C, 43·6; H, 10·8; N, 12·7%). This yielded a picrate, separating from ethanol as needles, m. p. 203° (Found: C, 39·5; H, 4·6. Calc. for $C_4H_{11}N$,$C_6H_3N_3O_7$: C, 39·8; H, 4·6%).

N-(2-*Methyl*-2-*nitropropyl*)-*t*-*butylamine*.—40% Aqueous formaldehyde (16·6 ml.) was added gradually to stirred t-butylamine (20·9 ml.) with water-cooling, followed by 2-nitropropane (18 ml.), which was added all at once. After being stirred for 3 hr. at room temperature, the mixture was treated with sodium sulphate (2 g.), and the aqueous layer was removed. The organic layer was kept for 5 days at room temperature, dried (Na_2SO_4), and distilled, yielding the *nitro-compound* (2·9 g.), m. p. 33°, b. p. 98°/20 mm. (Found: C, 55·25; H, 10·8. $C_8H_{18}N_2O_2$ requires C, 55·2; H, 10·35%). A similar experiment, conducted for only 2 days and at room temperature, yielded the base (5·5 g.).

1,1-*Dimethyl*-2-*t*-*butylaminopropylamine*.—The above nitro-compound (2·7 g.) in acetic acid (20 ml.) and water (30 ml.) was warmed for 2 hr. on the water-bath with zinc dust (12 g.), and the solution was filtered while hot. The filtrate was evaporated to dryness, and the residue was dissolved in water, basified with concentrated ammonia solution, and extracted with ether. The dried (K_2CO_3) extract was distilled, yielding the *diamine* (1·4 g.), b. p. 153° (Found: C, 66·05; H, 13·75. $C_8H_{20}N_2$ requires C, 66·65; H, 13·9%), which gave a dipicrate, m. p. 236° (decomp.) (from ethanol) (Found: C, 40·4; H, 4·1%). The *dihydrochloride* separated from ethanol as needles, m. p. 280° (decomp.) (Found: C, 44·6; H, 10·35. $C_8H_{20}N_2$,2HCl requires C, 44·25; H, 10·15%).

NN′-*Di*-*t*-*butylformamidine Monopicrate*.—A mixture of t-butylamine (dried over KOH and distilled) (22·8 ml.) and bromoform (4·8 ml.; containing 4% of ethanol) was heated in a sealed tube for 74 hr. at 100°. The resulting t-butylamine hydrobromide (9·3 g.) was filtered off and washed with ether. The combined filtrate and washings were washed with dilute sodium hydroxide solution, then dried (K_2CO_3), and the ether and unchanged t-butylamine were removed on a water-bath. An ethereal solution of the residue was shaken with 2N-hydrochloric acid, and the latter was then extracted with ether, basified with 40% sodium hydroxide solution, and re-extracted with ether. The latter extract was dried (K_2CO_3) and distilled, giving the formamidine, b. p. 100—110° (bath)/20 mm. (0·5 g.), which yielded a picrate, m. p. 197° (from ethanol), as needles (Found: C, 46·4; H, 5·95%). The *hydrochloride* (from ethanol–ether) had m. p. 288—289° (decomp.) (Found: C, 56·4; H, 10·75%).

Attempted Condensation of 2-*Nitropropane with Ethylene Dibromide*.—Ethylene dibromide (21·8 g.) was added in 2½ hr. to a stirred, refluxing solution of 2-nitropropane (18 g.) in 80% ethanol (160 ml.) and 15% sodium hydroxide solution (40 ml.). The ethanol was removed and the residue basified with sodium hydroxide and extracted with ether (4 × 15 ml.). The alkaline solution was then continuously extracted with chloroform for 24 hr. Evaporation

of the extract yielded a gum which crystallised when treated with ethanol–ether. Recrystallisation of the product from ethanol–ether afforded 2,3-dimethyl-2,3-dinitrobutane, plates, m. p. 210—211° (2·1 g.) (Found: C, 41·1; H, 6·9; N, 16·1. Calc. for $C_6H_{12}N_2O_4$: C, 40·9; H, 6·8; N, 15·9%).[62]

NN′-*Dibenzoyl*-2,5-*dimethylhexane*-2,5-*diamine*.—A solution of β-benzamido-β-methylbutyric acid [63] (4 g.) in methanol (15 ml.) was electrolysed in the way described by Linstead, Shepard, and Weedon,[35] with an anode current density of 0·1—0·2 amp./cm.^{2} for 5 hr. After the solution had been neutralised with dilute acetic acid, the bulk of the solvent was removed and the residue was kept in ether at 0°. The resulting solid (0·47 g.) was extracted with boiling ethyl acetate, an insoluble residue of m. p. >360° (0·28 g.) remaining. Concentration of the ethyl acetate solution gave a *diamide* which recrystallised from ethyl acetate as plates (0·1 g.), m. p. 220° (Found: C, 74·8; H, 8·4; N, 8·1. $C_{22}H_{28}N_2O_2$ requires C, 75·0; H, 8·0; N, 8·0%). The infrared spectrum confirmed its amide character. Evaporation of the ethereal filtrate gave an oil from which, after distillation [90—100° (bath)/2 mm.], benzamide separated from benzene as plates, m. p. 127° (0·23 g.) (Found: C, 69·7; H, 5·9; N, 11·6. Calc. for C_7H_7NO: C, 69·5; H, 5·8; N, 11·6%). The residue from the distillation was a gum (1·62 g.) which was refluxed for 24 hr. with ethanol (15 ml.) and concentrated hydrochloric acid (10 ml.). The cooled solution was extracted with ether (which removed benzoic acid), then evaporated to a gum, which was basified with 40% sodium hydroxide solution and extracted with ether. Distillation of this extract yielded a liquid (0·5 g.), b. p. 80—100° (bath)/15 mm., whose picrate separated from ethanol as needles, m. p. 197° (1·38 g.) [Found: C, 50·4; H, 4·4; N, 13·2%. *M* (spectroscopic [64]), 731 (as dipicrate)].

The above diamide (0·1 g.) was refluxed for 41 hr. with ethanol (8 ml.) and concentrated hydrochloric acid. The cooled solution was extracted with ether (affording 25 mg. of recrystallised benzoic acid) and then evaporated to a gum, which was basified with 40% sodium hydroxide solution and extracted with ether. The latter ethereal extract was treated with picric acid (0·13 g.), then concentrated. The first crystals to separate were picric acid (0·09 g.), followed by orange cubes (3 mg.) which were picked out by hand. A similar experiment with β-benzamido-β-methylbutyric acid (3 g.) yielded the diamide (0·08 g.) and hence the picrate separating as orange cubes (2 mg.). The combined yield of the latter (5 mg.) was recrystallised from ethanol, but the product was not homogeneous.

When the electrolysis was carried out in dimethylformamide solution,[65] instead of methanol, 95% of the original acid was recovered unchanged.

2,3-*Dimethylbutane*-2,3-*diamine*.—2,3-Dimethyl-2,3-dinitrobutane [62] was reduced by Bewad's method,[66] and also by hydrogen in the presence of Adams catalyst, to the diamine, whose *dipicrate* separated from dimethylformamide–ethanol as needles, m. p. 250° (decomp.) (Found: C, 38·1; H, 3·8; N, 19·7. $C_6H_{16}N_2,2C_6H_3N_3O_7$ requires C, 37·7; H, 3·8; N, 19·6%).

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