1.60) with stirring at room temperature according to the directions for the preparation of 6-ketocholestanyl acetate.[3] The reaction flask was then cooled in an ice–salt-bath and the remaining nitric acid mixture added with vigorous stirring during one hour. Stirring was continued for an additional half-hour and then the solution was poured into ice and water. The yellow precipitate was filtered, washed well with water and air-dried, m.p. 120–125° (dec.).

The crude nitrate was directly reduced in acetic acid solution (100 cc.) by adding 12.5 g. of zinc dust and heating on the steam-bath for two hours and then under reflux for 10 hours. After dilution with water the product was isolated by ether extraction and the resulting brown oil obtained after removal of the solvent was directly hydrolyzed with alcoholic hydrochloric acid for 1.5 hours. On working up the reaction only 520 mg. of crude oil was obtained, which was purified by chromatography on alumina in 25% benzene–hexane solution. The fraction eluted with 100% benzene gave 190 mg. of material, m.p. 174–175° after recrystallization from aqueous methanol. A mixture of this material with that isolated from the oxidation of androstanediol diacetate (m.p. 177–178°) melted at 173–176°.

Isolation of 3β,5,17β-Androstanetriol 3,17-Diacetate.—Fraction 3 of the previously mentioned chromatogram of the oxidation products of androstanediol diacetate was recrystallized from hexane and 1.6 g. (5.3%) of material, m.p. 180–182°, $[\alpha]^{23}\text{D}$ −9°.

Anal. Calcd. for $C_{23}H_{36}O_5$: C, 70.4; H, 9.3. Found: C, 70.2; H, 9.5.

Since the physical properties of this compound were the same as those of the androstane-3β,5α,17β-triol 3,17-diacetate previously described, a mixture of the two substances was made and this showed no depression of the melting point.

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NOTES

Reduction of Acyl Cyanides with Lithium Aluminum Hydride

BY ALFRED BURGER AND EDWIN D. HORNBAKER[1]

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Acyl cyanides have been hydrogenated to primary amino alcohols in good yields[2] but this method has not enjoyed wide use because of its relatively complicated mode of execution. It has now been observed that the same result can be achieved by reduction with lithium aluminum hydride. By this procedure it is also possible to preserve in the amino alcohols such substituents as aromatic halogen atoms which could be hydrogenolyzed in catalytic methods.

The preparation of amino alcohols from acyl cyanides complements related reduction methods of cyanohydrins which lead to amino alcohols[3–6] or amines.[4,7]

Experimental[8]

2-Phenylethanolamine.—A solution of 7.35 g. (0.056 mole) of benzoyl cyanide[9] in 100 ml. of dry ether was added dropwise to a stirred solution of 10 g. (*ca.* 0.26 mole) of lithium aluminum hydride in 300 cc. of ether so that refluxing was maintained. After another four hours of boiling the mixture was decomposed with water, and a 30% sodium hydroxide solution was added in small portions until a granular precipitate appeared. The latter was filtered, washed with ether, and the oily residue from the combined ether layers was distilled under reduced pressure. It yielded 6.5 g. (86%) of a colorless solid which, after recrystallization from benzene–petroleum ether melted at 56.5–58°.[10]

Anal. Calcd. for $C_8H_{11}NO$: C, 70.04; H, 8.08. Found: C, 69.81; H, 8.32.

When in another run only 30% excess of lithium aluminum hydride was used, the yield was reduced to 30%.

The N-benzoyl derivative crystallized from ethanol, m.p. 148–149°.[10]

***p*-Chlorobenzoyl Cyanide.**—A mixture of 65.5 g. (0.374 mole) of *p*-chlorobenzoyl chloride and 40.5 g. (0.45 mole) of cuprous cyanide was heated at 210–220° for one hour and then distilled under reduced pressure. The yield of colorless solid was 24.9 g. (40%), m.p. 37–40°. Redistillation raised the melting point to 41–42.5°.[11]

Anal. Calcd. for C_8H_4ClNO: C, 58.03; H, 2.44. Found: C, 57.76; H, 2.35.

2-(*p*-Chlorophenyl)-ethanolamine.—Reducing 8.3 g. (0.05 mole) of *p*-chlorobenzoyl cyanide with 10 g. (*ca.* 0.26 mole) of lithium aluminum hydride in a total of 300 ml. of dry ether for three hours, and working the reaction mixture up as described above, 7.7 g. (89%) of a colorless solid was obtained which crystallized from benzene, m.p. 93.5–94.5°.

Anal. Calcd. for $C_8H_{10}ClNO$: C, 55.98; H, 5.87. Found: C, 55.82; H, 5.84.

The benzoyl derivative crystallized from ethanol, m.p. 215.5–217.5°.

Anal. Calcd. for $C_{15}H_{14}ClNO_2$: C, 65.34; H, 5.12. Found: C, 65.15; H, 5.34.

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Tetraethyl Pyrophosphite as a Reagent for the Preparation of Anilides

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Tetraethyl pyrophosphite has been shown to be a useful reagent for forming peptide bonds.[1] We have found that it can be conveniently used to prepare anilides in good yield (Table I).

Experimental

Tetraethyl pyrophosphite was prepared as previously described.[1]

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