662. *Polymers Based on Hydrazine. Part I.*

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Polymers containing hydrazine and hydrazinium groups have been prepared from cross-linked, chloromethylated polystyrene. Nitrosation and reduction of polyethyleneimine does not afford polyethylenehydrazine (I). An attempt to prepare 1-aminoethyleneimine, the monomer corresponding to (I), failed but the polymer was obtained by pyrolysis of 3-amino-2-oxazolidone or its hydrochloride.

HYDRAZINE is a versatile source of resin intermediates and condensation polymers.[1-3] Polymeric hydrazides have been prepared by condensing hydrazine with dicarboxylic acids, esters, anhydrides,[4] and polymeric esters, *e.g.*, polyacrylates.[5] Polymeric hydrazones, formazans, and tetrazolium salts have been derived from polyaldehydes such as polyacraldehyde.[6] Polyvinyl ketones have been converted into polymeric hydrazones.[7] Hydrazine [8, 9] and hydrazides of dicarboxylic acids [10] have been condensed with formaldehyde and, similarly, with urea,[11] dicyandiamide, phenylthiourea, and guanidine [12] to give polymeric derivatives. Condensation polymers from di-isocyanates with hydrazine and dihydrazides have also been described.[13] Poly-1,2,4-triazoles and poly-4-amino-1,2,4-triazoles have been synthesised from dihydrazides of aliphatic dicarboxylic acids [14-16] and polyazines from polyfunctional aldehydes [17] and ketones.[18]

In contrast, there are but scant references to polymeric hydrazines, *i.e.*, systems incorporating the hydrazine residue $\cdot NH\cdot NH_2$, $\cdot NH\cdot NH\cdot$, or $\cdot N(NH_2)\cdot$, or the hydrazinium

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[1] Byrkit and Michalek, *Ind. Eng. Chem.*, 1950, **42**, 1866.

[2] Reed, *Roy. Inst. Chem. Lectures, Monographs, Reports*, 1957, No. 5. "Hydrazine and its Derivatives."

[3] *Rev. Prod. Chim.*, 1959, **62**, 178.

[4] Moldenhauer and Bock, U.S.P. 2,349,979; 2,378,571; 2,383,880.

[5] Kern, Hucke, Holländer, and Schneider, *Makromol. Chem.*, 1957, **22**, 31, 39.

[6] Kern, Schulz, and Braun, *J. Polymer Sci.*, 1960, **48**, 91.

[7] I.G. Farbenindustrie A.G., B.P. 497,031.

[8] Pulvermacher, *Ber.*, 1893, **26**, 2360.

[9] Neureiter, *J. Amer. Chem. Soc.*, 1959, **81**, 2910.

[10] Fisher and Wheatley, U.S.P. 2,597,467.

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[13] Campbell, Foldi, and Farago, *J. Appl. Polymer Sci.*, 1959, **2**, 155.

[14] Fisher, *J. Appl. Chem.*, 1954, **4**, 212.

[15] Moncrieff, B.P. 612,609; Geigy Co , Ltd., B.P. 824,163.

[16] Korshak, Chelnokova, and Shkolina, *Vysokomol. Soedineniya*, 1959, **1**, 1772.

[17] Marvel and Hill, *J. Amer. Chem. Soc.*, 1950, **72**, 4819.

[18] Zimmerman and Lochte, *J. Amer. Chem. Soc.*, 1936, **58**, 948; 1938, **60**, 2456.

group $\geq N^+(NH_2)$, attached to or linked by hydrocarbon units. Few polymerisable derivatives of hydrazine have been described. Arcus and Schaffer[19] prepared monomeric *m*-hydrazinostyrene but did not report its polymerisation. Conversion of a " styrylhydrazine " and 3,5-dihydrazinostyrene into polymers capable of removing aldehydes and ketones from dilute solution,[20] and the preparation and polymerisation of diallyl hydrazinedicarboxylate[21] have been reported in patents. Reduction of certain polymeric hydrazine derivatives, *e.g.*, polyhydrazides and polyhydrazones, offers a route to hydrazine polymers. Cohen and Minsk[22] exploited this method with lithium aluminium hydride as reducing agent. Conflicting claims have been made regarding the synthesis of hydrazine polymers by condensation of alkylene dihalides and hydrazine.[23,24] The reaction of *trans*-1,4-dibromobut-2-ene with hydrazine affords a polymer but its precise structure has not been defined.[25]

We have explored new routes to polymeric hydrazines. Our first approach was to incorporate the hydrazine group into existing polymeric systems. For example, chloromethylated cross-linked polystyrene resins were treated with hydrazine and some of its derivatives. In all cases, nitrogen-containing polymers were obtained; with hydrazine itself, there was evidence of extensive cross-linking and the resulting resins had only a very low capacity for aldehydes and ketones. 1,1-Dimethylhydrazine gave a polymer containing the hydrazinium group, which, after treatment with dilute sodium hydroxide solution, functioned as a strongly basic anion-exchange resin, with a capacity of 4 mequiv./g. Polyvinyl chloride reacts with hydrazine and 1,1-dimethylhydrazine, giving nitrogenous polymers. The reactions proved to be complex and were not studied in detail.

Nitrosation of polyethyleneimine, followed by reduction, was investigated as a possible route to polyethylenehydrazine (I):

$$[\cdot CH_2\cdot CH_2\cdot NH\cdot]_n \longrightarrow [\cdot CH_2\cdot CH_2\cdot N(NO)\cdot]_n \longrightarrow [\cdot CH_2\cdot CH_2\cdot N(NH_2)\cdot]_n \quad \text{(I)}$$

Commercial polyethyleneimine thus gave polymers with strong reducing properties but their composition did not correspond to (I). Leibnitz *et al.*[26] found evidence of considerable branching in samples of polyethyleneimine from the same commercial source. Of the total nitrogen content of the polymer, about 32% originated in primary amino-groups. They claimed that 2-aminoethyl groups are located on some of the nitrogen atoms along the polymer chain; our observation that polyethyleneimine condenses with benzaldehyde to give a polymeric Schiff base confirms this. In the above nitrosation, both the primary and the secondary amino-groups would be involved and this unexpected complication probably accounts for the presence of oxygen in the reduced polymer. Polyethyleneimine clearly is not a suitable starting material for the synthesis of (I). Lüttringhaus *et al.*[27] obtained cyclic hydrazines from sodium hypochlorite and diamines of the type $H_2N\cdot[CH_2]_n\cdot NH_2$ ($n = 3$ or 4) but made no comment on the possibility of forming polymeric hydrazines by intermolecular reaction, particularly with higher homologues.

An alternative approach to a polymer (I), synthesis and polymerisation of monomeric 1-aminoethyleneimine, was not successful. Attempts to convert 2-hydroxyethylhydrazine hydrochloride into the 2-chloro-derivative, a potential intermediate, failed. 1-Chloroethyleneimine was considered to be too hazardous a starting material, in view

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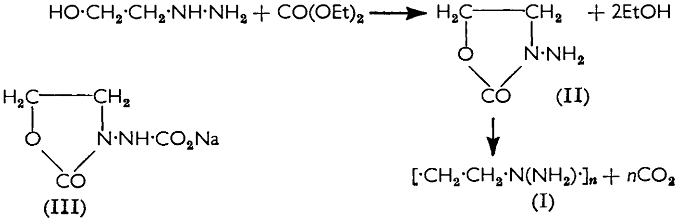
[19] Arcus and Schaffer, *J.*, 1958, 2428.
[20] Block, U.S.P. 2,851,445.
[21] Whitehill and McLamore, U.S.P. 2,583,980.
[22] Cohen and Minsk, *J. Org. Chem.*, 1959, **24**, 1404.
[23] Moncrieff, *Manuf. Chemist*, 1947, **18**, 177.
[24] Uraneck and Goertz, U.S.P. 2,822,354.
[25] Blood and Noller, *Chem. and Ind.*, 1959, 87.
[26] Leibnitz, Könnecke, and Gawalek, *J. prakt. Chem.*, 1958, **278**, 289.
[27] Lüttringhaus, Jander, and Schneider, *Chem. Ber.*, 1959, **92**, 1756.

of the experience of Graefe and Meyer.[28] After an earlier observation by one of us [29] that 2-oxazolidone gives polyethyleneimine on thermolysis, we attempted to use 3-amino-2-oxazolidone (II) for direct synthesis of the polymer (I). The amino-oxazolidone was prepared from 2-hydroxyethylhydrazine and ethyl carbonate in the presence of sodium methoxide.[30] There also appeared to be a side reaction, involving the catalyst and leading to some alcohol-insoluble sodium salt of the carbamic acid (III). On treatment with dilute acid, this salt (III) was readily converted into the oxazolidone (II). This decomposed with evolution of carbon dioxide around 165—170°; at 185°, gas evolution was vigorous, the salt progressively thickened, and after 25 minutes at this temperature, when the reaction was 90% complete (as assessed by the loss in weight due to carbon dioxide), a polymeric residue (I) was obtained as a solid froth. In order to obtain soluble polymer it is essential to conduct the pyrolysis at as low a temperature as possible, in a non-oxidising atmosphere, for a not undue period. Once decomposition had started, it was possible to reduce the temperature to about 140°, gas evolution then continuing, albeit at a slower rate. Finely divided inert material, *e.g.*, powdered glass, catalysed the reaction (cf. Newman and Caflisch [31]). At 200° and above, a small amount of ammonium carbonate was formed as a sublimate, and the polymers were insoluble or only partially soluble in water or ethanol, suggesting thermal breakdown of the polymer (I) with liberation of ammonia and formation of cross-linked structures. We did not find a suitable inert solvent. In boiling propionic acid, the oxazolidone (II) showed no signs of decomposition in 6 hours. In quinoline, carbon dioxide evolution was first noted at 214° and required 8 hours' heating at 220° for completion; there was evidence (ammonium carbonate) that the polymer was not stable at this temperature. In nitrobenzene, decomposition began at 195° and although the reaction proceeded slowly at 205° it seemed that the nitrobenzene reacted with the polymer or oxazolidone. In the presence of an equal weight of 2-hydroxyethylhydrazine, the oxazolidone began to lose carbon dioxide at 120° and reaction continued vigorously at this temperature; although the product was not characterised, it is thought that ring-opening, in this case, involved the 2-hydroxyethylhydrazine and yielded a simple rather than a polymeric derivative. Similarly, a polymer with reducing properties was obtained by heating polyvinyl alcohol with the oxazolidone at 150°. Just as 2-oxazolidone serves for the introduction of the 2-aminoethyl group into suitable systems,[29] compound (II) could serve as a source of 2-hydrazinoethyl groups.



The hydrochloride of compound (II) began to lose carbon dioxide at its melting point (139°) and continued to do so at a lower temperature (120°) until a glass-like, hygroscopic hydrochloride of polyethylenehydrazine was obtained.

To obtain, from the above pyrolytic reactions, polyethylenehydrazine uncontaminated with its precursor (II), a separation on ion-exchange resins was developed. By virtue of its strongly basic character the polymer was absorbed on a weakly acidic resin (Amberlite IRC-50) while the oxazolidone (II) passed through with the eluate. The polymer was

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[28] Graefe and Meyer, *J. Amer. Chem. Soc.*, 1958, **80**, 3939.

[29] Jones, *Chem. and Ind.*, 1956, 1454.

[30] Norwich Pharmacal Co., B.P. 735,169.

[31] Newman and Caflisch, *J. Amer. Chem. Soc.*, 1958, **80**, 862.

eluted from the resin with N-hydrochloric acid and recovered by passage down another column of strongly basic resin (Amberlite IRA-400).

Polyethylenehydrazine is almost colourless and soluble in water and ethanol, and in solution markedly reducing. It readily forms a polymeric picrate and condenses, through the NH_2-groups, with aldehydes and ketones. Polymeric derivatives were prepared with benzaldehyde, salicylaldehyde, pyridine-2-aldehyde, and pyridine-2,6-dialdehyde. An insoluble cross-linked polymer resulted from the reaction with the dialdehyde and this, like the polymer from pyridine-2-aldehyde, showed chelating properties.

EXPERIMENTAL

Treatment of Chloromethylated Cross-linked Polystyrene Resin with Hydrazine and its Derivatives.—(i) *Hydrazine hydrate.* Hydrazine hydrate (20 g.) was added to a chloromethylated cross-linked polystyrene [32] (10 g.), prepared in bead form from styrene containing 2% of divinylbenzene and chloromethylated to give a chlorine content of 23%. The mixture was heated under reflux at 100° for 12 hr. The product consisted of a mixture of resin and hydrazine hydrochloride. When washed with distilled water the resin was obtained as discrete beads (8·8 g.) (Found: C, 79·4; H, 7·1; N, 8·2; Cl, 0·7%). The resin had only a very low capacity for removal of aldehydes and ketones from aqueous solution, indicating extensive cross-linking with the hydrazine.

(ii) 1,1-*Dimethylhydrazine.* The same chloromethylated polystyrene resin (10 g.) was heated with 1,1-dimethylhydrazine (15 g.) under reflux at 100° for 3½ hr. More 1,1-dimethylhydrazine (10 g.) and ethanol (20 g.) were then added and heating continued for a further 8 hr. The resin beads were filtered off, washed with ethanol and water, and dried *in vacuo* over phosphorus pentoxide. This resin (12 g.) (Found: C, 63·8; H, 7·6; N, 13·3; Cl, 14·4%) contained the hydrazinium group $\cdot CH_2\cdot{}^+NMe_2\cdot NH_2\ Cl^-$ and after treatment with dilute sodium hydroxide solution behaved as a strongly basic ion-exchange resin and had a capacity of 4 mequiv./g.

(iii) *Phenylhydrazine.* Chloromethylated resin (10 g.), phenylhydrazine (20 g.), and ethanol (50 ml.) were heated under reflux at 100° for 7 hr. The resin was separated, washed with alcohol, sodium hydroxide solution, and water, and dried (yield, 13·2 g.) (Found: C, 80·4; H, 6·9; N, 11·6; Cl, 0·1%).

Similarly, treatment of the resin with 2-hydroxyethyl-, 1-acetyl-, 1,2-diacetyl-, or 1,2-diformyl-hydrazine, or 2-ethylhydrazine-1-carboxylate afforded nitrogen-containing resins.

Reactions of Polyvinyl Chloride with Hydrazine and 1,1-*Dimethylhydrazine.*—Polyvinyl chloride (12·5 g.), in powder form, was heated under reflux with hydrazine hydrate (35 g.) for 7 hr. The product obtained by filtration and washing with distilled water was an orange, insoluble solid (11·4 g.) (N, 7·0%). Similarly, unplasticised polyvinyl chloride film (0·009″ thick; 1 g.) was kept in hydrazine hydrate (70 g.) at 100° for 13 hr., then washed with deionised water; after being kept in dilute hydrochloric acid for ½ hr., the product behaved as an ion-exchange membrane. The same unplasticised film (1 g.), when kept for 11 days with anhydrous 1,1-dimethylhydrazine, became yellow and after being washed with deionised water functioned as an anion-exchange membrane with a reasonably low resistance. These reactions proved to be very complex and it was not possible to characterise the resulting polymers.

Nitrosation of Polyethyleneimine.—The polyethyleneimine was of commercial manufacture ("Polymin P") [Found: C, 55·8; H, 11·5; N, 31·8. Calc. for $(C_2H_5N)_n$: C, 55·8; H, 11·7; N, 32·5%]. A value of 3800 for $\bar{M}_n$ was obtained from osmometric measurements with cellulose acetate membranes.

In a typical experiment, concentrated hydrochloric acid (58 ml.) was added, with vigorous stirring, in 105 min. to a solution of polyethyleneimine (12·8 g.) and sodium nitrite (36 g.) in water (120 ml.) at 10—15°. The mixture was then left at room temperature for 1 hr. The pale yellow precipitate which had separated was washed continuously with distilled water for 2½ hr. and left in water overnight. It was recovered as a spongy solid (2·0 g., 9%) after drying *in vacuo* over phosphorus pentoxide [Found: C, 43·5; H, 7·6; N, 28·0. Calc. for the fully nitrosated, ideal polymer $(C_2H_4N_2O)_n$: C, 33·5; H, 5·5; N, 38·9%].

Reduction of the Nitrosated Polymers.—2·6% Sodium amalgam (8 g.) was added to a suspension of the nitrosated polymer (1·3 g.) in water (100 ml.). After being heated at 100° for 9 hr. the polymer was recovered, washed continuously with distilled water for 2 hr., and dried *in*

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[32] Pepper, Paisley, and Young, *J.*, 1953, 4097.

vacuo over phosphorus pentoxide (Found: C, 47·0; H, 7·1; N, 26·8%). The polymer, in this form, reduced ammoniacal silver nitrate and decolorised iodine solution.

A solution of sodium borohydride (5 g.) in water (100 ml.) was added to a suspension of polymer (1·4 g.) in water (200 ml.) made slightly alkaline with sodium hydroxide and kept for 2 days at room temperature. The solid polymer was separated and suspended in dilute acetic acid for 1 hr. and in dilute sodium hydroxide solution for 1 hr., then washed with water and dried *in vacuo* over phosphorus pentoxide (Found: C, 43·4; H, 8·7; N, 29·2%). It reduced ammoniacal silver nitrate solution and iodine solution.

The polymer (2·3 g.) was refluxed on the steam-bath for 1 hr. with 2-acetylthiophen (5 g.) ethanol (20 ml.), and glacial acetic acid (1 ml.). The recovered polymer was washed with boiling alcohol before drying *in vacuo* over phosphorus pentoxide (Found: C, 44·1; H, 7·6; N, 27·7; S, 0·5%).

Reaction of 2-*Hydroxyethylhydrazine Hydrochloride with Thionyl Chloride.*—Dry hydrogen chloride was passed into ice-cold ethanolic 2-hydroxyethylhydrazine (15 g. in 100 ml.). The dihydrochloride separated as a crystalline mass, m. p. 140° (decomp.) (13·3 g.) (Found: C, 16·4; H, 6·9; Cl, 47·6; N, 19·35%. Calc. for $C_2H_{10}Cl_2N_2O$: C, 16·1; H, 6·9; Cl, 47·6; N, 18·9%). Copious evolution of hydrogen chloride occurred when the dihydrochloride (5 g.) was refluxed with thionyl chloride (10 ml.) at 100°. After 4 hr. the excess of thionyl chloride was removed under a vacuum, leaving a black, intractable solid, from which, by treatment with boiling alcohol, only a small amount of elementary sulphur was extracted. Variation of the reaction conditions, including the use of benzene or other inert solvents as diluent, failed to produce the 2-chloroethyl derivative.

Synthesis of 3-*Amino*-2-*oxazolidone.*—A mixture of 2-hydroxyethylhydrazine (152 g.), diethyl carbonate (300 g.), and a solution of sodium (6 g.) in methanol (100 ml.) was heated at 105—110° under a short distillation column. When the distillation of methanol and the ethanol liberated in the reaction had ceased ($\sim$1 hr.; distillate 277 g.), the excess of diethyl carbonate (8·8 g.) was removed under reduced pressure. The residue was treated with boiling ethanol and filtered hot. The insoluble product was further washed with hot alcohol. From the filtrate, by crystallisation and recrystallisation from ethanol, 3-amino-2-oxazolidone, m. p. 71° (116·5 g.), was obtained. The insoluble residue (35·4 g.) proved to be *sodium* 2-*oxo-oxazolidin*-3-*ylcarbamate* (Found: C, 29·0; H, 3·2; N, 16·9; Na, 13·1. $C_4H_5N_2NaO_4$ requires C, 28·6; H, 3·0; N, 16·7; Na, 13·7%). On treatment with dilute acid it gave carbon dioxide and 3-amino-2-oxazolidone, characterised by mixed m. p. and as its *benzaldehyde derivative* (m. p. and mixed m. p. 146·5°) (Found: C, 63·2; H, 5·3; N, 14·7. $C_{10}H_{10}N_2O_2$ requires C, 63·6; H, 5·3; N, 14·7%). Anhydrous potassium carbonate was tried as catalyst in place of sodium methoxide in the above condensation but did not cause ester interchange.

When dry hydrogen chloride was passed into a warm solution of 3-amino-2-oxazolidone (10 g.) in ethanol (50 ml.) the *hydrochloride* (10·6 g.), m. p. 139° (decomp.), crystallised (Found: C, 26·2; H, 5·1; Cl, 25·6; N, 20·0. $C_3H_7ClN_2O_2$ requires C, 26·0; H, 5·1; Cl, 25·6; N, 20·2%). It was washed with a little cold ethanol, dried *in vacuo* over solid potassium hydroxide, and recrystallised from ethanol.

Preparation of Polyethylenehydrazine (I) *by Heating of* 3-*Amino*-2-*oxazolidone* (II).—3-Amino-2-oxazolidone (7·45 g.), when heated in a nitrogen atmosphere, began to lose carbon dioxide at 170°. Gas evolution was vigorous at 185° and after 25 min. at this temperature a polymeric rubbery residue was obtained as a froth. The loss in weight was 2·90 g. (90%). The polymer (I) dissolved slowly in ethanol and fairly readily in hot water.

In a series of experiments it was established that if the temperature exceeded 200° or if heating was continued for a prolonged period at lower temperatures (170—185°) the loss in weight exceeded that expected from mere loss of carbon dioxide and the polymers were insoluble or only partially soluble in water.

In 10% quinoline solution decomposition set in at 215° and evolution of carbon dioxide continued for 8 hr. when the temperature was held at 220°. A small amount of ammonium carbonate was deposited in the reflux condenser. When 3-amino-2-oxazolidone (5 g.) was heated with 2-hydroxyethylhydrazine (5 g.) and powdered glass (5 g.), decomposition was observed at 120° and was virtually complete after 3 hr. at this temperature. The product, a sticky viscous liquid, was not characterised; reaction between the two hydrazine derivatives had taken place.

The products derived from the thermolysis of 3-amino-2-oxazolidone possessed properties characteristic of a polymeric hydrazine. However, in all cases they were contaminated with 10—20% of unchanged starting material, removed as described below.

Ion-exchange Separation.—3-Amino-2-oxazolidone (30 g.) with an equal weight of powdered glass was heated to 170° in an atmosphere of nitrogen. As soon as evolution of carbon dioxide began the temperature was reduced to 140° and kept thereat for 2 hr. The viscous residue was then dissolved in water (100 ml.) and passed through Amberlite IRC-50 (H^+) (200 ml.). The column was washed with deionised water until the effluent was neutral. The basic polymer was washed from the column with N-hydrochloric acid (200 ml.) followed by water (100 ml.), and the column was drained. The combined effluents (~400 ml.) were passed through Amberlite IRA-400 (OH^-) (500 ml.) and the resin washed with water, giving ~1 l. of solution. This was concentrated under reduced pressure, yielding a viscous dope. Further removal of water was effected by evacuation at 0·05 mm. at room temperature and finally at 70° for 2 hr. The polymer gave a silver mirror with ammoniacal silver nitrate, reduced Fehling's solution, and decolorised iodine solution.

Preparation of Polyethylenehydrazine Hydrochloride.—3-Amino-2-oxazolidone hydrochloride (4·9420 g.) was heated to 140°. It melted and started to decompose, whereupon the bath temperature was reduced to 120° and kept thereat for 6 hr. during which decomposition continued. On cooling, a colourless, glass-like polymeric residue (3·5738 g.) was obtained (loss in wt. 90%). This was hygroscopic; when it was crushed and heated *in vacuo* at 100°, some further decomposition was noted (Found: C, 26·1; H, 7·3; Cl, 31·3; N, 27·6. Calc. for starting material: C, 26·0; H, 5·0; Cl, 25·6; N, 20·2. Calc. for polymer: C, 25·4; H, 7·4; N, 29·6; Cl, 37·6%). When 3-amino-2-oxazolidone was heated at 100°/0·1 mm. it sublimed without decomposition.

Reaction of 3-Amino-2-oxazolidone with Polyvinyl Alcohol.—3-Amino-2-oxazolidone (20·4762 g.) and polyvinyl alcohol (4·3872 g.; grade RH 349, du Pont) were heated at 155—160° for 3 hr. At 150° a homogeneous solution was obtained and decomposition started. The solution became increasingly viscous and frothed as decomposition progressed (final loss, 5·0919 g.). The hard polymeric residue dissolved in hot water and was precipitated in a large volume of ethanol as a fluffy, white, fibrous material (4·1 g.). It was taken up in water and reprecipitated in ethanol before analysis [Found: C, 47·4; H, 9·0. Calc. for $(C_4H_{10}N_2O)_n$: C, 47·0; H, 9·8%].

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