from *p*-bromobenzenediazomorpholide was refluxed for ten minutes with 1 g. of sodium hydroxide in 10 cc. of water. Ten cc. more of water was added and the solution filtered from a small amount of tar. On making the filtrate acid with concentrated hydrochloric acid, cream-colored needles separated. These needles dissolved in hot concentrated sulfuric acid to give a blue color; a mixed m. p. with a sample of *p*-bromobenzenesulfinic acid showed no depression.

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The Preparation of Cholesteryl *p*-Aminobenzoate

BY DAVID KRITCHEVSKY

In the preparation of cholesteryl *p*-aminobenzoate by reduction of cholesteryl *p*-nitrobenzoate, Shriner and Ko[1] were unable to effect reduction using iron, tin and amalgamated zinc with hydrochloric acid and finally reduced the nitro compound catalytically.

The reduction by chemical means was re-investigated and a suitable procedure using iron powder and acetic acid was found.

Experimental Part

Cholesteryl *p*-Nitrobenzoate.—The esterification was carried out by the method of Einhorn and Hollandt.[2] Cholesterol (25 g.) and *p*-nitrobenzoyl chloride (14.5 g.) (purified by vacuum distillation) were weighed into a 400-cc. beaker and 50 cc. of pyridine was added. The mixture was slowly heated to boiling; the acid chloride and the cholesterol dissolving during the heating. The solution was allowed to boil for one minute and then allowed to cool. A light brown solid began to crystallize instantly. Two recrystallizations from boiling methyl cellosolve gave large, white almost transparent plates, 25.7 g. (74% based on cholesterol used). The purest compound obtained melted at 190.5–191.5° and possessed a specific rotation in chloroform, $[\alpha]^{20}\mathrm{D}$ −6.97°.

Cholesteryl *p*-Aminobenzoate.—Cholesteryl *p*-nitrobenzoate (6 g.) was placed in a 200-cc. round-bottomed flask with 80 cc. of glacial acetic acid, 3.5 g. of 100 mesh iron filings was added and the mixture allowed to boil under gentle reflux. The color of the solution changed from colorless to dark brown within the first half hour. After one and one-half hours all the *p*-nitrobenzoate had dissolved. The solution was allowed to boil under reflux for one hour longer. The solution was then poured into a beaker and allowed to cool, crystals separating instantly. The crystals were washed with 1 *N* hydrochloric acid until the washings were colorless and then with water until the washings were neutral to litmus. The crude product weighed 5 g. Two recrystallizations from boiling amyl acetate yielded large tan needles, 4.2 g. (76% calculated). The purest compound obtained melted at 237.8–238.8° and possessed a specific rotation in chloroform, $[\alpha]^{20}\mathrm{D}$ +3.68°.

Saponification.—For the saponification of the cholesteryl *p*-aminobenzoate 0.1508 g. of the compound was boiled under reflux with 16 cc. of 0.9864 *N* alcoholic sodium hydroxide for two and one-half hours. A titer of 30.95 cc. of 0.5000 *N* hydrochloric acid was required to neutralize the excess alkali. Saponification equivalent found, 503: calculated, 505. The cholesterol recovered weighed 0.1036 g. (90% recovery based on *p*-aminobenzoate used) and melted at 147–148°. The melting point of the cholesterol used in these experiments was 145–146°. The *p*-aminobenzoic acid recovered from the saponification melted at 183° and did not depress the melting point of a known sample of *p*-aminobenzoic acid.

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[1] Shriner and Ko, *J. Biol. Chem.*, **80**, 1 (1928).

[2] Einhorn and Hollandt, *Ann.*, **301**, 95 (1898).

Hydrate Isomerism in the Hydrated Chromic Chlorides. Preparation of Triethylenediamine Chromium(III) Chloride from Hexaquo Chromium(III) Chloride[1]

BY LOUIS E. MARCHI[2] AND JAMES P. MCREYNOLDS

Triethylenediamine chromium(III) chloride, $[\mathrm{Cr(en)_3}]\mathrm{Cl_3}$,[3] may be prepared from the violet hexaquo-chromium(III) chloride by reaction with anhydrous ethylenediamine.

Procedure

Triethylenediamine Chromium(III) Chloride.—The violet hexaquo-chromium(III) chloride was prepared by the method of Biltz and Biltz.[4] Forty grams of the violet chloride was added to 100 ml. of anhydrous toluene in a 3-necked, 500 ml., round-bottomed flask equipped with a stirrer, thermometer and separatory funnel. The flask and its contents were cooled to 0° and anhydrous ethylenediamine[5] added slowly at first. The temperature was never allowed to rise above 15°. During the course of the reaction the mixture became red colored, due to the formation of some red dichlorodiethylenediamine chromium(III) chloride monohydrate, $[\mathrm{Cr\ en_2Cl_2}]\mathrm{Cl{\cdot}H_2O}$, which masked the yellow color of the $[\mathrm{Cr\ en_3}]\mathrm{Cl_3}$. The mixture was stirred for one-half hour after the addition of the ethylenediamine, after which time the toluene layer was poured off. The thick red aqueous solution was diluted to twice its volume and treated with "Super-cel."

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[1] Abstracted from a thesis presented to the Faculty of the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in August, 1942.

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[3] en = enthylenediamine, $\mathrm{NH_2{-}CH_2{-}CH_2{-}NH_2}$.

[4] Biltz and Biltz (trans. by Hall and Blanchard), "Laboratory Methods of Inorganic Chemistry," 1928, p. 200.

[5] The ethylenediamine was prepared by the method of Putnam and Kobe, *Trans. Electrochem. Soc.*, **74**, 610 (1938). The round-bottomed flask recommended was replaced by an iron container, the use of which circumvented the etching encountered by the contact of hot concentrated solutions of sodium hydroxide with glass.