thesis from 9-anthraldehyde described by Cook, Ludwiczak and Schoental.[4]

Experimental[5]

β-(9-Anthranyl)-propionic Acid (II).—A 1-l., three-necked flask with ground glass joints was fitted with a dropping funnel, condenser and mercury-sealed stirrer. The air in the system was replaced by dry nitrogen and 200 ml. of *t*-butyl alcohol[6] was added. After 4.88 g. (0.125 mole) of potassium was dissolved in the alcohol, 19.4 g. (0.1 mole) of anthrone,[7] m.p. 154–155°, was added with the aid of 10 ml. of *t*-butyl alcohol and the solution was stirred for one hour at room temperature. To this reddish-brown solution of potassium anthranolate was added dropwise over a period of one hour a solution of 7.3 ml. (0.11 mole) of acrylonitrile (Eastman Kodak Co.) in 40 ml. of anhydrous *t*-butyl alcohol. During the addition of the nitrile a bright red precipitate separated. The solution was refluxed for two hours and a clear deep red colored solution was obtained. After the addition of 11 ml. of concentrated hydrochloric acid (sp. gr. 1.18) in 225 ml. of water the *t*-butyl alcohol was removed by distillation during which time an additional 100 ml. of water was added. After the removal of 350 ml. of distillate the contents remaining in the flask were cooled and the aqueous layer was separated from a brown oil by decantation. The oily nitrile was refluxed for two hours with 100 ml. of concentrated hydrochloric acid during which time a solid acid separated. After cooling, the hydrochloric acid was removed with the aid of a sintered glass filter stick and the solid remaining in the flask was washed with 100 ml. of water. The solid acid was dissolved in 360 ml. of concentrated ammonium hydroxide and 240 ml. of water and the resulting solution was heated at 90–95° in an oil-bath for four hours with 60 g. of zinc dust (activated with copper sulfate). During the reduction the solution changed in color from reddish-orange to pale yellow. The cooled reaction mixture was filtered to remove excess zinc and the filtrate was extracted once with ether. The aqueous layer was acidified with hydrochloric acid and a tan oil separated which solidified on standing. The solid was filtered, washed with water and dried to give 22.5 g. (90% yield) of β-(9-anthranyl)-propionic acid (II), m.p. 190–193° (reported[4] m.p. 191–192°), as pale yellow crystals. Recrystallization of a small sample of the crude acid from glacial acetic acid gave pale yellow prisms, m.p. 194–195°.

In a larger run using 0.3 mole of anthrone and *t*-butyl alcohol (Eastman Kodak Co.) which had not been dried over sodium the yield of crude acid obtained was 71.3 g. (95% yield), m.p. 188–193°. When methyl acrylate was substituted for the nitrile in the condensation the yield of β-(9-anthranyl)-propionic acid (II) was lowered to 60%.

β-(9,10-Dihydro-9-anthranyl)-propionic Acid (III).—Twenty grams (0.08 mole) of crude β-(9-anthranyl)-propionic acid (II), m.p. 190–193°, was dissolved in 500 ml. of *n*-amyl alcohol (Eastman Kodak Co., practical grade) in a 1-l. round-bottomed flask equipped with a reflux condenser. To this refluxing solution was added 16.6 g. (0.72 mole) of sodium in small pieces over a period of five hours. The *n*-amyl alcohol was removed by steam distillation and the aqueous solution remaining in the flask was filtered and allowed to cool. The sodium salt of the dihydro acid crystallized in glistening plates and was filtered, washed with water, and redissolved in hot water. The resulting solution was acidified with hydrochloric acid to give 15.07 g. (74.5% yield) of almost colorless β-(9,10-dihydro-9-anthranyl)-propionic acid (III), m.p. 137–140° (reported[4] m.p. 139–140°). Acidification of the mother liquor from the crystallization of the sodium salt gave 5.9 g. of a yellow solid, m.p. 120–130°, which upon recrystallization from benzene gave an additional 2.32 g. (11.5% yield) of almost colorless dihydro acid (III), m.p. 134–140°. Recrystallization of a sample of the acid from benzene gave colorless crystals, m.p. 139–140°.

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(4) J. W. Cook, R. S. Ludwiczak and R. Schoental, *J. Chem. Soc.*, 1112 (1950).

(5) All melting points are uncorrected.

(6) Dried by refluxing over and distilling from sodium.

(7) K. H. Meyer, "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p. 60.

5-Ethoxyquinoxaline[1]

BY WILLIAM K. EASLEY[2] AND MICHAEL X. SULLIVAN

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The recent synthesis of 5-hydroxyquinoxaline[3,4] prompts us to report the synthesis of 5-ethoxyquinoxaline which had been prepared as an intermediate in this Laboratory. It was prepared from the known 2,3-dinitrophenetole[5] by catalytic reduction to the intermediate 2,3-diaminophenetole, which was not isolated but condensed with sodium glyoxal bisulfite to form 5-ethoxyquinoxaline. Both 5-ethoxyquinoxaline and copper-5-quinoxalinate have been found to produce 100% inhibition of the standard organism, *Aspergillus niger*, in 250 parts per million concentrations. Further investigation of the fungistatic properties of these compounds is in progress.

Experimental

2,3-Dinitrophenetole.—The method of Blanksma[5] as modified by Verkade and Witjens[6] was not found satisfactory for preparing the desired quantity of product. However, the following procedure was employed to obtain the 2,3-dinitrophenetole in reasonable yield and in a good state of purity. Twenty grams (0.088 mole) of 1-ethoxy-2,3-dinitro-4-aminobenzene[6] was dissolved in 200 ml. of concentrated sulfuric acid; 70 g. of water was added dropwise to the acid solution with mechanical stirring in an ice-bath. The suspension of the sulfate was diazotized at 0–5° with a solution of 6.07 g. (0.088 mole) of sodium nitrite in 25 g. of water, which was added dropwise in about 35 minutes. The diazonium solution was stirred for another hour at the same temperature and poured into a liter of boiling 95% ethanol. The mixture was boiled for 45 minutes, then diluted with enough water to give a final volume of about 4 liters. A dark brown precipitate formed during the dilution and was removed by filtration on a buchner funnel. The yield of the crude product was 13.6 g., m.p. 96–99°. The average yield from seven similar runs was 14.0 g. If further purification is desired, the product can be crystallized from 95% ethanol. For our use the product was not further purified.

5-Ethoxyquinoxaline.—Forty-eight grams (0.226 mole) of 2,3-dinitrophenetole was dissolved in 1800 ml. of 95% ethanol and reduced with hydrogen in the presence of 6 g. of 5% palladium-on-charcoal catalyst. During filtration from catalyst, the solution darkened considerably. To the filtrate was added 100 ml. of 2 *M* acetic acid and 50 ml. of 4 *M* sodium acetate solution. The resulting solution was heated to 60° and poured rapidly into a solution of 67.11 g. (0.226 mole) of sodium glyoxal bisulfite (Carbide and Carbon Chemicals Corp.) in 2 liters of water which had previously been heated to 60° and the mixture was stirred for one hour. It was then cooled in an ice-bath and made strongly alkaline by the addition of 120 g. of sodium hydroxide pellets and 500 g. of sodium carbonate. The mixture separated into two layers, a clear aqueous layer and a dark alcohol–water layer. The layers were separated, and the dark alcohol layer was reduced to less than half its volume at the water-pump. This dark mixture was then recombined with the clear layer, and a dark oil separated which was extracted with a pound of benzene. The benzene extract was dried over anhydrous calcium sulfate. The benzene was then removed at the water-pump, and the residual dark oil was vacuum distilled. The fraction that distilled from 106–117° at 0.5 to 2 mm. was collected. It was brownish-yellow in color and solidified in the receiving flask. Recrystallization from petroleum ether gave a white prod-

(1) Taken from the thesis submitted by William K. Easley in partial fulfillment of the requirements for the Ph.D. degree at The Division of Chemistry, Graduate School, Georgetown University, Washington, D. C.

(2) The Chemstrand Corporation, Marcus Hook, Pennsylvania.

(3) F. E. King, N. G. Clark and P. M. H. Davis, *J. Chem. Soc.*, 3012 (1949).

(4) S. K. Freeman and P. E. Spoerri, *J. Org. Chem.*, **16**, 438 (1951).

(5) J. J. Blanksma, *Rec. trav. chim.*, **27**, 49 (1908).

(6) P. E. Verkade and P. H. Witjens, *ibid.*, **65**, 361 (1946).

uct, m.p. 63–64°. Yield of crude product was 16.9 g., 41.9% of the theoretical yield.

Anal. Calcd. for $C_{16}H_{10}ON_2$: C, 68.94; H, 5.79; N, 16.08. Found: C, 69.11; H, 5.88; N, 16.24.

The reddish-orange salt of 5-ethoxyquinoxaline and methyl iodide was prepared by the procedure of Easley and Bahner,[7] m.p. 214–215° uncor. (with dec.).

Anal. Calcd. for $C_{11}H_{13}ION_2$: N, 8.85. Found: N, 8.60.

The scarlet salt with ethyl iodide was prepared in the same manner, m.p. 146–148° uncor. (with dec.).

Anal. Calcd. for $C_{12}H_{14}ION_2$: N, 8.50. Found: N, 8.22.

Acknowledgments.—The authors wish to thank Dr. E. Mosettig for use of his reduction apparatus and Miss Rita McCollum and Mr. T. S. Barker for microanalyses.

(7) W. K. Easley and C. T. Bahner, THIS JOURNAL, **72**, 3803 (1950).

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Ring Cleavage of 1-Benzenesulfonyl-2-benzylethylenimine with Hydrogen Bromide[1]

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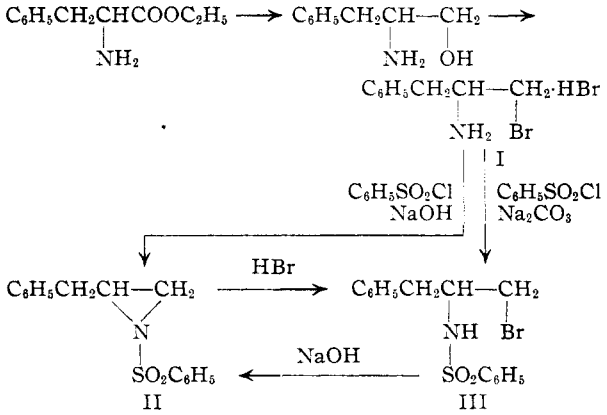
When 1-benzenesulfonyl-2-bromomethylethylenimine reacts with hydrobromic acid, ring cleavage occurs to form 1,3-dibromo-2-benzenesulfonamidopropane. In this process attack of the bromide ion occurs preferentially at the unsubstituted rather than at the substituted carbon of the three-membered ring.[2] We wish to record another example of this mode of cleavage in the production of 1-phenyl-2-benzenesulfonamido-3-bromopropane (III) from the action of hydrobromic acid on 1-benzenesulfonyl-2-benzylethylenimine (II). The



structure of the cleavage product was established by its identity with the product (III) obtained on treating 1-phenyl-2-amino-3-bromopropane hydrobromide (I) with benzenesulfonyl chloride and aqueous sodium carbonate. The ethylenimine compound (II) was prepared by treating the hydrobromide (I) with benzenesulfonyl chloride and aqueous alkali, or by treating 1-phenyl-2-benzenesulfonamido-3-propane (III) with alkali.

(1) Abstracted from a portion of the Thesis submitted by John C. Rockett to the Graduate School of Boston University in partial fulfillment of the requirements for the degree of Master of Arts.

(2) W. J. Gensler, THIS JOURNAL, **70**, 1843 (1948).

Experimental[3]

1-Phenyl-2-amino-3-bromopropane Hydrobromide (I).—*dl*-Phenylalanine ethyl ester was converted to *dl*-phenylalaninol, m.p. 67–68°, by reduction with lithium aluminum hydride.[4]

A sealed tube containing 1.0 g. (0.006 mole) of *dl*-phenylalaninol and 25 ml. of 48% hydrobromic acid was heated at 170–175° for five hours. The dark colored reaction mixture, in which some carbonized material was present, was diluted with 100 ml. of water and was decolorized with charcoal (Nuchar). The resulting water-white, strongly acid solution was taken to dryness under reduced pressure on the steam-bath. The dry residue after crystallization from absolute alcohol weighed 1.27 g. (65%) and melted at 173–176°. A second crystallization (from 3 ml. of absolute alcohol) afforded 0.97 g. (49%) of pure 1-phenyl-2-amino-3-bromopropane hydrobromide, m.p. 174–175°.

Anal. Calcd. for $C_9H_{13}NBr_2$: C, 36.8; H, 4.4. Found: C, 36.7; H, 4.4.

When the reaction was carried out at 100° instead of at 170°, the hydrobromide of *dl*-phenylalaninol was the only material isolated. This salt was prepared in a separate experiment by evaporating a mixture of 1.0 g. (0.0066 mole) of *dl*-phenylalaninol and 25 ml. of 48% hydrobromic acid under reduced pressure, and crystallizing the dry residual solids from ethyl alcohol. The hydrobromide obtained in this way (1.21 g. or 79%) melted at 148–149°, and showed no change in melting point after admixture with the material (m.p. 148–149°) obtained from the reaction at 100°.

Anal. Calcd. for $C_9H_{14}NOBr$: C, 46.5; H, 5.6. Found: C, 46.3; H, 5.3.

1-Benzenesulfonyl-2-benzylethylenimine (II) from 1-Phenyl-2-amino-3-bromopropane Hydrobromide (I).—To a vigorously stirred solution of 1.5 g. (0.0050 mole) of the hydrobromide (I) in 10 ml. of water was added 0.78 ml. (0.0060 mole) of benzenesulfonyl chloride followed immediately by a solution of 1.0 g. (0.0025 mole) of sodium hydroxide in 10 ml. of water. The mixture was stirred for 40 minutes at room temperature. The solids were collected by filtration, washed on the funnel with water and air-dried. The dry material (1.22 g. or 89%; m.p. 54–56°) was taken up in ether, the ether solution was washed with several portions of water, and was dried over sodium sulfate. On crystallizing the oil remaining after the ether solvent had been removed from ethyl alcohol, there was obtained 1.03 g. (75%) of 1-benzenesulfonyl-2-benzylethylenimine, m.p. 55–56°.

Anal. Calcd. for $C_{15}H_{15}NSO_2$: C, 65.9; H, 5.5. Found: C, 65.7; H, 5.6; ash, 0.3.

1-Benzenesulfonyl-2-benzylethylenimine (II) from 1-Phenyl-2-benzenesulfonamido-3-bromopropane (III).—A mixture of 0.5 g. (0.0014 mole) of compound III, 0.4 g. (0.010 mole) of sodium hydroxide and 10 ml. of water was shaken for 15 minutes. The crystalline solids (0.36 g. or 95%; m.p. 53–55°) were collected and crystallized from 5 ml. of ethyl alcohol. The product obtained weighed 0.31 g. (81%), and melted both before and after admixture with the 1-benzenesulfonyl-2-benzylethylenimine prepared as indicated above at 55–56°.

1-Phenyl-2-benzenesulfonamido-3-bromopropane (III) from 1-Benzenesulfonyl-2-benzylethylenimine (II).—A mixture of 10 ml. of 48% hydrobromic acid and 0.40 g. (0.00146 mole) of ethylenimine II was heated on the steam-bath for one hour. Twenty milliliters of water was added, and the cold mixture was thoroughly extracted with ether. The ether extract, after washing with water, was dried over anhydrous sodium sulfate. Removal of the solvent left a residual oil (0.44 g.) which, after crystallization from ethyl alcohol, furnished 0.34 g. (65%) of white crystalline 1-phenyl-2-benzenesulfonamido-3-bromopropane, m.p. 22–23°.

Anal. Calcd. for $C_{15}H_{16}NSO_2Br$: C, 50.8; H, 4.5. Found: C, 50.6; H, 4.6.

The mixed melting point with the same material prepared as described below was 22–23°.

(3) Melting points are uncorrected. The elementary analyses were carried out by Carol K. Fitz, 115 Lexington Avenue, Needham Heights 94, Mass.

(4) P. Karrer, P. Portmann and M. Suter, *Helv. Chim. Acta*, **31**, 1617 (1948); M. C. Rebstock, *et al.*, THIS JOURNAL, **73**, 3666 (1951).