TABLE IV

COMPOSITION OF ORIGINAL SOLUTION AND OF MOTHER LIQUOR EQUILIBRIUM WITH SODIUM SULFAMATE

Expt.	Original solution % H_2O	Original solution % NaCl	Mother liquor % H_2O	Mother liquor % NaCl	% H_2O in the solid, by calculation
1	31.22	3.880	36.85	4.539	−1.93
2	34.64	2.814	37.14	3.026	+1.46
3	35.83	7.125	38.42	7.627	−1.00
4	28.23	3.745	37.60	5.033	+1.00
5	28.70	3.115	36.88	4.043	+1.23

The results clearly indicate that the solid phase above the transition point is the anhydrous salt.

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γ-Isopropyl and γ-Cyclohexyl Valeric Acids

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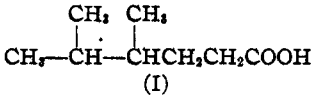
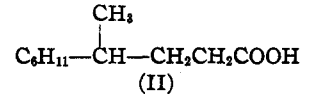
In connection with some experimental work in progress in these laboratories, it was necessary to prepare γ-isopropyl (I) and γ-cyclohexyl valeric acids (II).



(I)



(II)

The preparation of several γ-substituted alkanoic acid esters has been reported recently by Cason and co-workers.[2] According to the method of these workers, γ-substituted alkenoic acid esters, obtained from the corresponding γ,γ-disubstituted butyrolactones, were reduced catalytically to the corresponding saturated esters using platinum oxide catalyst. In our studies, attempts to reduce the ethyl ester of γ-isopropyl and γ-cyclohexyl pentenoic acids using platinum oxide catalyst failed completely. It was found, however, that these unsaturated acids, without further purification, could be reduced readily by nickel–aluminum alloy in alkaline solution according to the method used in these laboratories,[3] or catalytically, using Raney nickel. The presence of sulfur compounds apparently did not interfere with these reductions.

Experimental

γ-Methyl-γ-isopropylbutyrolactone.—This lactone was prepared essentially as described for the *n*-propyl analog.[2] A solution of isopropylmagnesium bromide in 500 cc. of ether was prepared in the usual manner from 72.9 g. (3.0 atoms) of magnesium and 230 cc. (2.45 moles) of isopropyl bromide. A portion of the solvent (200 cc.) was distilled off, the solution cooled, diluted with 300 cc. of anhydrous benzene and then added dropwise to a stirred solution of 317 g. (2.2 moles) of ethyl levulinate in 1.2 liters of benzene cooled to −5°. After decomposing the complex, the organic layer was separated, washed with water, 5% sodium bicarbonate solution, water, saturated sodium chloride solution and then dried over anhydrous sodium sulfate. The solvent was removed and the residue fractionated using an air-cooled Vigreux column 45 cm. in length. After a forerun of ethyl levulinate, the lactone distilled at 60–62° (1 mm.); yield 110 g. (35.1%).

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.58; H, 9.92. Found: C, 67.41; H, 10.29.

γ-Isopropylvaleric Acid (I).—Seventy and three-tenths grams (0.5 mole) of the above lactone and 99 cc. (1.5 moles) of thionyl chloride in 100 cc. of anhydrous benzene were refluxed on a steam-bath for three hours. The resulting solution was then added to a stirred solution of alcoholic hydrogen chloride at 0°. The solvents were removed and the residue heated under reflux at 185–190° for one and one-half hours and then distilled, b. p. 84–87° (10 mm.).

The crude unsaturated ester[4] was saponified by dissolving in 100 cc. of ethanol and refluxing with 200 cc. of 20% aqueous sodium hydroxide. After removing the ethanol, a solution of 60 g. of sodium hydroxide dissolved in 300 cc. of water was added, followed by the addition of 50 g. of nickel–aluminum alloy in the course of two to two and one-half hours. The saturated acid was isolated in the usual manner and distilled; b. p. 80–82° (1 mm.), $n^{24.5}$ 1.4315, yield 46 g. (64%).

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.19. Found: C, 66.79; H, 11.10.

The *p*-bromophenacyl ester melted at 56.0–57.5° after recrystallization from dilute alcohol.

Anal. Calcd. for $C_{16}H_{21}O_3Br$: C, 56.31; H, 6.20. Found: C, 56.42; H, 6.10.

γ-Methyl γ-Cyclohexylbutyrolactone.—A Grignard reagent was prepared from 31.1 g. (1.28 moles) of magnesium and 147.1 cc. (1.20 moles) of cyclohexyl bromide in 400 cc. of ether. The solvent (225 cc.) was removed, the mixture cooled, diluted with 300 cc. of anhydrous benzene and then added dropwise to a stirred solution of 144.1 g. (1.0 moles) of ethyl levulinate[5] in 750 cc. of benzene with cooling to −5°. The complex was then decomposed and the organic layer washed with water, 5% aqueous sodium carbonate, water and dried over anhydrous sodium sulfate. The residue remaining after removal of the solvent was fractionated. After a forerun of 30 g. of ethyl levulinate, there was obtained 70 g. (38.8%) of lactone, b. p. 120–122 (2 mm.), m. p. 55–56°. The yield of lactone was 48.5% based on ester consumed.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.61; H, 10.12.

Ethyl γ-Cyclohexylpentenoate.—A mixture of 109.4 g. (0.6 mole) of lactone and 131 cc. (1.8 moles) of thionyl chloride was refluxed on a steam-bath for three hours; the reaction mixture was then added to alcoholic hydrogen chloride; and, after removal of the solvents, the residue was heated for three hours at 195–200° and distilled. The yield of ester was 84 g. (66.6%), b. p. 91–93° (1 mm.), $n^{24.5}$ 1.4703.

Anal. Calcd. for $C_{13}H_{22}O_2$: C, 74.07; H, 10.50; sap. eq., 266.7. Found: C, 74.09; H, 9.99; sap. eq., 269.

γ-Cyclohexylpentenoic Acid.—The above ester (69.5 g., 0.33 mole) was refluxed for two hours with 40 g. (1.0

(1) Present address: Burroughs-Wellcome & Company, Inc., Tuckahoe, New York.

(2) Cason, Adams, Bennett and Register, THIS JOURNAL, 66, 1764 (1944).

(3) Schwenk, Papa, Whitman and Ginsberg, *J. Org. Chem.*, 9, 175 (1944).

(4) A sample of the saponification mixture was condensed with *p*-bromophenacyl bromide and the crude ester after recrystallization from dilute alcohol gave colorless crystals, m. p. 72–73°. *Anal.* Calcd. for $C_{18}H_{19}O_3Br$: C, 56.65; H, 5.65. Found: C, 56.50; H, 5.88.

(5) In an attempt to improve the yield of the butyrolactone, butyl levulinate was used in place of the ethyl ester. However, the yield of lactone amounted to only 33% of theory with a considerable amount of the butyl levulinate being recovered.

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.

SCHERING CORPORATION
CHEMICAL RESEARCH DIVISION
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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.

(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.

(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).