to belong to one or more than one of the sub-multiples $^1/_2$, $^1/_3$ or $^1/_6$ of the normal molecule. The molecular weights of these sub-multiples correspond to normal molecular weights of other proteins.

UPSALA, SWEDEN

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

# CYCLIC QUATERNARY AMMONIUM SALTS FROM HALOGENATED ALIPHATIC TERTIARY AMINES

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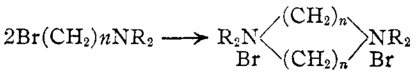
The formation of rings from open-chain compounds of various types has been the subject of many recent investigations. The work of Ruzicka[1] and his collaborators on the large carbon rings has led to this study of the nitrogen compounds in the hope of obtaining large rings containing a nitrogen atom in place of one of the carbon atoms. The largest simple ring containing a nitrogen atom heretofore described is the seven-membered ring, hexamethylene-imine, which has recently been characterized by Müller and Sauerwald.[2]

In a recent study of bromo tertiary amines[3] it was observed that 4-bromobutyldiethylamine on standing changed into a quaternary ammonium salt, which was thought to be a pyrrolidine derivative. The ease with which this reaction occurred suggested that other brominated tertiary amines might give the desired larger rings containing nitrogen.

Knorr and Roth[4] have studied bromo-ethyldimethylamine and chloropropyldimethylamine and have found that they reacted to give six- and eight-membered rings containing two nitrogen atoms, according to the general reaction



$$2\mathrm{Br(CH_2)}n\mathrm{NR_2} \longrightarrow \underset{\mathrm{Br}}{\mathrm{R_2N}}\left\langle\begin{matrix}\mathrm{(CH_2)}_n\\ \mathrm{(CH_2)}_n\end{matrix}\right\rangle\underset{\mathrm{Br}}{\mathrm{NR_2}}$$

Von Braun and his students[5] have studied bromo-alkyl primary amines of the type $\mathrm{Br(CH_2)}_n\mathrm{NH_2}$ and have found that when $n = 4, 5$ or 6 some of the cyclic nitrogen compound was obtained, although the yields were low and by-products due to secondary reactions formed the greater part of the final product. When $n = 7$, they were unable to obtain a reaction product that could be identified as the cyclic amine. In addition to these

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[1] The fourteenth paper on large carbocyclic rings by Ruzicka and his co-workers was published in *Helv. Chim. Acta*, **11**, 1174 (1928).

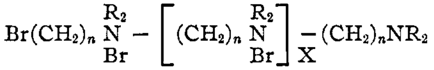
[2] Müller and Sauerwald, *Monatsh.*, **48**, 527, 731 (1927).

[3] Marvel, Zartman and Bluthardt, THIS JOURNAL, **49**, 2299 (1927).

[4] Knorr and Roth, *Ber.*, **39**, 1425 (1906).

[5] Von Braun and Steindorff, *ibid.*, **38**, 173, 3089 (1905); Von Braun and Müller, *ibid.*, **39**, 4116 (1906); Von Braun and Beschke, *ibid.*, **39**, 4121 (1906).

two types of reactions, bromo-alkylamines of this general type might be expected to unite to form long-chain molecules of the type



$$Br(CH_2)_n\overset{R_2}{\underset{Br}{N}} - \left[(CH_2)_n\overset{R_2}{\underset{Br}{N}}\right]_X - (CH_2)_nNR_2$$

According to the views recently expressed by Carothers,[6] ring formation would be the main reaction to be expected when $n$ has the value 4 or 5. When $n$ has a value greater than 5, the reaction would be expected to give the long open-chain polymeric type of compound.

The present paper describes the preparation and reactions of bromoamines of the general type $Br(CH_2)_nN(CH_3)_2$, where $n$ has a value of 4, 5, 6 and 7. All of these amines react with themselves to give cyclic quaternary ammonium salts to a greater or less degree. Where $n$ has the value 4, 5 or 6, ring formation proceeds as the major reaction and yields of more than 50% of the cyclic salt have been isolated. When $n$ has the value 7, the yield of cyclic compound is lowered to less than 50% but still represents a fairly large amount of the final product. These results are shown in Table I, where they are compared with the yields of the cyclic ketones which Ruzicka[7] has obtained by the distillation of the salts of dibasic acids.

TABLE I

COMPARISON OF THE YIELDS OF CYCLIC KETONES AND CYCLIC QUATERNARY AMMONIUM SALTS

| Ketone | Yield, % | Quaternary ammonium salt | Yield, % |
|---|---|---|---|
| $(CH_2)_4>CO$ | 45 | $(CH_2)_4>N(CH_3)_2Br$ | 76 |
| $(CH_2)_5>CO$ | 70 | $(CH_2)_5>N(CH_3)_2Br$ | 63 |
| $(CH_2)_6>CO$ | 50 | $(CH_2)_6>N(CH_3)_2Br$ | 56 |
| $(CH_2)_7>CO$ | 20 | $(CH_2)_7>N(CH_3)_2Br$ | 37 |

That the products isolated in this work were really rings was determined by comparing the five- and six-membered rings with known pyrrolidine and piperidine derivatives. The seven-membered ring was found to be identical with the corresponding derivative of Müller and Sauerwald's[2] hexamethylene-imine. The molecular weights of these salts were determined by freezing point depression in water. They showed the behavior of typical uni-univalent salts in that the values obtained were slightly over one-half the calculated value. No eight-membered ring containing nitrogen was available for comparison with the compound which was obtained from bromoheptyldimethylamine. However, its molecular weight from freezing point depression data checks with the value expected for the simple cyclic salt.

Attempts to determine the rate of the ring closing reaction quantitatively

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[6] Carothers, THIS JOURNAL, **51**, 2548 (1929).

[7] The figures in the table are the highest reported in the paper of Ruzicka, Brugger, Pfeiffer, Schinz and Stoll, *Helv. Chim. Acta*, **9**, 505 (1926).

by titration of ionic halogen and thus make it possible to compare the ease of formation of rings of different sizes were not successful. The side reactions proceeded to a sufficient extent to invalidate reaction rate studies.

## Experimental Part

**4-Phenoxybutyldimethylamine.**—To 180 cc. of a solution of dimethylamine (0.2 g. of amine per cc.) in absolute alcohol was added 46 g. of 4-phenoxybutyl bromide. The solution was allowed to stand overnight and then heated on a steam-bath for about one-half hour. The alcohol and excess dimethylamine were removed by distillation, the residue was treated with a 25% aqueous solution of sodium hydroxide and the amine was extracted with ether. The ether was evaporated and the amine was distilled under reduced pressure. The yield was 30 g. (77% of the theoretical amount) of a product, b. p. 122–124° (5 mm.); sp. gr. $^{20}_{20}$ 0.951; $n^{20}_{\mathrm{D}}$ 1.5017. This compound has previously been described by von Braun,[8] who prepared it by the distillation of 5-phenoxybutyltrimethylammonium hydroxide. The chloroplatinate was prepared and recrystallized from dilute alcohol; m. p. 104°.

*Anal.* Subs., 0.1382: Pt, 0.0338. Calcd. for $(C_{12}H_{19}ON)_2 \cdot H_2PtCl_6$: Pt, 24.52. Found: Pt, 24.45.

**5-Phenoxyamyldimethylamine.**—A solution of 163 g. of 5-phenoxyvaleric acid in 250 cc. of absolute alcohol containing 10 cc. of concentrated sulfuric acid was refluxed for about five hours. The ester was isolated in the usual way. The yield was 169 g. (90% of the theoretical amount) of ethyl 5-phenoxyvalerate; b. p. 151° (6 mm.); sp. gr. $^{20}_{20}$ 1.041; $n^{20}_{\mathrm{D}}$ 1.4982.

*Anal.* Subs., 0.2130: $CO_2$, 0.5025; $H_2O$, 0.1557. Calcd. for $C_{13}H_{18}O_3$: C, 64.48; H, 8.11. Found: C, 64.39; H, 8.10.

This ester was reduced to 5-phenoxyamyl alcohol by the method described by Marvel and Tanenbaum[9] for the preparation of 4-phenoxybutyl alcohol. From 110 g. of ester, 110 g. of sodium and 1 liter of absolute alcohol there was obtained 45 g. (50% of the theoretical amount) of 5-phenoxyamyl alcohol; b. p. 152–155° (5 mm.); m. p. 36°. This compound was previously described by von Braun, Deutsch and Schmatloch,[10] who prepared it by the action of oxygen on 5-phenoxyamylmagnesium iodide.

5-Phenoxyamyl bromide was prepared by mixing 55 g. of phosphorus tribromide and 90 g. of the alcohol at 0° and gradually allowing the mixture to come to room temperature. Water was added to the mixture and the product was separated and distilled. The yield was 63 g. (52% of the theoretical amount) of product; b. p. 154–155° (5 mm.); sp. gr. $^{20}_{20}$ 1.199; $n^{20}_{\mathrm{D}}$ 1.5240. Von Braun and Steindorff[11] have previously prepared this compound from sodium phenolate and pentamethylene bromide.

5-Phenoxyamyldimethylamine was prepared from 25 g. of the bromide and 18 g. of dimethylamine in alcohol solution. The yield was 15.5 g. (74% of the theoretical amount) of a product, b. p. 132–134° (5 mm.); sp. gr. $^{20}_{20}$ 0.945; $n^{20}_{\mathrm{D}}$ 1.4997. Von Braun[12] has previously prepared this amine by the distillation of 5-phenoxyamyltrimethylammonium hydroxide. The chloroplatinate was prepared. After crystallization from dilute alcohol it melted at 112°.

*Anal.* Subs., 0.2032: Pt, 0.0481. Calcd. for $(C_{13}H_{21}ON)_2 \cdot H_2PtCl_6$: Pt, 23.69. Found: Pt, 23.70.

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[8] Von Braun, *Ann.*, **382**, 35 (1911); von Braun and Deutsch, *Ber.*, **44**, 3701 (1911).

[9] Marvel and Tanenbaum, THIS JOURNAL, **44**, 2648 (1922).

[10] Von Braun, Deutsch and Schmatloch, *Ber.*, **45**, 1250 (1912).

[11] Von Braun and Steindorff, *ibid.*, **38**, 963 (1905).

[12] Von Braun, *Ann.*, **382**, 36 (1911).

**6-Phenoxyhexyldimethylamine.**—Ethyl 6-phenoxycaproate was prepared by esterifying with ethyl alcohol the crude 6-phenoxycaproic acid obtained from 147 g. of diethyl 4-phenoxybutylmalonate. The yield was 75 g. (63% of the theoretical amount) of a product, b. p. 157–159° (3 mm.); sp. gr. $^{20}_{20}$ 1.031; $n^{20}_{D}$ 1.4928.

*Anal.* Subs., 0.2103: $CO_2$, 0.5461; $H_2O$, 0.1592. Calcd. for $C_{14}H_{20}O_3$: C, 71.18; H, 8.46. Found: 70.86; H, 8.41.

By reduction of 70 g. of this ester with sodium and absolute alcohol, there was obtained 32 g. (55% of the theoretical amount) of 6-phenoxyhexyl alcohol; b. p. 152–154° (3 mm.); m. p. 31°. Von Braun, Deutsch and Schmatloch[10] have previously prepared this alcohol by the action of oxygen on 6-phenoxyhexylmagnesium bromide.

6-Phenoxyhexyl bromide was prepared by the action of 18 g. of phosphorus tribromide on 30 g. of the alcohol. The yield was 23 g. (54% of the theoretical amount) of a product; b. p. 155–156° (3 mm.); sp. gr. $^{20}_{20}$ 1.248; $n^{20}_{D}$ 1.5361.

*Anal.* Subs., 0.2376: 16.3 cc. of 0.0549 *N* $AgNO_3$. Calcd. for $C_{12}H_{17}OBr$: Br, 31.1. Found: Br, 30.8.

6-Phenoxyhexyldimethylamine was prepared from 22 g. of the bromide and 60 cc. of a 33% alcoholic dimethylamine solution. The yield was 14 g. (74% of the theoretical amount) of a product, b. p. 132–134° (3 mm.); sp. gr. $^{20}_{20}$ 0.942; $n^{20}_{D}$ 1.4988.

The chloroplatinate was prepared and after recrystallization from dilute alcohol melted at 126°.

*Anal.* Subs., 0.1920: Pt, 0.0438. Calcd. for $(C_{14}H_{23}ON)_2 \cdot H_2PtCl_6$: Pt, 22.91. Found: Pt, 22.86.

**7-Phenoxyheptyldimethylamine.**—Diethyl 5-phenoxyamylmalonate was prepared from 81 g. of 5-phenoxyamyl bromide. The yield was 67 g. (63% of the theoretical amount) of a product, b. p. 202–204° (4–5 mm.); sp. gr. $^{20}_{20}$ 1.508; $n^{20}_{D}$ 1.4882. The ester was impure and contained some unchanged bromide. It was not purified further but was used directly to give 7-phenoxyheptoic acid.

The crude malonic ester (65 g.) was saponified with boiling aqueous potassium hydroxide solution and the mixture was acidified. The malonic acid was separated and heated to drive out carbon dioxide. The crude 7-phenoxyheptoic acid thus obtained was esterified with ethyl alcohol. The yield was 31.5 g. (61% of the theoretical amount) of ethyl 7-phenoxyheptoate; b. p. 161–163° (3 mm.); sp. gr. $^{20}_{20}$ 1.015; $n^{20}_{D}$ 1.4932.

*Anal.* Subs., 0.1345: $CO_2$, 0.3524; $H_2O$, 0.1066. Calcd. for $C_{15}H_{22}O_3$: C, 72.00; H, 8.80. Found: C, 71.48; H, 8.87.

Reduction of 30 g. of this ester with sodium and absolute alcohol gave 16 g. (60% of the theoretical amount) of phenoxyheptyl alcohol; b. p. 157–158° (3 mm.); m. p. 34°.

*Anal.* Subs., 0.2545: $CO_2$, 0.6985; $H_2O$, 0.2214. Calcd. for $C_{13}H_{20}O_2$: C, 75.00; H, 9.62. Found: C, 74.81; H, 9.68.

The bromide was prepared by treating 13 g. of the alcohol with 13 g. of phosphorus tribromide. The yield was 13.5 g. (80% of the theoretical amount) of a product, b. p. 154–157° (3 mm.); sp. gr. $^{20}_{20}$ 1.199; $n^{20}_{D}$ 1.5240.

*Anal.* Subs., 0.1421: AgBr, 0.0981. Calcd. for $C_{13}H_{19}OBr$: Br, 29.52. Found: Br, 29.39.

7-Phenoxyheptyldimethylamine was obtained by treating 15 g. of the bromide with 4 cc. of 30% alcoholic dimethylamine solution. The yield was 12 g. (82% of the theoretical amount) of a product, b. p. 158–160° (8 mm.); sp. gr. $^{20}_{20}$ 0.939; $n^{20}_{D}$ 1.4980.

The chloroplatinate was prepared and after recrystallization from dilute alcohol melted at 162°.

*Anal.* Subs., 0.2029: Pt, 0.0446. Calcd. for $(C_{16}H_{25}ON)_2 \cdot H_2PtCl_6$: Pt, 22.20. Found: Pt, 22.00.

**ω-Bromo-alkyl Dimethylamines.**—The bromo-amines were prepared from the corresponding phenoxy derivatives by the action of hot 48% hydrobromic acid. The general procedure was to prepare a solution of 20 g. of the phenoxyamine in 100 cc. of 48% hydrobromic acid. This solution was distilled until the temperature of the vapors reached 123–125°. Then a second 100-cc. portion of 48% acid was added and the distillation was continued until the total distillate amounted to about 175 cc. This operation was carried out in all-glass apparatus to avoid contamination from the stoppers.

The residue in the distilling flask was evaporated to dryness under reduced pressure on a steam-bath. The crude bromo-amine hydrobromide was dissolved in about 30–35 cc. of water and the free amine was liberated by the addition of a 28% solution of sodium hydroxide. The solution was cooled in an ice-bath during the decomposition of the salt with the alkali. The amine was collected in ether and the ether then removed by evaporation under reduced pressure. If possible the amine was distilled under reduced pressure.

**4-Bromobutyldimethylamine.**—This amine was never definitely isolated due to too rapid formation of cyclic quaternary salt. Attempts were made at −10° and in a carbon dioxide–ether bath but no pure product could be obtained.

**5-Bromo-amyldimethylamine.**—This amine was obtained in ether solution at low temperatures, but attempts at distillation always resulted in the formation of the quaternary salt. The ether solution was extracted with dilute hydrochloric acid and the acid solution treated with an excess of gold chloride. The crystalline chloro-aurate was recrystallized from dilute alcohol and then melted at 57°.

*Anal.* Subs., 0.1943: Au, 0.0715. Calcd. for $C_7H_{16}NBr \cdot HAuCl_4$: Au, 36.95. Found: Au, 36.75.

**6-Bromohexyldimethylamine.**—This amine was distilled under reduced pressure without the formation of very large quantities of cyclic quaternary salt. It boiled at 78–80° (6 mm.). Attempts to determine the density and index of refraction gave very poor results since enough salt formed during the work to prevent any degree of accuracy. The chloro-aurate of some freshly distilled amine was prepared and crystallized from dilute alcohol. It melted at 111°.

*Anal.* Subs., 0.1199: Au, 0.0423. Calcd. for $C_8H_{18}NBr \cdot HAuCl_4$: Au, 35.98. Found: Au, 35.52.

**7-Bromoheptyldimethylamine.**—This amine was distilled under reduced pressure. Very little material was lost due to salt formation during the distillation. It boiled at 85–87° (7 mm.); sp. gr. $^{20}_{20}$ 1.029; $n^{20}_{D}$ 1.4695. The chloro-aurate was prepared and after crystallization from dilute alcohol it melted at 126°.

*Anal.* Subs., 0.1021: Au, 0.0361. Calcd. for $C_9H_{20}NBr \cdot HAuCl_4$: Au, 35.10. Found: Au, 34.96.

## Cyclic Quaternary Ammonium Salts

**N-Dimethylpyrrolidinium Bromide.**—Upon the addition of an excess of strong sodium hydroxide solution to 30–35 cc. of a solution of 4-bromobutyldimethylamine hydrobromide in water, prepared as described for the preparation of the bromo-amines from the corresponding phenoxy derivatives, the quaternary salt was precipitated as a crystalline mass. After filtration the product was crystallized from a mixture of 80% ethyl acetate and 20% absolute alcohol. There was obtained 13–14 g. of product (72–76% of the theoretical amount). The salt did not melt below 325° (uncorr.).

*Anal.* Subs., 0.0870: 8.36 cc. of 0.0549 *N* $AgNO_3$. Calcd. for $C_6H_{14}NBr$: Br, 43.5. Found: Br, 43.7.

The molecular weight of the N-dimethylpyrrolidinium bromide was determined cryoscopically. Subs., 0.6922: $H_2O$, 24.905; $\Delta t$, 0.556°. Calcd. for $C_6H_{14}NBr$: mol. wt., 180. Found: mol. wt., 92.6. A further check on the identity of this compound was made by converting it to the chloro-aurate of N-dimethylpyrrolidinium chloride, previously described by Willstätter and Huebner.[13]

Approximately 1 g. of the dimethylpyrrolidinium bromide was treated with an excess of an aqueous suspension of silver oxide. After shaking for one to two hours, all of the halogen was removed from the aqueous solution and the mixture filtered. The filtrate was then acidified with hydrochloric acid and to this solution was added an excess of gold chloride. The chloro-aurate so prepared melted at 282° (uncorr.) after recrystallization from water. Willstätter and Huebner have recorded the melting point as 286° (uncorr.), with decomposition. A second sample of the chloro-aurate showed no depression upon taking a mixed melting point with the chloro-aurate prepared from N-dimethylpyrrolidinium chloride which in turn had been prepared from pure pyrrolidine by the following method. Two to three g. of pyrrolidine was treated with an excess of methyl iodide in the presence of an excess of aqueous 20% sodium hydroxide solution. The insoluble N-dimethylpyrrolidinium iodide was removed by filtration, treated with an excess of an aqueous suspension of silver oxide, and converted to the chloro-aurate with hydrochloric acid and gold chloride as described above.

**N-Dimethylpiperidinium Bromide.**—This salt was obtained in two ways. A portion of a solution of 5-bromo-amyldimethylamine in alcohol was evaporated and the product purified by crystallization. The same product was obtained when an ether solution of the bromo-amine was evaporated and the residue allowed to solidify at room temperature. The crude salt was recrystallized from a mixture of 50% ethyl acetate and 50% absolute alcohol. The pure salt melted at 324° (uncorr.).

*Anal.* Subs., 0.1110: 10.14 cc. of 0.0549 $N$ $AgNO_3$. Calcd. for $C_7H_{16}NBr$: Br, 41.3. Found: Br, 41.2. The molecular weight was determined cryoscopically. Subs., 0.6166; $H_2O$, 24.904; $\Delta t$, 0.448°. Calcd. for $C_7H_{16}NBr$: Mol. wt., 194. Found: mol. wt., 100.

The structure of the N-dimethylpiperidinium bromide was confirmed by converting it to the chloroplatinate of N-dimethylpiperidinium chloride, which has been described by von Braun[14] as melting at 209–210°. The bromide was converted to the chloride as described under the pyrrolidinium salts. The chloroplatinate was prepared by the addition of chloroplatinic acid to the aqueous solution of dimethylpiperidinium chloride. It melted at 243° (uncorr.), with decomposition, after crystallization from water. Since this melting point did not agree with the one recorded by von Braun, a sample of the piperidine derivative was made for comparison.

Approximately 5 g. of piperidine was converted to N-dimethylpiperidinium chloride by the method used for the corresponding pyrrolidinium derivative. The aqueous, acid solution so obtained was treated with an excess of chloroplatinic acid and the salt crystallized from water. The chloroplatinate melted at 241° (uncorr.).

*Anal.* Subs., 0.1219: Pt, 0.0371. Calcd. for $(C_7H_{16}N)_2 \cdot PtCl_6$: Pt, 30.6. Found: Pt, 30.4.

Since pure 5-bromo-amyldimethylamine could not be isolated except in ether, the amount of ring compound formed was determined on a sample of amine which had been allowed to stand in alcohol for two months. About 5 cc. of bromo-amyldimethylamine hydrobromide solution which was equivalent to approximately 3 g. of bromo-amine was neutralized and extracted with ether as indicated in the general method. The

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[13] Willstätter and Heubner, *Ber.*, **40,** 3873 (1907).

[14] Von Braun, *ibid.*, **33,** 2735 (1900).

ether solution was transferred to a flask containing about 50 cc. of alcohol and the mixture allowed to stand. The quantity of bromo-amine lost during the neutralization as quaternary salt was not determined, although it was considerable. After standing the solvent was evaporated from the bromo-amine solution and the residue (0.65 g.) separated by fractional crystallization. The crude product thus obtained was dissolved in the minimum quantity of boiling solvent, composed of equal parts of ethyl acetate and absolute alcohol, and the solution cooled. After filtration, the filtrate was concentrated to incipient crystallization and again cooled. This process was repeated until the fractions became too small to handle, when the soluble end was mixed with all the previously used filter papers, extracted with alcohol, evaporated to dryness and the mixture again crystallized from the ethyl acetate–alcohol mixture. From the 0.65 g. of crude product there were obtained 0.413 g. of pure dimethylpiperidinium bromide and 0.23 g. of material that was slightly less pure.

**N-Dimethylhexamethylene-iminium Bromide.**—In one experiment a portion of the solution of 6-bromohexyldimethylamine in alcohol was evaporated and in another the pure distilled amine was allowed to solidify in the absence of a solvent. In either case the same product was obtained. Without a solvent the formation of quaternary salt seemed to take place more rapidly. The crude salt was crystallized from absolute alcohol, after which it melted at 289° (uncorr.).

*Anal.* Subs., 0.0940: 7.81 cc. of 0.0549 *N* $AgNO_3$. Calcd. for $C_8H_{18}NBr$: Br, 38.45. Found: Br, 38.70.

The molecular weight of N-dimethylhexamethylene-iminium bromide was determined cryoscopically. Subs., 0.2873: $H_2O$, 24.904; $\Delta t$, 0.165°. Calcd. for $C_8H_{18}NBr$: mol. wt., 208. Found: mol. wt., 130.

The structure of the N-dimethylhexamethylene-iminium bromide was determined by converting to a known derivative. Müller and Sauerwald[2] prepared the corresponding iodide and found it to melt at 265° (corr.).

About 1 g. of the dimethylhexamethylene-iminium bromide was shaken with an excess of an aqueous supension of silver oxide for one to two hours. After filtration the filtrate was acidified with hydriodic acid and evaporated to dryness. After crystallization from absolute alcohol the iodide thus obtained melted at 255° (uncorr.).

A sample of distilled 6-bromohexyldimethylamine was allowed to stand at room temperature until the mass solidified. The product was then dissolved in the minimum quantity of boiling solvent composed of 80% ethyl acetate and 20% absolute alcohol. The fractionation was carried out in the same way as for the corresponding piperidine derivative. From 10 g. of the distilled amine there was obtained 5.6 g. of the pure quaternary ammonium salt.

**N-Dimethylheptamethylene-iminium Bromide.**—This salt could be obtained in appreciable quantity only by reaction of the bromo-amine with itself in the absence of a solvent. The formation of quaternary ammonium salt in alcohol was so slow that practically no material could be isolated during a reaction period of several weeks. A sample of distilled 7-bromoheptyldimethylamine was allowed to stand overnight. The solid mixture which formed was crystallized from the minimum quantity of a mixture of equal parts of ethyl acetate and absolute alcohol. The pure N-dimethylheptamethylene-iminium bromide melted at 268° (uncorr.).

*Anal.* Subs., 0.1326: AgBr, 0.1114. Calcd. for $C_9H_{20}NBr$: Br, 36.02. Found: Br, 35.86.

The molecular weight of N-dimethylheptamethylene-iminium bromide was determined cryoscopically. Subs., 0.2433: $H_2O$, 24.890; $\Delta t$, 0.165°. Calcd. for $C_9H_{20}NBr$: mol. wt., 222. Found: mol. wt., 111.

A second sample of bromo-amine was allowed to solidify overnight and the ring compound separated by crystallization from the above ethyl acetate–alcohol mixture in the same way as the dimethylpiperidinium bromide. There was thus obtained 0.59 g. of pure quaternary ammonium salt from 1.57 g. of the amine.

## Summary

1. Halogenated aliphatic tertiary amines of the type $Br(CH_2)_nN(CH_3)_2$, in which $n$ has the values 4, 5, 6 and 7 have been prepared.

2. These amines react with themselves to form cyclic quaternary ammonium salts in yields which indicate that ring formation is the principal reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

# THE MECHANISM OF CARBOHYDRATE OXIDATION. XI. THE ACTION OF POTASSIUM HYDROXIDE ON MALTOSE

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The fact that maltose is a disaccharide makes a study of its behavior toward aqueous solutions of potassium hydroxide a much more complex problem than is the case with the monosaccharides for the reason that it may react in any one or all of three general ways. (a) The molecule of maltose may undergo hydrolysis[1] into two molecules of glucose. In this case one should expect the experimental data obtained from equivalent solutions of glucose and maltose to be quantitatively the same. (b) Since maltose is a reducing sugar like glucose, there exists the possibility of the disaccharide molecule undergoing enolization[2] and subsequent decomposition without hydrolysis having taken place previously. (c) It is evident that both reactions may take place simultaneously, the extent to which the maltose is changed in either direction being probably dependent on such experimental factors as alkali concentration and temperature. To obtain data with reference to the behavior of maltose in alkaline solutions, when examined from this general standpoint, was the first objective of these experiments.

If maltose is found to react in accordance with possibility (b) or (c), the mechanism of the alkaline decomposition of the disaccharide might depend upon the presence of an equilibrated mixture of six glucosido-hexoses, maltose and its isomers, analogs of the sugars in the well-known de Bruyn and van Ekenstein systems. These would be maltose (4-glucosido-*d*-glucose), 4-glucosido-*d*-mannose, 4-glucosido-*d*-fructose, 4-glucosido-pseudo-*d*-fructose, 4-glucosido-*d*-α-glutose and 4-glucosido-*d*-β-glutose.[3] Under the

[1] Lewis and Buckborough, THIS JOURNAL, **36**, 2385 (1914).

[2] Nef, *Ann.*, **403**, 381 (1914).

[3] Nef, *ibid.*, **403**, 382 (1914).