and refluxing were continued for 1 hr. The mixture was filtered while hot and the residue was washed with hot alcohol. The alcohol was removed under reduced pressure and the product, ethyl α-formamido-α-carbethoxy-β-2-methylphenylpropionate, was recrystallized from acetone-water, yield 68%, m.p. 92–94°.

Anal. Calcd. for $C_{16}H_{21}NO_5$: C, 62.54; H, 6.84; N, 4.56. Found: C, 62.60; H, 7.03; N, 4.67.

This product was reduced to compound VI with lithium aluminum hydride by the procedure used for making compound IV.

The corresponding sulfite was prepared as described for compound IV. The yield was 65%, m.p. 164–165°.

Anal. Calcd. for $C_{12}H_{18}ClNO_3S$: C, 49.39; H, 6.17; Cl, 12.17; N, 4.80; S, 10.97. Found: C, 49.30; H, 6.15; Cl, 12.40; N, 4.79; S, 10.89.

The corresponding dinicotinate, prepared by the method described for compound IV, melted at 193–194°, yield 38%.

Anal. Calcd. for $C_{24}H_{26}ClN_3O_4$: C, 63.22; H, 5.71; Cl, 7.79; N, 9.22. Found: C, 63.01; H, 6.05; Cl, 7.6; N, 8.92.

N-Methyl-1,1-di(hydroxymethyl)-2-(3-methylphenyl)ethylamine hydrochloride, VII. Ethyl α-formamido-α-carbethoxy-β-3-methylphenylpropionate was prepared by the procedure used for making α-formamido-α-carbethoxy-β-phenylpropionate except that *m*-methylbenzyl chloride was used in place of benzyl chloride. The yield was 84%, m.p. 94–96°.

Anal. Calcd. for $C_{16}H_{21}NO_5$: C, 62.54; H, 6.84; N, 4.56. Found: C, 62.50; H, 6.81; N, 4.76.

Ethyl α-formamido-α-carbethoxy-β-3-methylphenylpropionate was reduced with lithium aluminum hydride to compound VII.

The dinicotinate of VII was prepared in 38% yield, m.p. 185–186°.

Anal. Calcd. for $C_{24}H_{26}ClN_3O_4$: C, 63.22; H, 5.71; Cl, 7.79; N, 9.22. Found: C, 63.20; H, 5.88; Cl, 7.72; N, 9.37.

The sulfite of VII was prepared in 65% yield, m.p. 148–149°.

Anal. Calcd. for $C_{12}H_{18}ClNO_3S$: C, 49.39; H, 6.17; Cl, 12.17; N, 4.80; S, 10.97. Found: C, 49.26; H, 6.42; Cl, 12.20; N, 5.13; S, 10.75.

N-Methyl-1,1-di(hydroxymethyl)-2-(4-methylphenyl)ethylamine hydrochloride, VIII. Ethyl α-formamido-α-carbethoxy-β-4-methylphenylpropionate was prepared by the method used for making ethyl α-formamido-α-carbethoxy-β-phenylpropionate except that *p*-methylbenzyl chloride was used in place of benzyl chloride. The yield was 93%, m.p. 135–136°.

Anal. Calcd. for $C_{16}H_{21}NO_5$: C, 62.54; H, 6.84; N, 4.56. Found: C, 62.63; H, 7.26; N, 4.79.

Ethyl α-formamido-α-carbethoxy-β-4-methylphenylpropionate was reduced with lithium aluminum hydride to compound VIII.

The sulfite of VIII was prepared in 65% yield, m.p. 156–157°.

Anal. Calcd. for $C_{12}H_{18}ClNO_3S$: C, 49.39; H, 6.17; Cl, 12.17; N, 4.80; S, 10.97. Found: C, 49.68; H, 6.45; Cl, 12.15; N, 4.96; S, 10.81.

N-Ethyl-1,1-di(hydroxymethyl)-2-phenylethylamine hydrochloride, IX. Ethyl acetamidomalonate was the starting material for this preparation. Otherwise the procedure was similar to that used for making compound IV.

N-Methyl-1,1-di(hydroxymethyl)-2-(4-methoxyphenyl)ethylamine hydrochloride, X. Ethyl α-formamido-α-carbethoxy-β-4-methoxyphenylpropionate[4] was reduced with lithium aluminum hydride to compound X.

The dinicotinate of X melted at 172–173°, yield 33%.

Anal. Calcd. for $C_{24}H_{26}ClN_3O_5$: C, 61.08; H, 5.51; Cl, 7.52; N, 8.90. Found: C, 61.13; H, 5.56; Cl, 7.6; N, 8.95.

The corresponding sulfite melted at 167–168°, yield 73%.

Anal. Calcd. for $C_{12}H_{18}ClNO_4S$: C, 46.82; H, 5.85; Cl, 11.54; N, 4.55; S, 10.40. Found: C, 46.93; H, 5.82; Cl, 11.45; N, 4.68; S, 10.55.

N-Methyl-1,1-di(hydroxymethyl)-2-(4-hydroxyphenyl)ethylamine hydrochloride, XI. One gram of compound X was refluxed in 2 ml. of 48% hydrobromic acid and 5 ml. of acetic acid for 20 min. On diluting with 20 ml. of water a dark gummy material separated. The gum was washed with dilute sodium hydroxide solution and then with water. The residue was dissolved in ether, the solution dried and treated with dry hydrogen chloride. The hydrochloride, which was quite hygroscopic, was recrystallized from propanol and dry ether.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA 4, PA.

Synthesis of *N*-(2-Hydroxyethyl)-*N'*-(4-pentenyl)ethylenediamine

E. F. CLUFF AND H. F. MCSHANE, JR.

Received March 24, 1960

As an intermediate for the preparation of a certain polyurethane elastomer[1] the substituted ethylenediamine (I) was required in a state of high purity. Diamine syntheses involving alkylation reactions usually give mixtures which contain difficultly separable tertiary amine isomers. The latter materials act as chain terminating agents in polycondensation reactions and prevent the attainment of high molecular weight. Consequently the synthetic route shown in the flowsheet was chosen to provide a diamine of unequivocal structure.

Aminolysis of dimethyl oxalate (II) with *N*-(2-hydroxyethyl)ethylenediamine (III) provided crystalline *N*-(2-hydroxyethyl)piperazine-2,3-dione (IV) in 20–35% yield. This reaction has been shown to be general for many *N*-substituted ethylenediamines.[2] The present reaction most likely proceeds through the formation and subsequent breakdown of a linear polyamide. As the temperature was slowly raised to about 180°, an essentially quantitative yield of alcohol was obtained, and the reaction mass became increasingly more viscous. At this point, the product was insoluble in alcohol and no piperazinedione (IV) could be isolated. Increasing the temperature above 180° to about 220° produced a marked viscosity reduction in the reaction mass which was then alcohol soluble and deposited crystals of IV.

Conversion of IV to the monopotassium salt proceeded smoothly in refluxing *t*-butyl alcohol. The salt was not isolated but was alkylated directly with 1-bromo-4-pentene to provide the crystalline disubstituted piperazinedione (V) in 70% yield. Hydrolysis of V with aqueous-alcoholic potassium hydroxide provided an excellent yield of *N*-(2-hydroxyethyl) - *N'* - (4 - pentenyl)ethylenediamine (I). That alkylation of the piperazinedione (IV) had occurred on nitrogen and not on hydroxyl

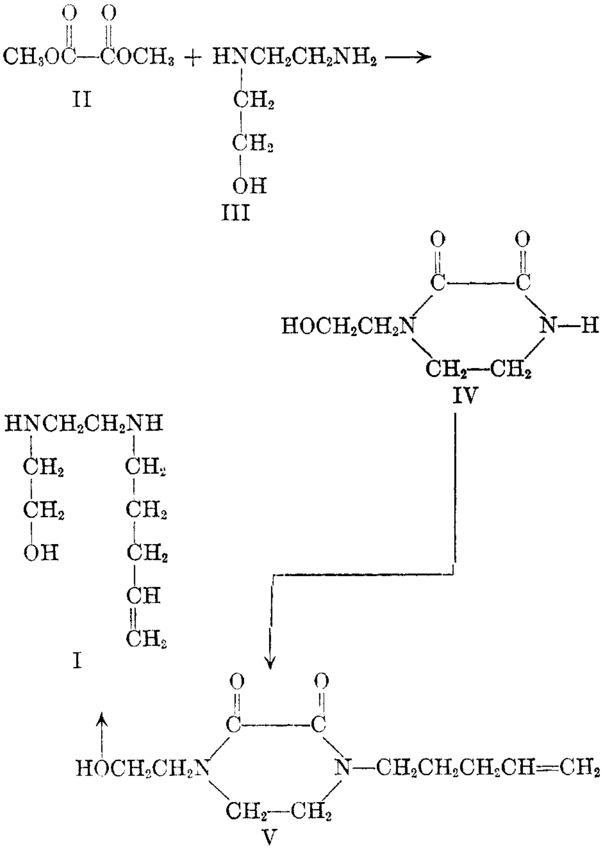
---

(1) E. F. Cluff and E. K. Gladding, Proceedings International Rubber Conf., Washington, D. C., 1959, p. 543.

(2) J. L. Riebsomer, *J. Org. Chem.*, **15**, 68 (1950).

was established by analysis of the diamine (I) for primary amino nitrogen which was absent. The purity of the diamine (I) was ultimately established by its polymerization with polytetramethylene-ether glycol bischloroformate to form a high molecular weight polyurethane.[1]

This sequence of reactions should provide a general route for the preparation of unsymmetrically *N,N'*-disubstituted ethylenediamines of high purity.



EXPERIMENTAL

N-(2-Hydroxyethyl)piperazine-2,3-dione (IV). A mixture of 343 g. (3.30 moles) of aminoethylethanolamine (III) and 5 ml. of concd. hydrochloric acid was added to 389 g. (3.30 moles) of dimethyl oxalate (II) over a period of 15 min. with good agitation. The temperature was raised gradually to 218° in about 1 hr., during which time 206 g. (6.44 moles, 97.6%) of methanol distilled from the reaction mixture. The reactants gradually formed a viscous polymer which broke down above 180° to form the piperazinedione (IV) and a red noncrystalline material which was not further investigated. The mixture was cooled to room temperature, taken up in 400 ml. of ethanol, cooled, and filtered. The crude product (199 g., 38%) was recrystallized from alcohol until pure, m.p. 163–164°.

Anal. Calcd. for $C_6H_{10}N_2O_3$: C, 45.56; H, 6.37; N, 17.72. Found: C, 45.2, 45.5; H, 5.9, 6.1; N, 17.4, 17.6.

N-(2-Hydroxyethyl)-N'-(4-pentenyl)piperazine-2,3-dione (V). A 3-l., four-necked flask equipped with a stirrer, thermometer, and reflux condenser fitted with a calcium sulfate drying tube was flamed out and cooled while being flushed with dry nitrogen. Distilled *t*-butyl alcohol (1600 ml.) was added followed by 61.4 g. (1.57 moles) of potassium. The mixture was refluxed and agitated until the metal had completely reacted. *N*-(2-Hydroxyethyl)piperazine-2,3-dione (248 g., 1.57 moles) was added, and the agitated suspension was refluxed overnight. The temperature was lowered to 70°, 234 g. (1.57 moles) of 1-bromo-4-pentene[3] was added, and the mixture was again refluxed overnight. After cooling, the solid potassium bromide was filtered (160 g., 86%), and the *t*-butyl alcohol was distilled. The last traces of solvent were removed under reduced pressure. The viscous residue was extracted with benzene (one 500-ml. and three 250-ml. portions) and then with tetrahydrofuran (three 500-ml., eight 250-ml., and six 100-ml. portions). The tetrahydrofuran was distilled, and the residue placed in a 0° coldbox overnight to crystallize. The solid was recrystallized from tetrahydrofuran (wt. 127 g.). The filtrate was diluted with 2 l. of tetrahydrofuran and the supernatant liquid was decanted from the precipitated oil. The tetrahydrofuran solution was again concentrated, seeded, and cooled to yield another 56 g. of solid. Further concentration of the filtrate yielded an additional 8.5 g. of product, bringing the total yield to 191.5 g. (54%). The residue from the benzene extract, combined with the end tetrahydrofuran filtrate from the recrystallizations, was chromatographed on 200-mesh activated alumina with tetrahydrofuran and ethanol. This resulted in the recovery of an additional 56.5 g. (16%) of material. Recrystallization of the combined solids from tetrahydrofuran afforded pure *N*-(2-hydroxyethyl)-*N'*-(4-pentenyl)piperazine-2,3-dione, m.p. 75–76.5°.

Anal. Calcd. for $C_{11}H_{18}N_2O_3$: C, 58.39; H, 8.02; N, 12.38. Found: C, 58.5, 58.5; H, 7.8, 7.9; N, 12.5, 12.7.

N-(2-Hydroxyethyl)-N'-(4-pentenyl)ethylenediamine (I). To a solution of 50 g. (0.770 mole) of 85% potassium hydroxide in 500 ml. of ethanol was added 0.1 g. of 2,6-di-*t*-butyl-*p*-cresol, a solution of 0.1 g. of sodium sulfite in 25 ml. of distilled water, and 83 g. (0.376 mole) of *N*-(2-hydroxyethyl)-*N'*-(4-pentenyl)piperazine-2,3-dione (V). The clear solution was refluxed overnight under an atmosphere of nitrogen. A precipitate began forming after about 15 min. The mixture was cooled, the solid potassium oxalate monohydrate was filtered (65.5 g., 96.8%), and the solvent was distilled from the filtrate. Vacuum distillation of the residue yielded hydroxyethylpentenylethylenediamine (57.6 g., 91.5% yield, b.p. 97.5° (0.15 mm.), n_D^{25} 1.4772).

Anal. Calcd. for $C_9H_{20}N_2O$: C, 62.75; H, 11.70; N, 16.27; primary amino N, absent. Found: C, 62.5, 62.8; H, 11.4, 11.5; N, 16.1, 16.1; primary amino N, absent.

A drop of amine added to aqueous oxalic acid yielded the bisoxalate, m.p. 236–237°.

Anal. Calcd. for $C_{13}H_{24}N_2O_9$: C, 44.31; H, 6.87; N, 7.95. Found: C, 44.0, 44.2; H, 6.8, 6.9; N, 7.8, 7.8.

The amine forms a solid hemihydrate, m.p. 41.5–42°, on admixture with 0.5 mole equivalent of water.

ELASTOMER CHEMICALS DEPARTMENT
E. I. DU PONT DE NEMOURS AND CO., INC.
WILMINGTON, DEL.

---

(3) Prepared according to the method of P. Gaubert, R. P. Linstead, and H. N. Rydon, *J. Chem. Soc.*, 1971 (1937) and E. M. Van Heyningen, *J. Chem. Soc.*, **76**, 2241 (1954), b.p. 124° (760 mm.), n_D^{25} 1.4615 (reported b.p. 124.5–128°, n_D^{25} 1.4642).

Decarboxylation of *N*-Methylaminoaromatic *ortho*-Carboxylic Acids

WAYLAND E. NOLAND AND GEORGE J. MEISTERS[1]

Received April 7, 1960

Dry distillation with soda-lime has been shown previously to produce *N*-demethylation (and con-