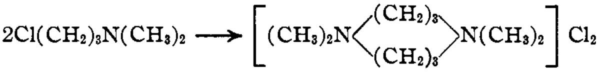
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Quaternary Ammonium Salts from Halogenated Alkyl Dimethylamines. II. The Polymerization of Gamma-Halogenopropyldimethylamines

BY C. F. GIBBS, E. R. LITTMANN AND C. S. MARVEL

Amines of the type $\mathrm{Br(CH_2)}_n\mathrm{N(CH_3)_2}$ have been found to react intramolecularly to produce cyclic quaternary ammonium salts in those cases where n has the value 4, 5 and 6.[1] Previously, Knoor and Roth[2] had studied the product formed when γ-chloropropyldimethylamine (I) was allowed to polymerize in aqueous solution and had assigned an eight-membered ring structure (II) to the quaternary ammonium salt thus obtained.



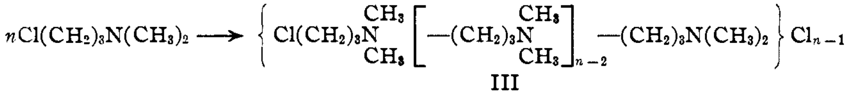
$$2\mathrm{Cl(CH_2)_3N(CH_3)_2} \longrightarrow \left[\mathrm{(CH_3)_2N}\begin{matrix}\mathrm{(CH_2)_3}\\ \\ \mathrm{(CH_2)_3}\end{matrix}\mathrm{N(CH_3)_2}\right]\mathrm{Cl_2}$$

I II

In support of this structure they showed that alkaline decomposition of the quaternary ammonium salt gave allyldimethylamine, tetramethyltrimethylenediamine and an oxygen containing compound believed to be isoallyl ether $\mathrm{(CH_2{=}C(CH_3))_2O}$ formed by the hydration of allene $\mathrm{CH_2{=}C{=}CH_2}$ which was expected as a primary decomposition product in the reaction.

It was also reported in the earlier work that when the chloro amine reacts with itself in water solution, the alkalinity of the solution diminishes but never completely disappears. It has now been found that the product resulting from this polymerization reaction is definitely basic and, moreover, contains some chlorine that is not ionic. These two facts cannot be explained by the cyclic formula (II) suggested by Knoor and Roth.

An alternative formula (III), which in view of the recent work of Carothers[3] on other bifunctional reactions seems to be more logical than the cyclic structure, does satisfactorily account for these reactions of the quaternary ammonium salt as well as for the alkaline decomposition products obtained by Knoor and Roth.



$$n\mathrm{Cl(CH_2)_3N(CH_3)_2} \longrightarrow \left\{\mathrm{Cl(CH_2)_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{N}}}\left[-\mathrm{(CH_2)_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{N}}}\right]_{n-2}-\mathrm{(CH_2)_3N(CH_3)_2}\right\}\mathrm{Cl}_{n-1}$$

III

A long chain molecule of the type indicated in formula III would still contain one chlorine atom which was of the alkyl halide type and one tertiary amine group which would make the molecule basic. From the ratio of the non-ionic chlorine to ionic chlorine in the product it has been

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[1] Littmann and Marvel, THIS JOURNAL, **52**, 287 (1930).

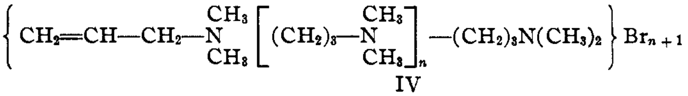
[2] Knoor and Roth, *Ber.*, **39**, 1425 (1906).

[3] See Carothers [*Chem. Rev.*, **8**, 353 (1931)] for a review of this field.

possible to estimate a mean molecular weight for the polymer. The mean value for *n* in the above formula falls between 12 and 13 and the approximate molecular weight is 1500. An attempt to check this value by titration of the amine group gave a value of about 4000 for the molecular weight.

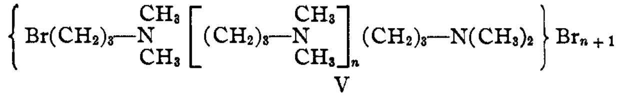
Some experiments on the polymerization of γ-bromopropyldimethylamine have given further evidence that linear polymerization is a characteristic reaction of the halogenopropyldimethylamines. A sample of the bromo amine of the correct bromine content gave a polymeric salt with less bromine in the molecule than was present in the amine. The product was always slightly basic and contained some non-ionic bromine. The low total bromine content suggested that during polymerization a side reaction was taking place which involved the loss of hydrogen bromide and the formation of an olefinic linkage. This surmise was corroborated by the fact that an aqueous solution of the polymer decolorized bromine water and potassium permanganate solution. A sample of the polymer was treated with silver nitrate in water solution and the resulting nitrate still contained a small amount of bromine. When this nitrate was treated with bromine evidence for the addition of bromine to the molecule was obtained.

The properties of this polymeric product are best explained by assuming it to be a mixture of the two types of compounds shown in formulas IV and V. Since the product obtained is a mixture no molecular weight could be calculated from the analytical data.



$$\left\{ CH_2{=}CH{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{N}} \left[(CH_2)_3{-}\overset{CH_3}{\underset{CH_3}{N}} \right]_n {-}(CH_2)_3N(CH_3)_2 \right\} Br_{n+1}$$

IV



$$\left\{ Br(CH_2)_3{-}\overset{CH_3}{\underset{CH_3}{N}} \left[(CH_2)_3{-}\overset{CH_3}{\underset{CH_3}{N}} \right]_n (CH_2)_3{-}N(CH_3)_2 \right\} Br_{n+1}$$

V

Experimental

γ-Phenoxypropyldimethylamine.—This amine was prepared by the general procedure of Knoor and Roth.[2] To a solution of 63 g. of dimethylamine in absolute alcohol was added 75 g. of phenoxypropyl bromide. The mixture was allowed to stand overnight, and then warmed on the steam-bath under a reflux condenser for about a half hour. The excess dimethylamine and the alcohol were distilled from a steam-bath, the residue in the flask was treated with an excess of 25% aqueous sodium hydroxide solution and the amine was collected in ether. On distillation 51 g. (81.5% of the theoretical amount) of a product boiling at 130–132° (20 mm.) was obtained.

The chloroplatinate was prepared by dissolving a sample of the amine in dilute hydrochloric acid and adding a slight excess of chloroplatinic acid. The derivative was crystallized from dilute alcohol and then melted at 147°.

Anal. Subs., 0.1693: Pt, 0.0430. Calcd. for $(C_{11}H_{17}ON)_2{\cdot}H_2PtCl_6$: Pt, 25.42. Found: Pt, 25.40.

When a large excess of dimethylamine was not used, a considerable amount of a product which seemed to be diphenoxypropyldimethylammonium bromide was formed.

γ-Chloropropyldimethylamine.—The method of Knoor and Roth[2] was used for this preparation. The yield was 4.5 g. of chloro amine from 12.5 g. of the phenoxy compound. The product boiled at 124–126°. A picrate melting at 105° was prepared. The melting point reported before was 110°.[2]

γ-Bromopropyldimethylamine.—A solution of 20 g. of γ-phenoxypropyldimethylamine in 140 cc. of concentrated hydrobromic acid was distilled in an all-glass apparatus until the temperature of the vapors reached 123–125°. A second portion of about 100 cc. of hydrobromic acid was added and the distillation repeated. If necessary a third and even a fourth portion of hydrobromic acid was used and distillation was continued until no more phenol distilled with the water, thus showing that the cleavage of the ether was complete. The residue in the flask was evaporated to dryness under reduced pressure and the bromo amine hydrobromide was dissolved in about 30 cc. of water. This solution was cooled and treated with an excess of cold 28% aqueous sodium hydroxide solution. The bromo amine was collected in ether and separated. The ether was removed by evaporation under reduced pressure and the bromo amine was then distilled as rapidly as possible. It boiled at 51° (15 mm.); 34–35° (6 mm.). Some polymerization occurred during distillation but the yield of distilled amine was 14 g. (75% of the theoretical amount); d_4^{20} 1.2312; n_D^{20} 1.4602.

Anal. Subs., 0.3496: 20.51 cc. of 0.1028 *N* $AgNO_3$. Calcd. for $C_5H_{12}NBr$: Br, 48.18. Found: Br, 48.20.

A sample of the hydrobromide was purified from absolute alcohol and analyzed.

Anal. Subs., 0.4925: 38.47 cc. of 0.1028 *N* $AgNO_3$. Calcd. for $C_5H_{13}NBr_2$: Br, 64.72. Found: Br, 64.32.

The chloroplatinate of the amine decomposed slowly at 125–130°.

Anal. Subs., 0.0557: Pt, 0.0144. Calcd. for $[C_5H_{12}NBr]_2 \cdot H_2PtCl_6$: Pt, 26.13. Found: Pt, 25.85.

Polymer of γ-Chloropropyldimethylamine.—Knoor and Roth[2] prepared the quaternary ammonium salt by allowing an aqueous solution of the chloro amine to stand for some time. The same compound was obtained by heating the liquid amine on the steam cone for about thirty-six hours. The solid which formed was washed with ether to remove a little unchanged amine and then purified by dissolving in anhydrous methyl alcohol and precipitating with ethyl acetate. The yield of quaternary ammonium salt from 1.5 g. of amine was 0.7 g. This compound melted with decomposition at 242–243°. The chloroaurate melted at 247–250° (Maquenne block) and the chloroplatinate at 275–280° (Maquenne block). The salts melted much lower if slowly heated in an oil-bath. Knoor and Roth have reported these salts as melting at 247–248° and 275–276°, respectively. The quaternary ammonium salt was amorphous. Its aqueous solution was alkaline toward methyl orange.

Anal. (Parr bomb) Subs., 0.1732: 78.19 cc. of 0.01826 *N* $AgNO_3$. Calcd. for $(C_5H_{12}NCl)_x$: Cl, 29.22. Found: Cl, 29.23. (Volhard) Subs., 0.1930: 81.72 cc. of 0.01826 *N* $AgNO_3$. Found: ionic Cl, 26.89.

From the ratio of non-ionic chlorine to total chlorine 2.39/26.89 it can be seen that the molecular weight of the polymer must be twelve to thirteen times the molecular weight of the simple substance or approximately 1500. Titration with standard acid gave a higher value.

Titration. Subs., 0.3321: 4.4 cc. of 0.0175 *N* HCl. Molecular weight: 4309.

Polymerization of γ-Bromopropyldimethylamine.—The bromo amine was polymerized by heating the pure liquid at steam-bath temperatures; by allowing the liquid to stand at room temperature; by allowing the solution in ethyl alcohol to stand at room temperature and at 0 to −10°; and by allowing the solution in anhydrous ether to stand at room temperature. The polymeric material which was formed under these various conditions did not vary greatly in physical properties. It was a white, non-crystalline, very hygroscopic solid which melted at temperatures varying from 225 to 240° with some decomposition. The water solution was distinctly basic to methyl orange but titration with standard acid gave unsatisfactory results. Samples were purified for analysis by dissolving the crude material in 90% methyl alcohol and precipitating the polymer with ethyl acetate. Very little product was lost. The samples were dried over phosphorus pentoxide in an Abderhalden dryer under reduced pressure at 76°. The properties of typical polymers are listed in Table I.

TABLE I

PROPERTIES OF TYPICAL POLYMERIC QUATERNARY AMMONIUM SALTS FROM γ-BROMOPROPYLDIMETHYLAMINE

Amine, g.	Conditions of reaction	Yield of polymer, g.	M. p., °C.	Br calcd. for $(C_5H_{12}NBr)_x$	Total Br found, %	Ionic Br found, %
10	Liquid on steam-bath	9	225–240	48.18	45.71	45.11
10	Liquid on steam-bath	9	225–240	48.18	47.17	46.40
10	Liquid on steam-bath	9	225–240	48.18	46.34	44.44
10	Liquid at room temp. (approx. 25°)	9.5	225–240	48.18	46.84	46.07
5	Soln. in 95% alcohol at 32°	3	235–245	48.18	47.37	46.60
10	Soln. in 95% alc. at −10 to 0°	6	230–245	48.18	48.00	46.80
10	Soln. in dry ether at room temp. (approx. 25°)	6	225–240	48.18	45.68	44.00

A 1-g. sample of the polymer was heated with an aqueous solution of trimethylamine at 100° in a sealed tube to see if the non-ionic bromine could be converted to ionic bromine. No significant change in ionic bromine could be detected.

A solution of the polymer in water decolorized potassium permanganate solution and also bromine water.

A solution of 2.64 g. of polymer (total Br, 47.37%; ionic Br, 46.6%) in water was made barely acid with nitric acid. A slight excess of aqueous silver nitrate was added and the silver bromide was filtered from the solution. The filtrate was treated with hydrogen sulfide and the silver sulfide was filtered. The filtrate was evaporated to dryness in a desiccator and dried in vacuum over phosphorus pentoxide. The nitrate thus obtained weighed 0.6 g. It was a resinous solid which decomposed at about 125°. It contained bromine as indicated by the following analysis.

Anal. Subs., 0.1687, 0.2422: 0.69, 1.75 cc. of 0.0213 *N* $AgNO_3$. Found: Br, 0.77, 1.05.

A solution of 7.88 g. of the polymer (total Br, 46.65; ionic Br, 45.85) was treated with silver nitrate and the nitrate obtained as described above. The nitrate in water solution was treated with bromine water until a slight excess of bromine remained in solution. This solution was evaporated to dryness and the residue analyzed.

Anal. Subs., 0.2595: 0.91 cc. of 0.1028 *N* $AgNO_3$. Found: Br, 2.95.

This increase of bromine in the nitrate polymer after treatment with bromine water indicates that some bromine had added to an olefinic linkage in the polymer.

Summary

1. γ-Chloropropyldimethylamine has been found to react intermolecularly to give a quaternary ammonium salt which contains non-ionic chlorine and which is slightly basic. These facts are not in harmony with

the cyclic structure previously assigned to the quaternary ammonium salt but are satisfactorily explained on the basis of an open chain polymeric structure.

2. γ-Bromopropyldimethylamine has been found to give a similar polymer but a side reaction involving loss of hydrogen bromide occurs along with the simple polymerization reaction.

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Carbon Suboxide

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The most satisfactory method for the synthesis of carbon suboxide is the pyrolysis of diacetyltartaric anhydride, details for which have been given by Ott and Schmidt.[1] Yields of 41% (32 g. of the suboxide from an original 250 g.) were obtained when the vapors of the anhydride were distilled at 11 mm. over a hot platinum filament. The specially designed apparatus, which calls for difficult glass blowing, is, however, objectionable. In the present work it was found that even better yields could be realized with simple apparatus and at ordinary pressure.

Carbon suboxide was found to react readily with hydroxylamine, giving malonhydroxamic acid: $O{=}C{=}C{=}C{=}O + 2NH_2OH \longrightarrow CH_2(CONHOH)_2$. This is analogous to the synthesis of acethydroxamic acid from ketene[2] and hydroxylamine. In a similar way, β-phenylhydroxylamine reacted with carbon suboxide to produce N,N′-diphenylmalonhydroxamic acid, $CH_2(CON(C_6H_5)OH)_2$. No products were isolated wherein carbon suboxide and the hydroxylamine added to each other except in the ratio of 1:2.

Experimental Part

A Pyrex combustion tube (1 cm. inside diam.) was constricted at one end and sealed to the side arm of a 50-cc. Pyrex distilling flask[3] which carried a dropping funnel in the stopper. Previously the tip of the funnel had been drawn out to a capillary. The tube was then placed within an electric furnace (36 cm. long, but longer furnaces have also been employed satisfactorily). The tube was closed with a one-holed stopper into which fitted a bent tube leading downward into a flask. A two-holed stopper closed this flask. A vertical, water-cooled condenser was fitted into the other hole. From the top of the condenser, the gases were delivered into a receiver which was cooled to −78° by solid carbon dioxide and acetone. Any gases which were still uncondensed were passed through an aniline trap. The exhaust gases, which contained much carbon monoxide, were conducted into a hood or outdoors.

Fifty grams of diacetyltartaric anhydride, which was readily made by the method of

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[1] Ott and Schmidt, *Ber.*, **55**, 2126 (1922); Ott, *ibid.*, **47**, 2391 (1914).

[2] Hurd and Cochran, THIS JOURNAL, **45**, 515 (1923).

[3] A larger flask could, of course, be used if desired.