240. *Some Reactions of the Dimethylamino Radical*, $\cdot NMe_2$.

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The radical $\cdot NMe_2$ has been obtained by pyrolysis of tetramethyltetrazen in a number of organic liquids. Some evidence of dehydrogenation of non-1-ene, cyclohexanol, and benzyl alcohol has been obtained, but there was no indication of nuclear substitution of naphthalene or anthracene. The $\cdot NMe_2$ radical combines with α-methylstyrene (isopropenylbenzene) to give a number of bases derived from the radicals $Me_2N\cdot CH_2\cdot CPhMe\cdot$ and $Me_2N\cdot CH_2\cdot CPhMe\cdot CH_2\cdot CPhMe\cdot$ by addition or disproportionation.

JUST as alkyl radicals can be formed by the pyrolysis of aliphatic azo-compounds, the dimethylamino radical can be obtained by the pyrolysis of tetramethyltetrazen:[1]

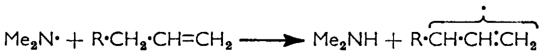
$$Me_2N\cdot N{:}N\cdot NMe_2 \longrightarrow N_2 + 2Me_2N\cdot$$

These radicals interact both by combination and by disproportionation, for the identified products of this pyrolysis, in the vapour phase,[2] are nitrogen, tetramethylhydrazine, dimethylamine, and a polymer of the Schiff's base, $CH_2{:}NMe$. From the few figures published, about as many radicals appear to interact by disproportionation as by combination.

Liquid-phase reactions of dimethylamino radicals have as yet been examined only by Erusalimsky, Dolgoplosk, and Kavunenko,[3] who have shown that these radicals can dehydrogenate cumene, forming dimethylamino (92%) and dicumyl (44%), and that they evidently combine with α-methylstyrene (isopropenylbenzene). No dimethylamine was generated from a dilute solution in the latter solvent, but the basic products were not examined.

$$Me_2N\cdot + Ph\cdot CHMe_2 \longrightarrow Me_2NH + Ph\cdot CMe_2\cdot$$
$$2Ph\cdot CMe_2\cdot \longrightarrow Ph\cdot CMe_2\cdot CMe_2Ph$$

We have now investigated the products of pyrolysis of tetramethyltetrazen in a number of organic liquids. From solutions in molten naphthalene, and in anisole containing anthracene, 62% of dimethylamine was involved but production of aromatic tertiary amines could not be detected. This appears to indicate that $\cdot NMe_2$ is less reactive than $\cdot NH_2$.[4] Decomposition of the tetrazen in a 5% solution in non-1-ene yielded 72% of dimethylamine and a high-boiling hydrocarbon mixture which appeared to contain both terminal ($\cdot CH{:}CH_2$) and *trans*-non-terminal ($\cdot CH{:}CH\cdot$) double bonds, but there was very little other basic material. Thus some allylic dehydrogenation seems to have occurred:



$$Me_2N\cdot + R\cdot CH_2\cdot CH{=}CH_2 \longrightarrow Me_2NH + R\cdot\overbrace{CH\cdot CH{:}CH_2}^{\cdot}$$

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[1] Rice and Grelecki, *J. Amer. Chem. Soc.*, 1957, **79**, 2679.

[2] Watson, *J.*, 1956, 3677; Watson and Waring, *Canad. J. Chem.*, 1960, **38**, 298.

[3] Erusalimsky, Dolgoplosk, and Kavunenko, *Zhur. obshchei Khim.*, 1957, **27**, 267.

[4] Seaman, Taylor, and Waters, *J.*, 1954, 4690; Albisetti, Coffmann, Hoover, Jenner, and Mochel, *J. Amer. Chem. Soc.*, 1959, **81**, 1489.

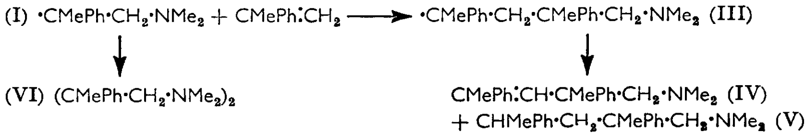
Decompositions in cyclohexanol, cyclohexanone, and benzyl alcohol gave 60—70% yields of dimethylamine, which again indicate that ·NMe_2 can effect some dehydrogenation of these liquids. Though reactions between amines and carbonyl compounds obscure the picture, yet, from the decomposition in benzyl alcohol, benzaldehyde has been isolated together with much smaller amounts of hydrobenzoin, benzil, benzyl benzoate, and a base which has proved to be *NN'*-dimethyl-1,2-diphenylethylenediamine, $(\cdot CHPh\cdot NHMe)_2$. Some of these minor products may have been formed from benzaldehyde, the reactions of which with dimethylamino radicals are very complex and will be reported later.

Products of the decomposition of tetramethyltetrazen in α-methylstyrene have been separated by distillation and chromatography and have been examined. From much more concentrated solutions than that used by Erusalimsky *et al.*, 12—26% of dimethylamine was evolved and 42—45% of the dimethylamino radicals could be accounted for as addition products of the α-methylstyrene. There was also formed a little 2,5-diphenylhex-1-ene and some hydrocarbon polymer. From the basic product a 15—20% yield of 3-dimethylamino-2-phenylpropene (II) was isolated and identified by reduction and methylation to give trimethyl-2-phenylpropylammonium iodide. Clearly, the base (II) has been formed by the following reactions:

$$Ph\cdot CMe{:}CH_2 + \cdot NMe_2 \longrightarrow \cdot CMePh\cdot CH_2\cdot NMe_2 \text{ (I)}$$
$$\cdot CMePh\cdot CH_2\cdot NMe_2 + \cdot R \longrightarrow CH_2{:}CPh\cdot CH_2\cdot NMe_2 \text{ (II)} + RH$$

in which a dimethylamino-radical has added, as would be expected, to the CH_2 group of the olefin to give radical (I).

A similar amount of the reaction product consisted of a mixture of related tertiary bases $C_{20}H_{25}N$ and $C_{20}H_{27}N$, probably 5-dimethylamino-4-methyl-2,4-diphenylpent-2-ene (IV) and 1-dimethylamino-2-methyl-2,4-diphenylpentane (V), whilst 3% consisted of a solid, $C_{22}H_{32}N_2$, possibly 1,4-bisdimethylamino-2,3-dimethyl-2,3-diphenylbutane (VI). These are the expected products of the following radical reactions, analogues of which, on use of trichloromethyl radicals, have been elucidated by Kharasch, Simon, and Nudenberg:[5]



$$\begin{array}{lcl}
\text{(I)}\ \cdot CMePh\cdot CH_2\cdot NMe_2 + CMePh{:}CH_2 & \longrightarrow & \cdot CMePh\cdot CH_2\cdot CMePh\cdot CH_2\cdot NMe_2 \text{ (III)} \\
\downarrow & & \downarrow \\
\text{(VI)}\ (CMePh\cdot CH_2\cdot NMe_2)_2 & & CMePh{:}CH\cdot CMePh\cdot CH_2\cdot NMe_2 \text{ (IV)} \\
 & & + CHMePh\cdot CH_2\cdot CMePh\cdot CH_2\cdot NMe_2 \text{ (V)}
\end{array}$$

EXPERIMENTAL

Tetramethyltetrazen was prepared by oxidizing *NN*-dimethylhydrazine (Eastman Kodak " Practical " material) with mercuric oxide[6] (yield 50%). It was redistilled from fused barium oxide and stored at 0° (b. p. 33—34°/15 mm.).

*Decomposition in Non-*1*-ene*.—The hydrocarbon (Shell Chemicals Co.), when freed from inhibitor, dried, and distilled from a little picric acid, had b. p. 37—38°/13 mm. A mixture of the tetrazen (3·5 g., 0·03 mole) and non-1-ene (64 g., ~0·5 mole) was refluxed for 44 hr. at 145—150° in a stream of dry, oxygen-free nitrogen. The issuing gases were passed through N-hydrochloric acid; titration, to Methyl Red, showed that 0·046 equiv. (77% of the ·NMe_2 groups) of base had been evolved. The acid solution was evaporated to dryness, the residue, covered with benzene (30 ml.), was basified with sodium hydroxide, and the benzene layer was dried. Addition to it of a saturated solution of picric acid in benzene gave yellow crystals, m. p. 154—156°, which after one recrystallisation did not depress the m. p. (158°) of dimethylamine picrate. The liquid product was extracted with water and then dilute acid but this procedure removed only 0·1 g. of brown, unsaturated, basic material. Non-1-ene was removed from the acid-washed liquid by distillation at 15 mm. and the remainder (12 g.) was chromatographed through alumina by use of light petroleum (b. p. 60—80°) and then fractionated at

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[5] Kharasch, Simon, and Nudenberg, *J. Org. Chem.*, 1953, **18**, 328.
[6] Bull, Seaton, and Audrieth, *J. Amer. Chem. Soc.*, 1958, **80**, 2516.

1·5 mm. into colourless oils: (*a*) 4 g., b. p. 142—180°, having strong infrared absorptions of almost equal intensity at 915 and 965 cm.$^{-1}$; (*b*) 3 g., b. p. 180—250°; (*c*) 2 g., b. p. >250°, having weaker absorptions at these frequencies. The absorption spectra of those oils indicated that they were mixtures of dimeric and polymeric unsaturated hydrocarbons.

Decomposition in boiling cyclohexanol (80 g.) was carried out similarly by using 4·64 g. of the tetrazen. 0·052 Equiv. (68%) of dimethylamine was liberated, but acid-extraction of the residue gave only a small amount of dark basic material. The neutral remainder contained ketonic material (<0·3 g.; absorption at 1700 cm.$^{-1}$) but the presence of cyclohexanone could not be established. A similar decomposition in cyclohexanone gave 76% of dimethylamine and yielded a deep brown liquid which, on acidification, deposited a black tar insoluble in ether. No identifiable products could be separated from the neutral remainder.

The decomposition at 145—150° of the tetrazen (11·6 g.) in molten naphthalene (51 g.) gave 0·124 equiv. (62%) of volatile base. Some basic tar was formed, but this gave only a few drops of a dark oil soluble in ether. The tetrazen (4·4 g.) and anthracene (6·7 g.) were refluxed at *ca.* 153° for 2 days in anisole (100 ml.) under nitrogen; 0·047 equiv. (62%) of dimethylamine was evolved. After removal of the anisole, extraction of the remainder gave 0·25 g. of basic tar, and 5 g. of anthracene were recovered.

Decomposition in Benzyl Alcohol.—A mixture of the tetrazen (11·6 g.) and benzyl alcohol (95 g.; b. p. 96—97°/15 mm.; purified by distillation from 2,4-dinitrophenylhydrazine) was heated at 145—150° for 43 hr. under nitrogen; 0·132 equiv. (66%) of volatile bases was evolved. The residual liquid was extracted with saturated aqueous sodium hydrogen sulphite. Decomposition of this extract with sodium carbonate followed by steam-distillation gave 2 ml. of an oil, consisting mainly of benzaldehyde [dinitrophenylhydrazone (4 g.), m. p. and mixed m. p. 234—237°].

The remaining product was distilled in steam to remove benzyl alcohol, and the residue, in ether, was extracted with 4N-hydrochloric acid. The remaining ether solution contained 8·1 g. of a green liquid which was dissolved in light petroleum and chromatographed on 5% deactivated alumina (500 g.). Light petroleum–benzene (9 : 1) eluted a yellow oil, A (0·64 g.), with $\nu_{max.}$ at 1715, 1265, and 1110 cm.$^{-1}$. Light petroleum–benzene (3 : 1) extracted 0·15 g. of an oil containing some crystals, B. Benzene eluted unchanged benzyl alcohol (2·8 g.), and ether–benzene eluted more benzyl alcohol (1·4 g.) together with yellow crystals, C (0·34 g.), with $\nu_{max.}$ at 3300, 1035, 1020, 758, and 700 cm.$^{-1}$.

Rechromatography of oil A gave a very pale yellow product (0·41 g.) with an infrared spectrum identical with that of benzyl benzoate. Hydrolysis of this with 25% aqueous potassium hydroxide gave benzoic acid (0·11 g.), m. p. and mixed m. p. 121°, and benzyl alcohol (3,5-dinitrobenzoate, m. p. and mixed m. p. 112°). Fraction B on rechromatography gave more benzyl benzoate together with benzil, m. p. and mixed m. p. 94—94·5°. Recrystallisation of the crystals C from ethanol gave colourless plates of hydrobenzoin, m. p. and mixed m. p. 135°. Basification of the acid extract gave a pale brown oil (4·15 g.) which, by chromatography through deactivated alumina, gave a little benzyl alcohol (1·12 g.), a yellow oil (1·09 g.), $\nu_{max.}$ 2750—2780m cm.$^{-1}$ (NMe), and a solid (0·48 g.) which, after crystallisation from acetone, gave prisms, m. p. 134° (Found: C, 80·0; H, 8·4; N, 11·6; NMe, 18·1%; *M*, 216. Calc. for $C_{16}H_{20}N_2$: C, 80·0; H, 8·4; N, 11·7%; *M*, 240), $\nu_{max.}$ (in Nujol) 3270, 2770, 1155, 1137, 1126, and 1105 cm.$^{-1}$. The infrared spectrum of the prisms in carbon tetrachloride solution had $\nu_{max.}$ at 3305 and 2805 cm.$^{-1}$, indicating the presence of a NHMe group.[7] The m. p. of this substance was not depressed on admixture with *NN'*-dimethyl-1,2-diphenylethylenediamine, prepared by Fischer and Römer's method,[8] and the two samples had coincident infrared spectra.

Decomposition in α-Methylstyrene.—The tetrazen (11·6 g.) and α-methylstyrene (75 g.; distilled from picric acid; b. p. 58°/16 mm.) were heated together at 145—150° for 2 days under purified nitrogen and gave 26% and 12% of dimethylamine in successive experiments. The mixture was extracted with 2N-hydrochloric acid, and the remaining neutral liquid was dried and distilled, to give a small residue (1·6 g.), b. p. 150—200°/8 mm., which, in light petroleum, was chromatographed through activated alumina. This yielded a colourless liquid (1·16 g.), n_D^{25} 1·5652, with absorptions at 1060, 895, 780, 765, and 700 cm.$^{-1}$, the absorption at 895 cm.$^{-1}$, typical of $RR'C{:}CH_2$, being relatively less intense than that of α-methylstyrene (Found: C, 91·6; H, 8·6. Calc. for $C_{18}H_{20}$: C, 91·5; H, 8·5%). These observations indicate

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[7] Hill and Meakins, *J.*, 1958, 760.

[8] Fischer and Römer, *J. prakt. Chem.*, 1906, **73**, 441.

that the liquid is 2,5-diphenylhex-1-ene, n_D^{25} 1·5621, which has been obtained by dimerising α-methylstyrene. Quantitative hydrogenation in glacial acetic acid over Adams catalyst indicated the presence of one double bond; the product absorbed only slightly at 895 cm.$^{-1}$.

The acid extract was basified and the organic bases (32 g.) were collected, dissolved in light petroleum, and chromatographed through 5% deactivated alumina. The successively eluted fractions were further separated by fractional distillation at reduced pressure. Three main products were obtained: X, b. p. 180—181°/11 mm., n_D^{25} 1·5486, $\nu_{max.}$ 2820, 2780, 1040, 1025, 900, 835, 780, 763, and 700 cm.$^{-1}$ (yields 19%, 25%) (Found: C, 85·0, 84·9; H, 9·4, 9·45; N, 5·4, 5·3%; *M*, 232. Calc. for $C_{20}H_{27}N$: C, 85·3; H, 9·7; N, 5·0%; *M*, 281); Y (more strongly adsorbed), b. p. 85°/8 mm., $\nu_{max.}$ 2820, 2780, 1035, 1020, 910, 855, 845, 780, 765, and 703 cm.$^{-1}$ (yields 20%, 16%) (Found: C, 81·8; H, 9·5; N, 8·5. $C_{11}H_{15}N$ requires C, 81·9; H, 9·4; N, 8·7%); and Z, which again slowly solidified, to give crystals, m. p. 100—101°, from light petroleum (b. p. 48—60°) (yield 3%) (Found: C, 81·9; H, 10·1; N, 7·9. $C_{22}H_{32}N_2$ requires C, 81·4; H, 9·9; N, 8·6%).

The liquid X gave a *picrate*, m. p. 152° (Found: C, 61·5; H, 5·7; N, 11·0. $C_{26}H_{30}N_4O_7$ requires C, 61·2; H, 5·9; N, 11·0%). Quantitative hydrogenation of X (from two different reactions) in glacial acetic acid over Adams catalyst indicated that 50% of X had one olefinic bond, the remainder being saturated. The hydrogenated product resembled X in all properties, except that its absorption at 900 cm.$^{-1}$ was very weak and it yielded the same picrate, m. p. 157°, as did untreated X. This evidence indicates that X is probably a 1 : 1 mixture of 5-dimethylamino-4-methyl-2,4-diphenylpent-2-ene and 1-dimethylamino-2-methyl-2,4-diphenylpentane, the picrate being that of the latter compound.

Liquid Y gave a *methiodide*, which formed cream-coloured crystals, m. p. 139°, from ethanol–ether (Found: C, 47·8; H, 5·9; N, 4·7; I, 41·3. $C_{12}H_{18}NI$ requires C, 47·5; H, 6·0; N, 4·6; I, 41·9%). Hydrogenation of Y indicated the presence of one olefinic bond: the product had very weak absorption at 910 cm.$^{-1}$ and gave a methiodide, m. p. 158—158·5°, corresponding in properties to trimethyl-2-phenylpropylammonium iodide [9] (Found: C, 47·2; H, 6·8; N, 4·6; I, 41·6. Calc. for $C_{12}H_{20}NI$: C, 47·2; H, 6·6; N, 4·6; I, 41·6%). This establishes that Y is 3-*dimethylamino*-2-*phenylpropene*.

Material Z, from its analysis, polar character, and spectrum seems to be 1,4-*bisdimethylamino*-2,3-*dimethyl*-2,3-*diphenylbutane*.

A synthesis of X was attempted; α-phenylpropionaldehyde was condensed with dimethylamine hydrochloride and paraformaldehyde in ethanol to give the Mannich base, β-*dimethylamino*-α-*methyl*-α-*phenylpropionaldehyde*, b. p. 118—124/9 mm., $\nu_{max.}$ 2830, 2780, 2730, 1730, 1040, 1030, and 865 cm.$^{-1}$ (Found: C, 75·8; H, 9·4; N, 6·8. $C_{12}H_{17}NO$ requires C, 75·4; H, 9·0; N, 7·3%), but attempts to condense this with the Grignard reagent of (1-bromoethyl)-benzene failed, only 2,3-diphenylbutane,[10] m. p. 126°, being obtainable. A similar self-coupling of this Grignard reagent has been reported previously.[11]

One of us (B. R. C.) thanks the D.S.I.R. for a Research Studentship.

The Dyson Perrins Laboratory, Oxford. [*Received, September* 1*st*, 1960.]

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[9] von Braun, Heider, and Neuman, *Ber.*, 1916, **49**, 2619.

[10] Heilbron and Bunbury, "Dictionary of Organic Compounds," II, Eyre and Spottiswoode, London, 1953, Vol. II, p. 273.

[11] Rupe and Tomi, *Ber.*, 1914, **47**, 3075.