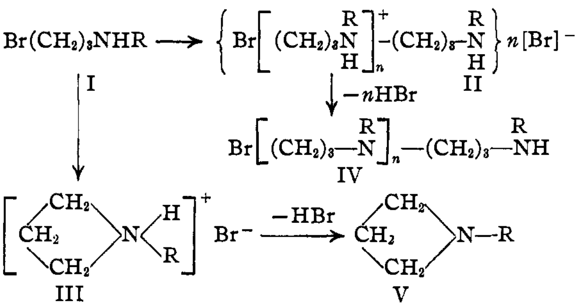
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Ammonium Salts from Bromopropylamines. VI. Salts of Polymeric Tertiary Amines[1]

BY JOHN CHARLES COWAN AND C. S. MARVEL

Previous work in this Laboratory has shown that halogenated tertiary amines of the type $Br(CH_2)_nNR_2$ undergo self-condensation intermolecularly or intramolecularly to give polymeric or cyclic quaternary ammonium salts, depending on the numerical value of *n* and the nature of the R group. The work described in this communication was undertaken in order to learn whether linear polymeric or cyclic tertiary amines would be obtained by a similar self-condensation of halogenated secondary amines.

It should be noted that halogenated secondary amines may be expected to give far more complex products than were obtained from related halogenated tertiary amines. For, whereas the latter give stable quaternary ammonium salts, the former give tertiary amine salts which may react further with unchanged bromoamine. On the basis of our earlier work, bromopropylalkylamines (I) would be expected to condense intermolecularly to give long-chain polymeric compounds (II), or with certain R groups to form monomeric cyclic salts (III) containing a four-membered ring. In the presence of an excess of the bromoalkylamine, these products might be expected to undergo double decomposition reactions to yield the hydrobromide salt of the simple bromoamine and the free polymeric (IV) or cyclic (V) tertiary amine, which then would react further with the bromoalkylamine to give quaternary ammonium salts of very complex type.



Our experiments have shown that when a free bromoalkylamine of type I in which R is methyl, ethyl, *n*-propyl, *n*-butyl or isobutyl is allowed to stand at room temperature in concentrated solution, the polymerization reaction occurs fairly smoothly, and is accompanied by few side reactions. However, in dilute solution, the products become very complex, due to the occurrence of secondary reactions, the exact nature of which has not as yet been elucidated. This observation is in accordance with the views which Salomon[2] has recently expressed in connection with rates of reactions of primary amines containing a haloalkyl group.

The polymers which are formed by the intermolecular condensation reactions vary greatly in size, depending on the size of the R group. In Table I are given the calculated values for the number of monomeric units in and the molecular weights of the various polymeric tertiary amine salts which have been prepared. The values for the number of monomeric units $(n + 1)$ in the polymers were calculated from the formula

$$\frac{n}{n+1} = \frac{\%\text{ ionic halogen}}{\%\text{ total halogen}}.$$

Since in a few cases the percentage of total halogen which we found in a polymer was lower than the theoretical value, we have used the theoretical value for total halogen in our calculations. It seems probable that any loss of halogen must be from the alkyl halide end-group, and not from the ionic fraction of the halogen.

TABLE I

MOLECULAR WEIGHTS OF POLYMERIC TERTIARY AMINE SALTS

$Br\{[(CH_2)_3NRH]_n{}^+(CH_2)_3NHR\}n[Br]^-$

R	$n + 1$	Approximate mol. wt.
CH_3	71–100	10800–15200
C_2H_5	22–23	3650–3820
n-C_3H_7	16–17	2880–3060
n-C_4H_9	20–21	3900–4100
i-C_4H_9	7–8	1350–1550

The polymeric salt from bromopropylmethylamine was treated with silver oxide to give the free base, which proved to be a viscous, semisolid, hygroscopic material. In 0.1 *N* solution, it gave a *p*H of approximately 9.3, indicating that it is a tertiary amine, and that it does not contain quaternary ammonium groups.

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[1] For the fifth paper in this series, see THIS JOURNAL, **57**, 1137 (1935).

[2] Salomon, *Helv. Chim. Acta*, **17**, 851 (1934); *Trans. Faraday Soc.*, **32**, 153 (1936).

TABLE II

γ-PHENOXYPROPYLALKYLAMINES

$C_6H_5OCH_2CH_2CH_2NHR$

R =	Yield of amine, %	B. p., °C.	Mm.	n^{20}_D	d^{20}_4	M. p. of hydrobromide, °C.	Br analyses, % Calcd.	Found
CH_3	60.5	133–138	23	1.5255	1.002	150–151	17.60[a]	17.65[a]
C_2H_5	66	147–148	26	1.5127	0.981	154–155	30.77	30.71
n-C_3H_7	66	154–155	25	1.5098	.971	160–161	29.20	29.27
n-C_4H_9	56.5	134–135	5	1.5060	.958	170–171	27.78	27.83
i-C_4H_9	79.8	153–156	20	1.5038	.955	174–175	27.78	27.65

[a] Chlorine in the hydrochloride was determined in this case. The hydrochloride melted at 155–156°.

The bromoalkylamines were prepared from phenoxypropylalkylamines by cleavage with hydrobromic acid by the general methods which have been described previously[3] for related compounds.

Experimental Part

γ-Phenoxypropylalkylamines.—The phenoxypropylamines were prepared by adding four times the theoretical amount of an alcoholic solution of the appropriate primary amine to γ-phenoxypropyl bromide and allowing the solution to stand for about twenty-four hours until reaction was complete. The alcohol and excess amine were removed by distillation from a steam-bath, and the residue was treated with a 25% aqueous solution of sodium hydroxide. The phenoxypropylamine was collected in ether, the ether removed and the amine distilled under reduced pressure. For analysis, the amines were converted to the hydrobromides, and ionic halogen was determined by direct titration with silver nitrate. The amines thus prepared are described in Table II.

γ-Bromopropylalkylamine Hydrobromides.—The γ-phenoxypropylamines were cleaved with hot 48% hydrobromic acid solution by the procedure used in previous work.[3] The best results were obtained when these cleavage reactions were carried out in an oil-bath held at 137–142°. The distillate was tested with bromine water from time to time, and when no phenol was distilling, the reaction was complete. The reaction mixture was diluted with water and evaporated under reduced pressure. The residue was again dissolved in water and evaporated under reduced pressure to remove the excess hydrogen bromide. If the distillate at this point was not neutral to methyl orange, this process was repeated. The dry residue, free from excess hydrogen bromide, was dissolved in absolute alcohol (dried with magnesium methylate[4]) and treated with Norite until the filtered solution was pale amber or yellow. After removal of the Norite, a part of the alcohol was distilled off under reduced pressure and a large excess of dry ether was added to the remaining solution. In some cases, the bromoamine hydrobromides precipitated at once; in other cases, the salts came out on standing. For analysis the salts were recrystallized by taking up in alcohol and precipitating with ether until no change in melting point was observed on repeating the purification. Less highly purified salts were used for conversion into polymers. The properties of the bromoamine hydrobromides are listed in Table III.

TABLE III

γ-BROMOPROPYLALKYLAMINE HYDROBROMIDES

$[BrCH_2CH_2CH_2NH_2R]^+Br^-$

R =	M. p., °C.	Analysis Ionic Bromine, % Calcd.	Found
CH_3	64–66	34.33	34.25
C_2H_5	144–146	32.38	31.77
n-C_3H_7	225–226	30.65	30.65
n-C_4H_9	253–255[a]	29.09	29.15
i-C_4H_9	255–257[a]	29.09	29.59

[a] Bloc Maquenne.

Polymeric Tertiary Amine Salts.—Each of the free γ-bromopropylalkylamines in which the alkyl group was methyl, ethyl and n-propyl, respectively, was obtained by treating the crude hydrobromide with 50% sodium hydroxide solution and then distilling the free bromoamine from the reaction mixture under reduced pressure. The amines thus obtained contained some water, and they were allowed to polymerize without drying. The n-butyl and isobutyl derivatives polymerized very rapidly at the temperatures at which they distilled. Hence, in these cases the free amines were obtained by treating the salts with 25% sodium hydroxide solution at about 0°, and then extracting the amine with ether. About 15 cc. of 95% alcohol was added to the ether extract and then the solution was evaporated to 10–15 cc. Titration indicated that this gave 1.5–2 molal solutions of the bromoamine. On standing for two or three days, these bromoamines polymerized.

All of the polymeric amine salts were colorless to light amber, sticky, hygroscopic solids. The experiments are summarized in Table IV.

In dilute solution the products of polymerization were complex, and the nature of the physical properties precluded the possibility of crystallizing and separating the substances which were formed. A solution of 5 g. of γ-bromopropylethylamine was treated with an excess of cold (0°) 25% sodium hydroxide solution, and the free amine was taken up in ether and diluted to 145 cc. Titration with standard acid showed that this ether solution was 0.14 molar. This dilute solution was allowed to stand for three days at room temperature. Then the ether was removed and the residue dried over phosphorus pentoxide at 100° under reduced pressure. This crude mixture contained 51.66% bromine, but the bromide ion was only 45.45%. When this product was taken up in absolute alcohol and

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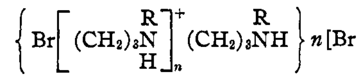
[3] Littmann and Marvel, THIS JOURNAL, **52**, 287 (1930).

[4] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, New York, 1932, p. 244.

TABLE IV

POLYMERIC SALTS FROM γ-BROMOPROPYLALKYLAMINES



$$\left\{ \mathrm{Br}\left[(\mathrm{CH_2})_3\overset{\mathrm{R}}{\underset{\mathrm{H}}{\mathrm{N}}} \right]^{+}_{n} (\mathrm{CH_2})_3\overset{\mathrm{R}}{\mathrm{N}}\mathrm{H} \right\} n[\mathrm{Br}]^-$$

R =	Amine salt, g.	B. p., Bromoamine, °C.	B. p., Bromoamine, Mm.	Yield, amine, g.	M. p. of polymers, °C.	Formula	Calcd. total	Analyses, Br % Found Total	Analyses, Br % Found Ionic
CH_3	10	29–30	4	2.5	205–210 dec.	$(C_4H_{10}NBr)_n$	52.63	52.56	51.89–52.10
C_2H_5	10	31–32	2	7.0	195–199	$(C_5H_{12}NBr)_n$	48.19	47.00	46.04
n-C_3H_7	8	37–38	3	1	.....	$(C_6H_{14}NBr)_n$	44.44	43.31	41.74
n-C_4H_9	5.2	...	..	3.6	100–120	$(C_6H_{16}NBr)_n$	41.23	41.33	39.16
i-C_4H_9	6.4	...	..	4.4	.....	$(C_7H_{16}NBr)_n$	41.23	41.30	35.23

precipitated with dry ether, the total bromine remained approximately constant at 51.96%, but the bromide ion fell to 43.38%. Further attempts to purify the mixture did not lead to any definite product.

A sample of the free polymeric tertiary amine was prepared from the polymeric salt obtained from γ-bromopropylmethylamine. The salt used in this experiment contained 50.3% bromine, and 49.07% bromide ion. A solution of 5 g. of this salt in water was treated with an excess of silver oxide, and then the solution was filtered. The filtrate was again treated with silver oxide to ensure complete removal of bromide ion. The mixture was centrifuged and the liquid filtered. The water was then removed under reduced pressure at room temperature (about 25°). The residue was an amber-colored, viscous, sticky, hygroscopic solid. This material still contained bromine which would react slowly with alcoholic silver nitrate. The water solution of the free polymer was tested with thymolphthalein, and showed a *p*H of about 9.3. This is slightly less basic than an aqueous solution of trimethylamine, showing that the polymer did not carry quaternary ammonium hydroxide groups. The polymeric amine could not be purified by reprecipitation, and the analysis was not especially significant.

Anal. Calcd. for $(C_4H_{10}N)_x$: N, 19.44. Found: N, 15.98.

Summary

γ-Bromopropylalkylamines in concentrated solution react intermolecularly to produce polymeric tertiary amine salts. The molecular weight of the linear polymeric salt is dependent on the alkyl group attached to the nitrogen atom, being about 10,000–15,200 when R is methyl, and falling to about 1350–1550 when R is isobutyl.

URBANA, ILLINOIS RECEIVED AUGUST 31, 1936

The Extraction of Europium from Monazite Residues and the Preparation of Pure Europium Compounds

BY HERBERT N. MCCOY

The method of separation of europium from other rare earths by reduction with zinc and precipitation as europous sulfate has been described in a preliminary note.[1] An account of further studies of some of the properties of europous salts is given in a later paper.[2]

The extraction of europium has now been carried out on a larger scale so that a more detailed description of the process of refinement can be given. In the earliest experiments, the starting material had been subjected to long-continued fractional crystallization as double magnesium nitrates in the presence of bismuth nitrate. It contained little besides samarium, europium and gadolinium. For this material, reduction in a Jones reductor two or three times repeated sufficed to give a pure product.[1]

When, later, material less rich in europium was used, it was found that modification of the process gave better recoveries of the desired element. Instead of running the rare earth solution through a reductor, it was found more expedient with low grade material to add zinc dust to the solution along with magnesium sulfate. It was also found that the addition of barium chloride as suggested by Selwood[3] for use in the electrolytic separation of europium was helpful in giving increased yields. The subsequent purification of the enriched europium concentrates so obtained was carried out in a large reductor as will be described later.

After europium had been extracted successfully from 12 to 15 lots of material varying in amounts from 20 g. to several kilograms and of varying degrees of richness, the separation of the europium

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[1] McCoy, THIS JOURNAL, **57**, 1756 (1935).

[2] McCoy, *ibid.*, **58**, 1577 (1936).

[3] Selwood, *ibid.*, **57**, 1145 (1935).