

mole) of sodium hydroxide in 200 cc. of water. The free acid was isolated and purified by distillation. The yield of unsaturated acid distilling at 115–118° (1 mm.) was 58 g. (96.6%); $n_D^{24.5}$ 1.4816.

Anal. Calcd. for $C_{11}H_{10}O_2$: C, 72.49; H, 9.96. Found: C, 72.47; H, 10.47.

The *p*-bromophenacyl ester melted at 68–69°.

Anal. Calcd. for $C_{19}H_{20}O_2Br$: C, 60.16; H, 6.11. Found: C, 60.25; H, 6.10.

γ -Cyclohexylvaleric Acid (II).—To a solution of 58 g. of γ -cyclohexylpentenoic acid in 300 cc. of ethanol there was added 10 cc. of Raney nickel catalyst. The hydrogenation was carried out in a conventional high pressure bomb at an initial pressure of 2,000 lb. At 150°, hydrogen adsorption became very rapid and was complete in approximately one hour. After filtering off the nickel catalyst, the alcohol was removed *in vacuo* and the residue taken up in ether. The ether solution was washed and the ether evaporated off. The residue was distilled; yield 52 g., b. p. 120–122° (2 mm.), $n_D^{24.4}$ 1.4780.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 72.27; H, 11.09.

SCHERING CORPORATION
CHEMICAL RESEARCH DIVISION
BLOOMFIELD, NEW JERSEY RECEIVED MARCH 11, 1947

Unsaturated Nitriles. V. The Preparation of *trans*-Cinnamitrile and Methacrylonitrile by Oxime Dehydration¹

BY DAVID T. MOWRY AND RICHARD R. MORNER

The acetic anhydride dehydration of aldoximes provides a convenient laboratory synthesis of α,β -unsaturated nitriles. Certain advantages of the method do not appear to be mentioned in the literature.

Cinnamaldehyde oxime has been dehydrated by this method to cinnamitrile.² Our experiments indicate that the product is the pure *trans*-isomer which has previously been obtained only after laborious fractional distillation and fractional crystallization of the mixture obtained from the reaction between benzaldehyde and cyanacetic acid.³

In contrast to the tedious, unsatisfactory methods in the literature,^{4,5} the preparation of methacrylonitrile from methacrolein by dehydration of the oxime proceeds smoothly in 57% yield. The intermediate oxime need not be isolated. We have also obtained a very pure product by the phosphorus pentoxide dehydration of methacrylamide, but the preparation by three steps from either acetone or methacrylic acid is tedious.

Experimental

trans-Cinnamitrile.—Cinnamitrile prepared according to Posner,³ in 84% yield has physical properties, b. p. 137° (16 mm.), n_D^{20} 1.6005, f. p. 22.5°, which agree well with those found by Ghosez,³ n_D^{20} 1.6032, m. p. 22.8–

23.6°, for a sample of pure *trans*-cinnamitrile. Prepared by the phosphorus pentoxide dehydration of *trans*-cinnamamide the *trans*-cinnamitrile, b. p. 140–141° (18 mm.), n_D^{20} 1.6000, f. p. 22.4°, is obtained in 64% yield.

Methacrylonitrile.—Technical 93% methacrolein (453 g., 6 moles) was added slowly to a solution of 487 g. (7.0 moles) of hydroxylamine hydrochloride and 484 g. (3.5 moles) of potassium carbonate in 650 cc. of water. The temperature was kept below 10° by stirring and cooling. The aqueous layer was separated, extracted with ether and the extract combined with the main portion.

After drying over anhydrous sodium sulfate, the material was distilled to give a 76% yield of methacrolein oxime,⁶ b. p. 46–47° (9.5 mm.), n_D^{20} 1.4815.

A very viscous thermally unstable residue (115 g.) remained in the distillation flask. Care must be taken to stop the distillation when the mixture becomes viscous and the temperature begins to rise; otherwise an explosive decomposition will result. The use of sodium hydroxide instead of potassium carbonate resulted in only a 33% yield of distilled oxime.

Methacrolein oxime (350 g., 4.12 moles) was slowly added to an excess of acetic anhydride (613 g., 6.0 moles) with stirring at 110–125°. The product was then slowly distilled through a 50-cm. Vigreux column at a 10:1 reflux ratio taking the fraction boiling at 88–100°. The crude nitrile was washed with potassium carbonate solution, dried over calcium chloride and refractionated to give 210 g. of methacrylonitrile,⁷ b. p. 89–91°, n_D^{20} 1.3977. This represents a 76% yield, or 57% based on methacrolein.

Approximately the same over-all yield was obtained if the crude, undistilled oxime was used for the dehydration. This, of course, avoided any difficulties with the oxime distillation.

In an alternate synthesis 85 g. (1.0 mole) of methacrylamide, m. p. 108–109° (obtained by the reaction of methacrylyl chloride and liquid anhydrous ammonia) and 186 g. (1.3 moles) of phosphorus pentoxide were thoroughly mixed and distilled. Methacrylonitrile, b. p. 89–91°, n_D^{20} 1.3999, was obtained in 85% yield.

(6) Hey, Nicholls and Pritchett, *J. Chem. Soc.*, 47 (1944), give b. p. 85° (14 mm.).

(7) Burns, Jones and Ritchie, ref. 5, give b. p. 90.0–90.5°.

CENTRAL RESEARCH LABORATORIES
MONSANTO CHEMICAL COMPANY.

DAYTON, OHIO RECEIVED MARCH 6, 1947

The Basicity of Phenylmercuric Hydroxide

BY RICHARD M. SCHRAMM

Phenylmercuric hydroxide has been reported to be strongly basic, turning red litmus blue and displacing ammonia from ammonium salts.¹ On the other hand, the chloride has been reported to be acidic, to evolve carbon dioxide from solutions of sodium carbonate,² and to be soluble in alkalis,³ while aqueous solutions of basic phenylmercuric nitrate, $C_6H_5HgNO_3 \cdot C_6H_5HgOH$, have been found to have a pH of 4.3.⁴ In view of these contradictory reports it was decided to determine the pH of a solution of the hydroxide.

The hydroxide was prepared from a pure commercial sample of basic phenylmercuric nitrate, m. p. 181–182°, by dissolving 40 g. in 4 liters of water containing 14 g.

(1) Otto, *J. prakt. Chem.*, [2] 1, 179 (1870).

(2) Dreher and Otto, *Ann.*, 164, 126 (1870); cf. Otto, *J. prakt. Chem.*, [2] 29, 137 (1884).

(3) Bradner, U. S. Patent 2,165,533 (July 11, 1939).

(4) Grave, Harris and Christiansen, *J. Am. Pharm. Assoc.*, 25, 752 (1936).

(1) Preceding paper, Mowry, *THIS JOURNAL*, 69, 573 (1947).

(2) Posner, *Ann.*, 339, 117 (1912).

(3) Ghosez, *Bull. soc. chim. Belg.*, 41, 477 (1932).

(4) Pieroh, U. S. Patent, 2,174,756 (1939); Loder, U. S. Patent 2,175,810 (1939); Kautter and Grafe, U. S. Patent 2,210,320 (1940); Marple, Evans and Borders, U. S. Patent 2,375,016 (1945); Kung, U. S. Patent 2,373,190 (1945); Haas, U. S. Patent 2,384,737 (1945).

(5) Burns, Jones and Ritchie, *J. Chem. Soc.*, 400, 714 (1935); British Patent 424,885 (1935).

(5 to 6 equivalents) of sodium hydroxide, filtering and evaporating the filtrate to 300 cc. The resulting phenylmercuric hydroxide, filtered off and dried, weighed 32 g. (86% yield) and melted at 226–227°.

Anal. Calcd. for C_6H_5HgOH : Hg, 68.07. Found: Hg, 67.93.

Recrystallization of this product from water did not produce any observable further purification.

A saturated solution measured at about 25° with a Coleman pH meter, Model 3B, gave values in the range pH 7.0 to 7.5. The solubility of phenylmercuric hydroxide at 0° per 100 cc. was found to be 0.52 g. in water, 0.48 g. in 0.0185 *N* sodium hydroxide and 0.36 g. in 1 *N* sodium hydroxide.

The previously reported solubility of phenylmercuric chloride in alkali was also observed in this Laboratory.

These observations indicate that phenylmercuric hydroxide is a very weak base but does not ionize as an acid. The solubility of the chloride in alkali is then explained by the formation of the moderately soluble and almost completely undissociated free base. In agreement with this, at least when an excess of sodium chloride is added, a solution of the hydroxide titrated with standard perchloric acid, using phenolphthalein as an indicator, requires 0.98 equivalent of the acid. Similarly, a solution of basic phenylmercuric nitrate, $C_6H_5HgNO_2 \cdot C_6H_5HgOH$, with phenolphthalein as indicator, requires an amount of sodium hydroxide equivalent to the nitrate present.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

RECEIVED FEBRUARY 17, 1947

Polarographic Behavior of Some Organic Compounds

By K. G. STONE¹

In order to answer some questions about the polarographic behavior of some sulfur and halogen compounds in the literature, the reducibility of the compounds described below was measured.

Experimental

A Leeds and Northrup Electrochemograph equipped with the cell arrangement described by Furman, Bricker and Whitesell² was used for the polarographic measurements. The work was done at room temperature (24 to 25°). The capillary was a 10-cm. length of selected marine barometer tubing and had the following characteristics: $m = 0.8173$ mg. per second; $m^2/v^{1/2}$ was 1.22 in acid solutions and 1.17 in neutral and alkaline solutions at the potential where the diffusion current started; the head of mercury was 46.5 cm. Oxygen was removed from all solutions polarographed by passing purified nitrogen for fifteen minutes. Polarograms were taken at $1/30$ sensitivity unless otherwise indicated.

The buffer solutions used were prepared by dissolving 0.25 mole of the first material in 600 ml. of distilled water neutralizing with a concentrated solution of the second material to the desired pH measured against the glass electrode, and diluting to 1000 ml.: acetate pH 4 and 5, acetic acid and sodium hydroxide; phosphate pH 6, 7, 8, 11 and 12, potassium dihydrogen phosphate and sodium hydroxide; acetate pH 7 and 8, ammonium hydroxide and acetic acid; borate pH 8 and 11, boric acid and sodium hydroxide; ammonia pH 9 and 10, ammonium hydroxide and hydrochloric acid; tartrate pH 11, tartaric acid and sodium hydroxide; 0.25 *M* potassium chloride was made up directly. In all cases, polarograms of the buffers showed no appreciable amount of reducible material before buffer breakdown.

(1) Present address: Sun Chemical Corporation, New York 13, N. Y.

(2) Furman, Bricker and Whitesell, *Ind. Eng. Chem., Anal. Ed.*, **14**, 333 (1942).

Dibenzyl sulfoxide, benzmorpholide and benzthiomorpholide were supplied in pure form by Robert Brown and Dr. Gregg Dougherty and were not further purified. Carbon tetrabromide was prepared by the procedure of Brisco, Peel and Rowlands³ from bromoform and hypobromite. The sample was kept in a desiccator over calcium chloride to slow down decomposition. Paragon carbostyryl was recrystallized three times from 50% ethanol and dried in a vacuum over concentrated sulfuric acid. Standard solutions of these materials were made as follows:—carbostyryl, 1.0 mg. per ml. in 20% ethanol; benzmorpholide, 1.0 mg. per ml. in 5% ethanol; benzthiomorpholide, 0.50 mg. per ml. in 15% ethanol; dibenzyl sulfoxide, 1.0 mg. per ml. in 15% dioxane; carbon tetrabromide, 2.0 mg. per ml. in 30% ethanol. The solutions polarographed were made by mixing 10.0 ml. of buffer with 5.0 ml. of standard solution, adding maximum suppressor if necessary, and diluting to 25.0 ml.

Preliminary experiments showed that amounts of organic solvents such as ethanol or dioxane up to about 6% by volume could be tolerated without any appreciable effects on the pH of the buffer or the half-wave potentials. It was further found that about 1% by volume of organic solvent was helpful in that the residual current was almost eliminated.

Results

It was found that carbostyryl (2-hydroxyquinoline) was reducible, but reasonable waves were found only in the borate buffer of pH 8 and potassium chloride. In both cases, the half-wave potential was estimated to be -1.9 volts vs. the saturated calomel electrode, but there is some uncertainty since the buffer decomposition wave came very soon after the reduction wave. This behavior was most unexpected by comparison with the relatively low half-wave potentials for 8-hydroxyquinoline.⁴

Carbon tetrabromide was found to be reducible, but in all cases the buffer decomposition overlapped and made a measurement impossible. This was not out of line with the reported measurements on carbon tetrachloride.⁵

TABLE I
POLAROGRAPHIC REDUCTION OF BENZTHIOMORPHOLIDE
0.48 mmolar in 2% ethanol

Buffer	pH	$E_{1/2}$, v. vs. S. C. E.	I , ma.
Acetate	4.0	-1.16	3.92
Acetate	5.0	1.16	3.68
Acetate	7.0	1.55	3.92
Acetate	8.0	1.57	4.00
Phosphate	8.0	1.64	3.60
Borate	8.0	1.71	3.04
Ammonia	9.0	1.56	3.84
Ammonia	10.0	1.62	3.76
Tartrate	11.0	1.59	2.56*
Phosphate	11.0	1.69	2.80
Borate	11.0	1.70	3.12
Phosphate	12.0	1.64	2.48
Potassium chloride	..	1.60	3.28

* Wave formation poor.

(3) Brisco, Peel and Rowlands, *J. Chem. Soc.*, 1766 (1929).

(4) Zan'ko, *Dokladi Akad. Nauk. URSR*, 27–35 (1940); Caruthers, *Ind. Eng. Chem., Anal. Ed.*, **18**, 412 (1942); Stone and Furman, *ibid.*, **16**, 696 (1944).

(5) Matheson and Nichols, *Trans. Electrochem. Soc.*, **73**, 193 (1938).