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Convenient Syntheses of Cyclopropanecarboxylic Acid, Ethyl Cyclopropanecarboxylate, Cyclopropanecarbonitrile, and Nitrocyclopropane

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Simplified procedures for the preparation of four monosubstituted cyclopropanes by 1,3-dehydrohalogenation are reported. Ethyl cyclopropanecarboxylate and cyclopropanecarbonitrile were prepared from ethyl 4-bromobutyrate and 4-iodobutyronitrile, respectively, employing sodium hydride as the base. Cyclopropanecarboxylic acid was prepared by hydrolysis of ethyl cyclopropanecarboxylate. Nitrocyclopropane was obtained from 1-iodo-3-nitropropane and aqueous sodium carbonate.

THE 1,3-DEHYDROHALOGENATION of various compounds is one of the best methods of preparing substituted cyclopropanes. Sodium hydride has been used previously as a base to prepare bicyclobutanes (*3, 15*) and cyclopropanes (*8, 12*) in high yields. This easily handled base and a simple apparatus have been employed here to give good yields of cyclopropanecarboxylic acid, ethyl cyclopropanecarboxylate, and cyclopropanecarbonitrile. In addition, a short scheme for preparing nitrocyclopropane is reported.

The synthesis of ethyl cyclopropanecarboxylate is a two-step scheme starting with γ-butyrolactone. The lactone is converted to ethyl 4-bromobutyrate (*9*) and then to the product with sodium hydride, in an over-all 76% yield. Sodium hydride is easier to handle, the work-up is easier, and the yields are higher than with other bases (*10, 13*). The ester can be hydrolyzed to provide a high-yield route to cyclopropanecarboxylic acid. This over-all three-step synthesis gives a 68% yield, as compared with 33% for the two steps of the most frequently used preparation (*11*).

The synthesis of cyclopropanecarbonitrile is a three-step synthetic scheme starting with 1-bromo-3-chloropropane. This halide is converted to 4-chlorobutyronitrile (*1*), then to 4-iodobutyronitrile, and finally to the product with sodium hydride. Although the over-all yield is less than the *Organic Syntheses* preparation (*14*), the present method employs a very simple apparatus and a more readily handled base.

Nitrocyclopropane has been prepared by a three-step synthetic scheme, starting with readily available 1-bromo-3-chloropropane. The halide is converted to 1-chloro-3-nitropropane, then to 1-iodo-3-nitropropane, and finally to the product with aqueous sodium carbonate (*2*). The major method for preparation has been the vapor phase nitration of cyclopropane, which is not an easy laboratory method (*7*).

An attempt was also made to prepare cyclopropylbenzene by a two-step scheme. The first step was the conversion of 3-phenyl-1-propanol to 1-iodo-3-phenylpropane, with phosphorus and iodine. However, only very small amounts of cyclopropylbenzene were isolated in the reaction of the iodide with sodium hydride in ether or refluxing benzene. No further attempts were made, in view of the established methods in the literature (*5, 6*).

EXPERIMENTAL

Ethyl Cyclopropanecarboxylate. To a 3-liter flask were added 67.2 grams (40.3 grams, 1.7 moles of sodium hydride) of a 60% sodium hydride dispersion in mineral oil (Metal Hydrides, Inc., Beverly, Mass.) and 300 ml. of anhydrous ether. This mixture was stirred magnetically for one hour and the ether removed by decantation. This process removed the mineral oil from the sodium hydride. To the washed hydride was added 1000 ml. of fresh anhydrous ether. The mixture was stirred magnetically as 195 grams (1.00 mole) of ethyl 4-bromobutyrate (*9*) was added. A reflux condenser and drying tube were added. There was an immediate evolution of hydrogen. The resulting slurry was stirred for 36 hours, after which time the reaction was essentially complete, as indicated by gas chromatography (Beckman GC-2, 6-foot silicone, Beckman 17449). The reaction mixture was suction-filtered through a coarse sintered glass filter and then through a fine one to remove the sodium bromide and excess sodium hydride. The solids were washed with two 50-ml. portions of ether, and then were added immediately to ethanol to destroy the sodium hydride. The filtrates were combined, and the ether was distilled through a 12-cm. column packed with glass helices. The residue was distilled through a 12-cm. Vigreux column to give 99.4 grams (88%) of ethyl cyclopropanecarboxylate: b.p. 133° to 135° C. (750 mm.), n_D^{23} 1.4182; lit. (*8*) b.p. 132° to 134° C., n_D^{25} 1.4174; NMR (Varian A-60 spectrometer, CCl_4 solvent) τ 8.47 (m,1), 9.17 (m,4), 5.94 (q,2), and 8.78 (t,3).

Cyclopropanecarboxylic Acid. Ethyl cyclopropanecarboxylate was hydrolyzed in aqueous sodium hydroxide, followed by acidification with concentrated hydrochloric acid and extraction with ether, to give a 90% yield of cyclopropanecarboxylic acid: b.p. 81° to 83° C. (12 mm.); lit. (*11*) b.p. 94° to 95° C. (26 mm.); NMR (CCl_4) τ 8.38 (m,1), 9.02 (m,4), and −1.95 (s,1).

4-Iodobutyronitrile. To a 3-liter flask fitted with a reflux condenser and drying tube were added 1700 ml. of acetone, 582 grams (3.88 moles) of sodium iodide, and 200.8 grams (1.94 moles) of 4-chlorobutyronitrile (*1*). The contents were heated under reflux for 48 hours with magnetic stirring. The acetone was removed under reduced pressure, water was added to dissolve the solids, and the layers were separated. The aqueous layer was extracted four times with 100-ml. portions of ether. The combined organic layers were dried over magnesium sulfate. The ether was removed under reduced pressure to give a dark red residue of 339 grams (90%) of 4-iodobutyronitrile, which was used directly without further purification.

Cyclopropanecarbonitrile. Sodium hydride was allowed to react with 4-iodobutyronitrile for 22 hours, as described in the ethyl cyclopropanecarboxylate preparation, to give a 44% yield of cyclopropanecarbonitrile: b.p. 31° C. (17 mm.) or 70° to 72° C. (87 mm.), the receiver cooled in a dry ice–acetone bath, n_D^{23} 1.4201; lit. (*14*) b.p. 69° to 70° C. (80 mm.) and lit. (*4*) n_D^{25} 1.4204; NMR (CCl_4) τ 8.64 (m,1), and 8.98 (m,4). The reaction of sodium hydride with 4-chlorobutyronitrile in ether at 25° C. and refluxing tetrahydrofuran gave only small amounts of cyclopropanecarbonitrile. Polymer was the primary product in the THF reaction, and dilution did not solve this problem.

1-Chloro-3-nitropropane. Into a 3-liter three-necked flask fitted with a stirrer and thermometer were placed 189 grams (1.2 moles) of 1-bromo-3-chloropropane and 460 ml. of dimethyl sulfoxide. The solution was cooled with an ice bath, and 82.8 grams (1.2 moles) of sodium nitrite (dried for four hours at 110° C.) was added over a period of 20 minutes, during which the temperature remained about 18° C. Two minutes after completing the addition of the sodium nitrite, a solid suddenly formed, accompanied by a rapid rise in temperature. During the next 45 minutes, cooling and stirring were maintained as the temperature climbed to 55° C. (30 minutes) and then dropped to 25° C. Water (1200 ml.) was added to dissolve the solids, and the reaction mixture was extracted seven times with 225-ml. portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate, and the ether was removed by distillation. The residue was distilled through a 12-cm. Vigreux column to give 61.0 grams of mainly unreacted 1-bromo-3-chloropropane: b.p. up to 75° C. (25 mm.), 19.1 grams of mainly the chloro nitrite ester: b.p. 81° to 98° C. (22 mm.), and 36.5 grams (25%) of 1-chloro-3-nitropropane (85% pure by gas chromatography): b.p. 98° to 110° C. (22 mm.); NMR (CCl_4) τ 5.42 (t,2,CH_2NO_2), 6.32 (t,2,CH_2Cl), and 7.45 (m,2). The residue consisted of a higher-boiling material, presumably 1,3-dinitropropane. An increase in the molar ratio of sodium nitrite to 1-bromo-3-chloropropane gave no larger yield of desired product, but increased the amount of 1,3-dinitropropane instead.

1-Iodo-3-nitropropane. Sodium iodide was allowed to react with 1-chloro-3-nitropropane in the manner described for the 4-iodobutyronitrile preparation to give an 87% yield of 1-iodo-3-nitropropane, which was used directly, without further purification. Gas chromatographic analysis showed this material to contain 60% of the iodide and 10% of unreacted chloride.

Nitrocyclopropane. Into a 250-ml. two-necked flask fitted with a steam inlet tube and a condenser were placed 55.0 grams (0.256 mole) of 1-iodo-3-nitropropane and a solution of 13.6 grams of sodium carbonate in 41 ml. of water. Steam was admitted to the flask, and 130 ml. of steam distillate was collected over a one-hour period. The distillate was extracted twice with 100-ml. portions of ether. The ether was removed by distillation and the residue (4.0 grams) distilled to give 3.7 grams (17%) of nitrocyclopropane: b.p. 77° to 81° C. (58 mm.), n_D^{23} 1.4416; lit. (*7*) b.p. 66° to 68° C. (58 mm.), n_D^{20} 1.4395; NMR (CCl_4) τ 5.71 (m,1), 8.47 (m,2), and 8.77 (m,2). Gas chromatographic analysis indicated the material to be of 95% purity. The reaction of sodium hydride with 1-chloro-3-nitropropane in ether at 25° C. and 1-iodo-3-nitropropane in ether at 25° C. and refluxing ether gave no nitrocyclopropane. Some nitrocyclopropane could be obtained from the reaction of sodium hydride with 1-iodo-3-nitropropane in refluxing benzene, but the major product was a polymer.

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