

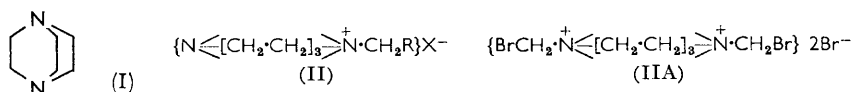
414. *Triethylenediamine (1,4-Diazabicyclo[2,2,2]octane) and Hexaethylenetetramine. Part IV.¹ The Interaction of Triethylenediamine and Dibromomethane, 1,2-Dibromoethane, and 1,3-Dibromopropane.*

By T. P. ABBISS and FREDERICK G. MANN.

The reaction of triethylenediamine with the three dibromoparaffins stated in the title is determined mainly by the reactivity of the bromine atoms in these three compounds. With dibromomethane, the diamine apparently undergoes only monoquaternisation: with 1,2-dibromoethane it undergoes ready monoquaternisation, but diquaternisation requires vigorous conditions: with 1,3-dibromopropane it undergoes very ready diquaternisation, and monoquaternary salts have not been isolated.

Many other products arising under different conditions are described.

THE structure of triethylenediamine (I) leaves the nitrogen atoms fully exposed to simple or quaternary salt formation, and the diquaternary salts are readily prepared.¹ We have investigated some of the products obtained by the reaction of the diamine with dibromomethane, 1,2-dibromoethane, and 1,3-dibromopropane. With these reagents there is clearly a possibility of obtaining simple quaternary salts and also complex products arising from extensive linear condensation of the diamine with the reactive dibromides. We have been interested mainly in the simple and more immediate derivatives, and vigorous reactions were sometimes subdued by cooling and dilution, to check the possible occurrence of a series of consecutive reactions leading to very complex products.



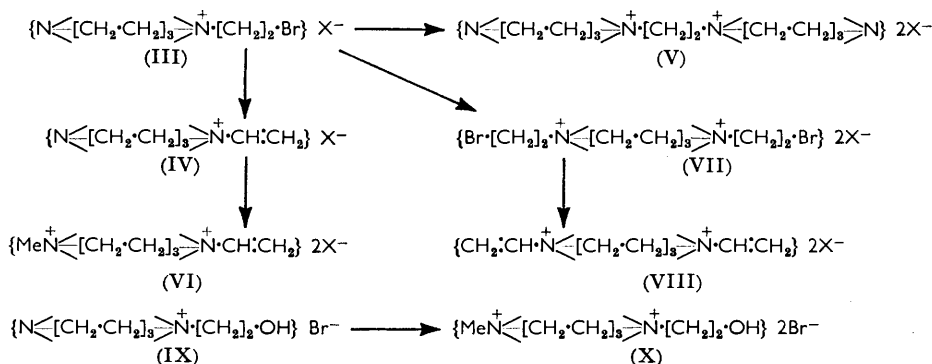
The diamine (I) reacted vigorously with methanolic dibromomethane (1 equivalent) to give the bromomethyl quaternary bromide (II; R = X = Br), which with silver oxide gave the hydroxymethyl salt (II; R = X = OH), identified as the dipicrate and diperchlorate. Aqueous sodium hydroxide, even under comparatively vigorous conditions, did not give this hydrolysis of the cation (II; R = Br): this was not unexpected in view of the structure of this cation, and the different mechanisms by which halogen atoms are removed by silver ions and by hydroxyl ions.² It should be noted that monoquaternary salts having a tertiary amine group, such as (II; R = Br or OH, X = Br), when treated with ethanolic sodium picrate usually gave solely the corresponding quaternary mono-picrate, but with an ethanolic solution of sodium picrate and picric acid usually gave the dipicrate: the use of an excess of perchloric acid similarly gave the diperchlorate. With similar but more complex bromides, the salts obtained by the action of sodium iodide, picrate, perchlorate, or thiocyanate thus showed the number of quaternary groups, and those obtained by sodium picrate-picric acid or by perchloric acid showed any additional tertiary amine groups.

¹ Part III, Mann and Baker, *J.*, 1957, 1881.

² Hughes, *Quart. Rev.*, 1951, 5, 245.

Experiments in which the diamine (I) was treated with dibromomethane (2 equivalents), or the bromide (II; X = Br) with one equivalent, gave mixtures from which no identified compound was isolated: in particular the compound (IIA) was not apparently formed, almost certainly because of the greatly reduced nucleophilic strength of the cation (II; R = Br) and the low reactivity of dibromomethane.

The reactions of the diamine (I) with 1,2-dibromoethane were more varied in type. Equimolecular quantities reacted vigorously in ethanol to give the 2-bromoethyl quaternary bromide (III; X = Br). This salt, when treated in ethanol with silver oxide, or less satisfactorily with aqueous sodium hydroxide, gave the quaternary vinyl hydroxide (IV; X = OH) identified as the mono- and di-picrate, diperchlorate, oxalate, and the metho-dipicrate (VI; X = C₆H₂N₃O₇).



The bromide (III; X = Br) reacted with the diamine (I) (one equivalent) in methanol at 45–50° to give the dibromide (V; X = Br), which could be readily isolated. The interaction of 1,2-dibromoethane with the diamine (I) (3 equivalents) also gave the dibromide (V; X = Br), accompanied, however, by various products, such as the bromide (III; X = Br), the bromide (IV; X = Br), and the hydrobromide of the diamine (I): it is clear that under these conditions the initial product is the bromide (III; X = Br), which then undergoes two different reactions with the diamine (I), namely, direct condensation to give the dibromide (V; X = Br), and loss of hydrogen bromide to give the bromide (IV; X = Br) and the diamine hydrobromide.

The bromide (III; X = Br), when treated with methanolic 1,2-dibromoethane at 100°, gave the bis-(2-bromoethyl) dibromide (VII; X = Br). The vigorous conditions required for this diquaternisation are in marked contrast to the exothermic monoquaternisation which afforded the bromide (III; X = Br), and indicate the marked deactivation of the tertiary nitrogen atom in the latter compound by the positive charge present on the quaternised nitrogen atom.³

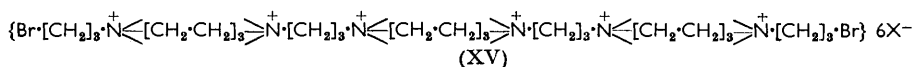
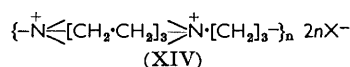
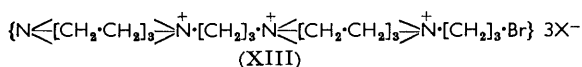
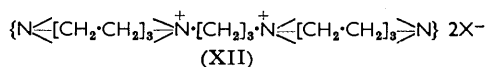
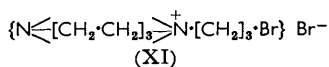
The bis-(2-bromoethyl) dibromide (VII; X = Br) was converted by silver oxide and (less readily) by aqueous sodium hydroxide into the divinyl derivative (VIII; X = OH), identified as the diperchlorate and dipicrate.

The 2-hydroxyethyl bromide (IX), which could not be obtained by hydrolysis of the salt (III), was prepared by the interaction of the diamine (I) with ethylene bromohydrin (one equivalent), and was further identified by quaternisation with methyl bromide to the dibromide (X). The bis-(2-hydroxyethyl) quaternary dibromide has been recorded by Oae *et al.*⁴

In our investigation of the products from 1,3-dibromopropane, we have failed to isolate the simple 3-bromopropyl quaternary bromide (XI), undoubtedly because of the greater reactivity of this 3-bromo-atom compared with that of the 2-bromo-atom in the bromide

³ Mann and Watson, *J. Org. Chem.*, 1948, **13**, 502.

⁴ Oae, Hovarth, Zalut, and Harris, *J. Org. Chem.*, 1959, **24**, 1348.

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(III; X = Br). At room temperature the diamine (I) (2 equivalents) reacted very vigorously with methanolic 1,3-dibromopropane to give the dibromide (XII; X = Br). The use of the diamine (I) and the 1,3-dibromopropane (2 equivalents) gave two products, one moderately soluble in methanol and the second insoluble. The soluble compound (XIII; X = Br) was the mono-3-bromopropyl quaternary salt of the compound (XII; X = Br), and it was identified as its triperchlorate, trithiocyanate, and tripicrate. Analysis of the insoluble product indicated that its cation consisted of the quaternised trimethylene-triethylenediamine units linked together to form a large overall cyclic structure as indicated by the formula (XIV): this was confirmed by the analysis of the corresponding perchlorate, iodide, thiocyanate, and picrate. Decisive evidence for the value of n is not available: the ionic nature of the compound and its very low solubility in solvents precluded the use of most methods for molecular-weight determination, and its very fine microcrystalline nature precluded the estimation of minimum molecular weights by X-ray methods. The use of Steuart and other models showed that the smallest strain-free cation was obtained when n was four: if this were true, the cation is octavalent. Some support for this formulation is the fact that if two of the cations (XIII) were to undergo mutual quaternisation of the head-to-tail type, the cation (XIV), having $n = 4$, would result: consequently the production of a mixture of the bromides (XIII; X = Br) and (XIV; X = Br) in this reaction may result from the initial formation of the simpler tribromide (XIII; X = Br) and its subsequent partial conversion into the bromide (XIV; X = Br). This in turn is supported by experiments in which the temperature of the reaction mixture was not allowed to rise above 5°: the yield of the tribromide (XIII; X = Br) was increased and that of the bromide (XIV; X = Br) decreased. Further, the bromide (XIV; X = Br) was also obtained when the dibromide (XII; X = Br) was heated with 1,3-dibromopropane (1.25 equivalents) in methanol at 70° for 6 hours: the first product of this reaction was almost certainly the tribromide (XIII; X = Br), which under these more rigorous conditions apparently underwent almost complete conversion into the bromide (XIV; X = Br). For purposes of clear reference the salt (XIV; X = Br) will be termed the octabromide, but it must be emphasised that this term is based solely on the above evidence.

When a concentrated methanolic solution of the diamine (I) was added dropwise from a fine capillary tube into an excess of vigorously stirred 1,3-dibromopropane at 45°, working up ultimately gave a salt whose composition indicated that it was the hexabromide (XV; X = Br): this was confirmed by its conversion into the bromine-containing hexapicrate (XV; X = C₆H₂N₃O₇). It is noteworthy that diquaternisation of the terminal bromine atoms of this cation with one molecule of the diamine (I) would produce the bromide (XIV; X = Br) having $n = 4$: unfortunately lack of material precluded this condensation being attempted experimentally.

EXPERIMENTAL

The systematic names are given for all new compounds, followed (for the simpler compounds) by the trivial name based on triethylenediamine.

All compounds were colourless except the yellow picrates. The m. p.s of certain compounds were dependent on the temperature of immersion, indicated as (T.I.-°) immediately after the recorded m. p.: occasionally a sealed evacuated tube (E.T.) had to be employed.

Dibromomethane Derivatives.—These were investigated less thoroughly than those of 1,2-dibromoethane and 1,3-dibromopropane.

1-Bromomethyl-4-aza-1-azoniabicyclo[2,2,2]octane bromide. (*Triethylenediamine bromomethobromide*) (II; R = X = Br). When dibromomethane (3.1 g.) was added to a solution of the diamine (I) (2 g., 1 mol.) in methanol (2 ml.), the temperature rose to *ca.* 80°. The stirred mixture was kept at 40° for 30 min., cooled, and poured into ether (25 ml.). The white precipitate (4.1 g., 80%), when recrystallised from *n*-propanol or ethanol, gave the *bromide* (II; R = X = Br), m. p. 176° (vigorous effervescence) (T.I. 170°) (Found: C, 29.3; H, 4.9; N, 9.9. $C_7H_{14}Br_2N_2$ requires C, 29.4; H, 4.9; N, 9.8%). Treatment with sodium picrate, both in ethanol, gave the *picrate* (II; R = Br, X = $C_6H_2N_3O_7$), m. p. 166° (decomp.) (from methanol) (Found: C, 36.2; H, 3.5; N, 16.0. $C_{13}H_{16}BrN_5O_7$ requires C, 35.9; H, 3.7; N, 16.1%). The bromide also gave a *dipicrate*, m. p. 183° (decomp.) (from water), and a *diperchlorate*, m. p. 182—184° (decomp.) (from aqueous ethanol).

1-Hydroxymethyl-4-aza-1-azoniabicyclo[2,2,2]octane hydroxide. (*Triethylenediamine hydroxymethohydroxide*) (II; R = X = OH). Silver oxide (1 g., 2.5 mol.) was added to a solution of the bromide (II; R = X = Br) (0.5 g., 1 mol.) in ethanol (10 ml.) which was shaken at 25° for 5 hr., and filtered through "Hyflo-supercel." The filtrate of the hydroxide (II; R = X = OH), treated with perchloric acid, deposited the *diperchlorate*, m. p. 296° (explodes) (from aqueous ethanol) (Found: C, 24.6; H, 5.0; N, 7.9. $C_7H_{16}ClN_2O_5.HClO_4$ requires C, 24.5; H, 4.7; N, 8.2%). The perchlorate, treated with ethanolic picric acid-sodium picrate, gave the *dipicrate hemihydrate*, m. p. 246—247° (decomp.) (from methanol) (Found: C, 37.2; H, 3.2; N, 18.2. $C_{13}H_{17}N_5O_8.C_6H_3N_3O_7.1/2H_2O$ requires C, 37.3; H, 3.5; N, 18.3%).

The bromide (II; R = X = Br) was unaffected when treated with an excess of 22% aqueous sodium hydroxide at 20—25° for 14 hr., or at 65—70° for 4.5 hr.

Derivatives of 1,2-Dibromoethane.—1-2'-Bromoethyl-4-aza-1-azoniabicyclo[2,2,2]octane bromide. (*Triethylenediamine 2-bromoethobromide*) (III; X = Br). 1,2-Dibromoethane (16.9 g.; 1 mol.) was added to a cold solution of the diamine (I) (11 g.; 1.1 mol.) in methanol (12 ml.). When the mixture started to boil, it was cooled to 0°, thoroughly stirred with ether, and filtered. The residue, recrystallised from *n*-propanol, afforded the *bromide* (III; X = Br) (25 g., 93%), m. p. 300° (decomp.) (Found: C, 32.0; H, 5.1; N, 9.1; ionic Br, 26.9. $C_8H_{16}Br_2N_2$ requires C, 32.0; H, 5.3; N, 9.3; ionic Br, 26.7%). It gave a *diperchlorate*, m. p. 306° (explosive decomp.) (T.I. 300°) (from methanol) (Found: C, 22.4; H, 3.9; N, 7.0. $C_8H_{16}BrClN_2O_4.HClO_4$ requires C, 22.8; H, 4.0; N, 6.7%), and a *dipicrate*, m. p. 200° (decomp.) (Found: C, 35.7; H, 3.4; N, 16.7. $C_{14}H_{18}BrN_5O_7.C_6H_3N_3O_7$ requires C, 35.4; H, 3.1; N, 16.4%) (from water).

The use of the diamine (2 mols.) under the above conditions also gave the bromide (III; X = Br): the reaction mixture, when boiled under reflux, or heated in sealed tubes, gave only unidentified decomposition products.

1-Vinyl-4-aza-1-azoniabicyclo[2,2,2]octane salts (IV). A solution of the bromide (III; X = Br) (1 g.) in ethanol (10 ml.) was shaken with silver oxide (2 g.; 2.5 mol.) for 45 min. and then filtered. Portions of the filtrate containing the hydroxide (IV; X = OH), with the appropriate reagents gave the following derivatives: *diperchlorate*, m. p. 268° (explosive decomp.) (from methanol) (Found: C, 28.8; H, 5.0; N, 8.4. $C_8H_{15}ClN_2O_4.HClO_4$ requires C, 28.4; H, 4.7; N, 8.3%), *monopicrate*, m. p. 200—202° (decomp.) (from methanol) (Found: C, 45.8; H, 4.7; N, 19.2. $C_{14}H_{17}N_5O_7$ requires C, 45.8; H, 4.7; N, 19.1%); *dipicrate*, m. p. 202—204° (decomp.) (from water) (Found: C, 40.0; H, 3.7; N, 19.0. $C_{14}H_{17}N_5O_7.C_6H_3N_3O_7$ requires C, 40.3; H, 3.3; N, 18.8%) [a mixture of the two picrates had m. p. 202° (decomp.)]; the *di(hydrogen oxalate)monohydrate*, deposited when the filtrate was added to saturated ethanolic oxalic acid, had m. p. 165° (vigorous effervescence) (Found: C, 42.4; H, 6.0; N, 8.5. $C_{10}H_{16}N_2O_4.C_2H_2O_4.H_2O$ requires C, 42.9; H, 5.9; N, 8.3%); heating at 70°/0.5 mm. for 11 hr. gave the anhydrous salt, m. p. 182—184° (decomp.) (Found: C, 44.9; H, 5.9; N, 9.0. $C_{10}H_{16}N_2O_4.C_2H_2O_4$ requires C, 45.2; H, 5.6; N, 8.8%). The presence of the vinyl group in the diperchlorate (IV; X = ClO_4) was confirmed by bands at 3130 ($C:CH_2$) and 1652 cm^{-1} (C=C) in the spectrum.

A mixture of the bromide (III; X = Br) (1 g.) in water (0.5 ml.) and 27.5% aqueous sodium hydroxide (1.0 ml.); 4 mol. of NaOH), when heated at 40° for 2 hr., cooled, neutralised with dilute hydrobromic acid, and added to aqueous picric acid-sodium picrate, deposited the above dipicrate, m. p. and mixed m. p. 202—204° (decomp.) after four recrystallisations from water (Found: C, 40.2; H, 3.6; N, 19.8%).

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1,1'-Ethylenedi-(4-aza-1-azoniabicyclo[2,2,2]octane) dibromide (V). Solutions of the bromide (III; X = Br) (3 g.) and the diamine (I) (1.68 g.; 1.5 mol.) in methanol (5 and 1.5 ml.) were mixed and heated at 45–50° for 3 hr., the pale yellow solution being then evaporated under reduced pressure. The residue was extracted with cold ether to remove unchanged diamine (0.9 g.) and then with hot n-propanol. Recrystallisation of the residue (1.65 g., 40%) from aqueous ethanol (charcoal) gave the *dibromide hemihydrate* (V; X = Br), m. p. 304° (decomp.) (Found: C, 40.1; H, 7.3; N, 13.3; ionic Br, 38.3. $C_{14}H_{28}Br_2N_4 \cdot \frac{1}{2}H_2O$ requires C, 39.9; H, 6.9; N, 13.3; ionic Br, 38.0%); recrystallisation from methanol followed by long heating at 100°/0.1 mm. gave the anhydrous hygroscopic *dibromide*, m. p. 316–318° (decomp.) (Found: C, 40.8; H, 6.7; N, 13.5. $C_{14}H_{28}Br_2N_4$ requires C, 40.8; H, 6.8; N, 13.6%). It gave a *dipicrate*, m. p. 282–284° (decomp.) (from water) (Found: C, 44.0; H, 4.9; N, 19.8. $C_{26}H_{32}N_{10}O_{14}$ requires C, 44.0; H, 4.5; N, 19.8%), and a *dithiocyanate monohydrate*, m. p. 232–234° (decomp.) (Found: C, 49.7; H, 7.8. $C_{16}H_{28}N_8S_2 \cdot H_2O$ requires C, 49.7; H, 7.8%).

1,2-Dibromoethane (1.68 g.) was added to a solution of the diamine (I) (3 g.; 3 mol.) in methanol (3 ml.), and when the preliminary exothermic reaction subsided, methanol (3 ml.) was added, and the clear solution heated at 40° for 3 hr.; a red colour had then developed and a mixture of white and red crystals had separated. The reaction mixture was evaporated to dryness under reduced pressure, and extracted with cold ether to remove unchanged diamine (I). The residue was then extracted in turn with cold acetone and boiling n-propanol. The acetone extract yielded the 1-vinyl bromide (IV; X = Br), identified as the dipicrate, m. p. 202–203° (Found: C, 40.5; H, 3.6; N, 18.8%), and, after being heated with methyl toluene-*p*-sulphonate, as the methobromide of the salt (IV; X = Br), identified as the 1-methyl-4-vinyl-1,4-diazoniabicyclo[2,2,2]octane dipicrate (VI; X = $C_6H_5N_3O_7$), m. p. 272° (decomp.) (from water) (Found: C, 41.3; H, 4.0; N, 18.0. $C_{21}H_{22}N_8O_{14}$ requires C, 41.3; H, 3.6; N, 18.4%). The n-propanol extract on evaporation gave a residue which, thrice recrystallised from ethanol (charcoal), gave the *monohydrobromide* of the diamine (I), m. p. 334° (decomp., vigorous effervescence) (Found: C, 37.4; H, 7.0; N, 14.2; ionic Br, 41.3. $C_8H_{12}N_2 \cdot HBr$ requires C, 37.3; H, 6.8; N, 14.5; ionic Br, 41.4%); it gave the dipicrate, m. p. 286° (decomp.) (lit.¹ 290°) (from water) (Found: C, 37.8; H, 3.2; N, 19.4. Calc. for $C_8H_{12}N_2 \cdot 2C_6H_5N_3O_7$: C, 37.9; H, 3.2; N, 19.6%).

The insoluble residue from the above extractions, recrystallised from methanol, gave the dibromide (V; X = Br), m. p. and mixed m. p. 317–320° (decomp.) (Found: C, 40.9; H, 7.1%). On one occasion, this residue when recrystallised from methanol-ethanol (1:4 v/v) gave the bromide (III; X = Br), m. p. and mixed m. p. 300° (decomp.) (Found: C, 32.3; H, 5.2%), which furnished the dipicrate, m. p. and mixed m. p. 200° (decomp.) (Found: C, 35.7; H, 3.0; N, 16.7%).

1,4-Bis-2'-bromoethyl-1,4-diazoniabicyclo[2,2,2]octane dibromide. (*Triethylenediamine bis-2-bromoethobromide*) (VII; X = Br). 1,2-Dibromoethane (0.96 g.; 1.5 mol.) was added to a solution of the bromide (III; X = Br) (1 g.) in methanol (2 ml.), which was heated in a sealed tube at 100° for 16 hr. The crystalline deposit from the cold mixture, when recrystallised from methanol or water, gave the *dibromide monohydrate* (1.2 g., 75%), m. p. 250° (vigorous effervescence) (T.I. 245°) (Found: C, 24.0; H, 4.1; N, 5.3. $C_{10}H_{20}Br_4N_2 \cdot H_2O$ requires C, 23.7; H, 4.4; N, 5.5%); heating at 100°/0.5 mm. gave the anhydrous *dibromide* of unchanged m. p. (Found: C, 24.6; H, 4.2. $C_{10}H_{20}Br_4N_2$ requires C, 24.6; H, 4.1%). It gave a *diperchlorate*, m. p. 242–243° (from aqueous ethanol) (Found: C, 22.6; H, 3.8; N, 5.4. $C_{10}H_{20}Br_2Cl_2N_2O_8$ requires C, 22.8; H, 3.8; N, 5.3%).

1,4-Divinyl-1,4-diazoniabicyclo[2,2,2]octane diperchlorate. (*Triethyldiamine divinylperchlorate*) (VIII; X = ClO_4). Silver oxide (2 g.) was added to a solution of the dibromide (VII; X = Br) (0.7 g.) in water (4.5 ml.), which was shaken for 2 hr. and filtered. The filtrate when treated in turn with 60% perchloric acid, methanol, and ether, deposited the *diperchlorate* (0.2 g., 40%), m. p. 279° (violent decomp.) (Found: C, 32.7; H, 4.8; N, 7.6. $C_{10}H_{18}Cl_2N_2O_8$ requires C, 32.9; H, 5.0; N, 7.7%). The i.r. spectrum of this salt showed bands at 3105 ($C:CH_2$) and 1658 cm^{-1} ($C:C$), confirming the presence of the vinyl groups. An aqueous solution of this salt when added to ethanolic sodium iodide gave the di-iodide, m. p. 211° (I.T. 200°) (from aqueous ethanol), and similarly gave the dipicrate, m. p. 256–257° (decomp.).

A solution of the dibromide (VII; X = Br) (0.5 g.) in water (1.5 ml.) was treated with 27.5% aqueous sodium hydroxide and, after 6 hr., with a slight excess of perchloric acid, and then ethanol. The deposited diperchlorate (Found: C, 33.3; H, 5.1%) gave the *dipicrate*

(VIII; $X = C_6H_2N_3O_7$), m. p. and mixed m. p. 256° (decomp.) (Found: C, 42.1; H, 3.7; N, 18.2. $C_{22}H_{22}N_8O_{14}$ requires C, 42.4; H, 3.6; N, 18.0%).

1,2'-Hydroxyethyl-4-aza-1-azoniabicyclo[2,2,2]octane bromide. (Triethylenediamine 2-hydroxyethobromide) (IX). Ethylene bromohydrin (1.11 g.; 1 mol.) was added to the diamine (I) (1 g.) in methanol (1 ml.), which was slowly heated to boiling, and then cooled, and volatile material removed under reduced pressure. The residual viscous oil when stirred with ether gave the bromide (IX; $X = Br$) as a white powder (1.9 g., 90%), too deliquescent for purification. Its solution in methanol, cooled in ice-salt, was therefore treated with methyl bromide (4 g.). The clear solution was allowed to reach room temperature, volatile material was removed as before, and the residue of 1,2'-hydroxyethyl-4-methyl-1,4-diazoniabicyclo[2,2,2]octane dibromide monohydrate (X) had m. p. $226-227^\circ$ after recrystallisation from methanol (Found: C, 31.1; H, 6.0; N, 8.1. $C_9H_{20}Br_2N_2O \cdot H_2O$ requires C, 30.9; H, 6.3; N, 8.0%): a sample, after long drying in a vacuum desiccator, gave the anhydrous dibromide (Found: Br, 47.7. $C_9H_{20}Br_2N_2O$ requires Br, 48.2%).

Derivatives of 1,3-Dibromopropane.—1,1'-Trimethylenedi(4-aza-1-azoniabicyclo[2,2,2]octane) dibromide (XII; $X = Br$). 1,3-Dibromopropane (3.62 g.; 1 mol.), when added to a solution of the diamine (I) (4 g.; 2 mol.) in methanol (4 ml.), caused a vigorous reaction, the temperature rising rapidly to ca. 100° . The cold product was thoroughly stirred with ether, collected (7.6 g., 100%), and crystallised from n-propanol-ethyl methyl ketone (4:1, v/v), giving the dibromide monohydrate (XII; $X = Br$), m. p. 297° (decomp.), $258-259^\circ$ (decomp.) (T.I. 225°) (Found: C, 40.0; H, 7.4; N, 12.6; ionic Br, 36.0. $C_{15}H_{30}Br_2N_4 \cdot H_2O$ requires C, 40.5; H, 7.3; N, 12.6; ionic Br, 36.0%). The dipicrate had m. p. $260-261^\circ$ (vigorous decomp.) (from water) (Found: C, 44.6; H, 4.3; N, 19.6. $C_{27}H_{34}N_{10}O_{14}$ requires C, 44.9; H, 4.7; N, 19.4%).

1-{3-(4-Aza-1-azoniabicyclo[2,2,2]octan-1-yl)propyl}-4,3'-bromopropyl-1,4-diazoniabicyclo[2,2,2]octane tribromide (XIII; $X = Br$) and salts of the cation (XIV). 1,3-Dibromopropane (7.25 g., 2 mol.) was added to the diamine (I) (2 g.; 1 mol.) in methanol (2 ml.) giving an exothermic reaction. The mixture was warmed under reduced pressure to remove methanol and dibromopropane, and the crude product was extracted with ether. The residue was then extracted with boiling methanol (5×50 ml.), leaving an insoluble residue.

The combined methanolic extracts were taken to dryness under reduced pressure, and the residue, when triturated with ether and then crystallised from methanol, gave the very hygroscopic tribromide (XIII; $X = Br$), m. p. $262-264^\circ$ (decomp.). An aqueous solution, treated with the appropriate sodium salts, gave the following crystalline derivatives: triperchlorate pentahydrate, m. p. 283° (explosive decomp.) (T.I. 270°) (Found: C, 28.1; H, 5.5; N, 7.0. $C_{18}H_{36}BrCl_3N_4O_{12} \cdot 5H_2O$ requires C, 27.8; H, 5.95; N, 7.2%); tripicrate, m. p. 292° (explosive decomp.) (E.T., T.I. 280°) after extraction with boiling water (Found: C, 39.9; H, 4.0; N, 16.6. $C_{36}H_{42}BrN_{13}O_{21}$ requires C, 40.3; H, 3.9; N, 17.0%) (the presence of bromine in the picrate was confirmed); triithiocyanate monohydrate, m. p. $239-240^\circ$ (decomp.) (from water) (Found: C, 43.1; H, 6.4; N, 17.2. $C_{21}H_{36}BrN_7S_3 \cdot H_2O$ requires C, 43.4; H, 6.6; N, 16.9%).

The insoluble white residue from the methanolic extracts was the octabromide (XIV; $X = Br$), m. p. $262-263^\circ$ (decomp.), 268° (vigorous decomp.) (T.I. 250°) (Found: C, 34.2; H, 6.1; N, 9.0; ionic Br, 50.4. $C_{36}H_{72}Br_8N_8$ requires C, 34.3; H, 5.8; N, 8.9; ionic Br, 50.9%). An aqueous solution, added to aqueous sodium iodide, gave the very hygroscopic octaiodide, m. p. $235-236^\circ$ (decomp.) (from water), which on exposure to air formed the nonhygroscopic pentahydrate (Found: C, 24.9; H, 5.3; N, 6.3. $C_{36}H_{72}I_8N_8 \cdot 5H_2O$ requires C, 25.0; H, 5.1; N, 6.5%). The octapicrate trihydrate had m. p. 267° (decomp.; markedly dependent on rate of heating), after thorough extraction with boiling water (Found: C, 40.5; H, 3.9; N, 17.7. $C_{84}H_{88}N_{32}O_{66} \cdot 3H_2O$ requires C, 40.4; H, 3.8; N, 17.8%). The octathiocyanate tetrahydrate had m. p. 247° (decomp.) after crystallisation from water (Found: C, 45.9; H, 6.8; N, 19.4; S, 21.9. $C_{44}H_{22}N_{16}S_8 \cdot 4H_2O$ requires C, 45.8; H, 7.0; N, 19.4; S, 22.2%).

When the above reaction was carried out with equimolecular quantities of the diamine (I) and 1,3-dibromopropane, the octabromide (XIV; $X = Br$) was again obtained in good yield, but the isolation of the tribromide (XIII; $X = Br$) was unsatisfactory.

Interaction of the Dibromide (XII; $X = Br$) and 1,3-Dibromopropane.—The dibromide (2 g.) and 1,3-dibromopropane (1.2 g.; 1.25 mol.) in methanol (8 ml.) was heated at $70-75^\circ$ for 6 hr. The cold semisolid product was stirred with cold methanol, and the collected solid extracted with boiling methanol (3×50 ml.), giving a residue of the octabromide (XIV; $X = Br$), m. p. and mixed m. p. 262° (decomp.). It was identified as the hydrated octaiodide, m. p. 235°

(decomp.) (Found: C, 25.0; H, 4.9; N, 6.7%), the hydrated octapicrate, m. p. and mixed m. p. 268° (decomp.) (T.I. 225°) (Found: C, 40.9; H, 4.0; N, 18.0%), the hydrated octathiocyanate, m. p. 239—240° (decomp.) (Found: C, 46.3; H, 7.0; N, 19.4%), and the *octaperchlorate hexahydrate*, recrystallised from water, m. p. 275—277° (explodes) (Found: C, 28.7; H, 5.8; N, 7.1. $C_{36}H_{72}Cl_8N_8O_{32} \cdot 6H_2O$ requires C, 28.4; H, 5.5; N, 7.4%).

1,4-*Di*(3-{4-3'-bromopropyl-1,4-diazoniabicyclo[2,2,2]octan-1-yl}propyl)-1,4-diazoniabicyclo[2,2,2]octane hexabromide (XV; X = Br).—The diamine (I) (1 g.) in methanol (1 ml.) was dropped from a fine capillary tube during 1½ hr. into vigorously stirred 1,3-dibromopropane (8.8 g.; *ca.* 5 mol.) at 45°, solid material being steadily deposited. Methanol was removed under reduced pressure, and the residue extracted first with cold ether and then with boiling methanol (2 × 50 ml.). The combined methanol extracts were taken to dryness, and the residue, when recrystallised from methanol, gave the *hexabromide* (XV; X = Br), m. p. 264—265° (decomp.) (Found: C, 31.1; H, 5.7; N, 7.3; ionic Br, 41.4. $C_{30}H_{60}Br_8N_8$ requires C, 31.5; H, 5.3; N, 7.3; ionic Br, 41.9%). It gave a *hexapicrate*, m. p. 300° (vigorous decomp.) (I.T. 290°), after three extractions with boiling water (Found: C, 39.2; H, 4.1; N, 17.1. $C_{66}H_{72}Br_2N_{24}O_{42}$ requires C, 39.0; H, 3.6; N, 16.5%): the presence of bromine was confirmed.

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