N-β-Bromoethylaniline Hydrobromide

By William M. Pearlman

Although a product designated[1,2] as N-β-bromoethylaniline hydrobromide has been reported to be formed by converting N-phenylethanolamine into its hydrobromide at 100° with gaseous hydrobromic acid and then heating to 150–160°, no identification was made and no yields were given. In addition, the indicated procedures are cumbersome. It was found that the desired product could be obtained in 85% yield from β-hydroxyethylaniline and hydrobromic acid by a slight modification of the procedure of Cortese.[3]

Experimental

β-Hydroxyethylaniline (100 g.) was precooled to 0° and 310 ml. of precooled (0°) 48% hydrobromic acid was added dropwise with stirring and cooling. When all of the hydrobromic acid had been added the mixture was distilled with an efficient fractionating column until a constant boiling distillate was reached. The residue was cooled slightly, placed in a large, open dish in a vacuum desiccator and evacuated with a water jet overnight. The resulting slurry was filtered and the solid recrystallized from absolute ethanol. The yield of nearly colorless needles was 180 g. (85.5%), m. p. 136–139°. A sample recrystallized from benzene was colorless, m. p. 137–138°.

Anal. Calcd. for $C_8H_{11}Br_2N$: C, 34.19; H, 3.95; N, 4.99. Found: C, 33.87; H, 4.16; N, 4.97.

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(1) French Patent 800,369; abstracted in *C. A.*, **30**, 8241^5 (1936).

(2) Julius v. Braun, *Ber.*, **70**, 979 (1937).

(3) "Organic Syntheses," Coll. Vol. II, 91, ed. by Blatt, John Wiley and Sons, Inc., New York, N. Y., 1943.

Research Laboratories
Parke, Davis & Company
Detroit 32, Michigan
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Oxidation–Reduction Potentials and Ionization Constants of the Reversible Series: Hexahydroxybenzene – Tetrahydroxyquinone – Rhodizonic Acid

By Paul W. Preisler, Louis Berger and Edgar S. Hill

Professor G. Schwarzenbach of the Universität at Zürich has recently called our attention to omission of reference in our publication[7] to the prior work and publication by Schwarzenbach and Suter[6] with the same substances. The oxidation–reduction potentials and ionization constants of this series of related compounds has been reported on several occasions.[1–7] It is regretted that there was no discussion of the work of Schwarzenbach and Suter[4,6] in our publications,[5,7] which oversight resulted from their being no abstract of the thesis of Suter[4] in *Chemical Abstracts* and no indication in the abstract[6a] of their joint publication[6] that they had worked with any compound of the rhodizonic acid series oxidation–reduction systems.

The two reports[6,7] differ mainly in the estimation of the ionization constants of rhodizonic acid. Our constants of $pK_1 = 4.1$ and $pK_2 = 4.5$ should be rejected in favor of those of Schwarzenbach and Suter, who found $pK_1 = 3.15$ and $pK_2 = 4.9$, since our values were estimated from the E_0'–pH curve of the rhodizonic acid–tetrahydroxyquinone system in a range where the curve is quite flat, while their values were determined by colorimetric and photometric methods.

Accepting their constants, 3.15 and 4.9, curves of $E_0' - p$H may be drawn which fit our experimentally determined points reasonably well. These changes do not affect the tetrahydroxyquinone–hexahydroxybenzene curve; the estimated ionization constant of tetrahydroxyquinone being unchanged at $pK_1 = 4.8$. Our E_0' values at $p\mathrm{H} = 0$ become altered: for rhodizonic acid–tetrahydroxyquinone to $E_0' = +0.426$ volt (increase of $+0.016$) and for tetrahydroxyquinone–hexahydroxybenzene to $E_0' = +0.388$ volt (increase of $+0.008$).

These extrapolated values for $p\mathrm{H} = 0$ and our measured potentials agree as well as may be expected for systems of this type with the potentials of Schwarzenbach and Suter. However, we experienced no difficulties in obtaining rapidly adjusting stable potentials in the entire pH range studied from 3.5 to 9.9. Therefore, where the slopes of our E_0'–pH curves are sufficiently well established, as for the tetrahydroxyquinone–hexahydroxybenzene system, we consider the ionization constants reported,[7] for tetrahydroxyquinone $pK_2 = 6.8$ and for hexahydroxybenzene $pK_1 = 9.0$, to be reliably estimated.

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(1) P. W. Preisler, E. S. Hill, E. Ronzoni and L. Young, *J. Biol. Chem.*, **123**, XCV (1938).

(2) G. E. Carpeni, Thesis, Paris, 1938.

(3) P. W. Preisler, *Cold Spring Harbor Symposia on Quantitative Biology*, **7**, 94 (1939).

(4) H. Suter, Thesis, Zürich, 1940.

(5) P. W. Preisler and L. Berger, paper presented at the meeting of the American Chemical Society, April, 1941; This Journal, **64**, 67 (1942).

(6) G. Schwarzenbach and H. Suter, *Helv. Chim. Acta*, **24**, 617 (1941).

(6a) *Chemical Abstracts*, **35**, 7806 (1941).

(7) P. W. Preisler, L. Berger and E. S. Hill, This Journal, **69**, 326 (1947).

Department of Biological Chemistry
Washington University Medical School
St. Louis 10, Mo.
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Freezing Point Depression of Sulfuric Acid by Siloxanes

By Fraser P. Price

Since sulfuric acid is used as an equilibrating agent in the preparation of silicones,[1] it is of interest to investigate the kinds of particles produced when siloxanes are dissolved in this acid. It was hoped that such an investigation would shed some light on the mechanism of siloxane rearrangement.

The molal freezing point depressions and the van't Hoff "*i*" factors in approximately 100% sulfuric acid were determined by the method of Hammett and Deyrup.[2] The only departure from their method was that the weight of solvent

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(1) Patnode and Wilcock, *ibid.*, **68**, 358 (1946).

(2) Hammett and Deyrup, *ibid.*, **55**, 1900 (1933).