766. *Polymers Based on Hydrazine. Part III.*[1] *The Reaction of* 1,1-*Dimethylhydrazine with Polymethylene Dihalides.*

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Polymethylenebis-(1,1-dimethylhydrazine) dihalides rather than polymeric materials were produced by reaction of 1,1-dimethylhydrazine with polymethylene dihalides. Some aspects of the infrared absorption spectra of hydrazine and hydrazinium compounds are discussed.

In further experiments designed to prepare linear polymers containing the hydrazine moiety, the reaction between 1,1-dimethylhydrazine (I) and a number of polymethylene dihalides (II) has been investigated. It was of interest to ascertain whether the hydrazine would behave as a bifunctional reagent and lead to polymers of type (III).

Ethylene dibromide reacted with two mol. of 1,1-dimethylhydrazine in boiling ethanol, yielding some crystalline material and a non-crystalline residue (A). The crystals were identified as ethylenebis-(1,1-dimethylhydrazinium) dibromide (VII; $n = 2$, X = Br), on the basis of analysis, the presence of ionic bromine, the similarity of its infrared spectrum to that of 1,1,1-trimethylhydrazinium iodide, and hydrogenolysis to *NNN'N'*-tetramethylethylenediamine (X; $n = 2$).

Ethylene dichloride behaved similarly. The crystalline product was assigned an analogous structure (VII; $n = 2$, X = Cl), since it proved to be identical with material derived from *NNN'N'*-tetramethylethylenediamine by quaternisation with chloramine in aqueous solution.[2] The amino groups in (VII; $n = 2$, X = Cl) possessed little basicity and did not condense with benzaldehyde[3] or with more ethylene dichloride to form a polymer.

Equimolecular amounts of 1,1-dimethylhydrazine and ethylene dibromide in boiling ethanol furnished crystalline 1-2'-bromoethyl-1,1-dimethylhydrazinium bromide (IV; $n = 2$, X = Br) and a residue (B). The former product, on condensation with another

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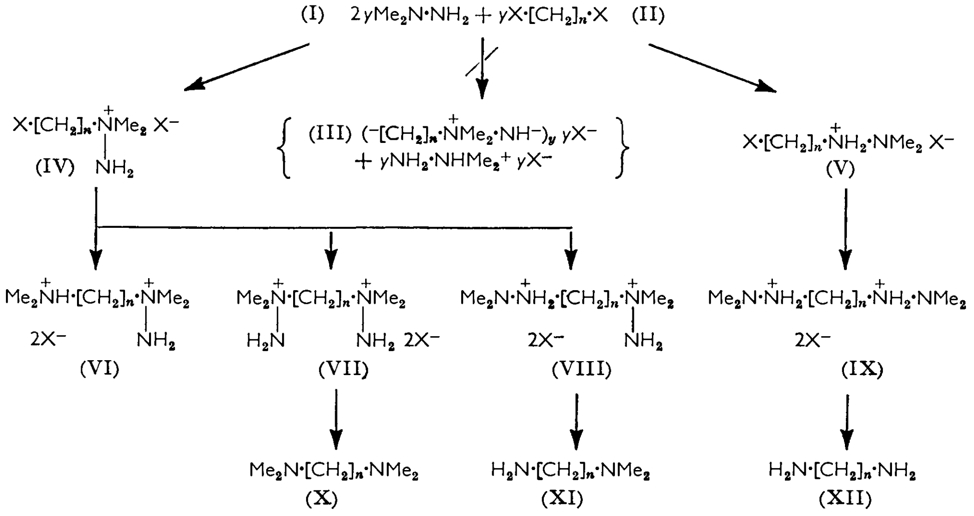
[1] Part II, preceding paper; for a preliminary note see Evans, *Chem. and Ind.*, 1959, 729.

[2] Omietanski and Sisler, *J. Amer. Chem. Soc.*, 1956, **78**, 1211.

[3] Smith and Most, *J. Org. Chem.*, 1957, **22**, 358.

mol. of dimethylhydrazine gave the dibromide (VII; $n = 2$, $X = Br$), as well as a residual product (C) whose infrared spectrum closely resembled that of (B). During several weeks at room temperature residue (B) partially crystallised and the crystals were found



to be a mixture of the hydrobromides of 1,1-dimethylhydrazine and 1-2′-dimethylaminoethyl-1,1-dimethylhydrazinium bromide (VI; $n = 2$, $X = Br$). The structure of the latter was confirmed by its synthesis from dimethylamine and 1-2′-bromoethyl-1,1-dimethylhydrazinium bromide (IV; $n = 2$, $X = Br$). Hydrogenolysis of the residue (B) afforded ammonia and *NNN′N′*-tetramethylethylenediamine (X; $n = 2$). Residue (C) deposited ammonium hydrogen oxalate on addition of oxalic acid and, when subjected to the same hydrogenolysis procedure as (B), yielded dimethylamine and the diamine (X; $n = 2$). Similarly, the residual product (A) liberated ammonia and dimethylamine on treatment with alkali, and, on hydrogenolysis after alkali treatment, yielded the diamine (X; $n = 2$) and a further quantity of ammonia. It was concluded on the basis of these hydrogenolysis experiments that the residual products (A), (B), and (C) were mixtures of ammonium bromide and the hydrobromides of dimethylhydrazine (I) and the dibromide (VI; $n = 2$, $X = Br$), no polymeric species being present.

Equimolecular quantities of 1,1-dimethylhydrazine and trimethylene dibromide in boiling ethanol rapidly formed trimethylenebis-(1,1-dimethylhydrazinium) dibromide (VII; $n = 3$, $X = Br$). In addition, 1,1-dimethylhydrazinium hydrobromide, 1,1-dimethylpyrazolidinium bromide (XIV), and some unchanged trimethylene dibromide were recovered. The identity of the pyrazole derivative was confirmed by its hydrogenolysis to 3-dimethylaminopropylamine (XV). Among the products of reaction of two molecular equivalents of 1,1-dimethylhydrazine with trimethylene dibromide were the dibromide (VII; $n = 3$, $X = Br$) and the same pyrazolidinium salt (XIV).

Methylene dichloride reacted comparatively slowly with two equivalents of the hydrazine in hot ethanol, but only two minor constituents of the complex reaction mixture —ammonium chloride and 1,1,1-trimethylhydrazinium chloride—were separated and identified. Ammonium bromide was the only identified product of the reaction with methylene dibromide.

Other polymethylene dihalides, chlorides, bromides, and iodides, under a variety of conditions, gave, as the main products, the corresponding polymethylene bis-(1,1-dimethylhydrazinium) dihalides (VII). Relevant data from the spectra of these salts in the 3 and the 6 μ region are given in Table 1 and are considered to support the structures postulated.

For comparison, the main absorption bands of some hydrazine derivatives are given in Table 2. Those of some salts are in listed Table 3.

TABLE 1.

Infrared maxima (cm.$^{-1}$) of polymethylenebis-(1,1-dimethylhydrazinium) dihalides (VII).

n	X						3 μ Region						6 μ Region
2	Cl		3220s	3096s		3024m	3010m	2930w					1637m
2	Br		3204s	3109s		3019m	3000m	2968w					1629m
3	Br		3233s	3097s		3027m	3006m	2988m	2963w				1631m
4	Br	3230s	3200s	3108s	3089s	3014m			2960w				1622m
5	I	3250m	3200s	3132s	3090s		3008w	2986w	2954w			2871w	1614m
5	Br		3196s	3100s			3018m		2953m			2873w	1629m
6	I		3244s	3132s	3089sh		3010w	2984w	2961w	2937m	2916w	2860w	1614m
10	Br		3206s	3111s		3047m	3017m			2934s		2859m	1630m

TABLE 2.

Infrared maxima (cm.$^{-1}$) of 1,1-dimethylhydrazine and some related hydrazinium compounds.

Compound				3 μ Region				
$NH_2{\cdot}NMe_2$	3308s	3223sh *	3142s			2978s	2950s	2896m
$NH_2{\cdot}NHMe_2^+ Cl^-$	3239s		3131s		3021m	2964m	2923m	2869msh
$NH_2{\cdot}NMe_3^+ I^-$	3282s	3231sh *	3142s	3007s		2937m		2890m
$NHEt{\cdot}NH_2Et^+ Cl^-$ †		3205s		3030s				

Compound			3 μ Region				6 μ Region	
$NH_2{\cdot}NMe_2$	2856s	2818s	2771s					1606s
$NH_2{\cdot}NHMe_2^+ Cl^-$		2726s	2676s	2632s	2519s	2484s	1609m	1624m
$NH_2{\cdot}NMe_3^+ I^-$								1615s
$NHEt{\cdot}NH_2Et^+ Cl^-$ †		2800—2720s	2540s	2420m	2280m	2180w		1597m, 1542m

* Probably overtone of a fundamental near 1600 cm.$^{-1}$. † Heacock and Marion, *Canad. J. Chem.*, 1956, **34**, 1782.

TABLE 3.

Infrared maxima (cm.$^{-1}$) of substituted hydrazinium compounds.

Compound			3 μ Region			
$Br{\cdot}CH_2{\cdot}CH_2{\cdot}N^+Me_2{\cdot}NH_2\ Br^-$ (IV)	3206s	3090s	3032s	2970sh		
$Me_2N^+H{\cdot}CH_2{\cdot}CH_2{\cdot}N^+Me_2{\cdot}NH_2\ 2Br^-$ (VI)	3205s	3104s	3032s	3000m	2947m	2909w
Bromide (XIV)	3142s		3014s	2977m	2930w	2896w

Compound		3 μ Region			6 μ Region
$Br{\cdot}CH_2{\cdot}CH_2{\cdot}N^+Me_2{\cdot}NH_2\ Br^-$ (IV)	2856w				1624m
$Me_2N^+H{\cdot}CH_2{\cdot}CH_2{\cdot}N^+Me_2{\cdot}NH_2\ 2Br^-$ (VI)		2607vs	2518m	2474s	1630m
Bromide (XIV)	2856w				1530w

The N–H stretching vibrations of uncharged NH_2 groups in primary amines in the solid state give rise to two bands[4,5] between 3400 and 3100 cm.$^{-1}$. 1,1-Dimethylhydrazine exhibits three bands in this region. Charged NH_2^+ groups, as occur in the salts of secondary amines, give rise to two N–H stretching vibration bands, at about 2920 and 2800 cm.$^{-1}$, respectively. Two other prominent bands, near 2500 and 2400 cm.$^{-1}$, may be due to vibrations of the NH_2^+ group lowered by hydrogen bonding.[6]

In 1,1,1-trimethylhydrazinium iodide, no charged NH_2^+ groups are present and the N–H stretching vibration bands are observed at 3282 and 3142 cm.$^{-1}$, respectively, very close to those of the parent 1,1-dimethylhydrazine. The spectra of the hydrazinium compounds (Table 1) include two strong bands between 3244 and 3200, and between 3132 and 3089 cm.$^{-1}$, respectively, and a series of bands of medium intensity between 3047 and

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[4] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, Ch. 14.

[5] Jones and Sandorfy, "Chemical Applications of Spectroscopy," Interscience Publ., Inc., London, 1956, p. 510.

[6] Stone, Craig, and Thompson, *J.*, 1958, 52.

2859 cm.$^{-1}$, but no bands between 2800 and 2000 cm.$^{-1}$. The bands between 3000 and 2859 cm.$^{-1}$ are due to the C–H stretching vibrations of methyl and methylene groups.[7] Bands of medium intensity between 3047 and 3000 cm.$^{-1}$ are probably due to the C–H stretching vibrations of a methyl group attached to a positively charged nitrogen atom. Tetramethylammonium chloride,[8] for example, has two such bands at 3100 and 3021 cm.$^{-1}$. By analogy with the conclusions deduced from the comparison of the spectra of 1,1-dimethylhydrazine and 1,1,1-trimethylhydrazinium iodide, the two strong bands between 3244 and 3089 cm.$^{-1}$ may be assigned to the N–H stretching of an amino-group. These two bands are at slightly lower frequencies than the N–H stretching bands of primary amines. Since the development of a positive charge on an NH_2 group brings about a decrease of several hundred cm.$^{-1}$ in the N–H stretching frequency, the slight lowering observed in the hydrazinium compounds may be ascribed to the inductive effect of the quaternary nitrogen atom in structure (VII) which causes a slight positive charge to develop on the NH_2 group.

The lack of absorption bands in the 2800—2000 cm.$^{-1}$ region indicates the absence of a structure analogous to that of a secondary amine salt. Structures (VIII) and (IX), which are possible alternatives to (VII), would be expected to absorb strongly in this region, just as 1,2-diethylhydrazinium chloride (Table 2) does.

Hence we conclude that the infrared spectra of the bishydrazinium compounds in the 3 μ region strongly support structure (VII).

It has been noted[4,9] that a primary amino-group gives rise to an infrared absorption band between 1650 and 1590 cm.$^{-1}$, which is shifted to lower frequencies when the nitrogen atom carries a positive charge. Heacock and Marion[9] assigned the band in the 1620—1560 cm.$^{-1}$ region of the spectra of secondary amine hydrohalides to the deformational mode of vibration of the $^+$N–H linkage. The N–H deformation absorption band at 1606 cm.$^{-1}$ in the spectrum of 1,1-dimethylhydrazine moves to 1615 cm.$^{-1}$ in the case of 1,1,1-trimethylhydrazinium iodide, while the polymethylenebishydrazinium compounds all have a strong absorption band between 1637 and 1614 cm.$^{-1}$. If the NH_2 group in the hydrazinium compounds had carried a positive charge, it would have been expected that this band would have moved to frequencies below 1606 cm.$^{-1}$. Consequently, it is concluded that the NH_2 groups in the polymethylenebis-(1,1-dimethylhydrazinium) halides do not carry positive charges and therefore formula (VII) rather than (VIII) or (IX) represents the structure of these halides.

Table 3 contains infrared data concerning three more compounds, two of which (IV and VI; $n = 2$, $X = Br$) contain the hydrazinium moiety. As expected by analogy with the bishydrazinium compounds (VII) discussed earlier, two N–H stretching bands occur in the 3244—3089 cm.$^{-1}$ region, while the N–H deformation band appears in the 1630—1624 cm.$^{-1}$ region. In addition, 1-2′-dimethylamino-1,1-dimethylhydrazinium bromide hydrobromide shows considerable absorption in the 2800—2400 cm.$^{-1}$ range which can be ascribed to the N–H stretching vibrations of an $\geqslant NH^+$ group and is in accord with the structure (VI; $n = 2$, $X = Br$) assigned to this compound. However, only one strong band occurs in the 3244—3089 cm.$^{-1}$ region in the spectrum of 1,1-dimethylpyrazolidinium bromide (XIV); in the 6 μ region, there is one band at 1530 cm.$^{-1}$ which is much weaker than the N–H deformation band of the bishydrazinium halides (VII) and of compounds (IV and VI; $n = 2$, $X = Br$). The position and intensity of the last band supports the cyclic structure (XIV) since the NH deformation band of secondary amines, unlike that of primary amines, is much weaker and can occur at a lower frequency.[4]

When 1,1-dimethylhydrazine reacts with polymethylene dihalides, the initial nucleophilic displacement at one end of the polymethylene dihalide chain can involve either the NMe_2 or the NH_2 group of the 1,1-dimethylhydrazine molecule and two intermediate

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[7] Ref. 5, p. 338.

[8] Kynaston, Larcombe, and Turner, *J.*, 1960, 1772.

[9] Heacock and Marion, *Canad. J. Chem.*, 1956, **34**, 1782.

products (IV and V) are possible. 1,1-Dimethylhydrazine can again attack each intermediate product in two different ways, giving three different products (VII, VIII, and IX). In 1.1-dimethylhydrazine, the inductive effect of the two methyl groups increases the electron availability at the nitrogen atom to which they are attached. This nitrogen atom therefore should be preferentially involved in any nucleophilic displacement of halogen from a carbon atom and indeed, Westphal [10] has shown that alkylation of alkylhydrazines occurs at the substituted nitrogen atom provided that steric effects do not interfere.

With tetra- and higher poly-methylene dibromides, the bis-(1,1-dimethylhydrazinium) dibromides are the major products (Table 4), so that the reaction route (I) ⟶ (IV) ⟶ (VII) must predominate. In the case of ethylene dibromide, the yield of bishydrazinium dibromide is low, but again it is unlikely that the reaction path departs markedly from the route cited; if it did, and significant quantities of compounds (VIII and IX; $n = 2$, $X = Br$) were formed, hydrogenolysis should yield the diamines (XI and XII; $n = 2$, respectively). We were unable to isolate either of these diamines on hydrogenolysis of the various products of the reaction of ethylene dibromide with 1,1-dimethylhydrazine. However, the evolution of dimethylamine when residue (A) was treated with aqueous alkali may indicate the weakness of the N–N linkages in the 1,1,3-trisubstituted hydrazine parts of structures (VIII) and (IX). The low yield of ethylenebis-(1,1-dimethylhydrazinium) dibromide is probably due to its instability under the reaction conditions. The positive charges on the two nitrogen atoms are close together and so the electrostatic repulsion between them is considerable. The consequent strain in the molecule will disappear if one nitrogen atom loses its positive charge. This it can do by expulsion of NH_2^+ (probably as NH_2Br which will ultimately be converted into ammonium bromide [11]). The remaining fragment has indeed been identified and isolated in the form of a hydrobromide (VI; $n = 2$, $X = Br$). Electrostatic repulsion between the two positive charges in the hydrobromide will not be as great as in the bishydrazinium dibromide because one positive charge can be shared with other atoms by hydrogen bonding,[12] $\geqslant N^+H\ Br^- \longrightarrow \geqslant N \cdots H \cdots Br$.

TABLE 4.

Yields of bromides (VII; $X = Br$) from 1,1-dimethylhydrazine and polymethylene dibromides $Br{\cdot}[CH_2]_n{\cdot}Br$.

n in dibromide	1	2	3	4	5
Yield (%)	0	24	36	95	83

In methylenebis-(1,1-dimethylhydrazinium) dibromide (VII; $n = 1$, $X = Br$) the two positively charged nitrogen atoms are closer than in the ethylene compound, and the electrostatic repulsion (which is inversely proportional to the square of the distance) is now so much greater that the molecule must disintegrate immediately it is formed. This explains our inability to isolate it (see Table 4).

With trimethylene dibromide, route (I) ⟶ (IV) ⟶ (VII) is still important (36% yield of hydrazinium dibromide) but a major product is the cyclic compound (XIV). In view of the lack of basicity exhibited by the amino-group of a hydrazinium group,[3] it is unlikely that the cyclic compound is formed by elimination of hydrogen bromide from the intermediate (IV; $n = 3$, $X = Br$). It is much more probable that unchanged 1,1-dimethylhydrazine liberates the free base, 1,1-dimethyl-2-3′-bromopropylhydrazine (XIII), from the other intermediate (V; $n = 3$, $X = Br$) and that this cyclises to 1,1-dimethylpyrazolidinium bromide.

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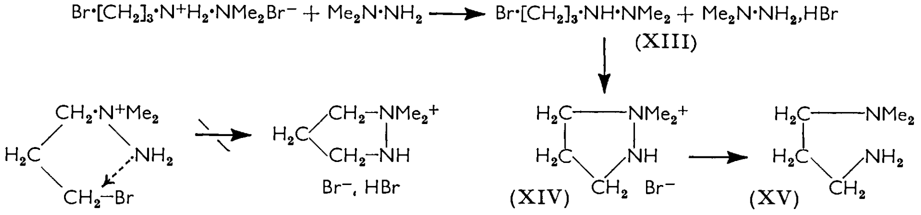
[10] Westphal, *Ber.*, 1941, **74**, 759.
[11] Moldenhauer and Burger, *Ber.*, 1929, **62**, 1615.
[12] Klages and Wolf, *Angew. Chem.*, 1956, **68**, 705.

In the intermediate ω-bromoalkyl compounds (IV), the positive charge on the nitrogen atom strongly activates the ω-bromine atom by its inductive effect so that the bromine atom in these intermediates is more reactive than in the parent polymethylene dibromides and will compete for the unused 1,1-dimethylhydrazine. Thus, equimolecular quantities of 1,1-dimethylhydrazine and tetramethylene dibromide gave as sole product the bishydrazinium compound (VII; $n = 4$, X = Br) and not the expected intermediate (IV; $n = 4$, X = Br). A similar experiment with trimethylene dibromide did not give any of the ω-bromo-intermediate, while with methylene dichloride the halogen atom in the intermediate was so highly activated that it was reduced and 1,1,1-trimethylhydrazinium chloride was formed. Only with ethylene dibromide was it possible to stop the reactions at the intermediate stage. This was probably due to the sharp increase in activation energy required to develop a second positive charge so near to the positive charge already present on the quaternary nitrogen atom of the intermediate (IV; $n = 2$, X = Br).



(XIII)

(XIV)

(XV)

Experimental

M. p.s are corrected. Microanalyses were by Miss M. Corner and her staff of this Laboratory.

Ethylenebis-(1,1-*dimethylhydrazinium*) *Dibromide.*—(i) Ethylene dibromide (37·5 g., 0·2 mole), 1,1-dimethylhydrazine (24 g., 0·4 mole), and ethanol (50 ml.) were refluxed on the steam-bath for 2 hr. After cooling, *ethylenebis-*(1,1-*dimethylhydrazinium*) *bromide* (15 g., 24%) was filtered off. Two recrystallisations from ethanol afforded needles, m. p. 207° (decomp.) (Found: C, 23·7; H, 6·0; Br, 51·5. $C_6H_{20}Br_2N_4$ requires C, 23·4; H, 6·5; Br, 51·9%). The filtrate was evaporated at 100°/20 mm.; the residue was dissolved in propan-1-ol, and the solution was cooled at −15° for a week and then filtered. Evaporation of the filtrate at 100°/20 mm. furnished a liquid residue (A) (31·7 g.).

(ii) 1-2′-Bromoethyl-1,1-dimethylhydrazinium bromide (40·5 g., 0·17 mole), 1,1-dimethylhydrazine (10 g., 0·17 mole), and ethanol (66 ml.) were refluxed for 1 hr. on the steam-bath, then cooled, and the crude product (7·7 g., 15%) was filtered off. After recrystallisation from aqueous ethanol, the product was identical with ethylenebis-(1,1-dimethylhydrazinium) dibromide mentioned above (m. p. and mixed m. p.). Evaporation at 50°/20 mm. of the ethanolic filtrate from the reaction mixture afforded a residue (C) (36·1 g.).

1-2′-*Bromoethyl-*1,1-*dimethylhydrazinium Bromide.*—Ethylene dibromide (64·4 g., 0·34 mole), 1,1-dimethylhydrazine (20·6 g., 0·34 mole), and ethanol (52 ml.) were refluxed on the steam-bath for 1 hr., then cooled to −5° for 1 hr., and 1-2′-*bromoethyl-*1,1-*dimethylhydrazinium bromide* (50·6 g., 60%) was filtered off. Evaporation of the filtrate at 50°/20 mm. furnished a liquid residue (B) (16·8 g.) whose infrared spectrum closely resembled that of (C).

The bromoethyl compound, after one recrystallisation from propan-1-ol and two subsequent crystallisations from ethanol, had m. p. 137·5—139·5° (decomp.) (Found: C, 19·6; H, 5·0; Br, 64·0; N, 11·1. $C_4H_{12}Br_2N_2$ requires C, 19·4; H, 4·9; Br, 64·5; N, 11·3%). The orange *picrate* separated from aqueous ethanol as needles, m. p. 106—109° (Found: C, 30·6; H, 4·2; Br, 19·9; N, 17·7. $C_{10}H_{14}BrN_5O_7$ requires C, 30·3; H, 3·6; Br, 20·2; N, 17·7%).

Hydrogenolysis. (i) Ethylenebis-(1,1-dimethylhydrazinium) dibromide (1·09 g.) in water (2 ml.) and acetic acid (8 ml.) with Adams catalyst (1 g.) was shaken under hydrogen at room temperature and pressure for 3 hr. The mixture was diluted with water, filtered, and evaporated at 100°/20 mm. Recrystallisation of the residue from aqueous methanol afforded NNN′N′-*tetramethylethylenediamine dihydrobromide* (0·29 g., 30%), m. p. 278° (decomp.), identical (m. p., mixed m. p., and infrared spectrum) with material prepared from hydrobromic acid and authentic diamine[13] (Found: C, 26·0; H, 6·6; Br, 56·9; N, 10·0. $C_6H_{18}Br_2N_2$ requires C, 25·9; H, 6·5; Br, 57·5; N, 10·1%).

(ii) Residue (A) (18·3 g.), dissolved in water (150 ml.) containing sodium hydroxide (10 g.), was distilled at 100°/20 mm. The distillate was treated with alcoholic picric acid and furnished the picrates of dimethylamine (m. p. 158—162·5°) and ammonia [m. p. 276—282° (decomp.)], identified by m. p. and mixed m. p.

The alkaline concentrate of (A), acidified with glacial acetic acid (50 ml.) was shaken over Adams catalyst (2 g.) under hydrogen at room temperature and pressure for 10 hr. The mixture was filtered, made alkaline with 4N-sodium hydroxide (500 ml.), and distilled. The distillate, smelling strongly of ammonia, was acidified with concentrated hydrobromic acid and evaporated to dryness at 100°/20 mm. Fractional crystallisation of the residue from propan-1-ol afforded ammonium bromide and *NNN'N'*-tetramethylethylenediamine dihydrobromide (m. p., mixed m. p., and infrared spectrum).

(iii) Residue (B) partially crystallised during several weeks at room temperature. The crystalline portion (6·3 g.) was separated into two components (soluble and sparingly soluble) by extraction with propan-1-ol. Three crystallisations of the sparingly soluble component from ethanol afforded 1-2'-dimethylaminoethyl-1,1-dimethylhydrazinium bromide hydrobromide, m. p. 203° (decomp.). The deliquescent soluble component, m. p. 45—73°, contained bromide ion and was identified as impure 1,1-dimethylhydrazinium bromide since picric acid precipitated the picrate, m. p. 141—144° (decomp.) (Found: C, 33·2; H, 3·8; N, 24·2. Calc. for $C_8H_{11}N_5O_7$: C, 33·2; H, 3·8; N, 24·2%).

Hydrogenolysis of a portion of material (B), before it crystallised, and under the conditions described in (ii), afforded ammonia and *NNN'N'*-tetramethylethylenediamine, identified as their hydrobromides by infrared spectroscopy.

(iv) Residue (C) (3 g.), when dissolved in ethanol containing anhydrous oxalic acid (2 g.), gave some crystals at −5°. Recrystallisation of these from aqueous ethanol afforded needles, m. p. 222—223° (decomp.), of ammonium hydrogen oxalate (Found: C, 22·0; H, 4·8; N, 12·7. Calc. for $C_2H_5NO_4$: C, 22·4; H, 4·7; N, 13·1%).

Residue (C) (5 g.) in water (5 ml.) and acetic acid (20 ml.) containing Adams catalyst (1 g.) was shaken under hydrogen at room temperature and pressure for 3½ hr. The mixture was diluted with water, filtered, and refluxed with concentrated aqueous sodium hydroxide for 15 min. Evolved gases were collected in ethanolic picric acid, yielding yellow plates, m. p. 159—162°, of dimethylamine picrate (m. p. and mixed m. p.). The alkaline mixture was then distilled and the aqueous distillate (15 ml.) was treated with ethanolic picric acid. A yellow solid, m. p. 216—225° raised to 266° (decomp.) on repeated crystallisation from aqueous acetone, was deposited. This was *NNN'N'*-tetramethylethylenediamine dipicrate (Found: C, 37·7; H, 4·2; N, 19·6. Calc. for $C_{18}H_{22}N_8O_{14}$: C, 37·7; H, 3·9; N, 19·5%).

1-2'-*Dimethylaminoethyl*-1,1-*dimethylhydrazinium Bromide Hydrobromide*.—1-2'-Bromoethyl-1,1-dimethylhydrazinium bromide (2·48 g.), anhydrous dimethylamine (5 ml.), and ethanol (70 ml.) were kept at room temperature for 18 hr. and then refluxed on the steam-bath for 1 hr. After removal of most of the ethanol on the steam-bath, the solution was diluted with ether and cooled to −15°, and the precipitate of dimethylamine hydrobromide filtered off. The filtrate was acidified with a few drops of concentrated hydrobromic acid and evaporated. Crystallisation of the residue from propan-1-ol and then from ethanol afforded needles, m. p. 203° (decomp.) (Found: C, 24·8; H, 6·1; Br, 54·0; N, 14·1. $C_6H_{19}Br_2N_3$ requires C, 24·6; H, 6·5; Br, 54·6; N, 14·3%). The picrate, crystallised from ethanol, had m. p. 243° (decomp.) (Found: C, 36·7; H, 4·2; N, 20·9. $C_{18}H_{23}N_9O_{14}$ requires C, 36·7; H, 3·9; N, 21·0%).

Ethylenebis-(1,1-*dimethylhydrazinium*) *Dichloride*.—(i) Ethylene dichloride (8·7 g., 0·088 mole) and 1,1-dimethylhydrazine (9·6 g., 0·16 mole) were refluxed on the steam-bath for 6 hr. The mixture was evaporated at 100°/20 mm., and the residue crystallised from methanol at −20°. The product (2·4 g., 11%) was recrystallised from methanol, affording *ethylenebis*-(1,1-*dimethylhydrazinium*) *dichloride* as rods, m. p. 212—214° (decomp.) (Found: C, 33·2; H, 9·0; Cl, 32·2; N, 26·0. $C_6H_{20}Cl_2N_4$ requires C, 32·9; H, 9·2; Cl, 32·4; N, 25·6%). The *picrate* crystallised from aqueous methanol as orange-yellow needles, m. p. 222° (decomp.) (Found: C, 36·3; H, 4·5; N, 22·9. $C_{18}H_{24}N_{10}O_{14}$ requires C, 35·8; H, 4·0; N, 23·2%).

No reaction was observed between the dichloride and benzaldehyde in methanol and acetic

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[13] Hanhart and Ingold, *J.*, 1927, 997.

acid, or with ethylene dichloride in methanol–propan-1-ol (10 hr.). 1-2′-Chloroethyl-1,1-dimethylhydrazinium chloride (0·2 g.) was obtained as a deliquescent solid when ethylene dichloride (4·4 g., 0·044 mole), 1,1-dimethylhydrazine (4·8 g., 0·08 mole), and methanol (50 ml.) were refluxed on the steam-bath for 3½ hr., then evaporated, and the residue crystallised from propan-1-ol at −20°. The *picrate* crystallised as orange needles, m. p. 136—139°, from ethanol (Found: C, 34·0; H, 3·9; Cl, 9·6; N, 20·0. $C_{10}H_{14}ClN_5O_7$ requires C, 34·1; H, 4·0; Cl, 10·1; N, 19·9%).

(ii) A solution of *NNN′N′*-tetramethylethylenediamine[13] (1 g.) in aqueous chloramine [200 ml.; obtained[14] by distilling a mixture of 0·3315N-sodium hypochlorite (370 ml.) and 0·3444N-ammonia (350 ml.) at 40°/22 mm.], was kept at 0° overnight, then evaporated at 100°/20 mm., and the residue was extracted with methanol. Evaporation of the methanolic extract furnished a solid which on two crystallisations from ethanol and one from methanol gave plates of ethylenebis-(1,1-dimethylhydrazinium) dichloride, identified by m. p., mixed m. p., and infrared spectrum.

Trimethylenebis-(1,1-*dimethylhydrazinium*) *Dibromide*.—(i) Trimethylene dibromide (8·1 g., 0·04 mole) and 1,1-dimethylhydrazine (4·8 g., 0·08 mole) in ethanol (50 ml.) were refluxed on the steam-bath for ½ hr. After cooling, the product (4·7 g., 36%), was collected and recrystallised from aqueous methanol, yielding *trimethylenebis*-(1,1-*dimethylhydrazinium*) *dibromide* as needles, m. p. 224·5° (decomp.) (Found: C, 26·3; H, 7·2; Br, 50·1; N, 17·4. $C_7H_{22}Br_2N_4$ requires C, 26·1; H, 6·9; Br, 49·6; N, 17·4%). The *picrate* crystallised as yellow needles (from aqueous ethanol), m. p. 196—198° (decomp.) (Found: C, 36·9; H, 4·5; N, 22·7. $C_{19}H_{28}N_{10}O_{14}$ requires C, 36·8; H, 4·61; N, 22·6%).

Treatment with ethanolic picric acid of a portion of the ethanolic filtrate from the reaction mixture afforded a picrate, which on repeated crystallisation from ethanol formed orange needles, m. p. 268° (decomp.).

(ii) Trimethylenebis-(1,1-dimethylhydrazinium) dibromide (7·8 g., 19%) was obtained when trimethylene dibromide (50·5 g., 0·25 mole), 1,1-dimethylhydrazine (15 g., 0·25 mole), and ethanol (500 ml.) were refluxed on the steam-bath for 10 min. After crystallisation from aqueous ethanol, the solid product was identified as the hydrazinium dibromide by m. p. and mixed m. p. determinations.

Concentration of the ethanolic reaction mixture on the steam-bath afforded an oil which was washed several times with ether. The ether washings, after being dried (K_2CO_3), were distilled and trimethylene dibromide (10·5 g.) was recovered. The ether-insoluble oil crystallised from acetone–propan-1-ol at −15°, affording 1,1-*dimethylpyrazolidinium bromide* (13 g., 30%), which recrystallised from propan-1-ol as needles, m. p. 206—207° (decomp.) (Found: C, 33·3; H, 7·4; Br, 44·0; N, 15·4. $C_5H_{13}BrN_2$ requires C, 33·2; H, 7·2; Br, 44·1; N, 15·5%). The *picrate* crystallised from aqueous methanol as orange needles and was identical with the second picrate [m. p. 268° (decomp.)] recorded under (i) (m. p. and mixed m. p.) (Found: C, 40·5; H, 4·6; N, 21·6. $C_{11}H_{15}N_5O_7$ requires C, 40·1; H, 4·6; N, 21·3%).

Evaporation of the acetone–propan-1-ol mother-liquor furnished an oil which crystallised at room temperature in 3 days. Repeated crystallisation from propan-1-ol afforded deliquescent white plates, m. p. 77—80°, of 1,1-dimethylhydrazine hydrobromide (Found: C, 17·1; H, 6·4; Br, 57·0; N, 20·4. Calc. for $C_2H_9BrN_2$: C, 17·0; H, 6·4; Br, 56·5; N, 19·9%), this identification being confirmed by conversion into 1,1-dimethylhydrazine picrate, m. p. and mixed m. p 141—144° (decomp.).

Hydrogenolysis of 1,1-*Dimethylpyrazolidinium Bromide*.—The bromide (2 g.) in water (5 ml.) and acetic acid (15 ml.) containing Adams catalyst (1 g.) was shaken under hydrogen at room temperature and pressure for 2½ hr. (absorption 1 mol.). After filtration, the solution was evaporated to dryness at 100°/20 mm. The residue, twice recrystallised from ethanol, furnished a product, m. p. 153·5—154·5° (Found: C, 23·1; H, 6·2; Br, 60·3; N, 10·2. Calc. for $C_5H_{16}Br_2N_2$: C, 22·8; H, 6·1; Br, 60·5; N, 10·6%), whose infrared spectrum was identical with that of authentic 3-dimethylaminopropylamine dihydrobromide. The *picrate* crystallised from aqueous ethanol as needles, m. p. 218—220° (decomp.) (Found: C, 36·6; H, 3·6; N, 19·8. $C_{17}H_{20}N_8O_{14}$ requires C, 36·4; H, 3·6; N, 20·0%).

Tetra- and Penta-methylenebis-(1,1-*dimethylhydrazinium*) *Dibromide*.—Tetramethylene dibromide (8·64 g., 0·04 mole), 1,1-dimethylhydrazine (4 g., 0·066 mole), and ethanol (20 ml.) were refluxed on the steam-bath for 10 min., then cooled and filtered. The product (10·55 g., 95%

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[14] *Inorg. Synth.*, Vol. I, p. 59.

calc. on 1,1-dimethylhydrazine consumed), on recrystallisation from methanol, gave *tetramethylenebis-*(1,1-*dimethylhydrazinium*) *dibromide*, m. p. 203—205° (decomp.) (Found: C, 28·7; H, 6·6; N, 16·9. $C_8H_{24}Br_2N_4$ requires C, 28·6; H, 7·2; N, 16·7%).

Pentamethylenebis-(1,1-*dimethylhydrazinium*) *dibromide* (14·5 g., 83%) was similarly obtained by refluxing pentamethylene dibromide (11·5 g., 0·05 mole), 1,1-dimethylhydrazine (6 g., 0·1 mole), and ethanol (20 ml.) on the steam-bath for 30 min. Recrystallisation from ethanol afforded needles, m. p. 187—188° (Found: C, 30·8; H, 7·2; Br, 45·0; N, 15·8. $C_9H_{26}Br_2N_4$ requires C, 30·9; H, 7·5; Br, 45·7; N, 16·0%).

Decamethylenebis-(1,1-*dimethylhydrazinium*) *Dibromide*.—Decamethylene dibromide (6·0 g., 0·03 mole), 1,1-dimethylhydrazine (2·4 g., 0·04 mole), and dry ether (20 ml.) were kept at room temperature for 1 week. The deliquescent product was filtered off and dried over phosphorus pentoxide for 3 weeks, finely crushed, and dried again for 1 week. The solid product (5·7 g., 68%), m. p. 110—131°, on repeated recrystallisation from ether–ethanol, gave *decamethylenebis-*(1,1-*dimethylhydrazinium*) *dibromide*, m. p. 136—138° (Found: C, 40·1; H, 8·6; Br, 37·5; N, 13·5. $C_{14}H_{36}Br_2N_4$ requires C, 40·0; H, 8·6; Br, 38·0; N, 13·3%. Schueler and Hanna[15] record m. p. 114—115·5° for a product which did not have the correct analysis.

Reactions with Alkylene Dichlorides.—The alkylene dichloride (0·04 mole), 1,1-dimethylhydrazine (4·8 g., 0·08 mole), and dry ether (40 ml.) were kept at room temperature for 3½ weeks, then the precipitate was filtered off and recrystallised twice from ethanol. Thus were obtained *pentamethylenebis-*(1,1-*dimethylhydrazinium*) *dichloride* (26%) m. p. 223° (decomp.) (Found: C, 41·5; H, 10·0; Cl, 26·5. $C_9H_{26}Cl_2N_4$ requires C, 41·4; H, 10·0; Cl, 27·1%) [corresponding *picrate* (from methanol), m. p. 176·5—178° (Found: C, 39·4; H, 4·3; N, 21·8. $C_{21}H_{30}N_{10}O_{14}$ requires C, 39·3; H, 4·6; N, 22·3%)], and *hexamethylenebis-*(1,1-*dimethylhydrazinium*) *dichloride* (19%), m. p. 223·5—224·5° (Found: C, 43·7; H, 10·0; Cl, 25·6; N, 20·1. $C_{10}H_{28}Cl_2N_4$ requires C, 43·6; H, 10·3; Cl, 25·8; N, 20·4%) [corresponding *picrate* (from ethanol), m. p. 191—192° (Found: C, 40·0; H, 5·0. $C_{22}H_{32}N_{10}O_{14}$ requires C, 40·0; H, 4·9%)].

Reactions with Alkylene Di-iodides.—The alkylene dichloride or dibromide (0·04 mole), sodium iodide (15 g.), and acetone were refluxed on the steam-bath for 3—6 hr., the precipitate of sodium halide was filtered off, and the filtrate evaporated to small bulk on the steam-bath. The residue was taken up in ether, washed with water, dried (Na_2SO_4), and evaporated on the steam-bath. The residual oil was refluxed with 1,1-dimethylhydrazine (4 g., 0·067 mole) and ethanol (25 ml.) for ½ hr., then cooled, and the precipitated polymethylenebis-(1,1-dimethylhydrazinium) di-iodide filtered off.

Thus were prepared *tetramethylenebis-*(1,1-*dimethylhydrazinium*) *di-iodide* (47%) (from methanol), m. p. 176° (decomp.) (Found: C, 22·6; H, 5·7; N, 13·4. $C_8H_{24}I_2N_4$ requires C, 22·6; H, 5·6; N, 12·8%) [corresponding *picrate* (from methanol), m. p. 219—220 (decomp.) (Found: C, 38·1; H, 4·4; N, 21·9. $C_{20}H_{28}N_{10}O_{14}$ requires C, 38·0; H, 4·5; N, 22·1%)], *pentamethylenebis-*(1,1-*dimethylhydrazinium*) *di-iodide* (73%), m. p. 159—171° (decomp.) (Found: C, 24·4; H, 5·5; N, 12·7. $C_9H_{26}I_2N_4$ requires C, 24·3; H, 5·9; N, 12·6%) [corresponding *picrate* (from methanol), m. p. 176·5—178° (Found: C, 39·4; H, 4·3; N, 21·8. $C_{21}H_{30}N_{10}O_{14}$ requires C, 39·0; H, 4·7; N, 21·7%)], and *hexamethylenebis-*(1,1-*dimethylhydrazinium*) *di-iodide* (44%) (from methanol–ethanol), rods, m. p. 175—176° (decomp.) (Found: C, 26·3; H, 5·8; I, 55·2; N, 12·2. $C_{10}H_{28}I_2N_4$ requires C, 26·2; H, 6·2; I, 55·7; N, 12·0%) [corresponding *picrate* (from methanol), m. p. 191—192° (Found: C, 40·1; H, 5·0. $C_{22}H_{32}N_{10}O_{14}$ requires C, 40·0; H, 4·9%)].

Reaction with Methylene Dihalides.—Methylene dichloride (5·3 g., 0·06 mole), 1,1-dimethylhydrazine (7·2 g., 0·12 mole), and ethanol (20 ml.) were refluxed on the steam-bath for 3 hr. and then evaporated at 100°/20 mm. The residual oil (5·3 g.) was dissolved in water, made alkaline with sodium hydroxide (5 g.), and continuously extracted with ether for 5 hr. The aqueous solution was made slightly acid with hydrochloric acid and evaporated to dryness at 100°/20 mm. The residue was extracted with boiling propan-1-ol. The extract, on cooling, deposited a solid (0·2 g.), m. p. >300° (Found: H, 7·6; Cl, 66·5. Calc. for NH_4Cl: H, 7·5; Cl, 66·4%), identified as ammonium chloride by its infrared spectrum. Addition of ethanolic mercuric chloride to a portion of the propan-1-ol solution precipitated a solid, m. p. 209—210·5°, whose infrared spectrum was identical with that of authentic 1,1,1-trimethylhydrazinium trichloromercuriate. After reaction of methylene dibromide (17·4 g., 0·1 mole) and 1,1-dimethylhydrazine (6 g., 0·1 mole) in boiling ethanol (50 ml.) for ¾ hr., only ammonium bromide (0·37 g.) was isolated.

[15] Schueler and Hanna, *J. Amer. Chem. Soc.*, 1952, **74**, 2112.

1,1,1-*Trimethylhydrazinium Trichloromercuriate.*—1,1-Dimethylhydrazine (3 g., 0·05 mole) and methyl iodide reacted violently when mixed in ethanol (20 ml.). 1,1,1-Trimethylhydrazinium iodide was filtered off and, when crystallised from ethanol, had m. p. 231·5—232° (decomp.) [lit., m. p. 235° (decomp.),[16] 258° [3]] (Found: C, 18·1; H, 5·5; I, 62·6; N, 13·5. Calc. for $C_3H_{11}IN_2$: C, 17·8; H, 5·5; I, 62·8; N, 13·9%). The *picrate* crystallised in rods (from ethanol), m. p. 246—248° (decomp.) (Found: C, 35·7; H, 4·0; N, 23·4. $C_9H_{13}N_5O_7$ requires C, 35·7; H, 4·3; N, 23·1%).

1,1,1-Trimethylhydrazinium iodide (0·5 g.), dissolved in water (100 ml.), was passed through Amberlite IRA-400 (OH^-). The eluate was acidified with concentrated hydrochloric acid and evaporated to dryness at 100°/20 mm. The residue, dissolved in methanol, was mixed with mercuric chloride (0·6 g.) in methanol, 1,1,1-*trimethylhydrazinium trichloromercuriate* being obtained as needles, m. p. 209—210·5° (Found: C, 9·9; H, 2·8; N, 7·1. $C_3H_{11}Cl_3HgN_2$ requires C, 9·4; H, 2·9; N, 7·3%).

Infrared Spectra.—The spectra were measured by using a modified Hilger D 209 double-beam spectrometer [17] or a double-beam grating spectrometer.[18] A quartz prism was used in conjunction with the Hilger spectrometer for measurements in the 3 μ region and a sodium chloride prism for measurements in the 6 μ region. Solid compounds were examined in pressed potassium chloride discs; 1,1-dimethylhydrazine was examined as a thin capillary film prepared in a dry-box.

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[16] Harries and Haga, *Ber.*, 1898, **31**, 58.
[17] Hales, *J. Sci. Instr.*, 1949, **26**, 359; 1953, **30**, 52.
[18] Hales, *J. Sci. Instr.*, 1959, **36**, 264.