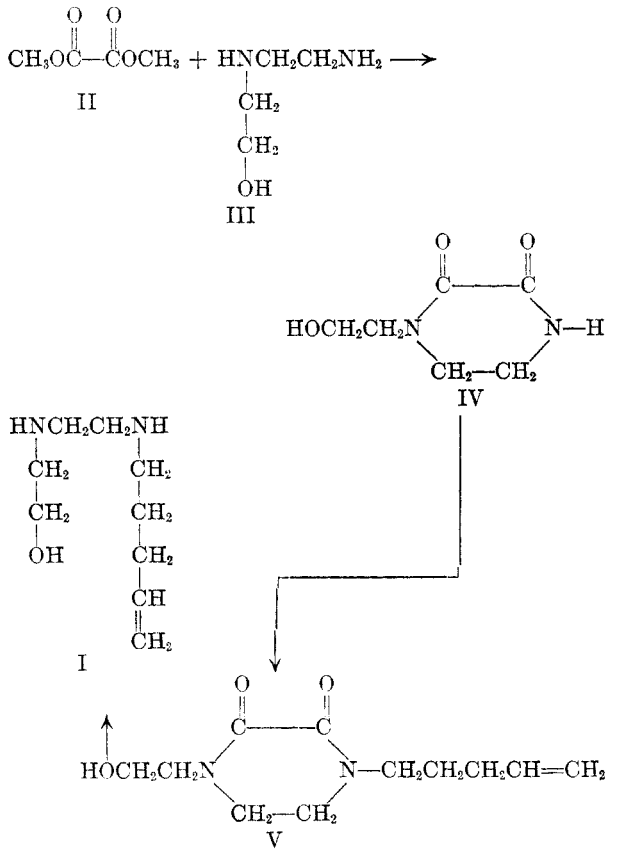
was established by analysis of the diamine (I) for primary amino nitrogen which was absent. The purity of the diamine (I) was ultimately established by its polymerization with polytetramethylene-ether glycol bischloroformate to form a high molecular weight polyurethane.[1]

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.

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(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).

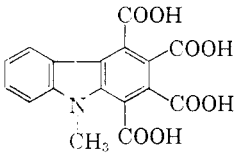
Decarboxylation of *N*-Methylaminoaromatic *ortho*-Carboxylic Acids

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

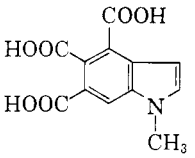
Received April 7, 1960

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

comitant decarboxylation to carbazole) of the salt of 9-methylcarbazole-1,2,3,4-tetracarboxylic acid (I).[2] No *N*-demethylation occurred under similar conditions, however, with 9-methylcarbazole[2] or with the salt of a triacid believed to be 1-methylindole-4,5,6-tricarboxylic acid (II).[3] The possibility that



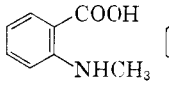
I



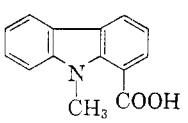
II

N-demethylation of I is occurring by neighboring group participation of the *ortho* carboxylate anion led us to test the generality of *N*-demethylation accompanying decarboxylation by use of selected *N*-methylaminoaromatic *ortho* carboxylic acids.

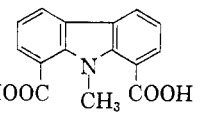
N-Methylanthranilic acid (III),[4] upon decarboxylation with soda-lime,[2] gave a liquid amine, which was isolated in 34% yield as the acetyl derivative, shown to be identical by mixed melting point and infrared comparison in Nujol with an authentic sample of *N*-methylacetanilide. 9-Methylcarbazole-1-carboxylic acid (IV)[5] and 9-methylcarbazole-1,8-dicarboxylic acid (V)[5] were similarly decarboxylated to 9-methylcarbazole in yields of 58% and 50%, respectively.



III

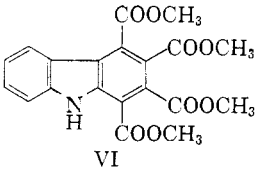


IV



V

These results show that *N*-demethylation accompanying decarboxylation of *N*-methylaminoaromatic *ortho* carboxylic acid salts is not a general phenomenon; that the presence of one or two *ortho* carboxylate groups is, in itself, insufficient cause for *N*-demethylation. It is concluded that, in the case in which it occurs (I), *N*-demethylation is favored by unusual stabilization of the resulting anion, attributable to the combined resonance and inductive effects of the four carboxylate substituent groups. In this connection, it is perhaps of interest to note that our efforts to *N*-methylate the sodium salt of the ester (VI)[2] of the corresponding unsubstituted



VI

compound have been unsuccessful. The results cited in this paper provide no evidence either for or against neighboring group participation by the *ortho* carboxylate group in *N*-demethylation in the case in which it occurs.[2]

Because of its importance to the conclusions drawn in this work, it appeared desirable to establish rigorously the position of the carboxyl group in 9-methylcarbazole-1-carboxylic acid (IV), prepared by action of *n*-butyllithium on 9-methylcarbazole, followed by reaction with carbon dioxide.[5] The structure had been logically assigned previously by analogy with numerous examples of *ortho* lithiation of aromatic amines[5] and with the fact that 9-ethylcarbazole-1-carboxylic acid, prepared similarly, had been shown to be identical with a sample prepared by ethylation of carbazole-1-carboxylic acid.[6]

Carbazole-1-carboxylic acid, most readily prepared from carbazole by reaction of its potassium salt[7] with carbon dioxide at 270°,[8] has been prepared unambiguously by two different methods,[9,10] and the product in the first case has been shown to be identical with a sample prepared from carbazole. After unsuccessful methylation attempts with dimethyl sulfate or methyl iodide in the presence of alkali,[11] we obtained 9-methylcarbazole-1-carboxylic acid (IV) in 11% yield from carbazole-1-carboxylic acid[8] by the action of sodamide and methyl iodide in liquid ammonia.[12] The sample was shown to be identical by mixed melting point (188.5–190°) and infrared comparison in Nujol with a sample[5] prepared from 9-methylcarbazole, thus constituting a proof of structure for 9-methylcarbazole-1-carboxylic acid (IV).

EXPERIMENTAL

Melting points were determined on a calibrated Kofler micro hot stage.

Decarboxylation of N-methylanthranilic acid (III). *N*-Methylanthranilic acid[4] (3.00 g., 0.0198 mole) was mixed thoroughly with powdered soda-lime (9 g.) and the mixture pyrolyzed under a stream of nitrogen with the aid of a Meker burner, in the manner previously described.[2] The liquid distillate was refluxed with acetic anhydride[13] for 30

(1) Graduate School research assistant, summer 1959. It is a pleasure to acknowledge the support of this work through a grant from the General Research Fund of the Graduate School of the University of Minnesota.

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min., yielding a colorless precipitate (1.01 g., 0.0068 mole, 34%), m.p. 97–98.5°. After recrystallization from ether the sample melted at 99.5–100.5°, mixed m.p. 100.5–101.5° with a sample of *N*-methylacetanilide prepared[13] from Eastman Kodak Co. White Label *N*-methylaniline. The infrared spectra of the two samples in Nujol were identical. ν_{NH} none; $\nu_{C=O}$ 1672 cm.$^{-1}$ in Nujol.

Decarboxylation of 9-methylcarbazole-1-carboxylic acid (IV), 9-Methylcarbazole-1-carboxylic acid[5] (0.50 g., 0.00221 mole) was mixed thoroughly with powdered soda-lime (2.5 g.) and the mixture decarboxylated as described previously. The white sublimate (0.23 g., 0.00127 mole, 58%), m.p. 87.5–89.0°, did not depress the melting point of authentic 9-methylcarbazole,[5] and the infrared spectra in Nujol were identical. ν_{NH} none.

Decarboxylation of 9-methylcarbazole-1,8-dicarboxylic acid (V). 9-Methylcarbazole-1,8-dicarboxylic acid[5] (0.50 g., 0.00186 mole) was decarboxylated as described previously. The white sublimate (0.17 g., 0.00094 mole, 50%), m.p. 84–86°, did not depress the melting point of authentic 9-methylcarbazole[5] (it is interesting to note, however, that the mixed melting point of equal quantities of carbazole and 9-methylcarbazole is 83–87°) and the infrared spectra in Nujol were essentially identical, except for the presence of a medium weak NH or OH band at 3500 cm.$^{-1}$, suggesting contamination by a small amount of carbazole, the *N*-demethylation product.

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A New Synthesis of Benzothiazoline

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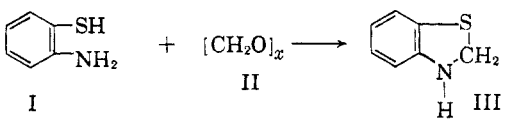
Received April 25, 1960

Although a number of syntheses for benzothiazoline have been reported in the literature,[1–4] none offers the convenience of the method which we report here.

We found that benzothiazoline (III) was formed in good yields by refluxing 2-aminobenzenethiol (I) with paraformaldehyde (II) followed by distillation under reduced pressure.



I II III

EXPERIMENTAL

To 12.5 g. (0.1 mole) of 2-aminobenzenethiol (American Cyanamid, tech. grade) dissolved in 20 ml. of anhydrous methyl alcohol was added a mixture of 4 g. of paraformaldehyde (Eastman Kodak, pract. grade) suspended in 10 ml. of anhydrous methyl alcohol. The mixture was refluxed until the original yellow color disappeared (about 12 hr.).

Upon cooling to room temperature, two distinct layers formed. The bottom layer was withdrawn and distilled. The fraction collected at 146–149°/18 mm. was identified as benzothiazoline. The yield was 75–80% based on 2-aminobenzenethiol.

Identification of the product was accomplished as follows: (a) The infrared spectrum showed an intense nitrogen-hydrogen stretching band at 3.0 μ. (b) The boiling point was identical with that reported,[1,5] in the literature (b.p. 270°). (c) The phenylisocyanate derivative melted at 161–162°. The literature[5] value was 162°.

Acknowledgment. The authors are grateful to the American Cyanamid Co. for graciously supplying 2-aminobenzenethiol.

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Schiff Bases from 4-(4-Aminostyryl)quinoline and Aldose Sugars[1]

CARL TABB BAHNER, NORVELL HUNT, AND LYDIA M. RIVES

Received May 2, 1960

4-(4-Aminostyryl)quinoline (I) reacted readily with 4-dimethylaminobenzaldehyde to form a Schiff base that was less toxic than I.[2] It seemed that aldose sugars might produce similar products and that the sugar moiety might cause the compounds to be water soluble. The use of a small amount of dimethylformamide made it possible to bring the reactants into a homogeneous liquid reaction mixture at the desired temperature, 120–130°. Glyceraldehyde, ribose, galactose(II), glucose(III), lactose, and maltose all seemed to react smoothly under these conditions, but only II formed crystals that were purified readily by recrystallization. The other products tended to precipitate as gels or amorphous solids.

EXPERIMENTAL

Galactose Schiff base of 4-(4-aminostyryl)quinoline. A mixture of 30.0 g. of I and 15.0 ml. of dimethylformamide was heated to 130° to produce a clear solution. This solution was cooled to 110°, 21.6 g. of II was added slowly with stirring, and the mixture was heated 10 min. at 120–130°. The resulting solid mass was washed with benzene and with water to remove excess starting materials. One gram of solid was dissolved in 30 ml. of dimethylformamide, 20 ml. of the solvent was removed by distillation at 60° at 2.5 mm. The bright yellow crystals which formed were recrystallized

(1) This research was supported by a grant from the National Cancer Institute.
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