765. *Polymers Based on Hydrazine. Part II.* Reaction of Hydrazine Hydrate with Ethylene Dihalides.*

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Ethylene dihalides react with hydrazine hydrate to give ethylenedihydrazine, 1,4-diaminopiperazine, and poly(ethylenehydrazine). The yield of polymer is increased if the reaction is carried out in the presence of a hindered base, *e.g.*, ethyldi-isopropylamine. Ethylenedihydrazine only is produced from ethylene dichloride with a large excess of hydrazine hydrate. The structure of the polymer has not been determined. Failure to obtain ethylenediamine as a product of hydrogenolysis of the polymer suggests that the group $\cdot NH\cdot NH\cdot CH_2\cdot CH_2\cdot$ cannot be a recurring unit in the chain; nor is the polymer made up entirely of $\cdot N(NH_2)\cdot CH_2\cdot CH_2\cdot$ units.

Moncrieff[1] claimed without details that ethylene dichloride and hydrazine hydrate give cross-linked polymers. This contrasts with a statement in a patent[2] that alkylene dichlorides react with a 6—24 mol. proportion of hydrazine to yield alkylenedihydrazines $H_2N\cdot NH\cdot [CH_2]_n\cdot NH\cdot NH_2$, but with a smaller proportion of hydrazine to yield a polyhydrazine $H\cdot [NH\cdot NH\cdot (CH_2)_n]_x\cdot NH\cdot NH_2$ ($x > 1$; $n = 1$—8 in both formulæ).

Since we were interested in preparing polymers containing the hydrazine residue, this reaction was reinvestigated. In boiling ethanol, equimolecular quantities of hydrazine hydrate and ethylene dichloride reacted rapidly, about half the hydrazine being converted into the monohydrochloride; ethylenedihydrazine and 1,4-diaminopiperazine were isolated as their condensation products with benzaldehyde. The major product, however, was a polymeric hydrazine which was also isolated as its condensation product with benzaldehyde. When the reaction was carried out in the presence of one mol. of ethyldi-isopropylamine (which reacted with the hydrogen chloride liberated in the reaction but did not quaternise with the ethylene dichloride for steric reasons[3]), the yield of polymer increased. However it was confirmed that ethylenedihydrazine was the only product from ethylene dichloride and a 24-molar excess of hydrazine hydrate.

The benzaldehyde derivative of poly(ethylenehydrazine) contained a small amount of chlorine, probably present in 2-chloroethyl end groups. The infrared spectrum showed the presence of secondary amine groups. Hydrochloric acid brought about hydrolysis to benzaldehyde and poly(ethylenehydrazine) hydrochloride, the latter substance appearing from its analysis to contain oxygen. On hydrogenolysis, ammonia was formed, presumably by cleavage of $N\cdot NH_2$ groups though the uptake of hydrogen was greater than that calculated from the amount of ammonia formed. The reduction of 2-chloroethyl end groups and fission of other N–N linkages, of a different type, probably accounts for this discrepancy. If these other N–N linkages formed part of the polymer chain, then the polymer would thereby be degraded—the polymer had in fact suffered a considerable

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* Part I, *J.*, 1963, 3523.

[1] Moncrieff, *Manuf. Chem.*, 1947, **18**, 177.

[2] Uraneck and Goertz, U.S.P. 2,822,354/1958.

[3] Hünig and Kiessel, *Chem. Ber.*, 1958, **91**, 380.

reduction in molecular weight (to $\ngtr 800$). The existence in the polymer of hydrazine linkages other than $\cdot N(NH_2)\cdot$ was confirmed by condensation of the polyethylenehydrazine hydrochloride with thiophen-2-aldehyde. If all the hydrazine linkages were of the form $\cdot N(NH_2)\cdot$ and each of these condensed with the aldehyde, the resulting derivative would contain nitrogen and sulphur in the ratio 2 : 1; the ratio found was 3·2 : 1. This suggests the occurrence of NH–NH linkages (or other N·N groups) which do not condense with aldehydes. [The complicating possibility of branching along the polymer chain (as in polyethyleneimine) with the existence of units such as $\cdot CH_2\cdot CH_2\cdot N(CH_2\cdot CH_2\cdot NH\cdot NH_2)\cdot NH\cdot$ cannot be ruled out.] If no chain branching is assumed a polymer containing 5 $\cdot N(NH_2)\cdot$ groups for every 3 $\cdot NH\cdot NH\cdot$ groups would afford a thiophen-2-aldehyde derivative with this N : S ratio, if we assume complete reaction. However, this conclusion does not accord with the results of hydrogenolysis.

Polyethylenehydrazine generated from the hydrochloride was a viscous reducing oil, rapidly oxidising in air. On hydrogenolysis, it evolved ammonia and again there was a discrepancy between the amount of hydrogen absorbed and the amount of hydrogen required to produce the quantity of ammonia obtained.

Poly(ethylenehydrazine) could be cross-linked (and an insoluble polymer obtained) by condensation with dialdehydes such as pyridine-2,6-dialdehyde. Condensation with decamethylene dibromide afforded an ethanol-soluble product containing ionic bromine. The dibromide had probably reacted with single chains of the poly(ethylenehydrazine) producing small closed loops in preference to cross-linking different chains.[4]

The reaction with hydrazine of ethylene dibromide, alone or in the presence of ethyldiisopropylamine, was essentially similar to that of ethylene dichloride. Hydrogenolysis, however, suggested that the poly(ethylenehydrazine) produced contained a smaller proportion of $\cdot N(NH_2)\cdot$ groups than were in the polymer obtained from ethylene dichloride.

In an attempt to discover whether ethylenedihydrazine and 1,4-diaminopiperazine were intermediates in the formation of poly(ethylenehydrazine), these two substances were separately condensed with ethylene dibromide. Ethylenedihydrazine was converted into 1,4-diaminopiperazine and poly(ethylenehydrazine), but 1,4-diaminopiperazine produced a crystalline product which on hydrogenolysis yielded ammonia. Condensation had thus been effected on the tertiary amino-groups of 1,4-diaminopiperazine but the crystalline product was not 1,4-diamino-1,4-diazoniabicyclo[2,2,2]octane dibromide (VIII; $R = NH_2$, $X = Br$) since its infrared spectrum differed from that of the dichloride (VIII; $R = NH_2$, $X = Cl$), which, together with 1-amino-1,4-diazoniabicyclo[2,2,2]octane chloride hydrochloride (VIII; $R = H$, $X = Cl$), was synthesised by quaternation of triethylenediamine with chloramine (cf. Sisler, Ahuja, and Smith [5] and Rudner [6]). A possible structure for the condensation product from ethylene dibromide and the diaminopiperazine is (IX) [the polymeric structure (X) is considered unlikely because of the highly crystalline nature of the material].

Some alternative methods for the synthesis of 1,4-diaminopiperazine were explored. In one approach, piperazine was coupled with diazotised 2,5-dichloroaniline,[7] and the resultant 1,4-bis-(2,5-dichlorophenylazo)piperazine was reduced. However, fission of the N–N linkage occurred in preference to that of the N=N linkage, and the product proved to be 2,5-dichlorophenylhydrazine rather than the desired 1,4-diaminopiperazine. The synthesis was successfully accomplished by nitrosating piperazine and reducing the dinitroso-derivative with zinc and acetic acid (reduction by sodium and alcohol or catalytically proved inferior, the latter causing hydrogenolysis of 1,4-diaminopiperazine to ammonia and piperazine).

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[4] Shepherd and Kitchener, *J.*, 1957, 86.

[5] Sisler, Ahuya, and Smith, *J. Org. Chem.*, 1961, **26**, 1819.

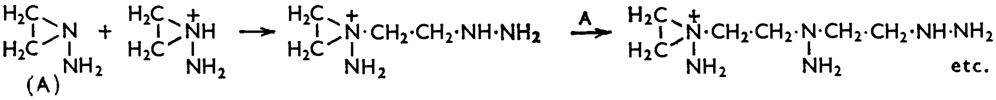
[6] Rudner, U.S.P. 2,973,361.

[7] Drumm, O'Connor, and Reilly, *Sci. Proc. R. Dublin Soc.*, 1940, **22**, 223.

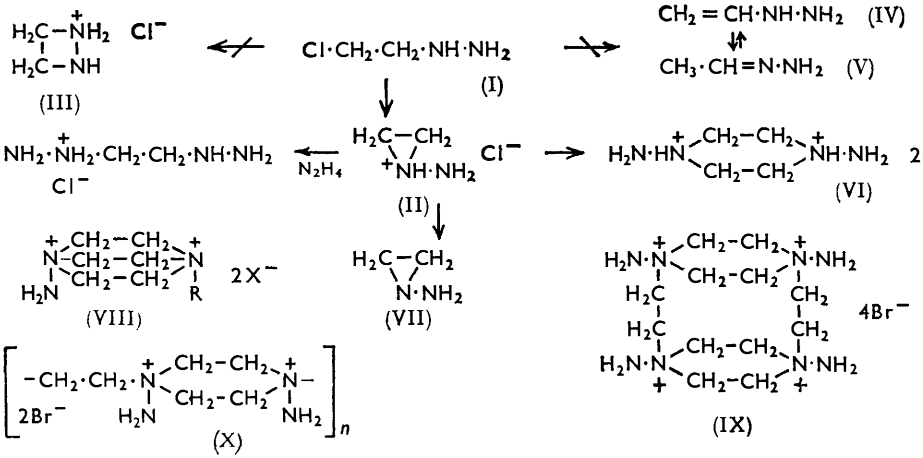
The following mechanism is suggested for the reaction of hydrazine with ethylene dihalides (the dichloride is used for illustration). Initially nucleophilic displacement of one of the halogen atoms occurs:

$$(CH_2Cl)_2 + N_2H_4 \longrightarrow Cl\cdot CH_2\cdot CH_2\cdot{}^{+}NH_2\cdot NH_2\ Cl^-$$

The 2-chloroethyl group reduces the basicity of the hydrazine. Consequently, unchanged hydrazine or ethyldi-isopropylamine (if present) displaces 2-chlorethylhydrazine from its hydrochloride. This undergoes an internal nucleophilic displacement, affording *N*-aminoethylenimine hydrochloride (II) in preference to the four-membered ring structure (III).[8] Elimination of hydrogen chloride and formation of vinylhydrazine (IV) is also unlikely; this product is tautomeric with acetaldehyde hydrazone (V) and no acetaldehyde, produced by hydrolysis, was detected experimentally during working-up of the various reaction mixtures. Three reactions of product (II) appear probable: (*a*) ring opening with hydrazine to form ethylenedihydrazine hydrochloride (this would predominate if a large excess of hydrazine were present); (*b*) reaction [9] with 2-chloroethylhydrazine (I) to yield 1,4-diaminopiperazine dihydrochloride (VI); and (*c*) liberation of *N*-aminoethyleneimine and chain-condensation between the free base (VII) and its ion and subsequent substituted ions, leading to poly(ethylenehydrazine).[10] However, it is clear from what has been said earlier that the polymer chain is not exclusively made up of $\cdot N(NH_2)\cdot CH_2\cdot CH_2\cdot$ units.



Further, since we were unable to isolate ethylenediamine after hydrogenolysis of the polymer it seems unlikely that the grouping $\cdot NH\cdot NH\cdot CH_2\cdot CH_2\cdot$ is a repeating unit in the chain. It is possible, however, that units such as $\cdot\underset{\displaystyle CH_2\cdot CH_2\cdot NH\cdot NH_2}{\underset{|}{N}}\cdot NH\cdot CH_2\cdot CH_2\cdot$ occur together with $\cdot N(NH_2)\cdot CH_2\cdot CH_2\cdot$ units. A further complication probably arises from the use of ethanol as the reaction medium. Indeed, there is some evidence in the infrared spectra of the polymers of the existence of ether linkages, probably arising from ethoxy-groups.



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[8] King, *J.*, 1949, 1318.

[9] Fruton in Elderfield's "Heterocyclic Compounds," Chapman and Hall, London, 1950, Vol. I, p. 69.

[10] Jones, Langsjoen, Neumann, and Zomlefer, *J. Org. Chem.*, 1944, **9**, 125.

EXPERIMENTAL

Melting points are corrected.

Reaction of Ethylene Dichloride with Hydrazine.—The reaction was followed by titrating unused hydrazine with hydrochloric acid to Methyl Red.[11] When ethanolic ethylene dichloride (9·9 g. in 50 ml.) and hydrazine hydrate (5 g.) were refluxed on the steam-bath, the reaction occurred to the extent of 11% complete in ½ hr., 77% in 7½ hr., and 92% in 21½ hr.

Ethylene dichloride (99 g.) and 100% hydrazine hydrate (50 g.) in ethanol (500 ml.) were refluxed for 24 hr. No vinyl chloride was evolved. The bulk of the solvent was removed by distillation and the distillate diluted with water (1600 ml.) and extracted twice with ether. The extracts were dried (Na_2SO_4) and distilled, yielding ethylene dichloride (44 g.), b. p. 82—85°. The involatile portion of the original mixture partially crystallised on cooling. The deliquescent crystals, m. p. $<100°$, were identified as hydrazine hydrochloride by conversion into hydrazine dihydrochloride, m. p. and mixed m. p. 196—199° (decomp.).

The reaction mixture was refluxed with concentrated hydrochloric acid (100 ml.) and water (500 ml.) for 10 min., and the evolved gases were passed through an acetic acid–sulphuric acid solution of 2,4-dinitrophenylhydrazine. No acetaldehyde 2,4-dinitrophenylhydrazone was isolated. The aqueous mixture was evaporated to crystallisation at 100°/20 mm., acidified with concentrated hydrochloric acid (100 ml.), and set aside overnight. On filtration, hydrazine dihydrochloride (52·3 g.), m. p. 196—199° (decomp.), was obtained. The filtrate was evaporated to dryness at 100°/20 mm., and the residue (50 g.) was dissolved in water (250 ml.) containing sodium hydroxide (20 g.) and shaken with acetic acid (20 ml.) and benzaldehyde (49 g.) for 15 min. The mixture was extracted with chloroform, and the chloroform extract was dried (Na_2SO_4) and evaporated on the steam-bath. The residue was extracted twice with hot light petroleum (b. p. 60—80°) and hot ethanol. Insoluble benzaldehyde poly(ethylenehydrazone) (31·3 g.) remained (Found: C, 71·9; H, 8·0; Cl, 2·4; Cl^-, 1·3; N, 16·2%). The infrared spectrum of a thin film exhibited a medium band at 3220 $cm.^{-1}$ (tentatively assigned to the N–H stretching vibration of $>$N·NH groups), and strong bands at 3058 and 3028 (aromatic CH), 2957 and 2856 (CH_2 stretching), 1672 (C=N), 1445 (CH_2 deformation), and 755 and 694 $cm.^{-1}$ (monosubstituted benzene). In addition, a strong band appeared at 1137 $cm.^{-1}$, suggesting the existence of a C–O–C linkage. An upper limit of 3600 for the number average molecular wight ($\overline{M}_n$) of the polymer was obtained from osmometric measurements with a cellulose acetate membrane, in fair agreement with the value 3230 obtained by assuming that the organic chlorine in the polymer was in an end group.

Evaporation of the combined ethanol and light-petroleum extracts obtained in the isolation of the polymer furnished a solid (24 g.) which was extracted twice with hot methanol. The methanol-insoluble portion (9 g.), after two crystallisations from chloroform, furnished 1,4-dibenzylideneaminopiperazine, m. p. 212—213·5° (lit.,[12] 205°) (Found: C, 73·9; H, 6·7; N, 18·9. Calc. for $C_{18}H_{20}N_4$: C, 73·9; H, 6·9; N, 19·2%). Evaporation of the methanolic extracts furnished a solid, which on repeated crystallisation from methanol, afforded 1,3-dibenzylideneamino-2-phenylimidazolidine, m. p. 137·5—138° (decomp.) [lit.,[11] m. p. 130—132° (decomp.)] (Found: C, 77·9; H, 6·1; N, 16·3. Calc. for $C_{23}H_{22}N_4$: C, 77·9; H, 6·3; N, 15·8%).

Reaction of Ethylene Dichloride with an Excess of Hydrazine.—Ethylene dichloride (19·8 g.), 100% hydrazine hydrate (240 g.), and ethanol (100 ml.) were refluxed for 8 hr. on the steam-bath in an apparatus arranged for gas collection. No vinyl chloride was evolved. The mixture was poured into water (800 ml.) and concentrated hydrochloric acid (1000 ml.) and cooled to 0° and the hydrazine dihydrochloride was filtered off. The filtrate was concentrated at 100°/20 mm. to crystallisation, cooled, and filtered. The process of concentration, cooling, and filtration was continued until the filtrate did not give a precipitate on addition of concentrated hydrochloric acid. This final filtrate was evaporated to dryness at 100°/20 mm. and the residue, on crystallisation from aqueous methanol, afforded ethylenedihydrazine dihydrochloride (11·9 g.), m. p. 167° (decomp.) (lit.,[13] 159°) (Found: C, 14·8; H, 7·2. Calc. for $C_2H_{12}Cl_2N_4$: C, 14·7; H, 7·4%). The aqueous-methanolic mother-liquor, on treatment with benzaldehyde and

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[11] Audrieth and Ogg, "The Chemistry of Hydrazine," Chapman and Hall, Ltd., London, 1951, p. 157.

[12] Schmidt and Wichman, *Ber.*, 1891, **24**, 3245.

[13] Daeniker and Druey, *Helv. Chim. Acta*, 1957, **40**, 919.

sodium acetate, afforded a trace of 1,4-dibenzylideneaminopiperazine and 1,4-dibenzylideneamino-2-phenylimidazolidine (12·0 g.), giving a total yield of ethylenedihydrazine derivatives of 53%.

No reaction was observed between ethylene dichloride and hydrazine monohydrochloride in boiling methanol in 29½ hr., or between ethylene dichloride and hydrazine hydrate in the presence of acetic acid and potassium acetate.

Reaction of Ethylene Dichloride with Hydrazine Hydrate in the Presence of a Proton-acceptor.—Ethyldi-isopropylamine [3] was used in preference to anhydrous sodium carbonate or an anion-exchange resin (Deacidite H) in order to avoid a heterogeneous reaction mixture.

An ethanolic solution (100 ml.) containing ethylene dichloride (19·8 g.), 100% hydrazine hydrate (10 g.), and ethyldi-isopropylamine (25·8 g.) was refluxed for 24 hr. No vinyl chloride was evolved. The mixture was decomposed with 10% aqueous sodium hydroxide (200 ml.), and the upper layer of ethyldi-isopropylamine (23 g.) was removed. After extraction with ether, the aqueous mixture was shaken with benzaldehyde (20 g.) and acetic acid (30 ml.) for 15 min., then extracted with chloroform, and the chloroform extract was washed with aqueous sodium hydroxide, dried (Na_2SO_4), and evaporated at 100°/20 mm. Recrystallisation of the solid residue from methanol–chloroform afforded a mixture (1·7 g.) of 1,4-dibenzylideneaminopiperazine and 1,3-dibenzylideneamino-2-phenylimidazolidine. A further 1·1 g. of this mixture was obtained by evaporation of the mother-liquor and crystallisation of the residue from chloroform–light petroleum (b. p. 60—80°). Evaporation of the final mother-liquor afforded a red oil which was separated by extraction with boiling light petroleum (b. p. 60—80°) into benzaldehyde azine (7·8 g.) (soluble) and benzaldehyde poly(ethylenehydrazone) (10·6 g.). The infrared spectrum of a thin film of this polymer was substantially the same as that of the specimen prepared earlier. Osmometric measurements placed an upper limit of 2400 on the value of $[\bar{M}_n]$.

Poly(ethylenehydrazine) Hydrochloride.—Benzaldehyde poly(ethylenehydrazone) (40·4 g.) was heated slowly with concentrated hydrochloric acid (60 ml.) and water (200 ml.), until no more benzaldehyde distilled (1 hr.). The mixture was filtered and evaporation of the filtrate at 100°/20 mm. furnished a red viscous liquid (18·1 g.) (Found: C, 30·0; H, 7·7; Cl, 34·1; Cl^-, 33·8; N, 21·2%; Cl^-: N, 0·63). The infrared spectrum of the polymeric hydrochloride had intense absorption between 3240 and 2520 cm.$^{-1}$, with medium-strong bands at 2067 and 1950 cm.$^{-1}$. Very similar bands occur in the spectrum of hydrazine dihydrochloride (at 3000—2400, 2067, and 1940 cm.$^{-1}$). An intense band at 1594 cm.$^{-1}$ was assigned to the N–H deformation vibration of the NH_3^+ group.[14]

Reactions of the hydrochloride. (i) Poly(ethylenehydrazine) hydrochloride (0·3 g.) in aqueous solution (30 ml.) was shaken with glacial acetic acid (5 ml.) and thiophen-2-aldehyde (0·6 g.) for 15 min., then extracted twice with ether and once with chloroform. Evaporation of the dried (Na_2SO_4) chloroform extract furnished a brown residue (Found: N, 17·7; S, 12·84%; N : S = 3·2 : 1).

(ii) The hydrochloride (1·7956 g.) in water (5 ml.) and glacial acetic acid (15 ml.) was shaken with hydrogen and Adams catalyst (0·98 g.) (absorption 334 ml. at N.T.P.). A control experiment showed that 0·98 g. of the catalyst absorbed 161 ml., hence that the hydrochloride had absorbed 173 ml. The reaction mixture was filtered, treated with N-sodium hydroxide (230 ml.), and distilled. The distillate was absorbed in concentrated hydrobromic acid (5 ml.) and water (10 ml.) and evaporated to dryness. The residue (1·0994 g.) contained ammonium bromide (0·581 g.) estimated by the sodium cobaltinitrite method.[15] This quantity of ammonium bromide would be produced by the absorption of 132·8 ml. (N.T.P.) of hydrogen. Consequently 40 ml. were used in the reduction of CH_2Cl end groups and the splitting of other N–N linkages.

The alkaline reaction mixture was acidified with concentrated hydrochloric acid, filtered, and evaporated at 100°/20 mm. The residue was dissolved in the minimum quantity of water and reacidified with concentrated hydrochloric acid. This solution was cooled to −10°, filtered, and evaporated at 100°/20 mm., furnishing a residue, from which ethanol extracted an oil (Found: C, 36·6; H, 7·5; N, 15·3; Cl, 31·0%), whose infrared spectrum had a broad intense band between 3000 and 2450 cm.$^{-1}$ (NH stretching of NH_2^+) and a band at 1594 cm.$^{-1}$ (N–H deformation vibration of NH_2^+). Comparison with the spectrum of authentic ethylenediamine

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[14] Snyder and Decius, *Spectrochim. Acta*, 1959, **13**, 280.

[15] Gove, Baum, and Stanley, *Analyt. Chem.*, 1951, **23**, 721.

dihydrobromide showed that it was unlikely that a salt of ethylenediamine was present in the mixture.

The oil (0·5 g.) in water (100 ml.) was passed through resin IRA-400 (OH^-) and then evaporated at 100°/20 mm. The residual brown oil dissolved in ethanol and did not develop pressure in an osmometer fitted with a cellulose acetate membrane which was impermeable to substances of molecular weights greater than 800.

Cross-linking experiments. (i) Poly(ethylenehydrazine) hydrochloride (4·7 g.) in water (26 ml.) and ethanol (100 ml.) containing sodium hydroxide (2 g.) was refluxed for 15 min. with pyridine-2,6-dialdehyde (1·7 g.) in ethanol (100 ml.), acidified with a few drops of glacial acetic acid. The precipitate was filtered off, washed with ethanol and water, and air-dried (Found: C, 59·0; H, 6·0; N, 26·0%).

(ii) The hydrochloride (4·7 g.) in water (26 ml.) containing sodium hydroxide (2 g.) was refluxed with decamethylene dibromide (7·5 g.) in ethanol (175 ml.) on the steam-bath for 2 hr. Ethanol was removed by distillation and the residue extracted with ether (3 × 50 ml.). Evaporation of the dried (Na_2SO_4) extract furnished decamethylene dibromide (4·4 g.). The ether-insoluble portion was an oil which was insoluble in water but soluble in methanol or ethanol and after several days over phosphorus pentoxide set to a hard red resin (Found: C, 55·2; H, 9·1; N, 11·1; Cl, 2·8; Br, 19·4; Br^-, 19·4%).

Poly(ethylenehydrazine).—Poly(ethylenehydrazine) hydrochloride (5 g.) in water (300 ml.) was passed through resin IRA-400 (OH^-) and evaporated to dryness at 100°/20 mm. The residual oil had $\bar{M}_n$ 2900 (Found: C, 53·1; H, 9·2; N, 31·8; Cl, 0·4%) and reduced Fehling's and ammoniacal silver nitrate solutions.

Poly(ethylenehydrazine) (0·608 g.), Adams catalyst (0·6 g.), water (1 ml.), and acetic acid (17 ml.) were shaken with hydrogen for 6 hr. 209 ml. of hydrogen (N.T.P.) were absorbed, of which 113 ml. had been absorbed by the polymer. The mixture was filtered, treated with 2·5N-sodium hydroxide (220 ml.), and distilled. The distillate was collected in concentrated hydrobromic acid (3 ml.) and this was then evaporated to dryness. Infrared analysis revealed that the residue (0·4315 g.) was substantially ammonium bromide. This quantity of ammonium bromide accounted for 98·6 ml. of the hydrogen absorbed, so that 14·4 ml. of hydrogen were used up in the reduction of $CH_2{\cdot}CH_2Cl$ end groups and fission of other N–N linkages.

Reaction of Ethylene Dibromide with Hydrazine Hydrate.—When an ethanolic solution (20 ml.) of ethylene dibromide (7·6 g.) and 100% hydrazine hydrate (2 g.) was refluxed on the steam-bath, titration as above showed 82% of reaction in ½ hr. and 92% in 2 hr.

Ethylene dibromide (15·1 g.) was caused to react with 100% hydrazine hydrate (4 g.) in refluxing ethanol (40 ml.) for 1 hr. Dilution with water and extraction with ether led to the recovery of ethylene dibromide (4·9 g.). The pH of the aqueous solution was adjusted to 3 by means of sodium acetate–acetic acid and the mixture was shaken with benzaldehyde (10·4 g.) for ¾ hr. Dibenzaldehyde azine (9·0 g.) was filtered off. The filtrate was treated with fresh benzaldehyde (7 g.), and the precipitate (6·4 g.) shown to be a mixture of 1,3-dibenzylideneamino-2-phenylimidazolidine, 1,4-dibenzylideneaminopiperazine, and benzaldehyde poly(ethylenehydrazone) by methods described above.

The experiment was repeated in the presence of ethyldi-isopropylamine (10·3 g.). No vinyl bromide was evolved and after 1 hr. the mixture was decomposed with concentrated hydrochloric acid (10 ml.) and water (90 ml.). Ether-extraction of the solution led to the recovery of ethylene dibromide (0·75 g.). After concentration at 100°/20 mm., the residual aqueous solution was made alkaline with sodium hydroxide (10 g.) in water (50 ml.) and twice extracted with ether. Evaporation of these dried (Na_2CO_3) ether extracts afforded ethyldi-isopropylamine (8·3 g.). The aqueous mixture was then shaken with benzaldehyde (8·5 g.) in the presence of acetic acid and extracted with chloroform. The dried chloroform (Na_2SO_4) extract furnished a semi-solid residue (13 g.) on evaporation. Hot light petroleum (b. p. 60—80°) removed dibenzaldehyde azine (5 g.). Addition of hot methanol caused 1,4-dibenzylideneaminopiperazine (0·3 g.) to be precipitated. Evaporation of the methanolic mother-liquor afforded benzaldehyde poly(ethylenehydrazone) (8 g., 70%).

This benzaldehyde poly(ethylenehydrazone) (8 g.) was heated with concentrated hydrochloric acid (20 ml.) and water (120 ml.) until no more benzaldehyde distilled (1 hr.). The acid mixture was filtered and evaporated to dryness at 100°/20 mm., affording poly(ethylenehydrazine) hydrochloride (4 g.) as a deliquescent rubbery mass whose infrared spectrum closely resembled that of the specimen prepared earlier.

The polymeric hydrochloride (4 g.) in water (400 ml.) was passed through resin IRA-400 (OH^-) form, and the eluate, collected under nitrogen, was evaporated at 100°/20 mm., furnishing poly(ethylenehydrazine) as a dark viscous oil (1·1 g.) with $\bar{M}_n$ 1735. The infrared spectrum of a thin capillary film exhibited an intense band at 3277 $cm.^{-1}$ with a shoulder at 3160 $cm.^{-1}$ (N–H stretching vibration of NH_2 groups), a pair of strong bands at 2938 and 2819 $cm.^{-1}$ (CH_2 stretching), a broad intense band at 1594 $cm.^{-1}$ (NH deformation vibration of NH_2), and a sharp intense peak at 1451 $cm.^{-1}$ (CH_2 deformation).

This poly(ethylenehydrazine) (0·5176 g.) ($\bar{M}_n$ 2280), prepared in a second experiment with ethylene dibromide, was shaken with Adams catalyst (1·0013 g.), water (5 ml.), and acetic acid (15 ml.) under hydrogen at room temperature and pressure for 5½ hr. [86·5 ml. (N.T.P.) absorbed by the polymer]. The mixture was filtered and then distilled with 2N-sodium hydroxide, and the distillate was collected in dilute hydrochloric acid. Evaporation of the distillate furnished ammonium chloride (0·1094 g.) (identified by its infrared spectrum), which accounted for 45·8 ml. of hydrogen. Consequently 40·7 ml. of hydrogen must have been used for reduction of $CH_2{\cdot}CH_2Br$ end groups and other N–N linkages.

Reaction of Ethylene Dibromide with Ethylenedihydrazine.—Ethylenedihydrazine was prepared by neutralising its dihydrochloride (10 g.), in a small quantity of water with sodium hydroxide (4·9 g.) in water (7 ml.) and ethanol (150 ml.), and filtering the mixture. The filtrate, mixed with ethylene dibromide (11·5 g.) and diluted to 250 ml. with ethanol, was refluxed on the steam-bath for 18 hr. Most of the ethanol was removed by distillation. The residue was diluted with water and shaken with benzaldehyde (13 g.) in the presence of acetic acid (7 ml.). The precipitate, on fractional crystallisation from chloroform–methanol, furnished 1,3-dibenzylideneamino-2-phenylimidazolidine (1·1 g.), 1,4-dibenzylideneaminopiperazine (2·6 g.) and benzaldehyde poly(ethylenehydrazone) (2·8 g.; $\bar{M}_n$ ~1600). The infrared spectrum of the polymer, in Nujol mull, was very similar to that of earlier specimens. A C=N band was observed at 1664 $cm.^{-1}$, and the two intense bands characteristic of a monosubstituted benzene appeared at 756 and 694 $cm.^{-1}$, respectively.

1,4-*Diaminopiperazine.* (*a*) Piperazine hexahydrate (34·2 g.) in water (65 ml.) and concentrated hydrochloric acid (80 ml.) was added in 2 hr. to an ice-cold, stirred solution of sodium nitrite (56 g.) in water (112 ml.). The dinitroso-compound (23·4 g., 92%) was filtered off and air-dried. After two crystallisations from water, it had m. p. 158·5—159·5° (lit.,[16] m. p. 158°) (Found: C, 33·5; H, 6·1; N, 38·8. Calc. for $C_4H_8N_4O_2$: C, 33·3; H, 5·6; N, 38·9%).

Sodium sulphite,[17] sodium dithionite,[18] and hydrazine [19] failed to reduce dinitrosopiperazine.

1,4-Dinitrosopiperazine (4·8 g.), ethanol (100 ml.), and Adams catalyst (1 g.) were shaken with hydrogen at room temperature and pressure for 1½ hr. The mixture, smelling strongly of ammonia, was filtered and the filtrate evaporated. The residue was shaken in ethanol (15 ml.) with benzaldehyde (3 ml.) and acetic acid (2 ml.). The white precipitate was filtered off and recrystallised from water–ethanol–acetic acid as needles m. p. 217—219° (decomp.), identified as piperazine diacetate by comparison of its infrared spectrum with that of an authentic specimen (Found: N, 13·4. Calc. for $C_8H_{18}N_2O_4$: N, 13·6%).

Sodium (9·2 g.) was added in 1 hr., in small quantities, to the dinitroso-compound (4·8 g.) in ethanol (150 ml.). The mixture was acidified with aqueous hydrochloric acid and the alcohol removed by distillation. The solution was shaken with sodium acetate and benzaldehyde and 1,4-dibenzylideneaminopiperazine (1·8 g., 22%) was filtered off.

A slurry of dinitroso-compound (21·8 g.) with glacial acetic acid (82 ml.) was added in portions during 1¼ hr. to a stirred ice-cold mixture of zinc dust (78 g.) and water (102 ml.). After a further ½ hr., the mixture was filtered and shaken with acetic acid (10 ml.) and distilled benzaldehyde (32 ml.) for 15 min. On filtration, 1,4-dibenzylideneaminopiperazine (36·9 g., 84%) was obtained.

Steam was passed into a suspension of the dibenzylidene derivative (27·3 g.) in water (400 ml.) and concentrated hydrochloric acid (200 ml.) until no more benzaldehyde distilled (½ hr.). The acid solution was filtered and evaporated at 100°/20 mm. The residue (15·1 g.), dissolved in the minimum quantity of water, was titrated with concentrated aqueous sodium hydroxide to phenolphthalein and evaporated to dryness at 100°/20 mm. The residue was

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[16] Ladenburg, *Ber.*, 1891, **24**, 2400.

[17] Lauer, Sprung, and Langkammerer, *J. Amer. Chem. Soc.*, 1936, **58**, 225.

[18] *Org. Synth.*, Vol. I, p. 69.

[19] Rothenburg, *Ber.*, 1893, **26**, 2060.

extracted with ethanol; the ethanolic extract, when kept at 0° for 3 days, deposited 1,4-*diaminopiperazine dihydrate* (7·5 g., 81%), m. p. 75—84° raised to 77—81° on recrystallisation from propan-1-ol (Found: C, 31·8; H, 9·9; N, 36·8. $C_4H_{16}N_4O_2$ requires C, 31·6; H, 10·6; N, 36·8%). Drying over calcium chloride afforded the anhydrous material, m. p. 117—119° (Found: C, 41·1; H, 10·4. Calc. for $C_4H_{12}N_4$: C, 41·3; H, 10·4%).

Alternatively, 2,5-dichloroaniline (16 g.) was diazotised according to the procedure of Noelting and Kopp,[20] and the diazo-solution, after filtration, was poured rapidly into an ice-cold solution of hydrated sodium acetate (300 g.) and piperazine (17·2 g.) in water (500 ml.). The precipitate was filtered off, air-dried, and extracted with hot ethanol. The ethanolic extract deposited 1,4-bis-(2,5-dichlorophenylazo)piperazine (4·3 g., 20%), m. p. 142—148° (decomp.) (lit.,[7] 146°). Zinc dust (8 g.) was added in 20 min., with swirling, to a suspension of the azo-compound (4·3 g.) in alcohol (160 ml.) and acetic acid (40 ml.). After 1½ hr., the mixture was heated under reflux at 80° for 1½ hr., then filtered, made alkaline with sodium hydroxide (30 g.) in water (500 ml.), and steam-distilled for 2 hr. The distillate was acidified with concentrated hydrochloric acid and evaporated at 100°/20 mm. The residue (1·2 g.) in hot ethanol and 20% aqueous sodium acetate (8 ml.) was shaken with benzaldehyde (1 g.) and cooled, furnishing plates of *benzaldehyde* 2,5-*dichlorophenylhydrazone*, m. p. 93—95·5° (Found: C, 59·1; H, 4·0; Cl, 26·4; N, 10·8. $C_{13}H_{10}Cl_2N_2$ requires C, 58·9; H, 3·8; Cl, 26·8; N, 10·6%).

Reaction of Ethylene Dibromide with 1,4-*Diaminopiperazine*.—Ethylene dibromide (9·1 g.), 1,4-diaminopiperazine (6·0 g.), and ethanol (200 ml.) were refluxed on the steam-bath. Colourless needles (0·3 g.) separated after 1¼ hr. and were filtered off. More needles (1·23 g.) were obtained by refluxing the filtrate for 16 hr. A third crop (0·7 g.) was obtained after 8 hours' refluxing. The three crops had identical infrared spectra and crystallised from aqueous ethanol as needles, decomp. 160—180° (Found: C, 23·9; H, 5·6; Br, 52·3; Br^-, 53·4. $[C_6H_{16}Br_2N_4]_n$ requires C, 23·7; H, 5·3; Br, 52·6; Br^-, 52·6; N, 18·4%). The infrared spectrum, measured in a potassium chloride disc, exhibited intense peaks at 3172 and 3066 cm.$^{-1}$ (NH stretching) and a medium-intense peak at 1635 cm.$^{-1}$ (NH deformation), characteristic of the trialkylhydrazinium groups.[21]

This polymer (0·15 g.) in water (5 ml.) and acetic acid (6 ml.) were shaken with Adams catalyst (0·15 g.) and hydrogen at room temperature and pressure for 5 hr. The mixture was filtered, made alkaline with sodium hydroxide (5 g.) in water (200 ml.), and steam-distilled. The alkaline distillate was acidified with concentrated hydrobromic acid and evaporated at 100°/20 mm. The residue, after crystallisation from ethanol, was identified as ammonium bromide by its infrared spectrum. The aqueous reaction mixture was acidified with concentrated hydrobromic acid and evaporated at 100°/20 mm. The residue, dissolved in the minimum of hot water, was acidified strongly with concentrated hydrobromic acid, kept at $-15°$ for 12 hr., and filtered. The filtrate was evaporated at 100°/20 mm. and the residue was extracted with methanol. The infrared spectrum of the methanol-insoluble portion was different from that of triethylenediamine dihydrobromide but the appearance of six absorption peaks between 2790 and 2470 cm.$^{-1}$ indicated the presence of a protonated tertiary amino-group.

Reaction of Triethylenediamine with Chloramine.—A solution of triethylenediamine in aqueous chloramine (96 ml.), obtained by the distillation [22] of a mixture of 1·211N-ammonia (273 ml.) and 1·179N-sodium hypochlorite (262 ml.) at 45°/20 mm., was kept at 0° for 6 hr. and then at room temperature for 2 days. The mixture was evaporated at 100°/25 mm. and the residue continuously extracted with ethanol. The ethanol-insoluble portion (3 g.) was dissolved in water (40 ml.) containing sodium hydroxide (4 g.) and this solution was evaporated at room temperature and 20 mm. until the smell of ammonia disappeared. The solution was acidified with concentrated hydrochloric acid (20 ml.), evaporated at 100°/20 mm. to crystallisation, and filtered. The filtrate was evaporated to dryness at 100°/20 mm., and the residue dissolved in water (2 ml.) and acidified with concentrated hydrochloric acid (10 ml.). After filtration, the filtrate was evaporated at 100°/20 mm. and the residue crystallised in turn from methanol and ethanol, affording 1,4-*diamino*-1,4-*diazoniabicyclo*[2,2,2]*octane dichloride* as rods, m. p. >300° (decomp.) (Found: C, 33·6; H, 7·2; Cl, 32·8; N, 26·1. $C_6H_{16}Cl_2N_4$ requires C, 33·5; H, 7·5; Cl, 32·9; N, 26·1%). The infrared spectrum (potassium chloride disc) had peaks at

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[20] Noelting and Kopp, *Ber.*, 1905, **38**, 3506.
[21] Evans, Jones, and Kynaston, following paper.
[22] *Inorg. Synth.*, Vol. I, p. 59.

3180s and 3096s (NH stretching) and 1598m cm.$^{-1}$ (NH deformation). These are characteristic of a hydrazinium grouping.[21] The spectrum also differed from that of the product decomposing at 160—180° that was isolated after reaction of ethylene dibromide with 1,4-diaminopiperazine.

The ethanolic extract, on evaporation, furnished a solid (2·6 g.) which was dissolved in water (260 ml.) and passed through Amberlite IRA-400 (OH$^-$). The eluate was concentrated at 100°/20 mm. until the ammonia was removed, acidified with concentrated hydrobromic acid (5 ml.) and evaporated at 100°/20 mm. The residue (1·5 g.), on recrystallisation from aqueous ethanol, afforded 1-*amino*-1,4-*diazoniabicyclo*[2,2,2]*octane bromide hydrobromide*, m. p. >300° (decomp.) (Found: C, 25·0; H, 5·2; Br, 55·3; N, 14·4. $C_6H_{15}Br_2N_3$ requires C, 24·9; H, 5·2; Br, 55·3; N, 14·5%). The infrared spectrum (potassium chloride disc) revealed a protonated tertiary amino-group (intense bands between 2793 and 2474 cm.$^{-1}$) [23] and a hydrazinium group (NH stretching bands at 3206 and 3119 and NH deformation band at 1624 cm.$^{-1}$).

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