# **894.** *Photolysis of Diethylamine and Triethylamine*

By L. T. ALLAN and G. A. SWAN

Photolysis of diethylamine yielded *meso*- and racemic *NN'*-diethylbutane-2,3-diamine (IV), 1,3-diethyl-2,4,5-trimethylimidazolidine (V), tetraethylhydrazine (VII), and *N*-but-2-enylidene-ethylamine (II). Triethylamine, on photolysis, gave *meso*- and racemic *NNN'N'*-tetraethylbutane-2,3-diamine (VIII), *NN'*-diethylbutane-2,3-diamine, 1,3-diethyl-2,4,5-trimethylimidazolidine, and tetraethylhydrazine.

WE have already shown [1,2] that $\gamma$-radiolysis of diethylamine yields *meso*- and racemic *NN'*-diethylbutane-2,3-diamine (IV), 1,3-diethyl-2,4,5-trimethylimidazolidine (V), and tetraethylhydrazine (VII). Similar radiolysis of triethylamine afforded *meso*- and racemic *NNN'N'*-tetraethylbutane-2,3-diamine.[3] Pfordte and Leuschner [4] claim to have isolated the stereoisomeric forms of *NN'*-diethylbutane-2,3-diamine and of *NNN'N'*-tetraethylbutane-2,3-diamine from diethylamine and triethylamine, respectively, after photolysis. Whilst we agree that these products are in fact formed, we were led to study these photolyses because several features of Pfordte and Leuschner's work seemed very unsatisfactory.

According to these authors, *meso*- and racemic *NN'*-diethylbutane-2,3-diamine (IV) have b. p. 240° and 165°, respectively; and for *meso*- and racemic *NNN'N'*-tetraethylbutane-2,3-diamine they give b. p. 208° and 135°, respectively. Such a great difference between the boiling points of these isomers is unbelievable and it seems likely that the higher-boiling material, in each case, is of more complex structure. Pfordte and Leuschner also ascribed comparably widely divergent boiling points to the *meso*- and racemic forms of other diamines, which they claimed to have obtained by the photolyses of n-propylamine, n-butylamine and isobutylamine. We have not had the pure isomers in sufficient quantities for accurate boiling-point determinations, but we can quote the following, approximate values. For *meso*- and racemic *NN'*-diethylbutane-2,3-diamine, b. p. 50—65° (bath temp.)/12 mm., and for *meso*- and racemic *NNN'N'*-tetraethylbutane-2,3-diamine, b. p. 70—80° (bath temp.)/5 mm. Judged by their behaviour on gas–liquid chromatography, the *meso*-isomers probably have slightly lower boiling points than the corresponding racemic forms.

The configurations allotted by Pfordte and Leuschner to their so-called *meso*- and racemic forms were based on reactions with periodic acid, phthalic anhydride, picric acid, and cupric hydroxide. The reaction with periodic acid does not apply to those diamines in which the nitrogen atoms are tertiary and that with phthalic anhydride applies only to

---

[1] G. Smith and G. A. Swan, *J.*, 1962, 886.
[2] L. T. Allan and G. A. Swan, *J.*, 1965, 4434.
[3] G. A. Swan, P. S. Timmons, and D. Wright, *J.*, 1959, 9.
[4] K. Pfordte and G. Leuschner, *Annalen*, 1961, **646**, 25.

primary amines. They state that periodic acid degrades 1,2-diamines in the same way as 1,2-diols, but that, whereas *meso*-1,2-diols are rapidly degraded, racemic 1,2-diols react only during several hours. However, they state that the " racemic diamines " react only slightly slower with periodic acid than do the " *meso*-diamines," although no experimental details are given. Actually it is the racemic 1,2-diols which one might expect to react more rapidly than the *meso*-1,2-diols, and this has been proved experimentally.[5]

Pfordte and Leuschner also state that reaction of the " racemic diamines " with phthalic anhydride (in equimolecular proportions) in acetone yields phthalimidic acids containing a free amino-group and that the product from the " *meso*-diamines " are quite different, having high melting points and containing neither a free amino nor carboxyl group. Analyses were not reported on these latter compounds. These observations might be due to the " *meso*-diamines " having a more complex structure.

The same authors also state that the " *meso*-diamines " yield blue copper complexes, which are not given by the " racemic diamines." As with periodic acid, this is the opposite of what one might have guessed. They also state that only the " racemic diamines " yield crystalline mono-picrates, the " *meso*-diamines " giving no well-defined picrates. This, again, might point to the " *meso*-diamines " being of more complex nature and perhaps consisting of mixtures of stereoisomers. Moreover, there is a lack of evidence that the compounds referred to as " mono-picrates " are not, in fact di-picrates. Pfordte and Leuschner quote only nitrogen values on their picrates and it should be noted that the calculated values for the mono- and di-picrates of 2,5-dimethylhexane-3,4-diamine and of *NN'*-diethylbutane-2,3-diamine (both bases $C_8H_{20}N_2$) are 18·8 and 18·6%, respectively (Found: 18·65 and 18·72%). Actually, we have prepared di-picrates from both *meso*- and racemic *NN'*-diethylbutane-2,3-diamine, m. p. 214° (decomp.) and 160° (decomp.), respectively;[1] the German authors give m. p. 153° for their supposed " racemic monopicrate." From their racemic *NNN'N'*-tetraethylbutane-2,3-diamine they obtained a picrate, m. p. 177° and compared this with our value of 178°. We must point out, however, that our value, as clearly stated in our Paper, refers to the *meso*-picrate. The corresponding racemic picrate has m. p. 137° and both of them are dipicrates.

We therefore conclude that the lower-boiling materials, the so-called " racemic diamines," obtained by Pfordte and Leuschner by photolyses of amines were probably mixtures of *meso*- and racemic diamines and that the high-boiling materials, the so-called " meso-diamines," were more complex in nature. They prepared a bisnitrosamine from " racemic " *NN'*-diethylbutane-2,3-diamine and this had m. p. 77°, compared with 74·5° for the same compound prepared from a sample of the diamine obtained by Picon's method.[6] For the bisnitrosamines of the *meso*- and racemic diamines, we found m. p. 108—109° and 92—93°, respectively.

We irradiated diethylamine with a quartz, medium-pressure lamp and fractionated the product. The material, which was less volatile than diethylamine, was analysed by gas–liquid chromatography and found to contain *meso*- and racemic *NN'*-diethylbutane-2,3-diamine (IV), 1,3-diethyl-2,4,5-trimethylimidazolidine (V) and tetraethylhydrazine (VII) (Table 1). However, another compound was present in amount greater than any

TABLE 1

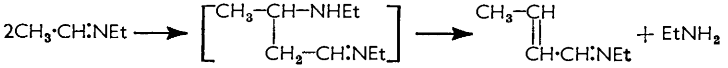
Composition of photolysis products of diethylamine, less volatile than diethylamine (wt.-%)

| Product | Period of irradiation (hr.) 24 | 46 | 89 | 108 |
|---|---|---|---|---|
| Tetraethylhydrazine | 0·6 | 1·3 | 1·6 | 1·4 |
| 1,3-Diethyl-2,4,5-trimethylimidazolidine | 9·9 | 6·6 | 10·6 | 14·4 |
| *meso-NN'*-Diethylbutane-2,3-diamine | 4·9 | 7·7 | 9·1 | 20·4 |
| Racemic *NN'*-diethylbutane-2,3-diamine | 4·1 | 11·1 | 12·8 | 19·5 |
| *N*-But-2-enylidene-ethylamine | 72·4 | 58·7 | 49·2 | 30·7 |

---

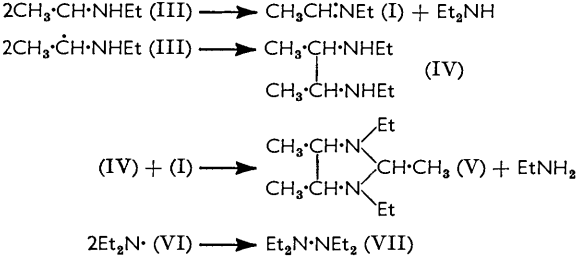
[5] F. R. Duke and V. C. Bulgrin, *J. Amer. Chem. Soc.*, 1954, **76**, 3803.
[6] M. Picon, *Bull. Soc. chim. France*, 1923, [4], **33**, 86.

of these, although the proportion of this product decreased as the time of irradiation increased, suggesting it to be an unstable compound. Attempts to isolate this compound by fractional distillation or preparative gas chromatography were unsuccessful, owing to its ready polymerisation. When the photolysis products were treated with picric acid or other acids, the only crystalline salts isolated were of either *meso-* or racemic *NN'*-diethylbutane-2,3-diamine. Mass-spectrometric examination of the products of a short-period irradiation indicated the presence of a compound, *M* 97, and this proved to be *N*-but-2-enylidene-ethylamine (II). The same compound was obtained by refluxing crotonaldehyde with ethylamine, or by refluxing *N*-ethylidene-ethylamine for 13 hr. The latter reaction (cf. analogous cases reported in the literature [7]) and the formation of 1,3-diethyl-2,4,5-trimethylimidazolidine (V) (cf. ref. 2) suggest the formation of *N*-ethylidene-ethylamine (I) as a main photolytic product of diethylamine. The identified products could be explained on the assumption of the primary formation of the radical $CH_3{\cdot}\dot{C}H{\cdot}NHEt$ (III). Disproportionation could then give *N*-ethylidene-ethylamine (I) and dimerisation would lead to *NN'*-diethylbutane-2,3-diamine (IV); interaction of these two products could yield 1,3-diethyl-2,4-5-trimethylimidazolidine (V). The formation of tetraethylhydrazine (VII) would suggest the intervention of the radical $Et_2N{\cdot}$ (VI), which could be a photolytic product, or could be formed by hydrogen abstraction by the radical $CH_3{\cdot}\dot{C}H{\cdot}NHEt$. The gas chromatogram showed that small amounts of four other compounds were formed by photolysis of diethylamine.



$$2CH_3{\cdot}CH{:}NEt \longrightarrow \left[\begin{array}{l} CH_3{-}CH{-}NHEt \\ \qquad | \\ \qquad CH_2{-}CH{:}NEt \end{array}\right] \longrightarrow \begin{array}{l} CH_3{-}CH \\ \qquad \| \\ \qquad CH{\cdot}CH{:}NEt \end{array} + EtNH_2$$

(I) (II)



$$2CH_3{\cdot}\dot{C}H{\cdot}NHEt\ (III) \longrightarrow CH_3CH{:}NEt\ (I) + Et_2NH$$

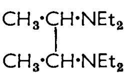
$$2CH_3{\cdot}\dot{C}H{\cdot}NHEt\ (III) \longrightarrow \begin{array}{l} CH_3{\cdot}CH{\cdot}NHEt \\ \qquad | \\ CH_3{\cdot}CH{\cdot}NHEt \end{array}\ (IV)$$

$$(IV) + (I) \longrightarrow \begin{array}{l} CH_3{\cdot}CH{\cdot}N{<}^{Et} \\ \qquad |\qquad\quad {>}CH{\cdot}CH_3 \\ CH_3{\cdot}CH{\cdot}N{<}_{Et} \end{array}\ (V) + EtNH_2$$

$$2Et_2N{\cdot}\ (VI) \longrightarrow Et_2N{\cdot}NEt_2\ (VII)$$

Our failure to detect *N*-but-2-enylidene-ethylamine among the $\gamma$-radiolysis products of diethylamine may be associated with the facts that this compound is unstable and that the $\gamma$-irradiation lasted 32 days, whilst the photolytic experiment in which the highest yield was obtained lasted only 1 day.

We studied the photolysis of triethylamine similarly and the gas chromatogram of the product showed 18 peaks, this situation contrasting very sharply with the $\gamma$-radiolysis of the same amine, where 89% of the material consisted of *meso-* and racemic *NNN'N'*-tetraethylbutane-2,3-diamine, and another product was present to the extent of nearly 5%. Among the photolysis products of triethylamine, the following were identified: *meso-* and racemic *NNN'N'*-tetraethylbutane-2,3-diamine (VIII), *NN'*-diethylbutane-2,3-diamine (IV), 1,3-diethyl-2,4,5-trimethylimidazolidine (V), and tetraethylhydrazine (VII) (Table 2). It was thought that *NN'*-diethylvinylamine might be present, as this compound has been shown to be formed by the action of benzoyl peroxide or chloranil on triethylamine.[8] However, a synthetic sample [9] polymerised on the gas-chromatographic column.



$$\begin{array}{l} CH_3{\cdot}CH{\cdot}NEt_2 \\ \qquad | \\ CH_3{\cdot}CH{\cdot}NEt_2 \end{array}$$

(VIII)

---

[7] M. S. Kharasch, I. Richlin, and F. R. Mayo, *J. Amer. Chem. Soc.*, 1940, **62**, 494; W. S. Emerson, S. M. Hess, and F. C. Uhle, *ibid.*, 1941, **63**, 872.

[8] C. Walling and N. Indictor, *J. Amer. Chem. Soc.*, 1958, **80**, 5814; D. Buckley, S. Dunstan, and H. B. Henbest, *J.*, 1957, 4901.

[9] G. Opitz and H. Mildenberger, *Annalen*, 1961, **649**, 26.

The formation of these products could be explained on the assumption that during the photolysis of triethylamine, the radical $CH_3\cdot\dot{C}H\cdot NEt_2$ is formed, but that C–N bond fission also occurs, to give the radical $Et_2N\cdot$ and hence diethylamine and its photolysis products.

TABLE 2

Composition of photolysis products of triethylamine, less volatile than triethylamine (wt.-%)

| | Period of irradiation (hr.) | | | | |
|---|---|---|---|---|---|
| | 77·25 | 77·5 | 97·75 | 87·0 | 136·0 |
| Product | Glass vessel | | | Quartz vessel | |
| | a | b | c | d | e |
| Tetraethylhydrazine | 1·1 | 0·2 | 0·3 | 3·0 | 0·9 |
| Unknown X | 15·3 | 20·9 | 19·5 | 6·8 | 7·6 |
| *NN'*-Diethylbutane-2,3-diamine | 18·6 | 26·6 | 28·4 | 7·8 | 10·2 |
| 1,3-Diethyl-2,4,5-trimethylimidazolidine | 5·4 | 3·9 | 1·8 | 10·9 | 11·0 |
| Unknown Y | 4·2 | 2·1 | 0·9 | 10·7 | 8·2 |
| *meso-NNN'N'*-Tetraethylbutane-2,3-diamine | 13·8 | 13·2 | 8·2 | 21·0 | 24·8 |
| Racemic *NNN'N'*-tetraethylbutane-2,3-diamine | 14·2 | 11·1 | 10·2 | 20·9 | 21·1 |

In comparing the results of our $\gamma$-radiolyses with those of our photolyses, it must be remembered that the former were carried out at temperatures around 10° and the latter at approximately the boiling points of the amines concerned.

## EXPERIMENTAL

*General Directions.*—For the photolyses, a 125-w, quartz medium-pressure lamp was employed. The amines were irradiated in an atmosphere of nitrogen (oxygen-free) in a quartz flask, the nearest face of which was 2 in. away from the lamp. In three experiments on triethylamine, a glass vessel was used at a distance of (a) 2 in., (b) 4 in., and (c) 11 in., respectively (77·25, 77·5, and 97·75 hr.).

The gas-chromatographic analyses were carried out as described elsewhere.[2]

*Irradiation of Diethylamine.*—Diethylamine (225 ml.) was irradiated, then fractionated, the fraction of b. p. 80—100° (bath temp.)/10 mm. being collected. The weight of this, with different times of irradiation, was as follows: 0·40 g. (24 hr.), 1·95 g. (46 hr.), 1·53 g. (89 hr.), and 1·32 g. (108 hr.). Analysis was on Carbowax 1000 at 72° (flow rate 30 ml./min.), retention times being as follows: tetraethylhydrazine, 2·75 min., 1,3-diethyl-2,4,5-trimethylimidazolidine, 11·0 min., *meso-* and racemic *NN'*-diethylbutane-2,3-diamine, 15·75 and 17·75 min., respectively, and *N*-but-2-enylidene-ethylamine, 32·75 min.

N-*But-2-enylidene-ethylamine* (II).—Freshly distilled crotonaldehyde (20 ml.) was added during 45 min., with stirring and cooling in an ice–salt freezing mixture, to anhydrous ethylamine (26 ml.). After the addition, stirring was continued for 1 hr. with cooling, followed by 1 hr. at room temperature. The mixture was shaken with potassium carbonate (5 g.). The organic layer was separated, dried ($K_2CO_3$), and distilled to give the base, b. p. 65—70° (bath temp.)/10 mm. (2·6 g.). This decomposed too rapidly for analysis, but had the same gas-chromatographic behaviour as the main product of the photolysis of diethylamine.

*Irradiation of Triethylamine.*—Triethylamine was irradiated, then fractionated, the fraction of b. p. 90—130° (bath temp.)/15 mm., being collected. The volumes of triethylamine and weights of products were: (a) 155 ml., 0·13 g., (b) 180 ml., 0·04 g., (c) 230 ml., 0·03 g., (d) 140 ml., 0·63 g., (e) 230 ml., 0·79 g. Analysis was on liquid paraffin at 95° (flow rate 30 ml./min.), retention times (min.) being as follows: tetraethylhydrazine 3·5, unknown X 9·75, *NN'*-diethylbutane-2,3-diamine 11·75, 1,3-diethyl-2,4,5-trimethylimidazolidine 19·75, unknown Y 23·0, *meso-* and racemic *NNN'N'*-tetraethylbutane-2,3-diamine, 44·75 and 53·5, respectively.

meso-NN'-*Diethyl*-NN'-*dinitrosobutane*-2,3-*diamine.*—Prepared from the *meso*-diamine[1] in dilute hydrochloric acid, with sodium nitrite, and crystallised from ethanol, the *dinitrosamine* had m. p. 108—109° (Found: C, 47·6; H, 8·85; N, 27·75. $C_8H_{18}N_4O_2$ requires C, 47·5; H, 8·95; N, 27·7%).

*Racemic* NN′-*Diethyl*-NN′-*dinitrosobutane*-2,3-*diamine.*—When similarly prepared, this had m. p. 92—93° (Found: C, 46·8; H, 8·6; N, 27·6%).

This work was sponsored by Air Force Materials Laboratory, Research and Technology Division, A.F.S.C. through the European Office of Aerospace Research, U.S.A.F. We thank Mr. P. Kelly, M.Sc., for the mass-spectrometric measurement. The Pye Argon Chromatograph used in this work was purchased through a grant from the D.S.I.R.

DEPARTMENT OF ORGANIC CHEMISTRY, THE UNIVERSITY OF NEWCASTLE UPON TYNE,
NEWCASTLE UPON TYNE 1.
[*Received, March 4th*, 1965.]