146. *Reactions of Tertiary Bases with Polyhalogeno-paraffins.*

By W. Cule Davies, (Miss) Elaine B. Evans, and H. R. Whitehead.

The densities, refractive indices, and viscosities of binary mixtures of dimethylaniline and methylene dichloride or chloroform show little departure from ideal behaviour. Trimethylamine and triethylamine in the presence of air or oxygen react readily with bromoform in ethereal or xylene solution, giving the hydrobromide of the base and formaldehyde or acetaldehyde, respectively, as main products. Chloroform does not react with trimethylamine under these conditions.

Numerous physicochemical investigations have shown that chloroform and other polyhalogeno-paraffins form complexes with ethers. The structures given by Earp and Glasstone (J., 1935, 1709) for the compounds of ether with chloroform and carbon tetrachloride are $R_2O{\rightarrow}H{\cdot}CCl_3$ and $R_2O{\rightarrow}Cl{\cdot}CCl_3$. On the other hand, a compound of ether with, *e.g.*, methyl chloride, would probably be given an oxonium salt structure. In an attempt to obtain further information on these structures, we commenced a study of the systems formed between tertiary amines and polyhalogeno-paraffins, since tertiary amines have greater donor power than ethers, and the number of possible compounds would be less, as the amine has only one lone pair of electrons. The results obtained were unexpected and the work has been abandoned, but in view of recent papers by Zellhoefer, Copley, and Marvel (*J. Amer. Chem. Soc.*, 1938, **60**, 1337) and by Hammick, Norris, and Sutton (J., 1938, 1755), our results are recorded.

Determinations of the densities, refractive indices, and viscosities of binary mixtures of dimethylaniline with methylene dichloride or chloroform at several temperatures showed that there was little departure from ideal behaviour. Deviations in the viscosity measurements could be explained by association. Similarly, cryoscopic and ebullioscopic measurements gave no indications of unusual behaviour.

Trimethylamine and triethylamine, however, in the presence of air or oxygen, reacted readily with bromoform in ethereal or xylene solution at room temperature, the main products being the hydrobromide of the base and formaldehyde or acetaldehyde, respectively. Chloroform and carbon tetrachloride, on the other hand, were unaffected under these conditions. Again, carbon tetrabromide reacted with trimethylamine with production of an unidentified crystalline solid and formaldehyde. It is noteworthy that triethylphosphine reacts with chloroform and carbon tetrachloride, giving quaternary phosphonium salts, *e.g.*, $CCl[P(C_2H_5)_3Cl]_3$ (Hantzsch and Hibbert, *Ber.*, 1907, **40**, 1508).

Experimental.

Methylene dichloride, chloroform, and bromoform were thoroughly washed with water, dried over calcium chloride, and fractionally distilled (bromoform under diminished pressure). They were kept in the dark, and were only used if they gave no indication of free hydrogen halide. Dimethylaniline, purified by treatment with acetic anhydride, was fractionated. Liquid trimethylamine was distilled through a tube containing solid potassium hydroxide into the reaction vessel.

The mixtures of the organo-chlorides and dimethylaniline were made up by weighing. Densities are corrected for buoyancy of the air, and were determined in a 10-c.c., glass-capped, Ostwald pyknometer. Refractive indices were taken in a Zeiss–Pulfrich refractometer. Viscosities were determined in a U-tube viscometer for pipette filling, No. 0 (British Standards Institution, No. 188, 1937), standardised with water. The kinetic-energy correction was applied, and the results are expressed in centipoises.

The densities and refractive indices of the methylene dichloride- and chloroform–dimethylaniline mixtures, when plotted against the volume % of methylene dichloride or chloroform, fall accurately on a straight line. When the viscosities of the methylene dichloride–dimethylaniline mixtures are plotted against the volume % of the former, there is considerable departure from linearity, but plotting against g.-mols. % gives a linear relation, though there is a slight deviation at the lower temperature. With chloroform–dimethylaniline mixtures the deviation in the volume % plot is smaller than with methylene dichloride, though when the results are plotted against weight % the deviations are very small. The graph of log η against volume %

is very closely linear in this case. The deviations can be explained by association of one or both of the constituents.

Dimethylaniline and methylene dichloride at 25°.

CH_2Cl_2, wt. %	0	13·85	26·37	37·92	49·68	59·00	68·78	76·78	84·12	92·30	100
$d_{4°}^{25°}$	0·9520	0·9886	1·0250	1·0614	1·1019	1·1359	1·1739	1·2073	1·2401	1·2790	1·3181
η	1·302	1·090	0·935	0·815	0·712	0·641	0·578	0·532	0·491	—	0·414
$n_D^{24·8°}$	1·5562	1·5419	1·5276	1·5138	1·4992	1·4868	1·4726	1·4615	1·4493	1·4356	1·4220

Dimethylaniline and methylene dichloride at 0°.

CH_2Cl_2, wt. %	0	18·48	37·67	57·33	79·83	100
$d_{4°}^{0°}$	0·9722	1·0246	1·0864	1·1598	1·2579	1·3620
η	2·072	1·562	1·167	0·893	0·675	0·531
n_D	1·5677	1·5484	1·5266	1·5017	1·4697	1·4361

Dimethylaniline and chloroform at 25°.

$CHCl_3$, wt. %	0	15·35	29·11	40·40	52·00	60·09	69·28	78·06	85·59	92·89	100
$d_{4°}^{25°}$	0·9520	1·0065	1·0610	1·1114	1·1677	1·2108	1·2637	1·3186	1·3689	1·4234	1·4794
η	1·302	1·195	1·093	1·006	0·914	0·848	0·775	—	0·645	0·590	0·537
$n_D^{24·8°}$	1·5562	1·5442	1·5323	1·5218	1·5097	1·5005	1·4896	1·4780	1·4669	1·4556	1·4437

Dimethylaniline and chloroform at 40°.

$CHCl_3$, wt. %	0	14·39	33·75	50·24	64·17	77·50	89·35	100
$d_{4°}^{40°}$	0·9396	0·9894	1·0660	1·1412	1·2140	1·2929	1·3715	1·4501
η	1·041	0·966	0·861	0·765	0·682	0·602	0·528	0·465
$n_D^{39·5°}$	1·5495	1·5385	1·5217	1·5053	1·4894	1·4720	1·4538	1·4357

Measurements by Weissenberger, Schuster, and Lielacher (*Sitzungsber. Akad. Wiss. Wien*, 1925, **134**, Abt. 2*B* Chemie, 301) of the vapour pressures of mixtures of chloroform and dimethylaniline were considered to indicate the formation of a 1 : 1 molecular compound. The high solubility of dichlorofluoromethane in dimethylaniline suggests the formation of a hydrogen bond (C—H$\leftarrow$N) according to Zellhoefer, Copley, and Marvel (*loc. cit.*).

Most substances behave abnormally in freezing dimethylaniline, and the cryoscopic constant apparently decreases with increasing concentration in a range of from 8 to 3 (Ampola and Rimatori, *Gazzetta*, 1897, I, **27**, 51). The mean value of $K = 5·8$ given by these authors is, therefore, subject to considerable uncertainty. Using pure chlorobenzene as solute, we found that extrapolation of the K values, obtained for a series of concentrations, to zero depression gave a value of $K = 7·0$ as the cryoscopic constant of dimethylaniline. This value was supported by the results of some preliminary measurements of the latent heat of fusion of dimethylaniline, from which a value of $K = 6·8$—$7·2$ was calculated. The value $K = 5·8$ must be taken as low. There is, however, some difficulty in obtaining constant freezing points with dimethylaniline solutions. With the cryoscopic constant, $K = 7·0$, methylene dichloride, chloroform, and bromoform appear to be associated in freezing dimethylaniline : Found : average values of M, 130, 162, 281. Calc. : 85, 119, 253, respectively.

The behaviour of dimethylaniline ($M = 121$) in boiling methylene dichloride ($K = 2·6$; Walden, *Bull. Acad. Imp. Sci. Petrograd*, 1915, **9**, 1485) and chloroform ($K = 3·8$; Centnerszwer and Lazniewski, *Z. physikal. Chem.*, 1932, *A*, **160**, 257) was found to be almost normal.

G. of $Ph·NMe_2$/1000 g. of CH_2Cl_2	7·679	13·90	25·19	36·25
Δt	0·145°	0·288°	0·508°	0·772°
M	137·7	125·5	128·9	122·1
G. of $Ph·NMe_2$/1000 g. of $CHCl_3$	5·310	9·886	24·06	32·41
Δt	0·180°	0·328°	0·780°	1·040°
M	112·1	114·5	117·2	118·4

When trimethylamine (0·14 g.-mol./l.) was mixed with chloroform (large excess) in 90% acetone, there was a slight fall in the concentration of the base (determined by titration with standard hydrochloric acid), but subsequent readings remained constant. No precipitate appeared even after 1 month in a mixture of trimethylamine and excess of chloroform in ether. There was still no precipitate when oxygen was bubbled through. Chloroform and trimethylamine, therefore, do not react under these conditions.

Trimethylamine in 90% acetone (25 c.c.; 0·2819 g.-mol./l.) was mixed with a solution (25 c.c.) of bromoform (6·25 g.) in 90% acetone. Initially, 6·08 c.c. of this mixture would require

17·1 c.c. of N/20-hydrochloric acid; after 10 minutes, 5 c.c. of acid were required, and a corresponding amount of halide ion was produced.

When trimethylamine (2·5 g.) and bromoform (8 g.) were mixed with 25 c.c. of ether in an open flask, there was an immediate precipitate (2 g.), which, crystallised from alchol, had m. p. 243° (decomp.; partial sublimation at about 200°) (Found: Br, 57·3. Calc. for NMe_3,HBr: Br, 57·1%). The main crystalline product is, therefore, trimethylamine hydrobromide. The filtrate from the reaction was distilled. The ethereal fraction contained formaldehyde (gallic acid–sulphuric acid test; Fenton, J., **1907**, 91, 690); the liquid remaining was bromoform. There was no indication of a fraction boiling higher than bromoform (*e.g.*, tetrabromoethylene). If dry trimethylamine vapour was passed into a dry ethereal solution of bromoform in an atmosphere of nitrogen, there was no salt precipitation. As soon as oxygen was admitted, precipitation commenced and continued rapidly, and there was a considerable evolution of heat. Water was added, and the mixture gently warmed. A little carbon dioxide was evolved, showing that carbonyl bromide, if produced at all, was only a minor product. With xylene as solvent, similar results were obtained. We have failed to find dimethylamine hydrobromide among the products.

Similarly, a mixture of triethylamine (1·4 c.c.) and bromoform (1 c.c.) in ether (25 c.c.) gave on admission of oxygen an immediate precipitate of triethylamine hydrobromide. The ethereal filtrate was distilled. The first runnings contained acetaldehyde, but did not give the test for formaldehyde.

An ice-cold mixture of trimethylamine (2 g.), carbon tetrabromide (5 g.), and ether (25 c.c.) through which oxygen was passed gave after several hours 2·4 g. of precipitate, and the filtrate gave the usual test for formaldehyde. The precipitate, m. p. 209—210° (decomp.), is readily recrystallised from ethyl alcohol, but has not been identified.

Crystals of dimethylamine hydrobromide (m. p. 133° from alcohol–ether) slowly appear in a mixture of bromoform (5 c.c.), dimethylamine (3 g.), and ether (20 c.c.). The filtrate does not give the gallic acid test for formaldehyde.

TATEM LABORATORIES, UNIVERSITY COLLEGE, CARDIFF.

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