acid, the corresponding chloride III (X = Cl) was obtained, m.p. 93–96°.

Anal. Calcd. for $C_{17}H_{15}Cl$: C, 80.16; H, 5.89; Cl, 13.95. Found: C, 80.48; H, 5.91; Cl, 13.66.

Synthesis of 1,4-Naphthohydroquinone-2-carboxanilide and 1,4-Naphthoquinone-2-carboxanilide[1]

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Truit[2] reported that various derivatives of 2-acylamino-3-alkyl-1,4-naphthoquinone possess amebicidal activity. Buu-Hoi[3] reported that 1-naphthylamine, 1,5-naphthylenediamine, and similar derivatives of 2-chloro-1,4-naphthoquinone were capable of inhibiting the growth of *Mycobacterium tuberculosis*. N,N-Diethyl-4-chloro-1-hydroxy-2-naphthamide, ethyl 4-chloro-1-hydroxy-2-naphthalate and N-phenethyl-4-chloro-1-hydroxy-2-naphthamide were shown by Franzen and Binkley[5] to exhibit low antiprotozoal activity. It seemed quite likely that various substituted amide derivatives of 1,4-dihydroxy-2-naphthoic acid and the corresponding 1,4-naphthoquinone-2-carboxamide should be interesting biologically.

Experimental[5,6]

1,4-Dihydroxy-2-naphthoic Acid.[7]—When this compound was made according to the procedure of Homeyer and Wallingford,[7] a red oil was often obtained in the preparation of the intermediate compound, diethyl 1,4-dihydroxy-2,3-naphthalate. This difficulty was overcome when NaH was substituted for $NaOC_2H_5$ in the condensation of ethyl phthalate and ethyl succinate, and by running the reaction in anhydrous ether. The melting point of diethyl 1,4-dihydroxy-2,3-naphthalate[7] was raised from 62–64° to 74–74.5° when the product was recrystallized twice from petroleum ether (b.p. 30–60°).

1,4-Naphthohydroquinone-2-carboxanilide.—To a suspension of 16 g. (0.123 mole) of aniline hydrochloride in 800 ml. of acetonitrile was added 17.5 ml. of triethylamine followed by 25 g. (0.123 mole) of 1,4-dihydroxy-2-naphthoic acid and 54 g. (0.125 mole) of 1-cyclohexyl-3-(2-morpholinyl-(4)-ethyl) carbodiimide metho-*p*-toluenesulfonate. After stirring for 48 hr. at room temperature, the 1-cyclohexyl-3-(2-morpholinyl-(4)-ethyl)urea metho-*p*-toluenesulfonate was removed by filtration, and washed with 100 ml. of acetonitrile. The organic layers were combined and the solvent removed under reduced pressure. The crude product was dissolved in ether and the solution washed with *N* hydrochloric acid, *N* sodium bicarbonate, and finally water until the aqueous layer remained clear. Drying over $MgSO_4$ and removal of the ether yielded 12 g. of a mixture of yellow and red crystals. The crude material was dissolved in hot 95% ethanol, and subsequent cooling to room temperature gave red crystals (135 mg.), m.p. 215° dec. The structure of this compound remains unknown.

Anal. Calcd. for $C_{34}H_{24}N_2O_6$ (quinhydrone): C, 73.17; H, 4.39; N, 5.07. Found: C, 74.83; H, 4.47; N, 7.20.

Concentration of the mother liquor gave 10 g. of crude 1,4-naphthohydroquinone-2-carboxanilide. Five recrystallizations from benzene gave 3.70 g. (11%) of light tan crystals, m.p. 212° dec.

Anal. Calcd. for $C_{17}H_{13}NO_3$: C, 73.28; H, 4.71; N, 5.06. Found: C, 73.12; H, 4.87; N, 5.24.

Infrared absorption in KBr, 2.9 (OH), 3.1 (N–H), 6.2, and 6.3 μ (C=O); ultraviolet absorption in EtOH, λ_{max} 270 and 360 mμ; λ_{min} 245 and 328 mμ.

1,4-Naphthoquinone-2-carboxanilide.—To 260 mg. of 1,4-naphthohydroquinone-2-carboxanilide in anhydrous ether was added 2 g. of silver oxide and 2 g. of $MgSO_4$. The reaction mixture was stirred in the dark for 4 hr. The solution was filtered to remove the excess silver oxide and the $MgSO_4$. The ether solution was concentrated to yield 240 mg. of bright red-orange crystals. Recrystallization from anhydrous ether yielded 212 mg. (82%) of product, m.p. 140–141°.

Anal. Calcd. for $C_{17}H_{11}NO_3$: C, 73.50; H, 4.00; N, 5.05. Found: C, 73.26; H, 4.04; N, 5.36.

Infrared absorption in KBr, 3.1 (N–H), 6.1, 6.3 (C=O), and 5.9 μ (quinone C=O); ultraviolet absorption in EtOH, λ_{max} 252 and 334 mμ; λ_{min} 310 mμ.

Reaction of 1,4-Dihydroxy-2-naphthoic Acid with Benzyl Bromide.—To 10 g. (0.05 mole) of 1,4-dihydroxy-2-naphthoic acid in 50 ml. of ethanol and 25 ml. of water was added 40 ml. of 7 *N* KOH and 33 ml. of benzyl bromide over a 20 min. period. After cooling to room temperature, 300 ml. of water was added and the aqueous solution acidified with glacial acetic acid. Extraction of the solution with $CHCl_3$ and distillation of the $CHCl_3$ layer at 45° (0.58 mm.) resulted in a yellow sirup. The sirup was layered with anhydrous ether in a stoppered flask. White crystals separated after 2 weeks, 7 g., m.p. 142–143° (from ether). The analytical results are not in agreement with those expected for benzyl 1-hydroxy-4-O-benzyl-2-naphthalate.

Anal. Calcd. for $C_{25}H_{20}O_4$: C, 78.12; H, 5.20. Found: C, 85.00; H, 5.70. Calcd. for $C_{24}H_{20}O_2$: C, 84.70; H, 5.88.

When 1,4-naphthalenediol was treated with benzyl bromide and 7 *N* KOH and the reaction mixture worked up in the usual manner, dibenzyl 1,4-naphthohydroquinone was isolated. Recrystallization from ether gave white crystals, m.p. 142–143°. A mixture melting point with the product isolated previously caused no depression. The compound isolated was dibenzyl-1,4-naphthohydroquinone.

Acetylation of 1,4-Dihydroxy-2-naphthoic Acid with Acetic Anhydride or Isopropenyl Acetate.—Refluxing 1 g. of 1,4-dihydroxy-2-naphthoic acid with 10 ml. of acetic anhydride and 0.5 g. of sodium acetate for 1.5 hr. yielded 1,4-diacetoxynaphthalene,[8] recrystallized from ethanol, m.p. 124–125° (lit.[7,8] 125–127°). Refluxing 1 g. of 1,4-dihydroxy-2-naphthoic acid with 10 ml. of isopropenyl acetate and 1 drop of sulfuric acid for 2 hr. gave upon work-up, 220 mg. of 1,4-diacetoxynaphthalene, m.p. 125–126°.

(1) Supported by Grant CY3231, U. S. Public Health Service.

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(3) N. P. Buu-Hoi, *Bull. Soc. Chim.*, **11**, 578 (1944).

(4) J. S. Franzen and S. B. Binkley, *J. Org. Chem.*, **24**, 992 (1959).

(5) Analyses by Micro-Tech Laboratories, Skokie, Ill.

(6) All melting points are corrected. The infrared spectra were run on a Perkin-Elmer Infracord spectrophotometer and the ultraviolet spectra were taken on a Beckman DU spectrophotometer.

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(8) F. Russig, *J. Prakt. Chem.*, **62**, 30 (1900).

Book Reviews

Steroid Reactions: An Outline for Organic Chemists. By CARL DJERASSI. Holden-Day, Inc., San Francisco, Calif., 1963. vi + 657 pp. $9.75.

The last two decades have seen an enormous increase in the volume of literature on steroid chemistry. In a survey of reactions characteristic of this field both the steroid chemist and the general organic chemist face the dilemma of a complete literature search without sacrificing a significant slice of one's working time which, otherwise, could be spent in the laboratory. Prof. Djerassi, who is so well known for his contributions to steroids, has now come out with a book which every chemist in the field will receive with relief.

The book under review can be considered more appropriately as a catalog or atlas rather than a text book as it illustrates the examples without much description. It is divided into 14 sections, each devoted to a given reaction. Each section is composed of a comprehensive collection of examples of some particular reaction, which has been widely employed for steroids, and has been modified to suit specific requirements in individual cases.