819. *The Chemical Effects of γ-Radiation on Organic Systems. Part XI.*[1] *The Action of Radiation on Triethylamine, Diethylamine, n-Butylamine, and 1-Methylpiperidine*

By L. T. Allan and G. A. Swan

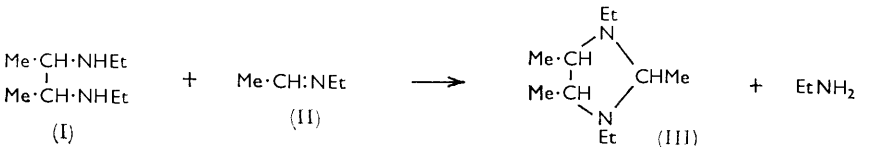
Gas-chromatographic studies of the radiolysis products of diethylamine have shown the presence of 1,3-diethyl-2,4,5-trimethylimidazolidine (III) and tetraethylhydrazine (IV). The radiolysis products of n-butylamine include *N*-butylidenebutylamine (VIII), *N*-(2-ethyl-2-hexenylidene)butylamine (X), 1,2-dibutylhydrazine (XII), *meso*- and racemic octane-4,5-diamine (VI), and 2,4,5-tripropylimidazolidine (IX).

We have previously isolated a considerable number of γ-radiolysis products of a variety of amines by the use of the classical methods of organic chemistry and partition chromatography.[2] As it seemed likely that other products had escaped detection, we have re-examined those radiolysis products which are less volatile than the original amine by gas–liquid chromatography in the case of triethylamine, diethylamine, and 1-methylpiperidine. We have also investigated the radiolysis products of n-butylamine. The new *G* values quoted here are calculated from peak areas on the gas chromatograms.

The distilled residue from the irradiation of triethylamine contained *meso*- (*G* 0·72) and racemic (*G* 0·81) 2,3-bisdiethylaminobutane, which together accounted for 89% of the residue. Separation of these products by gas–liquid chromatography was possible with a non-polar liquid phase, but was better achieved on a polar phase such as Carbowax 1000.

Irradiation of diethylamine, earlier reported to yield *meso*-(*G* 0·77) and racemic (*G* 0·78) *NN'*-diethylbutane-2,3-diamine (I),[2] has now been found to give the following products: *meso*- (*G* 0·97) and racemic (*G* 0·55) *NN'*-diethylbutane-2,3-diamine, 1,3-diethyl-2,4,5-trimethylimidazolidine (III) (*G* 0·33), and tetraethylhydrazine (IV) (*G* 0·002). These four products accounted for 85% of the residue. The imidazolidine (III) was isolated by preparative gas–liquid chromatography and its structure deduced from its mass spectrum. This structure was proved by the synthesis of the same compound by reaction of *NN'*-diethylbutane-2,3-diamine with acetaldehyde, the racemic diamine reacting faster than its *meso*-isomer. Complete separation of the *meso*- and racemic imidazolidines was not achieved by gas–liquid chromatography, and the *G* value quoted would therefore include both isomers.

We have previously pointed out that *N*-ethylidene-ethylamine (II) might be expected as a radiolysis product of diethylamine.[2] The imidazolidine could be formed by reaction of this with the diamine:



[1] Part X, G. A. Swan and P. S. Timmons, *J.*, 1962, 1120.
[2] G. A. Swan, P. S. Timmons, and D. Wright, *J.*, 1959, 9; G. Smith and G. A. Swan, *J.*, 1962, 886.

The apparent anomaly in the *G* values found for the *meso*- and racemic diamines by the two different methods of analysis can thus be explained. Probably approximately equal amounts of the two diamines are formed radiolytically but preferential reaction of the racemic diamine with *N*-ethylidene-ethylamine results in the remaining diamine's becoming enriched with respect to the *meso*-isomer. In the chemical analysis, the acid treatment would decompose the imidazolidine to give back the original (mainly racemic) diamine.

The formation of tetraethylhydrazine (IV) points to the formation of the radical $Et_2N\cdot$ during the radiolysis of diethylamine; but this radical may not be formed by direct radiolysis, as it could arise through hydrogen abstraction by the radiolytically formed EtNH·ĊHMe radical.

$$2Et_2N\cdot \longrightarrow Et_2N\cdot NEt_2$$
(IV)

When 1-methylpiperidine was irradiated, it had been earlier reported that the unchanged base recovered by distillation contained piperidine and that the residue (b. p. >107°) contained 1,2-dipiperidinoethane, *meso*-1,1′-dimethyl-2,2′-bipiperidyl, and 1-methyl-2-(piperidinomethyl)-piperidine.[2] We failed to find a liquid phase which would allow a complete separation of the three last components by gas–liquid chromatography. By using Carbowax 1000 as stationary phase, synthetic 1,1′-dimethyl-2,2′-bipiperidyl (previously thought to be the *meso*-form) gave two peaks on the chromatogram, although these were not completely resolved. It therefore appears to be a mixture of *meso*- and racemic forms. By analogy with other cases, the *meso*-configuration was ascribed to the first isomer to be eluted. Unfortunately the *meso*-isomer had the same retention time as 1-methyl-2-(piperidinomethyl)piperidine, so gas–liquid chromatography was able to give only a *G* value (1·28) for the total of the latter compound, together with *meso*- and racemic 1,1′-dimethyl-2,2′-bipiperidyl; the presence of the latter isomer in the irradiation product was indicated by a shoulder on the chromatogram. The previously determined *G* values for these compounds were 0·39 + 0·75 (*i.e.*, 1·14). On the same column, 1,2-dipiperidinoethane was well separated from these other isomers, leading to a *G* value of 0·39, as compared with the previously reported 0·37. The residue (b. p. >107°) also contained small amounts of 1-methylpiperidine and piperidine. These, together with 1,2-dipiperidinoethane, 1,1′-dimethyl-2,2′-bipiperidyl, and 1-methyl-2-(piperidinomethyl)piperidine constituted 59% of the residue. A further twelve peaks appeared on the chromatogram, although many of these were very small.

Separation of the radiolysis products of n-butylamine was also best achieved on Carbowax 1000, the following being identified: *N*-butylidenebutylamine (VIII) (*G* 0·27), *N*-(2-ethyl-2-hexenylidene)butylamine (X) (*G* 0·23), 1,2-dibutylhydrazine (XII) (*G* 0·002), *meso*- and racemic octane-4,5-diamine (VI) (*G*, combined 0·05) and 2,4,5-tripropylimidazolidine (IX) (*G* 0·17). The formation of these products could be explained if butylamine underwent radiolysis to yield the radical (V), which could then dimerise to give (VI), or disproportionate to yield butyraldimine (VII).

$$Pr^n\cdot CH_2\cdot NH_2 \rightsquigarrow Pr^n\cdot \dot{C}H\cdot NH_2 + H\cdot$$
(V)

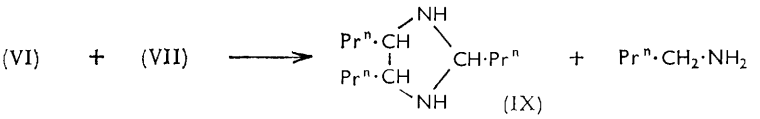
$$2Pr^n\cdot \dot{C}H\cdot NH_2 \longrightarrow Pr^n\cdot CH(NH_2)\cdot CH(NH_2)\cdot Pr^n$$
(VI)

$$2Pr^n\cdot \dot{C}H\cdot NH_2 \longrightarrow Pr^n\cdot CH{:}NH + Pr^n\cdot CH_2\cdot NH_2$$
(VII)

N-Butylidenebutylamine (VIII) could be formed by interaction of butyraldimine with

butylamine and the imidazolidine (IX) by reaction of butyraldimine with octane-4,5-diamine (VI). For its synthesis, we used butyraldehyde instead of the imine.

$$Pr^n{\cdot}CH{:}NH + Pr^n{\cdot}CH_2{\cdot}NH_2 \longrightarrow Pr^n{\cdot}CH{:}N{\cdot}CH_2Pr^n + NH_3$$
(VIII)



N-(2-Ethyl-2-hexenylidene)butylamine (X) is known to result when *N*-butylidenebutylamine (VIII) is heated for 3 hours at 140—150°.[3] It might therefore be produced in a similar way during the irradiation or the subsequent working-up.

$$Pr^n{\cdot}CH{:}CEt{\cdot}CH{:}N{\cdot}Bu^n$$
(X)

The formation of 1,2-dibutylhydrazine (XII) would imply the intervention of the radical (XI).

$$2Bu^n{\cdot}NH{\cdot} \longrightarrow Bu^n{\cdot}NH{\cdot}NH{\cdot}Bu^n$$
(XI) (XII)

The above compounds account for only 39% of the residue from irradiated butylamine; the gas chromatogram showed a further nine peaks. This stands in sharp contrast to the case of triethylamine, where the residue contains little except the two isomeric diamines.

A mixture of *meso*- and racemic octane-4,5-diamine (VI) was obtained by reduction of the dioxime of octane-4,5-dione with Raney nickel alloy and sodium hydroxide solution. 1,2-Dibutylhydrazine (XII) was synthesised by Schmitz and Schinkowski's method.[4] Reduction of butaldazine with lithium aluminium hydride or with hydrogen in the presence of Adams catalyst gave mixtures of products. 1-Butyl-2-butyrylhydrazine was isolated from the reaction of 1,2-dibutyrylhydrazine with lithium aluminium hydride; but further reduction of this compound could not be effected.

Experimental

General Directions.—The arrangements for the irradiations and dosimetry were as described in Part I.[5] The amines, which were all irradiated under nitrogen (oxygen-free) at room temperature, were commercial samples which had been purified by fractional distillation and checked for purity by gas chromatography.

A Pye Argon Chromatograph was used for gas chromatography. The stationary, liquid phases were supported on 100—120 mesh Celite 545 (L. Light and Co., Ltd.,), which had been washed with alkali. The weight of the liquid was 10% of the solid phase. In the analyses, compounds are given in their order of elution from the column. The retention time was taken as the interval between the point when the sample was injected and the point when the peak height reached its maximum. Identification was based on comparison with authentic compounds which were also used for calibration, in terms of peak areas.

Irradiation of Triethylamine.—Triethylamine (260 ml.) was irradiated for 504 hr. (total dose $4{\cdot}13 \times 10^{23}$ ev) and unchanged base was removed by fractional distillation. The residue yielded a fraction, b. p. 225—260°/750 mm. (2·36 g.), which was analysed by gas chromatography. With liquid paraffin as liquid phase, a complete separation of the isomeric diamines could be achieved only at low temperatures, where the retention times were inconveniently long (290·25 and 334·75 min. for the *meso* and racemic diamines, respectively, at 48°, with a flow rate of 80 ml./min.). Analysed thus, the product contained *meso*- (41·8%) and racemic (47·0%) 2,3-bisdiethylaminobutane and a compound of retention time 403 min. (4·6%). At 48° silicone oil MS 550 gave only a partial separation, but Carbowax 1000, with a flow rate of

[3] W. S. Emerson, S. M. Hess, and F. C. Uhle, *J. Amer. Chem. Soc.*, 1941, **63**, 872.
[4] E. Schmitz and K. Schinkowski, *Chem. Ber.*, 1964, **97**, 49.
[5] G. A. Swan and P. S. Timmons, *J.*, 1958, 4669.

30 ml./min. gave good separation, with retention times of the *meso* and racemic isomers of 51 and 61·5 min., respectively.

Irradiation of Diethylamine.—Diethylamine (275 ml.) was irradiated for 766 hr. (total dose $6·65 \times 10^{23}$ ev) and unchanged amine was removed by fractional distillation. The residue (3·71 g.) was chromatographed on Carbowax 1000 at 48° and flow rate of 50 ml./min. and thus found to contain tetraethylhydrazine [2] (1·1%), 1,3-diethyl-2,4,5-trimethylimidazolidine (16·8%), and *meso*- (41·8%) and racemic (24·9%) *NN'*-diethylbutane-2,3-diamine. The retention times of these were 5·75, 29, 51·5, and 61 min., respectively. On Apiezon L, the imidazolidine was eluted after the diamines and on silicone oil MS 550 or liquid paraffin at 48°, the isomeric diamines were incompletely separated. The use of *o*-toluidine and hendecanol, previously recommended for the separation of amines,[6] gave prolonged retention times.

Reaction between NN'-*Diethylbutane*-2,3-*diamine and Acetaldehyde.*—The *meso*-diamine (0·1 g.) in ether (100 ml.) was refluxed with acetaldehyde (0·04 g.) for 5 hr. After addition of acetaldehyde (0·04 g.) the solution was kept overnight at room temperature, then refluxed for 11 hr. Distillation of the dried (Na_2SO_4) solution gave meso-1,3-*diethyl*-2,4,5-*trimethylimidazolidine*, b. p. 60—70° (bath temp.)/30 mm. (Found: C, 69·8; H, 12·6. $C_{10}H_{22}N_2$ requires C, 70·5; H, 13·0%), shown by gas chromatography to be free from the original diamine. Reaction was faster in refluxing benzene and when a mixture of *meso* and racemic diamine was allowed to react with less than an equivalent amount of acetaldehyde, preferential formation of the racemic imidazolidine occurred.

Irradiation of 1-*Methylpiperidine.*—1-Methylpiperidine, purified as described earlier,[2] (240 ml.) was irradiated for 738 hr. (total dose $3·95 \times 10^{23}$ ev) and unchanged material was removed by fractional distillation. The residue, b. p. >107° (4·39 g.), was chromatographed on Carbowax 1000, at 117°, with a flow rate of 30 ml./min. and thus found to contain 1-methylpiperidine (3·4%), piperidine (6·2%), 1,1'-dimethyl-2,2'-bipiperidyl, and 1-methyl-2-(piperidinomethyl)piperidine (combined, 37·6%) and 1,2-dipiperidinoethane (11·5%). The retention times of these were 1·75, 2·25, 36·75, and 46·5 min., respectively.

Irradiation of n-Butylamine.—n-Butylamine (175 ml.) was irradiated for 978 hr. (total dose $3·82 \times 10^{23}$ ev) and the unchanged amine was removed by fractional distillation. The residue (2·22 g.) was chromatographed on Carbowax 1000 at 95°, with a flow rate of 30 ml./min., and thus found to contain butylamine (4%), *N*-butylidenebutylamine [7] (9·9%), *N*-(2-ethyl-2-hexenylidene)butylamine [3] (11·8%), 1,2-dibutylhydrazine [4] (1%), *meso*- and racemic octane-4,5-diamine (combined, 2·3%) and 2,4,5-tripropylimidazolidine (9·5%). The retention times of these were 1·25, 3·0, 21·5, 27·5, 42, 52, and 119·5 min., respectively.

Octane-4,5-*diamine* (VI).—Butyroin [8] was oxidised by Rigby's method [9] to octane-4,5-dione, the dioxime of which (5·0 g.), together with sodium hydroxide (16·5 g.) were dissolved in water (100 ml.). Raney nickel alloy (11·3 g.) was added gradually, with stirring, during 1 hr. at 45—50°. The mixture was kept overnight, filtered, and the filtrate distilled until no more base came over. The distillate was acidified with hydrochloric acid (6N, 7 ml.) and evaporated to dryness. The residue was treated with a solution of sodium (2 g.) in methanol (80 ml.) and the mixture distilled rapidly. Fractional distillation of the distillate yielded the *diamine*, b. p. 208° (Found: C, 65·45; H, 13·7. $C_8H_{20}N_2$ requires C, 66·6; H, 14·0%). Gas chromatography indicated this to be a mixture of *meso* and racemic forms. It yielded a *dipicrolonate* which, after recrystallisation from acetone, had m. p. 247—248° (Found: N, 20·3. $C_8H_{20}N_2,2C_{10}H_8N_4O_5$ requires N, 20·85%).

2,4,5-*Tripropylimidazoldine* (IX).—This was obtained by refluxing octane-4,5-diamine (0·41 g.) and acetaldehyde (0·2 g.) in ether for 7 hr. and had b. p. 260—270°.

NN'-*Dibutyrylhydrazine.*—n-Butyryl chloride (20·6 g.) was added during 45 min. to a stirred and cooled mixture of 80% hydrazine hydrate (7·1 g.), potassium carbonate (13·5 g.), and water (60 ml.). The mixture was stirred for a further 45 min. and the resulting solid was collected and crystallised from ethanol to yield the *product*, m. p. 169—170° (Found: C, 55·8; H, 8·85; N, 16·4. $C_8H_{16}N_2O_2$ requires C, 55·8; H, 9·35; N, 16·25%).

Reduction of this compound with lithium aluminium hydride (Soxhlet, 30 hr.) in tetrahydrofuran yielded a product which after distillation and recrystallisation from light petroleum

[6] A. R. Amell, P. S. Lamprey, and R. C. Schiek, *Analyt. Chem.*, 1961, **33**, 1805.
[7] C. W. C. Stein and A. R. Day, *J. Amer. Chem. Soc.*, 1942, **64**, 2569.
[8] J. M. Snell and S. M. McElvain, *Org. Synth.*, 1933, **13**, 24.
[9] W. Rigby, *J.*, 1951, 793.

(b. p. 60—80°) had m. p. 62—63° and appeared to be 1-*butyl*-2-*butyrylhydrazine* (Found: C, 61·6; H, 11·45; N, 16·95. $C_8H_{18}N_2O$ requires C, 60·75; H, 11·45; N, 17·7%). This gave a *picrolonate*, from ethanol–ether, m. p. 142—144° (Found: N, 19·75. $C_8H_{18}N_2O,C_{10}H_8N_4O_5$ requires N, 19·85%).

This work was sponsored by the (U.S.) Air Force Materials Laboratory, Research and Technology Division, A.F.S.C.

We thank Mr. P. Kelly, M.Sc., for the mass spectrometric measurement. The Pye Argon Chromatograph was purchased through a grant from the D.S.I.R.

Department of Organic Chemistry, University of Newcastle upon Tyne,
Newcastle upon Tyne 1. [*Received, February 9th*, 1965.]