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

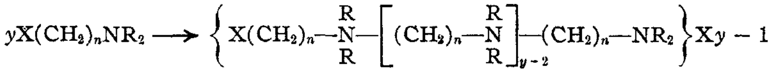
Quaternary Ammonium Salts from Halogenated Alkyl Dimethylamines. III. Omega-Bromo-Heptyl-, -Octyl-, -Nonyl- and -Decyl-dimethylamines

BY M. R. LEHMAN, C. D. THOMPSON AND C. S. MARVEL

The reaction of an ω-halo-alkyl dialkylamine (I) with itself has been shown to occur in such a way as to produce three distinct types of quaternary ammonium salts depending on the number (n) of carbon atoms between the halogen atom and the nitrogen atom. The reactions which have been demonstrated are as follows

$$\underset{\text{I}}{X(CH_2)_nNR_2} \longrightarrow [(CH_2)_n > NR_2]X \qquad (1)$$

$$2X(CH_2)_nNR_2 \longrightarrow \left[R_2N\begin{matrix}(CH_2)_n\\ \\ (CH_2)_n\end{matrix}NR_2\right]X_2 \qquad (2)$$



$$yX(CH_2)_nNR_2 \longrightarrow \left\{X(CH_2)_n-\overset{R}{\underset{R}{N}}-\left[(CH_2)_n-\overset{R}{\underset{R}{N}}\right]_{y-2}-(CH_2)_n-NR_2\right\}Xy - 1 \qquad (3)$$

Reaction 1 has been established definitely[1] for amines in which n has the value 4, 5 or 6. Reaction 2 has been observed[2] for chloroethyldimethylamine in which n has the value 2. Knorr and Roth[3] also reported the formation of an eight-membered ring containing two nitrogen atoms when chloropropyldimethylamine was allowed to stand. However, recent work has shown[4] that the product formed is really a polymeric compound such as that indicated in reaction 3.

It is of interest to note that these results are in accordance with predictions made on the basis of the work of Carothers[5] on other bifunctional reactions. In the earlier work[1] from this Laboratory it was reported that ω-bromoheptyldimethylamine gave a cyclic quaternary ammonium salt. Since this observation is not in agreement with the expected results, this case has now been reëxamined and the work has been extended to include haloalkylamines with eight, nine and ten carbon atoms between the bromine atom and the nitrogen atom.

The method of synthesis of the amines was the same as was used in the earlier work,[1,4] and may be indicated by the following equations.

$$C_6H_5O(CH_2)_nBr \xrightarrow{(CH_3)_2NH} C_6H_5O(CH_2)_nN(CH_3)_2 \xrightarrow{HBr}$$
$$Br(CH_2)_nN(CH_3)_2{\cdot}HBr \xrightarrow{NaOH} Br(CH_2)_nN(CH_3)_2$$

The conditions under which the amine was allowed to polymerize had some influence on the molecular size of the product obtained, but this in-

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

[2] Knorr, *Ber.*, **37**, 3507 (1904).

[3] Knorr and Roth, *ibid.*, **39**, 1425 (1906).

[4] Gibbs, Littmann and Marvel, THIS JOURNAL, **55**, 753 (1933).

[5] Carothers, *Chem. Rev.*, **8**, 353 (1931).

fluence was not great. The amines gave products which indicated that the polymerization reaction (3) was the only important one. Even ω-bromoheptyldimethylamine, which was formerly believed to produce a simple cyclic salt, gave a product which was obviously polymeric in nature when a sufficiently large sample was available for examination. The polymers varied in physical properties from thick viscous liquids, through glassy substances to amorphous powdery solids. They were all extremely hygroscopic and because of this property, difficult to purify and analyze. The molecular weights calculated from the ratio of non-ionic bromine to total bromine ranged from 3350 to 28,000. Each sample was undoubtedly a mixture and the apparent molecular weight was only an average value. The number of amine units per molecule of polymer varied from about 15 to 127. Owing to difficulties of purification, no progress could be made in separating fractions of polymers of different sizes. For the same reason it is impossible to say that no simple rings were produced. However, it can be stated with assurance that the amines of the type $Br(CH_2)_nN(CH_3)_2$, where n has the value 7, 8, 9 or 10, readily undergo a polymerization reaction to give chiefly long chain polymeric quaternary ammonium salts in accordance with equation 3 above. The side reaction involving the loss of hydrogen bromide which was noted in the case of bromopropyldimethylamine[4] was unimportant in the higher homologs.

Experimental

ω-Phenoxyalkyl Bromides.—ω-Phenoxyheptyl bromide was prepared from the corresponding alcohol as previously described.[1] It was found that this alcohol could be readily prepared by a new combination of reactions starting with hexamethylene bromide. Hexamethylene bromide was treated with sodium phenolate in water solution according to the method previously described for the preparation of ω-phenoxypropyl bromide.[6] The yield of ω-phenoxyhexyl bromide was 80% of the calculated amount. This was converted to the cyanide[7] which was esterified in the usual manner by boiling with ethyl alcohol and sulfuric acid.[6] Reduction of the ethyl-ω-phenoxyheptanoate with sodium and alcohol[1] gave the desired ω-phenoxyheptyl alcohol. The yield based on the hexamethylene bromide was 51.5% of the calculated amount.

The eight carbon chain was prepared by converting ω-phenoxyhexyl bromide to the malonic ester derivative,[8] followed by hydrolysis; elimination of carbon dioxide; preparation of ethyl ω-phenoxyoctanoate; reduction of this ester to ω-phenoxyoctylalcohol;[1] and conversion of this alcohol to the bromide.[1]

The nine and ten carbon chains were built up from the corresponding dibasic acids through the esters, glycols and dibromides. The phenoxyalkyl bromides were prepared as previously described for the propyl derivative[6] except that the reaction was carried out in approximately 30% alcohol solution instead of in water solution.

The new compounds which were prepared and characterized in these various syntheses are listed in Table I.

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(6) Marvel and Tanenbaum, THIS JOURNAL, **44**, 2647 (1922).

(7) V. Braun and Müller, *Ber.*, **39**, 4113 (1906), have prepared this cyanide from the corresponding chloride.

(8) Marvel, MacCorquodale, Kendall and Lazier, THIS JOURNAL, **46**, 2840 (1924).

TABLE I

PROPERTIES OF VARIOUS PHENOXY ALKYL DERIVATIVES

	Formula	Yield, %	M. p., °C.	B. p., °C.; press., mm.	Sp. gr., $^{20}_{20}$	n^{20}_D	Analyses Calcd.	Analyses Found
1	$C_6H_5O(CH_2)_6CH(CO_2C_2H_5)_2$	71		222–225 (7)	1.054	1.4908	C, 67.86; H, 8.33	C, 67.86; H, 8.24
2	$C_6H_5O(CH_2)_7CO_2C_2H_5$	83		172–174 (3)	1.013	1.4952	C, 72.68; H, 9.16	C, 72.62; H, 9.20
3	$C_6H_5O(CH_2)_8OH$	76	41–42	177 (4)	...	....	C, 75.61; H, 9.98	C, 75.05; H, 10.03
4	$C_6H_5O(CH_2)_8Br$	77		178 (5)	1.192	1.5272	Br, 28.07	Br, 28.04
5	$C_6H_5O(CH_2)_9Br$	57		141–143 (3)	...	....	Br, 26.7	Br, 26.5
6	$C_6H_5O(CH_2)_{10}Br$	50	32.5	170–176 (3)	...	....	Br, 25.5	Br, 25.3

ω-Phenoxyalkyldimethylamines.—The phenoxyalkyl bromides were treated with a 25% solution of dimethylamine in alcohol as described for the lower homologs.[1] The octyl derivatives were isolated as described for the lower homologs. The nonyl and decyl derivatives were first purified as the hydrobromides by washing with ether and recrystallizing the salts from hot water. Chloroplatinates were prepared and crystallized from dilute alcohol.

ω-Phenoxyoctyldimethylamine was obtained in yields of 47% of the calculated amount; b. p. 159–161° (5 mm.); d^{20}_4 0.9023, n^{20}_D 1.4987. The chloroplatinate melted at 94–95.5°. The picrate melted at 97–98°.

Anal. Calcd. for $(C_{16}H_{27}ON)_2 \cdot H_2PtCl_6$: Pt, 21.49. Found: Pt, 21.50. Calcd. for $C_{22}H_{30}O_8N_4$: N, 11.72. Found: N, 11.85.[9]

ω-Phenoxynonyldimethylamine hydrobromide, m. p. 114–115°, was obtained in 71% of the calculated amount. The free amine boiled at 147–148° (5 mm.); d^{20}_4 0.9221; n^{20}_D 1.4914. The chloroplatinate melted at 136–137°.

Anal. Calcd. for $C_{17}H_{29}ON$: N, 5.32. Found: N, 5.36.[9] Calcd. for $(C_{17}H_{29}ON)_2 \cdot H_2PtCl_6$: Pt, 20.8. Found: Pt, 20.8.

ω-Phenoxydecyldimethylamine hydrobromide, m. p. 105°, was obtained in 89% yield and gave a 75% yield[10] of the free base; b. p. 173–176° (3 mm.); d^{20}_4 0.9218; n^{20}_D 1.4918. The chloroplatinate melted at 104°.

Anal. Calcd. for $C_{18}H_{31}ON$: N, 5.05. Found: N, 5.05.[9] Calcd. for $(C_{18}H_{31}ON)_2 \cdot H_2PtCl_6$: Pt, 20.25. Found: Pt, 20.03.

ω-Bromoalkyldimethylamines.—The amines were prepared from the phenoxyalkylamines by the procedure described in the previous work.[1] In the case of the nonyl and decyl derivatives the hydrobromides of the amines were purified by recrystallization for a mixture of alcohol and ether. The heptyl and octyl derivatives were characterized in the form of the chloroplatinates. The free amines usually polymerized on attempted distillation, although one sample of ω-bromoheptyldimethylamine was found to distil undecomposed at 107° (15 mm.). The new compounds and their properties are recorded in Table II.

Polymerization of the ω-Bromoalkyldimethylamines.—The free ω-bromoalkyldimethylamines were obtained from the hydrobromides. The salt was dissolved in

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(9) This micro analysis was made by Mr. K. Eder.

(10) These yields are based on the ω-phenoxydecyl bromide used.

TABLE II

SALTS OF ω-BROMOALKYLDIMETHYLAMINES, $Br(CH_2)_nN(CH_3)_2$

n =	Salt	M. p., °C.	Analyses, % Calcd.	Found
7	Chloroplatinate	Oily	Pt, 22.85	Pt, 22.89
8	Chloroplatinate	91–92	Pt, 22.13	Pt, 21.74[8]
9	Chloroplatinate	...	Pt, 21.9	Pt, 22.1
10	Hydrobromide	...	HBr, 23.5	HBr, 23.9

water, the free base was liberated with cold 25% sodium hydroxide solution and the amine was taken up in ether. The polymerizations were carried out under different conditions as will be noted in Table III. The products were hygroscopic, amorphous substances which in water solution gave an alkaline reaction to methyl orange. In every case, the polymer had more total bromine than ionic bromine. Total bromine was determined by Stepanow's method or by use of the Parr bomb. Ionic bromine was determined by the Volhard method. The polymers were purified by solution in absolute alcohol and precipitation with ethyl acetate. They were dried over phosphorus pentoxide in a vacuum desiccator.

A few of the more important properties of these polymeric compounds are listed in Table III.

TABLE III

PROPERTIES OF THE POLYMERS

	Polymers of	Description	Conditions for polymerization
1	ω - Bromoheptyldimethylamine	1[a] Amorphous, white, hygroscopic powder, m. p. 247°	Heating to 75° at 3 mm.
2	"	2[a] Amorphous, white, hygroscopic powder, m. p. 250°	Heating to 75° at 3 mm.
3	"	3 Amorphous, white, hygroscopic powder	Standing overnight at 25°
4	ω - Bromooctyldimethylamine	1 Thick resinous product	Heating to 114–115° at 10 mm.
5	ω - Bromononyldimethylamine	1 Opaque, sticky solid	Allowing ether solution of amine to stand two weeks
6	"	2 Opaque solid	Heating bromoamine at 125°
7	ω - Bromodecyl - dimethylamine	1 Amorphous, white solid, m. p. 206–208°	Allowing ether soln. to stand at room temp. two weeks
8	"	2 Hard, glassy substance	Allowing bromoamine to stand without solvent
9	"	3 White amorphous solid, m. p. 160–175°	Heating to 150°

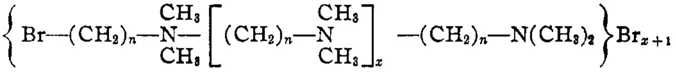
	Formula of polymer	Analyses, % Total bromine Calcd.	Found	Ionic bromine Found	Indicated mol. wt.
1	$(C_9H_{20}NBr)_x$	36.0	35.5	33.6	3350
2	$(C_9H_{20}NBr)_x$	36.0	35.8	33.85	3750
3	$(C_9H_{20}NBr)_x$	36.0	35.63	35.35	28,000
4	$(C_{10}H_{22}NBr)_x$	33.85	33.58	31.55	3470
5	$(C_{11}H_{24}NBr)_x$	32.0	31.6	30.54 30.2	5000–6000
6	$(C_{11}H_{24}NBr)_x$	32.0	31.5	30.1 29.6	5000
7	$(C_{12}H_{26}NBr)_x$	30.3	30.2	29.4	10,000
8	$(C_{12}H_{26}NBr)_x$	30.3	30.4	29.1	6000
9	$(C_{12}H_{26}NBr)_x$	30.3	30.4	29.3	7000

[a] 1 and 2 obtained from same reaction; 1 is the more soluble portion.

Summary

1. ω-Bromoalkyldimethylamines of the series $\mathrm{Br(CH_2)_nN(CH_3)_2}$, where n has the value 7, 8, 9 or 10, have been prepared.

2. These amines have been found to polymerize readily to give products of the type



$$\left\{\mathrm{Br}-(\mathrm{CH_2})_n-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{N}}}-\left[(\mathrm{CH_2})_n-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{N}}}\right]_x-(\mathrm{CH_2})_n-\mathrm{N(CH_3)_2}\right\}\mathrm{Br}_{x+1}$$

The polymers are basic to methyl orange in water solution. The molecular weights calculated from the ratio of non-ionic to total bromine vary from 3350 to 28,000 for different samples. The polymers are hygroscopic substances which vary in physical state from resinous gums through glass-like products to amorphous solids.

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Relation of Concentration to Action of Gelatinizing Agents on Starch[1]

BY C. E. MANGELS AND C. H. BAILEY

Aqueous solutions of certain substances are known to have the power of swelling or gelatinizing starch granules at ordinary temperatures. This property of alkalies, strong acids and other reagents has long been known.

Reychler[2] studied qualitatively the gelatinizing effect of a number of reagents on starches, but more recently Ostwald and Frankel[3] have followed the reaction by means of viscosity determinations. There is comparatively little or no information on record, however, regarding the action of starch gelatinizing reagents over a wide range of concentration. This paper presents a contribution in that field.

Experimental

The swelling or gelatinizing effect of different reagents over a series of concentrations was followed by means of viscosity determinations supplemented in some cases by microscopic examinations. An Ostwald pipet, similar in design to that used by Ostwald and Frankel[3] and having a capillary 3.0 mm. in diameter, was used for the determinations. A starch, prepared in the laboratory from a hard red winter wheat patent flour, was used in all cases. Solutions of strong bases, neutral salts and urea were used as cold gelatinizing agents.

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[1] Joint contribution from North Dakota Agricultural Experiment Station and Minnesota Agricultural Experiment Station. Condensed from one section of a thesis presented by C. E. Mangels to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Paper No. 1177, Journal Series, Minnesota Agricultural Experiment Station.

[2] Reychler, *Bull. soc. chim. Belg.*, **29**, 118, 309 (1920).

[3] Ostwald and Frankel, *Kolloid-Z.*, **43**, 296 (1927).