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%); $n^{24.5}$ 1.4816.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.47; H, 10.47.

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

Anal. Calcd. for $C_{19}H_{23}O_3Br$: 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.), $n^{24.4}$ 1.4780.

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

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Unsaturated Nitriles. V. The Preparation of *trans*-Cinnamonitrile and Methacrylonitrile by Oxime Dehydration[1]

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 cinnamonitrile.[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 cyanoacetic 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*-Cinnamonitrile.**—Cinnamonitrile prepared according to Posner,[2] in 84% yield has physical properties, b. p. 137° (16 mm.), n^{25}D 1.6005, f. p. 22.5°, which agree well with those found by Ghosez,[3] n^{20}D 1.6032, m. p. 22.8–23.6°, for a sample of pure *trans*-cinnamonitrile. Prepared by the phosphorus pentoxide dehydration of *trans*-cinnamamide the *trans*-cinnamonitrile, b. p. 140–141° (18 mm.), n^{25}D 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^{25}D 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^{25}D 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^{25}D 1.3999, was obtained in 85% yield.

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

[2] Posner, *Ann.*, **389**, 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).

[6] Hey, Nicholls and Pritchett, *J. Chem. Soc.*, 47 (1944), give b. p. 65° (14 mm.).

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

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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 alkalies,[3] while aqueous solutions of basic phenylmercuric nitrate, $C_6H_5HgNO_3 \cdot C_6H_5HgOH$, have been found to have a *p*H of 4.3.[4] In view of these contradictory reports it was decided to determine the *p*H 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.

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

[2] Dreher and Otto, *Ann.*, **154**, 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).