Continuing the reaction beyond this stage results in the formation of an insoluble and very large oxygen-rich macromolecule.

Conclusions

Based on the investigation of the polymeric products formed during the condensation of paraformaldehyde with dibenzothiophene, the following conclusions are made. (1) The conversion of dibenzothiophene to polymethylene dibenzothiophene was 71% in 24 hr. (2) The molecular weight of the polymer increases with increasing conversion. (3) The polymeric products formed during the early stage of the condensation appear to be composed of at least four oligomeric species having linear structures. (4) The polymeric products formed at the higher conversions appear to contain large amounts of branched, high molecular weight fractions in addition to low molecular weight fractions. (5) The low molecular weight polymer fractions contain methylene bridges and hydroxymethyl end groups. The higher molecular weight fractions contain, in addition to these groups, oxymethylene bridges.

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Reactions of *N,N,N',N'*-Tetramethyl-α,ω-diaminoalkanes with α,ω-Dihaloalkanes. I. 1–*y* Reactions[1]

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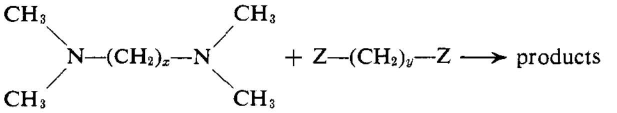
ABSTRACT: The reactions of *N,N,N',N'*-tetramethyldiaminomethane with a number of α,ω-dihaloalkanes were investigated in dimethylformamide (DMF), DMF–methanol (1:1 by volume), and acetonitrile. The most important products of these reactions consisted of dimethylaminohaloalkanes, dimethylamine hydrohalides, cyclic and linear mono- and diammonium salts, as well as polyelectrolytes. The course of the reaction was influenced by the solvent. The reaction of tetramethyldiaminomethane with 1,4-dibromobutane yielded unexpectedly in DMF–methanol a linear diammonium compound containing two methoxy groups. A mechanism accounting for the reaction products is proposed and experimental evidence for the isolated compounds is presented.

A detailed study was carried out of the reactions of I with II in which *x* and *y* are integers and Z represents a halogen.



$$(CH_3)_2N-(CH_2)_x-N(CH_3)_2 + Z-(CH_2)_y-Z \longrightarrow \text{products} \quad (1)$$

I II

A large variety of products consisting mainly of mono-, di-, and polyammonium salts was obtained, depending on the reaction mechanism. The latter varied not only with the structure of reagents and the values of *x* and *y*, but also with the solvent medium. The most significant intermediate species formed during the course of reaction 1 were the dimethylaminohaloalkanes $(CH_3)_2N(CH_2)_yBr$. The chemical behavior of the latter was investigated by Marvel[3–7] and Knorr.[8] The reaction of *N,N,N',N'*-tetramethyl-α,ω-diaminoalkanes with α,ω-dihaloalkanes (1) was also studied by Kern,[9] McElvain,[10] and Cadogan.[11]

Because of the considerable general interest in the synthesis of this type of compounds and in particular in the synthesis of polyelectrolytes in which the distances between positive nitrogens can be varied almost at will,[12] we have carried out a systematic study of reaction 1 using various combinations of *x* and *y*. In this paper a detailed account of the reaction of tetramethyldiaminomethane with a number of α,ω-dibromo- or diiodoalkanes, *i.e.*, the 1–*y* reaction, is presented, and some corrections to previously published data[13] are pointed out. The results of *x*–*y* reactions leading to low and high molecular weight ammonium compounds ($x \geq 2$) will be described in part II of this work.

Results and Discussion

Synthesis. The present study covers the reactions of tetramethyldiaminomethane with $Br(CH_2)_yBr$ (y = 1–8, 10, and 16) and $I(CH_2)_yI$ (y = 1, 4, and 5) in such solvents as dimethyl-

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(1) This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract No. NAS-7100.

(2) NRC–NASA Resident Research Associate.

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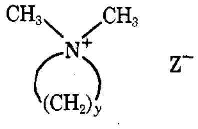
(13) H. Noguchi and A. Rembaum, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **10**, 718 (1969); *Polym. Lett.*, **7**, 383 (1969). We reported that the 1–5 reaction in DMF–methanol (1:1) yielded the cyclic dimer of dimethylaminobromopentane. Further investigations of the 1–*y* reactions established, however, that the 1–5 reaction product is a monoammonium salt.

formamide (DMF), DMF–methanol (1:1 by volume), and acetonitrile. All the reactions were carried out in solution and at room temperature (*ca.* 22°), using the diamine and the dihalide in a molar ratio of 1:1. The results of these reactions, which to our knowledge have not been reported before, are described below.

The product of the 1–1 reaction in DMF–methanol was identified as dimethylamine hydrobromide by comparing it with the authentic specimen prepared from dimethylamine and hydrobromic acid. In contrast to this, the 1–1 reaction in acetonitrile or in DMF alone yielded dimethylaminobromomethane, the structure of which was determined by synthesizing this compound[14] from tetramethyldiaminomethane and hydrogen bromide as well as by elemental, ir, and nmr analyses. Similarly, when diiodomethane was used in the 1–1 reaction in acetonitrile, dimethylaminoiodomethane was isolated. The 1–2 reaction in DMF–methanol and acetonitrile yielded a six-membered cyclic diammonium salt, *i.e.*, 1,1,4,4-tetramethylpiperazinium dibromide (IX) in place of the expected five-membered cyclic compound. This surprising result can be well understood on the basis of the proposed mechanism (Scheme II).

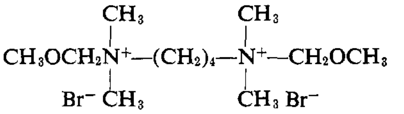
The isolation of products from the 1–3 reaction carried out in DMF–methanol was not successful. In acetonitrile a solid product of the composition $C_5H_{12}BrN$ was obtained. It was found to consist of a low molecular weight 3–3 ionene polymer (XII) and probably of a four-membered cyclic monoammonium salt (IIIa). However the presence of the latter has not yet been proven unambiguously (see Experimental Section).

The 1–4 reaction showed a remarkable dependence on solvent and halogen. With 1,4-dibromobutane in acetonitrile only 1,1-dimethylpyrrolidinium bromide (IIIb) could be isolated. With 1,4-diiodobutane, dimethylaminoiodomethane crystallized from the reaction mixture and 1,1-dimethylpyrrolidinium iodide (IIIc) was obtained from the filtrate.



IIIa, $y = 3$; Z = Br IIId, $y = 5$; Z = Br
b, $y = 4$; Z = Br e, $y = 5$; Z = I
c, $y = 4$; Z = I f, $y = 6$; Z = Br

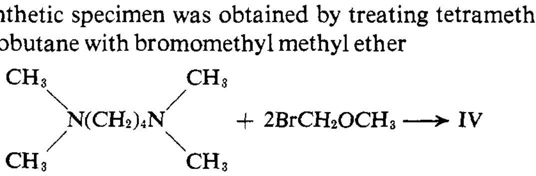
When the solvent medium for the 1–4 reaction was changed to DMF–methanol, a crystalline oxygen-containing compound was isolated (IV).



$$CH_3OCH_2\overset{CH_3}{\underset{Br^-\ CH_3}{N^+}}-(CH_2)_4-\overset{CH_3}{\underset{CH_3\ Br^-}{N^+}}-CH_2OCH_3$$

IV

The structure of IV, *i.e.*, tetramethylenebis(methoxymethyldimethylammonium bromide), was established by an independent synthesis, chemical analysis, and ir and nmr spectra. The synthetic specimen was obtained by treating tetramethyldiaminobutane with bromomethyl methyl ether



$$(CH_3)_2N(CH_2)_4N(CH_3)_2 + 2BrCH_2OCH_3 \longrightarrow IV \quad (2)$$

The elemental analysis agreed well with the proposed structure. In addition, the ir spectrum exhibited ether linkage bands in the region of 1000–1200 cm^{-1} and showed no absorption due to OH stretching vibrations.[15] Finally, the nmr spectrum (Figure 1) was found to be identical with that of the synthetic sample. Although the structure of compound IV is well proven, no details of the mechanism of the 1–4 reaction can be given at present. From the 1–6 reaction in DMF–methanol, an oxygen-containing material was also isolated, the structure of which remains to be established.

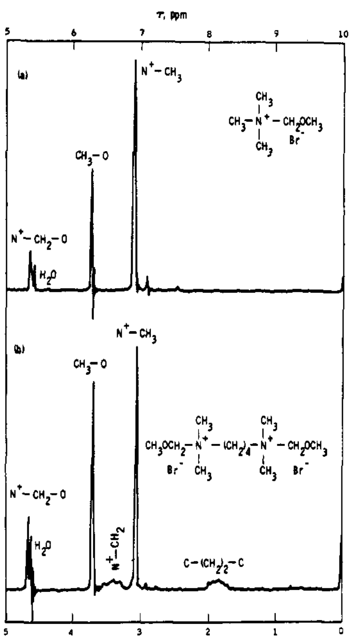


Figure 1. Nmr spectrum of (a) a model compound and (b) the 1–4 reaction product prepared in DMF–methanol.

In contrast to the solvent participation in the 1–4 reaction, the 1–5 reaction, whether carried out in DMF, DMF–methanol, or acetonitrile, yielded invariably 1,1-dimethylpiperidinium bromide (IIId) or iodide (IIIe). The structures of cyclic monoammonium salts (IIIb, IIIc, IIId and IIIe) were confirmed by comparison with specimens synthesized from *N*-methylpyrrolidine and *N*-methylpiperidine. The ir and nmr spectra were identical with those of the authentic samples.

The 1–6 reaction in pure DMF or acetonitrile yielded a seven-membered cyclic monoammonium salt (IIIf), namely, hexahydro-1,1-dimethylazepinium bromide (=1,1-dimethylhexamethyleniminium bromide).

The main products of 1–y reactions in which $y > 6$ were dimethylaminobromomethane, in some cases easily isolated in pure form (*e.g.*, in the 1–8 and 1–10 reactions using acetonitrile as a solvent), and low molecular weight polymers (intrinsic viscosity in aqueous 0.4 *M* KBr solution ranging from 0.025 to 0.051).

Mechanism. The first step of the 1–y reaction is most probably a 1:1 addition of the starting reagents to form the monosalt V (Scheme I). The latter undergoes bond scission at a to yield VI and VII, and this proposed second step is based on the structures of isolated products as well as on previous investigations.[16–18] The subsequent steps depend on the values of y (see reactions 5–8).[3–8]

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(14) H. Bohme, W. Lehners, and G. Keitzer, *Chem. Ber.*, **91**, 340 (1958).

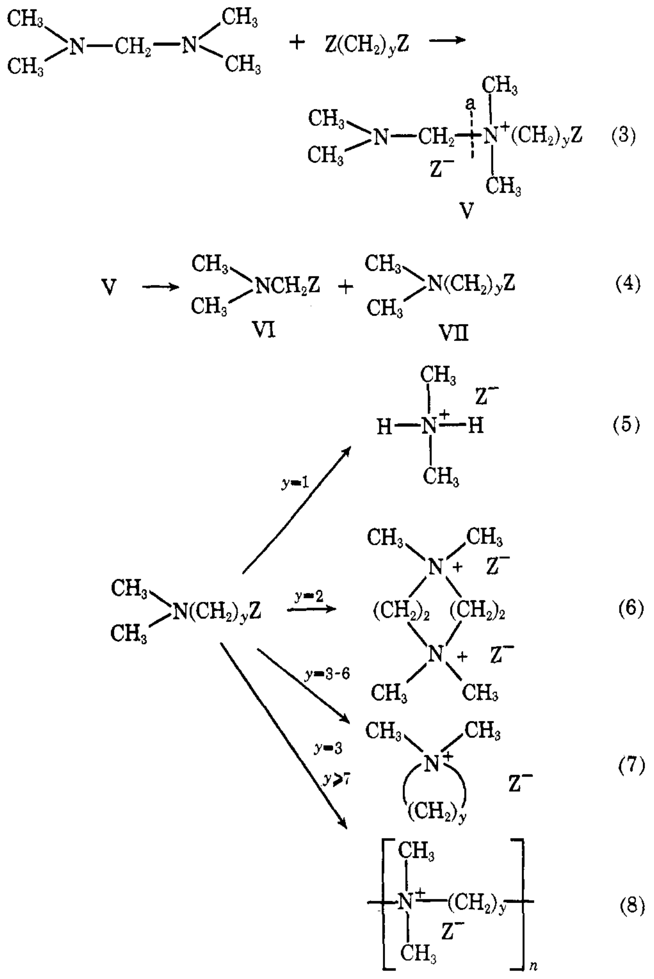
(15) The product is hygroscopic, and the band at 3400 cm^{-1} is due to absorbed water.

(16) W. C. Hunt and E. C. Wagner, *J. Org. Chem.*, **16**, 1792 (1951).

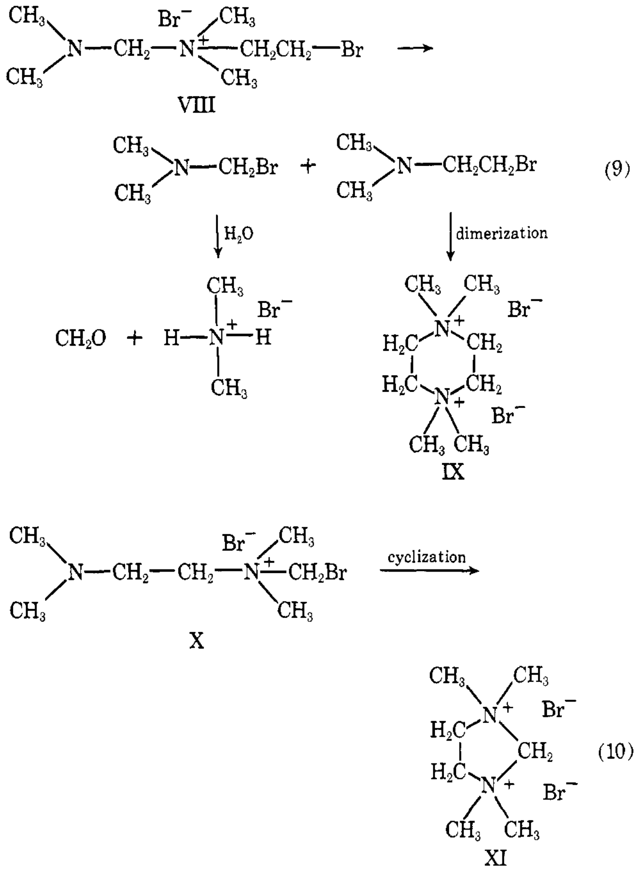
(17) H. Bohme and W. Lehners, *Justus Liebigs Ann. Chem.*, **595**, 169 (1955).

(18) H. Bohme, E. Mundlos, W. Lehners, and O. E. Herboth, *Chem. Ber.*, **90**, 2008 (1957).

SCHEME I
MECHANISM OF 1–y REACTIONS



SCHEME II
MECHANISM OF THE 1–2 AND 2–1 REACTIONS



The formation of dimethylamine hydrobromide in the 1–1 reaction can be understood on the basis of findings by Bohme and Lehners,[17] who showed that the decomposition of dimethylaminobromomethane takes place spontaneously by reaction with water to form dimethylamine hydrobromide and formaldehyde. If we assume that methanol reacts in a similar way as water, then the mechanism of Bohme and Lehners would also apply in our case.

We have found that in the absence of water or methanol (in dry acetonitrile or DMF), pure dimethylaminobromo- or -iodomethane (VI) could be obtained in yields ranging from 9 to 25% (see Experimental Section, reactions 1–1, 1–4, 1–8, and 1–10), and formaldehyde was produced on exposure to moisture.

It is remarkable that whereas the 1–2 reaction (9) leads to a six-membered cyclic diammonium salt, the 2–1 reaction (10) produces a five-membered cyclic diammonium salt.[1] This unexpected result is easily understood on the basis of Scheme II.

VIII undergoes bond scission because of resonance effects[17] different in X, which therefore undergoes cyclization without bond scission. Both compounds IX and XI have been isolated in pure form, and their structure was proven unequivocally.

Nmr Spectroscopy. Evidence for the proposed mechanisms and structures is derived mainly from the study of the nmr spectra and elemental analyses (see Experimental Section). A careful examination of a variety of nmr spectra of mono-, di-, and polyammonium salts (some of which were previously published[18,19]) permits the assignment of the proton resonances. The established τ values for various proton resonances yield evidence for the structure of the 1–2 reaction product IX, for the reaction of dimethylaminobromomethane (VI) in water, for the dimethoxy compound IV, and for polyelectrolytes (XII).

Identical nmr spectra of VI were obtained irrespective of whether the latter was prepared from tetramethyldiaminomethane by reaction with a mineral acid or from the 1–y reactions (y = 1, 4, 8, and 10; see Experimental Section). The nmr spectrum of VI determined in D_2O (Figure 2) is apparently due to two components, namely, dimethylaminobromomethane and dimethylamine hydrobromide. This is, of course, not surprising, since VI reacts with D_2O. Thus, if we assume that the mechanism[17] is correct, then the peaks at τ 7.27 and 7.15 can be assigned to N^+–CH_3 of dimethylamine hydrobromide and N–CH_3 of dimethylaminobromomethane, respectively. The τ 5.36 peak is due to DOH and that at τ 5.17 to the proton resonance of the CH_2 group in dimethylaminobromomethane. However, no resonance peak due to formaldehyde could be detected.

The assignment is in agreement with the integration values. In addition, the nmr spectrum of VI admixed with dimethylamine hydrobromide showed that the assignment of the τ value of 7.27 was correct. The low value of τ for the N–CH_3 resonance is consistent with results obtained with similar compounds containing polar atoms in the vicinity of the nitrogen atom. Thus the τ value for N–CH_3 in O=CHN–$(CH_3)_2$ is 7.03 or 7.12 (Varian Catalog No. 39). It appears that in water (or D_2O) an equilibrium between dimethylamine hydro-

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(19) A. Rembaum, S. Singer, and H. Keyzer, *J. Polym. Sci., Part B*, 7, 395 (1969).

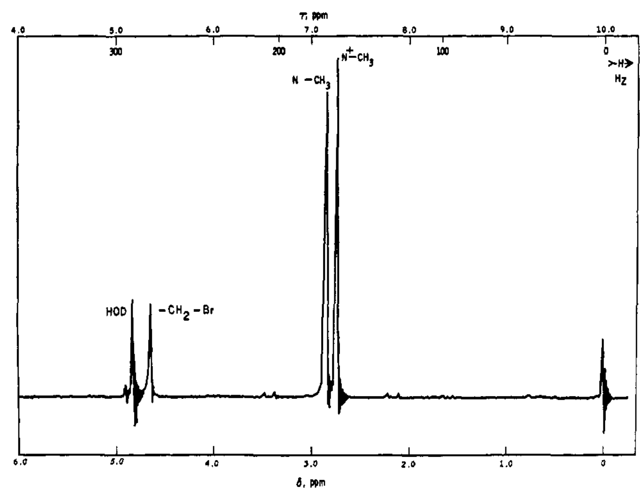


Figure 2. Nmr spectrum of dimethylaminobromomethane.

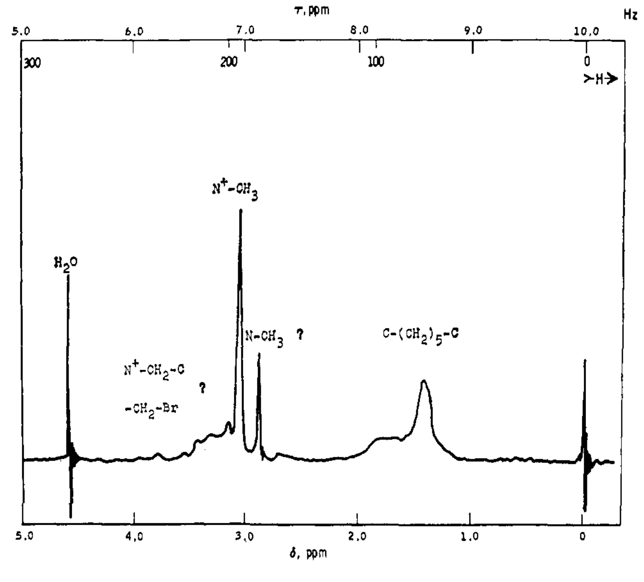


Figure 3. Nmr spectrum of the 1–7 reaction product, low molecular weight polymer ([η] = 0.043).

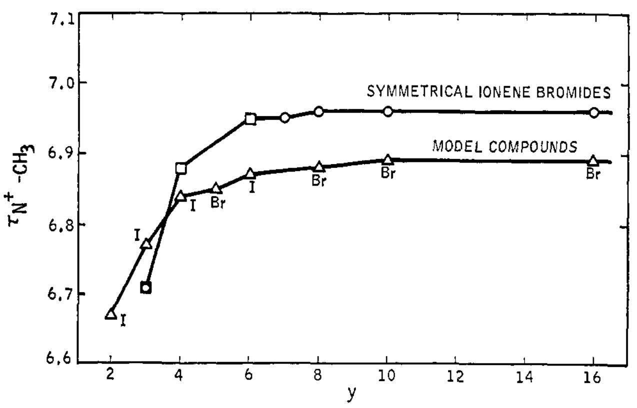
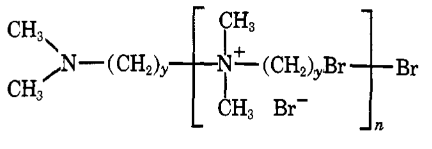


Figure 4. Values for N^+-CH_3 proton resonance as a function of the number of CH_2 groups (y) in compounds: XII, —○—○—; XIII, —□—□—; and XIV, —△—△—.

bromide and dimethylaminobromomethane is established, since no change of the nmr spectrum (measured in a sealed tube) was observed with time.

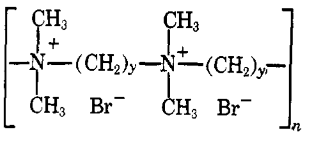
The nmr spectrum of the 1–2 reaction product was found to be identical with that of the diammonium salt published previously[13] and consisted of two peaks at τ 5.97 and 6.54 which were assigned to $N^+CH_2CH_2N^+$ and N^+CH_3 protons, respectively. This therefore is in agreement with the mechanism of Scheme II.

The nmr spectra of IV (Figure 1b), when compared with the nmr spectrum of a synthetic specimen of a model compound (Figure 1a), yielded unequivocal evidence for the solvent dependence of the 1–4 reaction and for structure IV. Finally, nmr data together with intrinsic viscosity measurements yielded evidence for the formation of low molecular weight polyammonium salts (polyelectrolytes) in the 1–7, 1–8, 1–10, and 1–16 reactions. A typical nmr spectrum of the polyelectrolytes isolated from the above reaction products is shown in Figure 3. The spectrum is in agreement with structure XII (y = 7). The sharp singlet at τ 6.95 and the broad peaks at τ 7.9–8.9 are due to N^+–CH_3 and C–$(CH_2)_5$–C protons, respectively. The peaks at the lower field than the N^+–CH_3 peak are due to N^+–CH_2–C (triplet) and possibly also to –CH_2Br end groups. The τ 7.16 peak is assigned to the protons of the terminal dimethylamino group or of some impurity. The nmr spectra of other polymeric 1-y reaction products were very similar to the spectrum of Figure 3 and to the nmr spectra of high molecular weight polyelectrolytes which will be described in the second part of this paper. This similarity is clearly illustrated in Figure 4 in which τ values of N^+–CH_3 proton resonance for the polymeric 1-y reaction products (XII) and y-y ionene bromides (XIII, see part II) as well as for model compounds (XIV) are plotted against the number (y) of CH_2 groups. The τ values for the two series of polymers fit the same curve, indicating that both have the same type of recurring unit, *i.e.*, $-N^+(CH_3)_2(CH_2)_y-\ Br^-$, or that XII is a symmetrical ionene analogous to XIII and hence supporting the assigned structure XII for the polymeric 1-y reaction products. In this case, the saturation of shielding effect of CH_2 groups was reached at y = 8 (highest value of τ for N^+–CH_3 = 6.96). This was found to be also true in the case of model compounds (XIV) where the saturation of the shielding effect was reached at y = 10 (highest value of τ for N^+–CH_3 = 6.89) and cyclic ammonium compounds (III) where the saturation of shielding already occurs at y = 5 (highest value of τ for N^+–CH_3 = 6.89), the τ values being independent of the type of counteranions.[20]



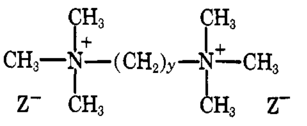
$$\mathrm{(CH_3)_2N{-}(CH_2)_y{-}\left[{-}\overset{CH_3}{\underset{CH_3\ \ Br^-}{\overset{+}{N}}}{-}(CH_2)_yBr{-}\right]_n{-}Br}$$

XII, $x = 1, y = 3$ and $y \geqslant 7$



$$\left[{-}\overset{CH_3}{\underset{CH_3\ \ Br^-}{\overset{+}{N}}}{-}(CH_2)_y{-}\overset{CH_3}{\underset{CH_3\ \ Br^-}{\overset{+}{N}}}{-}(CH_2)_{y'}{-}\right]_n$$

XIII, $x = y \geqslant 3$



$$\mathrm{CH_3{-}\overset{CH_3}{\underset{Z^-\ \ CH_3}{\overset{+}{N}}}{-}(CH_2)_y{-}\overset{CH_3}{\underset{CH_3\ \ Z^-}{\overset{+}{N}}}{-}CH_3}$$

XIV, Z = Br or I, $y \geqslant 2$

Conclusion

With the exception of the reactions where solvent participation occurred, all results of the 1-*y* reactions are readily understood on the basis of mechanisms shown in Schemes I and II and on the basis of the fact that five-, six-, and seven-membered cyclic structures are formed preferentially whenever the geometrical configuration of the reactants or primary reaction products permits it. When cyclization is unlikely, the major products of reaction 1 are low molecular weight polyelectrolytes.

Experimental Section

Reagents. The purity of all reagents was checked by gas chromatography. After drying with Drierite, most of the dibromides were distilled at atmospheric pressure or under reduced pressure. When very impure, the dibromides were washed with concentrated sulfuric acid, water, 10% sodium carbonate, and water, successively, and dried over calcium chloride. The dibromides were further purified by repeated distillation, 1,10-dibromodecane was purified by repeated fractional crystallization, and 1,16-dibromohexadecane was recrystallized from *n*-hexane. *N,N,N′,N′*-Tetramethyldiaminomethane was dried over Drierite and fractionally distilled under atmospheric pressure. All the solvents were reagent or spectroscopic grade and were used without further purification.

Elemental Analysis. Most of the samples were dried *in vacuo* at 40° overnight before analysis. Dimethylaminohalomethanes were analyzed without any pretreatment. Elemental analyses were carried out by the Spang Microanalytical Laboratory, Ann Arbor, Mich. Ionic bromine content was also checked by the Mohr method in our laboratory.

Melting Point. Melting points were measured in open capillary tubes with the Mel-Temp, Laboratory Devices, Cambridge, Mass., at a heating rate of *ca.* 1°/min near the melting points. The immersion temperature was far below the temperature at which apparent discoloration occurred. No particular attention was paid to the heating rate at temperatures far below the melting point.[20] Melting points are not corrected.

Intrinsic Viscosity. The intrinsic viscosity of the polymeric 1–7, 1–8, and 1–10 reaction products was measured in an Ubbelohde viscometer at 25.0 ± 0.01°, using a 0.4 *M* KBr aqueous solution as solvent. The intrinsic viscosity of the polymeric 1–16 reaction product was measured similarly, using a 0.4 *M* KBr solution in 2:1 mixture (by volume) of methanol and water as solvent.

Infrared Spectroscopy. The infrared spectra were taken with a Perkin-Elmer grating spectrophotometer, Model 421, using the KBr disk method.

Nuclear Magnetic Resonance Spectroscopy. The 60-MHz proton magnetic resonance spectra were taken at *ca.* 37° (probe temperature) in deuterated water by means of a Varian A-60 spectrometer, using sodium 2,2-dimethyl-2-silapentane-5-sulfonate as an internal standard.

Synthesis. (A) Dimethylaminobromomethane. This compound was prepared by the method of Bohme, Lehners, and Keitzer.[14] To a solution of 50.0 g (0.618 mol) of hydrogen bromide in 160 ml of DMF, 31.5 g (0.308 mol) of tetramethyldiaminomethane was added at −12° with stirring. The mixture was warmed up to room temperature to give a white precipitate. It was left at room temperature overnight. The precipitate was filtered, taking care to exclude moisture, washed with DMF and then with absolute ether, and dried *in vacuo* at room temperature: yield 35.5 g (83.4% based on hydrogen bromide), for nmr spectrum see Figure 2.

Anal. Calcd for C_3H_8BrN: Br, 57.90. Found: Br(ionic),[22] 57.98.

(B) Methoxymethyltrimethylammonium Bromide. To a solution of 12.55 g (0.100 mol) of bromomethyl methyl ether in 150 ml of acetonitrile, 6.60 g (0.112 mol) of trimethylamine was added with stirring. The reaction appeared to be instantaneous, and initially the reaction temperature reached *ca.* 40°. After standing for 23 hr at room temperature, the colorless, homogeneous mixture was evaporated to dryness by means of a rotary evaporator. The residue was transferred to a glass filter with *n*-hexane and dried *in vacuo* at 40°: yield 18.12 g (98.1% based on the ether); mp 118.5–119.5°; nmr τ 5.36 (s, 2.0, 2 H,[23] N^+CH_2O), 6.27 (s, 3.2, 3 H, OCH_3), 6.90 (s, 8.8 9 H, N^+CH_3).

Anal. Calcd for $C_5H_{14}BrNO$: C, 32.62; H, 7.67; Br(ionic), 43.41; N, 7.61. Found: C, 32.61; H, 7.61; Br(ionic), 43.40; N, 7.66.

(C) Tetramethylenebis(methoxymethyldimethylammonium bromide). To a solution of 17.35 g (0.139 mol) of bromomethyl methyl ether in 150 ml of acetonitrile, a solution of 9.52 g (0.0660 mol) of *N,N,N′,N′*-tetramethyl-1,4-diaminobutane in 100 ml of acetonitrile was added with stirring at 20–35°. A white precipitate was formed when approximately half of the amine solution was introduced. The whole reaction seemed to be complete in several minutes. After standing overnight at room temperature, the precipitate was filtered, washed with acetonitrile three times and then with benzene, and dried *in vacuo* at 40°, yield 21.55 g (82.8% based on the diamine). It was recrystallized from absolute ethanol, mp 174–176° dec. The ir and nmr spectra were the same as those of the 1–4 reaction product obtained in a 1:1 mixture of DMF and methanol.

Anal. Calcd for $C_{12}H_{30}Br_2N_2O_2$: Br(ionic), 40.54. Found: Br(ionic), 40.49.

(D) 1,1-Dimethylpyrrolidinium Halides and 1,1-Dimethylpiperidinium Halides. A solution of methyl halide in methanol was added to a solution of amine in methanol with stirring. The mixture was cooled with ice water for a short time initially. The homogeneous mixture was evaporated to dryness by use of a rotary evaporator. The residue was collected on a glass filter with benzene, washed with benzene, and dried *in vacuo* at 40°. The results are summarized in Table I.

1-*y* Reactions. (A) 1–1 Reaction. (a) In DMF–Methanol (1:1). Tetramethyldiaminomethane (20.48 g, 0.200 mol) was mixed with 34.85 g (0.200 mol) of dibromomethane in 130 ml of the solvent, and the mixture was left at room temperature for 72 hr. The homogeneous solution was then poured into a large excess of benzene. The white precipitate was filtered, washed with benzene, and dried *in vacuo* at 40°, yield 12.21 g (24.4%). No precipitate was obtained when the mixture was poured into a large excess of acetone. It was recrystallized from a 7.5:1 mixture (by volume) of acetone and 95% ethanol: mp 139.5–140° (lit.[24] 133.5°), nmr τ 7.27 (s, 6 H, N^+CH_3) (lit.[25] τ for dimethylamine hydrochloride 7.28). All the properties including ir and nmr spectra were the same as those of dimethylamine hydrobromide prepared by the reaction of dimethylamine with hydrobromic acid.

Anal. Calcd for C_2H_8BrN (dimethylamine hydrobromide): C, 19.06; H, 6.40; Br(ionic), 63.42; N, 11.12. Found: C, 19.09; H, 6.26; Br(ionic), 63.48; N, 11.00.

(b) In Acetonitrile. Tetramethyldiaminomethane (10.31 g, 0.101 mol) was allowed to react with 17.53 g (0.101 mol) of dibromomethane in 65 ml of acetonitrile for 168 hr at room temperature. The homogeneous reaction mixture was poured into 800 ml of benzene with stirring. The white precipitate was filtered with exclusion of moisture, washed with benzene, and dried *in vacuo*

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[20] Most of the ammonium compounds began to decompose at temperatures far below the melting points. Thus, as pointed by Mann and Senior,[21] the melting points depended on the thermal history. Therefore, a difference of several degrees in the melting points of two samples is not significant. A typical example is the 1–2 reaction product. When heated from *ca.* 150°, both the 1–2 and the 2–2 (ref 13) reaction products, which have the same structure, melted at 314–315° with decomposition and sublimation. However, when the same sample of the 2–2 reaction product was heated from *ca.* 240°, partial melting with decomposition occurred at 331–332°, much of the decomposed solid product remaining even at 360°.

[21] F. G. Mann and A. Senior, *J. Chem. Soc.*, 4476 (1954).

[22] The halogen contents of dimethylaminobromomethane and dimethylaminoiodomethane could be determined by the Mohr method.

[23] Result of integration shown by a relative value followed by the number of protons in the molecule.

[24] I. Heilbron and H. M. Bunbury, Ed., "Dictionary of Organic Compounds," Vol. II, Eyre and Spottiswoode, London, 1953, p 275.

[25] K. Tori, T. Iwata, K. Aono, M. Ohtsuru, and T. Nakagawa, *Chem. Pharm. Bull.*, **15**, 329 (1967).

TABLE I
1,1-DIMETHYLPYRROLIDINIUM AND 1,1-DIMETHYLPIPERIDINIUM HALIDES

Product	Amine, g/CH_3OH, ml	Halide, g/CH_3OH, ml	Time, hr	Yield,[a] g (%)	Br^-, I^-, % found (calcd)	Mp dec,[b] °C
$C_6H_{14}BrN$	8.51[c]/100	10.95[e]/50	70	17.63 (97.9)	44.24 (44.37)	323–324
$C_6H_{14}IN$	8.52[c]/50	14.19[f]/50	19	22.20 (97.7)	55.91 (55.88)	314–316
$C_7H_{16}BrN$	9.92[d]/100	12.40[e]/50	65	19.04 (98.1)	41.25 (41.16)	339–340
$C_7H_{16}IN$	9.92[d]/100	14.19[f]/50	22	22.90 (95.0)	52.53 (52.63)	323–323.5

[a] Yield in per cent is based on diamine. [b] Recrystallized from isopropyl alcohol, absolute ethanol, *n*-propyl alcohol, or 95% ethanol, respectively. [c] *N*-Methylpyrrolidine. [d] *N*-Methylpiperidine. [e] Methyl bromide. [f] Methyl iodide.

at room temperature, yield 6.79 g (24.4%). The nmr spectrum was the same as that shown in Figure 2.

Anal. Calcd for C_3H_8BrN (dimethylaminobromomethane): Br, 57.90. Found: Br(ionic), 57.50.

(c) In DMF. Tetramethyldiaminomethane (10.23 g, 0.100 mol) was allowed to react with 17.40 g (0.100 mol) of dibromomethane in 65 ml of DMF for 168 hr at room temperature. The pale yellow mixture was poured into 1.3 l. of benzene with stirring. The precipitate was treated as in (b), yield 7.46 g (27.0%). Its nmr spectrum was substantially the same as that of Figure 2.

Anal. Calcd for C_3H_8BrN (dimethylaminobromomethane): Br, 57.90. Found: Br(ionic), 56.75.

(d) 1–1 (Iodide) Reaction in Acetonitrile. Tetramethyldiaminomethane (10.25 g, 0.100 mol) was mixed with 26.86 g (0.100 mol) of diiodomethane in 65 ml of acetonitrile, and the reaction mixture was left at room temperature for 168 hr. The yellow mixture was then treated as described in the 1–1 reaction (b), yield 9.20 g (24.8%). The nmr spectrum was the same as that in Figure 2.

Anal. Calcd for C_3H_8IN (dimethylaminoiododomethane): I, 68.59. Found: I(ionic),[22] 68.17.

(B) 1–2 Reaction. (a) In DMF–Methanol (1:1). Tetramethyldiaminomethane (20.79 g, 0.204 mol) was allowed to react with 38.23 g (0.204 mol) of dibromoethane in 130 ml of the solvent for 70 hr at room temperature. The white crystalline precipitate was filtered, washed with a small amount of the solvent three times and then with acetone, and dried *in vacuo* at 40°, yield 2.53 g (8.2%).

Anal. Found: Br(ionic), 52.61.

It was recrystallized from a 3:1 mixture (by volume) of methanol and water: mp 314–315° dec[20] (lit.[21] 370°); nmr τ 5.97 (s, 8.0, 8 H, $N^+CH_2CH_2N^+$), 6.56 (s, 12.3, 12 H, N^+CH_3).

Anal. Calcd for $C_8H_{20}Br_2N_2$ (1,1,4,4-tetramethylpiperazinium bromide): C, 31.60; H, 6.63; Br(ionic), 52.56; N, 9.21. Found: C, 31.52; H, 6.60; Br(ionic), 52.50; N, 9.13.

More of the same product was obtained when the filtrate was poured into a large excess of acetone. The precipitate was filtered, washed with acetone, and dried as before, yield 0.58 g (1.9%).

Anal. Calcd for $C_8H_{20}Br_2N_2$: Br(ionic), 52.56. Found: Br(ionic), 51.77.

When the reaction was carried out for 361 hr under the same conditions, the yields of the first and the second fractions were 14.0 and 2.1%, respectively.

(b) In Acetonitrile. Tetramethyldiaminomethane (10.22 g, 0.100 mol) was mixed with 18.78 g (0.100 mol) of dibromoethane in 65 ml of acetonitrile, and the mixture was left for 120 hr at room temperature. The crystalline precipitate was then filtered, washed with a small amount of acetonitrile and then with acetone, and dried *in vacuo* at 40°, yield 5.49 g (36.1%).

Anal. Calcd for $C_8H_{20}Br_2N_2$ (1,1,4,4-tetramethylpiperazinium bromide): Br(ionic), 52.56. Found: Br(ionic), 52.92.

The pale yellow filtrate was treated as in (a), yield 0.035 g (0.2%). All the properties of the products were the same as those of the products in (a).

(C) 1–3 Reaction in Acetonitrile. Tetramethyldiaminomethane (10.31 g, 0.101 mol) was allowed to react with 20.36 g (0.101 mol) of 1,3-dibromopropane in 65 ml of acetonitrile for 168 hr at room temperature. The fluffy precipitate was filtered, washed with a small amount of acetonitrile and then with acetone, and dried *in vacuo* at 40°, yield 8.16 g (48.7% as $(C_5H_{12}BrN)_n$). Chemical analysis data indicated that it contained a considerable amount of oxygen which could be attributed to absorbed water. The data corrected for the water agreed fairly well with the formula $C_5H_{12}BrN$.

Anal. Calcd for $(C_5H_{12}BrN)_n$: C, 36.16; H, 7.28; Br(total), 48.12; N, 8.43. Found: C, 33.03; H, 7.21; Br(total), 44.63; Br(ionic), 44.29; N, 7.39. Found (after correction): C, 36.18; H, 6.83; Br(total), 48.89; Br(ionic), 48.52; N, 8.10.

Comparison of the nmr spectrum of this product with that of a 3–3 ionene bromide[13] resulted in the following assignments: τ 6.11 (triplet, J = 5.8 Hz, N^+–CH_2–C of IIIa), 6.4 (broad peak, N^+–CH_2–C of XII (y = 3)), 6.45 (sharp singlet overlapped on the broad peak at τ 6.4, N^+–CH_3 of IIIa), 6.71 (broad singlet, N^+–CH_3 of XII), 7–8 (broad multiplet, C–CH_2–C of IIIa and XII), 7.27 (singlet, N^+–CH_3 of dimethylamine hydrobromide converted from VI).

Recrystallization of this product from methanol gave a powdery substance only. It is considered to be a polymeric product, XII (y = 3).[6] Slow evaporation of the filtrate at room temperature gave a very small amount of needles (probably dimethyltrimethyleneammonium bromide, IIIa).[4] Based on these results it was concluded that this product was likely to be a mixture of IIIa and XII (y = 3).

The filtrate of the reaction mixture was poured into 1.5 l. of acetone. The precipitated substance was a sticky paste and could not be isolated.

(D) 1–4 Reaction. (a) In DMF–Methanol (1:1). Tetramethyldiaminomethane (10.21 g, 0.100 mol) was allowed to react with 21.58 g (0.100 mol) of 1,4-dibromobutane in 65 ml of the solvent for 264 hr at room temperature. The reaction mixture was poured into a large excess of acetone with stirring. The precipitated crystal was filtered, washed with acetone, and dried *in vacuo* at 40°, yield 17.62 g (89.5% based on the diamine). It was recrystallized from absolute ethanol: mp 174–176° dec; nmr τ 5.35 (s, 4.5, 4 H, N^+-CH_2O), 6.30 (s, 5.7, 6 H, OCH_3), 6.62 (t, J = *ca.* 8 Hz, 4.2, 4 H, N^+CH_2C), 6.94 (s, 11.8, 12 H, N^+CH_3), 8.17 (quintet, J = *ca.* 4.2 Hz, 4.0, 4 H, $C(CH_2)_2C$).

Anal. Calcd for $C_{12}H_{30}Br_2N_2O_2$ (tetramethylenebis(methoxymethyldimethylammonium bromide)): C, 36.56; H, 7.67; Br (ionic), 40.54; N, 7.11. Found: C, 36.57; H, 7.66; Br(ionic), 40.52; N, 7.04.

(b) In Acetonitrile. Tetramethyldiaminomethane (10.39 g, 0.102 mol) was allowed to react with 21.95 g (0.102 mol) of 1,4-dibromobutane in 65 ml of acetonitrile for 25 hr at room temperature. The precipitated crystal was filtered, washed with a small amount of acetonitrile three times and then with acetone, and dried *in vacuo* at 40°, yield 6.76 g (36.9%).

Anal. Found: Br(ionic), 44.30.

It was recrystallized from isopropyl alcohol: mp 332–333° dec (lit. 335–336°,[26] 342°[27]); nmr τ 6.44 (m, 4.0, 4 H, N^+CH_2C),

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(26) G. Wittig and T. F. Burger, *Justus Liebigs Ann. Chem.*, **632**, 85 (1960).

(27) F. Weygand and H. Danniel, *Chem. Ber.*, **94**, 1688 (1961).

6.82 (s, 6.1, 6 H, N^+CH_3), 7.77 (m, 4.0, 4 H, $C(CH_2)_2C$). The ir and the nmr spectra of this product were the same as those of 1,1-dimethylpyrrolidinium bromide.

Anal. Calcd for $C_6H_{14}BrN$ (1,1-dimethylpyrrolidinium bromide): C, 40.02; H, 7.84; Br(ionic), 44.37; N, 7.78. Found: C, 40.07; H, 7.72; Br(ionic), 44.40; N, 7.79.

More of the same product was obtained when the filtrate was poured into a large excess of acetone. It was filtered, washed with acetone, and dried as above, yield 0.16 g (0.9%).

The 1–4 reaction was carried out in acetonitrile for 168 hr under the same conditions as above. The crystalline precipitate was filtered, washed with a small amount of acetonitrile and then with benzene, and dried as before, yield 12.80 g. It yielded formaldehyde in moist air.

Anal. Calcd for $C_6H_{14}BrN$ (1,1-dimethylpyrrolidinium bromide): Br(ionic), 44.37. Found: Br(ionic), 48.03.

The bromine content and the nmr spectrum indicated that it consisted of 74% 1,1-dimethylpyrrolidinium bromide and 26% dimethylaminobromomethane.

The filtrate was poured into 1.5 l. of benzene. The precipitate was sticky and could not be filtered. The benzene layer was decanted. The residual paste became powdery when treated with 1 l. of acetone with stirring. It was isolated as in (b), yield 3.64 g (19.1%).

Anal. Calcd for $C_6H_{14}BrN$ (1,1-dimethylpyrrolidinium bromide): Br(ionic), 44.37. Found: Br(ionic), 44.94.

(c) 1–4 (Iodide) Reaction in Acetonitrile. Tetramethyldiaminomethane (10.30 g, 0.100 mol) was allowed to react with 31.23 g (0.100 mol) of 1,4-diiodobutane in 65 ml of acetonitrile for 168 hr at room temperature. The precipitated crystal was filtered, with exclusion of moisture, washed with acetonitrile three times and then with benzene, and dried *in vacuo* at room temperature, yield 8.93 g (47.9%), mp 217–218 dec (in a sealed capillary); nmr in Figure 2.

Anal. Calcd for C_3H_8IN (dimethylaminoiodomethane): C, 19.48; H, 4.36; I, 68.59; N, 7.57. Found: C, 19.44; H, 4.42; I(ionic), 68.45; N, 7.53.

The filtrate was poured into a large excess of benzene with stirring. The precipitate was filtered, washed with benzene, and dried *in vacuo* at 40°, yield 15.59 g (68.2%).

Anal. Found: I(ionic), 55.62.

It was recrystallized from absolute ethanol: mp 318–320° dec (lit.[27] 323–326°); nmr τ 6.45 (m, 4.0, 4 H, N^+CH_2C), 6.83 (s, 6.1, 6 H, N^+CH_3), 7.77 (m, 4.0, 4 H, $C(CH_2)_2C$). The ir and the nmr spectra of the product were the same as those of 1,1-dimethylpyrrolidinium iodide.

Anal. Calcd for $C_6H_{14}IN$ (1,1-dimethylpyrrolidinium iodide): I(ionic), 55.88. Found: I(ionic), 55.93.

(E) 1–5 Reaction. (a) In DMF–Methanol (1:1). Tetramethyldiaminomethane (20.71 g, 0.203 mol) was allowed to react with 46.67 g (0.203 mol) of 1,5-dibromopentane in 130 ml of the solvent for 48 hr at room temperature. The crystal formed was filtered, washed with a small amount of the solvent and then with acetone, and dried *in vacuo* at 40°, yield 9.57 g (24.3%).

Anal. Found: Br(ionic), 40.62.

It was recrystallized from *n*-propyl alcohol: mp 328–330° dec (lit. 324°,[3] 345–346°[28]); nmr τ 6.63 (t, J = 5.3 Hz, 4.0, 4 H, N^+CH_2C), 6.89 (s, 5.9, 6 H, N^+CH_3), 8.25 (tallest peak of the diffuse multiplet at 7.8–8.6, 6.0, 6 H, $C(CH_2)_3C$). The ir and the nmr spectra of the product were the same as those of 1,1-dimethylpiperidinium bromide.

Anal. Calcd for $C_7H_{16}BrN$ (1,1-dimethylpiperidinium bromide): C, 43.31; H, 8.31; Br(ionic), 41.16; N, 7.22. Found: C, 43.53; H, 8.29; Br(ionic), 41.01; Br(total), 41.19; N, 7.17.

The filtrate was poured into a large excess of acetone with stirring. The precipitate was filtered, washed with acetone, and dried as above, yield 8.01 g (20.4%). The properties of this fraction were the same as those of the first one.

Anal. Calcd for $C_7H_{16}BrN$: Br(ionic), 41.16. Found: Br (ionic), 40.62.

(b) In Acetonitrile. Tetramethyldiaminomethane (10.35 g, 0.101 mol) reacted with 23.29 g (0.101 mol) of 1,5-dibromopentane in 65 ml of acetonitrile for 48 hr at room temperature. The precipitated crystal was filtered, washed with a small amount of acetonitrile and then with benzene, and dried as in (a), yield 11.05 g (56.2%). It contained 41.72% ionic bromine and smelled of formaldehyde.

The per cent ionic bromine and the nmr spectrum of the product indicated that the dimethylaminobromomethane content was of the order of 3%. It was recrystallized as in (a).

Anal. Calcd for $C_7H_{16}BrN$ (1,1-dimethylpiperidinium bromide): Br(ionic), 41.16. Found: Br(ionic), 41.21.

The filtrate was poured into a large excess of benzene with stirring. The precipitate was filtered, washed with benzene, and dried as before, yield 1.69 g.

Anal. Calcd for $C_7H_{16}BrN$ (1,1-dimethylpiperidinium bromide): Br(ionic), 41.16. Found: Br(ionic), 52.98.

Its nmr spectrum had a strong peak at τ 7.27 due to the presence of dimethylamine hydrobromide, in addition to the peaks due to 1,1-dimethylpiperidinium bromide. The ionic bromine content of the product indicated that about 50% of it was 1,1-dimethylpiperidinium bromide.

When the reaction was carried out for 168 hr under the same conditions, the yields of the first and the second fractions were 15.50 and 3.56 g, respectively. The purities as 1,1-dimethylpiperidinium bromide of the first and the second fractions were 78 and *ca.* 20%, respectively.

(c) In DMF. Tetramethyldiaminomethane (10.26 g, 0.100 mol) was allowed to react with 23.08 g (0.100 mol) of 1,5-dibromopentane in 65 ml of DMF for 48 hr at room temperature. The crystal formed was filtered, washed with a small amount of DMF three times and then with acetone, and dried as in (a), yield 12.21 g.

Anal. Calcd for $C_7H_{16}BrN$ (1,1-dimethylpiperidinium bromide): Br(ionic), 41.16. Found: Br(ionic), 43.93.

The ionic bromine content and the nmr spectrum of the product indicated that it consisted of 83% 1,1-dimethylpiperidinium bromide and 17% dimethylaminobromomethane.

The filtrate was poured into 1.5 l. of acetone with stirring. The precipitate was filtered, washed with acetone, and dried as before, yield 0.011 g (0.06%).

(d) 1–5 (Iodide) Reaction in DMF–Methanol (1:1). Tetramethyldiaminomethane (10.35 g, 0.101 mol) and 32.81 g (0.101 mol) of 1,5-diiodopentane were mixed in 65 ml of the solvent. The mixture was cooled with ice water for a short while at the beginning of reaction and then left for 96 hr at room temperature. The homogeneous solution was poured into 1.5 l. of benzene. The benzene layer was decanted and 500 ml of acetone was added with stirring to the residual cloudy oil. The product became powdery. It was filtered, washed with acetone, and dried *in vacuo* at 40°, yield 11.20 g (45.9%).

Anal. Found: I(ionic), 52.65.

It was recrystallized from 95% ethanol: mp 313–313.5° dec (lit. 334°,[29] 346–349°[30]); nmr τ 6.63 (t, J = 5.5 Hz, 4.0, 4 H, N^+CH_2C), 6.88 (s, 6.1, 6 H, N^+CH_3), 8.23 (tallest peak of the diffuse multiplet at 7.8–9.6, 6.3, 6 H, $C(CH_2)_3C$). The ir and the nmr spectra of it were the same as those of 1,1-dimethylpiperidinium iodide.

Anal. Calcd for $C_7H_{16}IN$ (1,1-dimethylpiperidinium iodide): C, 34.87; H, 6.69; I(ionic), 52.63; N, 5.81. Found: C, 34.84; H, 6.69; I(ionic), 52.71; N, 5.81.

(F) 1–6 Reaction. (a) In Acetonitrile. Tetramethyldiaminomethane (10.22 g, 0.100 mol) and 24.40 g (0.100 mol) of 1,6-dibromohexane were allowed to react in 65 ml of acetonitrile for 8 hr at room temperature. The crystalline precipitate was filtered, washed with a small amount of acetonitrile and then with acetone, and dried *in vacuo* at 40°, yield 2.70 g (13.0%).

Anal. Found: Br(ionic), 38.35.

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(28) R. Lukes and Z. Vesely, *Chem. Listy*, **50**, 1643 (1956).

(29) A. Tzschach and W. Lange, *Z. Anorg. Allg. Chem.*, **326**, 280 (1964).

(30) G. Opitz and H. Mildenberger, *Justus Liebigs Ann. Chem.*, **649**, 26 (1961).

It was recrystallized from absolute ethanol: mp 269–269.5° dec (lit.[27] 285–288°); nmr τ 6.63 (t, J = 4.5 Hz, 4.0, 4 H, N^+CH_2C), 6.88 (s, 5.9, 6 H, N^+CH_3), 8.26 (tallest peak of the diffuse multiplet at 7.8–8.6, 7.9, 8 H, $C(CH_2)_4C$).

Anal. Calcd for $C_8H_{18}BrN$ (1,1-dimethylhexahydroazepinium bromide): C, 46.16; H, 8.72; Br(ionic), 38.39; N, 6.73. Found: C, 46.12; H, 8.64; Br(ionic), 38.41; N, 6.73.

The filtrate was poured into a large excess of acetone with stirring, and the mixture was left at room temperature overnight. The precipitate was filtered, washed with acetone, and dried as above, yield 2.79 g (13.4%). The ir and nmr spectra were the same as those of the first fraction.

Anal. Calcd for $C_8H_{18}BrN$: Br(ionic), 38.39. Found: Br (ionic), 38.45.

When the reaction was carried out for 120 hr under the same conditions, the yields of the first and the second fractions were 26.3 and 6.5%, respectively.

(b) In DMF. Tetramethyldiaminomethane (10.21 g, 0.100 mol) was allowed to react with 24.38 g (0.100 mol) of 1,6-dibromohexane in 65 ml of dimethylformamide for 169 hr at room temperature. The crystalline precipitate was filtered, washed with a small amount of DMF (three times) and then with benzene, and dried *in vacuo* at 40°, yield 10.01 g. The crude product contained 41.72% of ionic bromine and smelled of formaldehyde, indicating the presence of dimethylaminobromomethane. Its purity as 1,1-dimethylhexahydroazepinium bromide was 84%, and the corrected yield 40.4%. It was recrystallized from absolute ethanol.

Anal. Calcd for $C_8H_{18}BrN$ (1,1-dimethylhexahydroazepinium bromide): Br(ionic), 38.39. Found: Br(ionic), 38.16.

The filtrate was poured into 1.5 l. of benzene to give an oily product. The isolation of a solid product was unsuccessful.

(G) 1–7 Reaction in Acetonitrile. Tetramethyldiaminomethane (4.86 g, 0.0476 mol) was allowed to react with 12.20 g (0.0474 mol) of 1,7-dibromoheptane in 31 ml of acetonitrile for 168 hr at room temperature. A crystalline compound, considered to be dimethylaminobromomethane according to the mechanism in Scheme I, and a polymeric product were observed to separate out simultaneously. The mixed precipitate was filtered, washed with a small amount of acetonitrile and then with acetone, and dried *in vacuo* at 40°, yield 1.78 g (16.9% as $(C_9H_{20}BrN)_n$). It was dissolved in methanol and the solution was left at room temperature for a day. It was then poured into a large excess of acetone with stirring. The precipitate was filtered, washed with acetone, and dried as before, $[\eta]$ = 0.043.

Anal. Calcd for $(C_9H_{20}BrN)_n$: C, 48.65; H, 9.07; Br, 35.97; N, 6.30. Found: C, 44.31; H, 8.56; Br(ionic), 35.80; Br(total), 36.40; N, 6.25.

The filtrate was poured into a large excess of acetone. The precipitate was filtered, washed with acetone, and dried as before, yield 2.00 g (19.0% as $(C_9H_{20}BrN)_n$). It was reprecipitated as above, $[\eta]$ = 0.025.

(H) 1–8 Reaction in Acetonitrile. Tetramethyldiaminomethane (10.29 g, 0.101 mol) and 27.40 g (0.101 mol) of 1,8-dibromooctane were allowed to react in 65 ml of acetonitrile for 168 hr at room temperature. The long needles formed were filtered with exclusion of moisture, washed with a small amount of acetonitrile and then with benzene, and dried *in vacuo* at room temperature: yield 1.29 g (9.3%), nmr the same as the nmr spectrum of dimethylaminobromomethane (see Figure 2).

Anal. Calcd for C_3H_8BrN (dimethylaminobromomethane): C, 26.11; H, 5.84; Br, 57.90; N, 10.15. Found: C, 26.09; H, 5.94; Br(ionic), 57.73; N, 10.12.

The filtrate was poured into 1.5 l. of a 2:1 mixture of acetone and benzene. The precipitate was filtered, washed with acetone, and dried *in vacuo* at 40°: yield 5.40 g (22.7% as $(C_{10}H_{22}BrN)_n$), $[\eta]$ = 0.028. The product was reprecipitated as described in the 1–7 reaction: recovery 32%, $[\eta]$ = 0.036.

Anal. Calcd for $(C_{10}H_{22}BrN)_n$: C, 50.85; H, 9.39; Br, 33.83; N, 5.93. Found: C, 47.16; H, 8.93; Br(ionic), 37.92; Br(total), 38.11; N, 5.79.

(I) 1–10 Reaction in Acetonitrile. Tetramethyldiaminomethane (10.31 g, 0.101 mol) was allowed to react with 30.29 g (0.101 mol) of 1,10-dibromodecane in 65 ml of acetonitrile for 168 hr at room temperature. The long needles formed were isolated as in the 1–8 reaction: yield 1.28 g (9.2%), nmr as in Figure 2.

Anal. Calcd for C_3H_8BrN (dimethylaminobromomethane): C, 26.11; H, 5.84; Br, 57.90; N, 10.15. Found: C, 25.91; H, 5.96; Br(ionic), 57.93; N, 10.13.

The filtrate was poured into 1.5 l. of benzene with stirring. A pastelike substance precipitated in the benzene layer. The layer was decanted and the residue was dissolved in a small amount of methanol. The solution was poured into 1 l. of acetone. An oil-containing powdery substance separated which became a powder on standing for a week at room temperature. It was filtered, washed with acetone, and dried *in vacuo* at 40°: yield 2.84 g (10.7% as $(C_{12}H_{26}BrN)_n$), $[\eta]$ = 0.036. It was reprecipitated as before: recovery 46%, $[\eta]$ = 0.040.

Anal. Calcd for $(C_{12}H_{26}BrN)_n$: C, 54.54; H, 9.92; Br, 30.24; N, 5.30. Found: C, 50.76; H, 9.33; Br(ionic), 34.54; Br (total), 34.76; N, 4.85.

(J) 1–16 Reaction in Benzene–Tetrahydrofuran–Methanol (1:1:1). Tetramethyldiaminomethane (3.41 g, 0.0334 mol) and 12.81 g (0.0333 mol) of 1,16-dibromohexadecane were allowed to react in 70 ml of a 1:1:1 mixture (by volume) of benzene, tetrahydrofuran, and methanol for 168 hr at room temperature. The homogeneous mixture was then evaporated by means of a rotary evaporator. The pastelike residue was treated with 200 ml of acetone for 5 days, during which it gradually became powdery. The mixture was poured into 1 l. of acetone and stirred for 5 hr. The precipitate was filtered, washed with acetone, and dried *in vacuo* at 40°: yield 4.57 g (39.3% as $(C_{18}H_{38}BrN)_n$), $[\eta]$ = 0.048. It was reprecipitated as before: recovery 42%, $[\eta]$ = 0.051.

Anal. Calcd for $(C_{18}H_{38}BrN)_n$: C, 62.05; H, 10.99; Br, 22.93; N, 4.02. Found: C, 56.91; H, 10.18; Br(ionic), 25.81; Br(total), 26.00; N, 4.07.

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