oid oxidation product recently mentioned by Fieser, *et al.*[4] The latter authors gave no biological data for the oxidation product and stated that the tocopherol was active at 0.3 mg. We found that 1 mg. of the tocopherol was totally inactive, but the oxidation product was fully active at that dose.[5]

Experimental

2 - Methyl - 5,6,7,8 - tetrahydro - 1,4 - naphthoquinone.—A solution of 1.72 g. of 2-methyl-1,4-naphthoquinone in glacial acetic acid was completely hydrogenated using platinum oxide catalyst. The reaction mixture was decanted from the catalyst, diluted with water and extracted with ether. The ethereal solution was washed, dried and the solvent evaporated. The quinone was obtained by steam distilling a suspension of the crude hydroquinone in a ferric chloride solution. The distillate was extracted with ether, the extract dried and the solvent evaporated. The residue after recrystallization from light petroleum ether yielded 1.6 g. (94%) of quinone melting at 58–59°.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 74.95; H, 6.71.

β,γ-5,6,7,8-Hexahydro Vitamin K_1.—One gram of the synthetic vitamin was hydrogenated as described above. The hydroquinone was oxidized with silver oxide in dry ether. The yield was 0.95 g. (95%) of yellow oil giving with alcoholic alkali a pink color which darkened to brown on standing.

Anal. Calcd. for $C_{31}H_{52}O_2$: C, 81.52; H, 11.47. Found: C, 81.17; H, 11.60.

Naphthotocopherol.—A mixture of 3.5 g. of 2-methyl-1,4-naphthoquinone, 5 g. of phytol, 5 g. of anhydrous zinc chloride and 50 cc. of xylene[6] was refluxed for twenty-four hours. The solvent was removed *in vacuo* and the residue taken up in ether. The ethereal solution was washed repeatedly with 2% potassium hydroxide solution containing hydrosulfite and finally with dilute hydrochloric acid and water. After drying and removal of the solvent, the remaining brown oil was taken up in petroleum ether (b. p. 40–60°), and extracted with Claisen alkali. The small amount of yellow oil obtained on working up the soluble portion gave the typical Dam–Karrer reaction for vitamin K_1.

The petroleum ether portion was washed, dried and the solvent evaporated. The residue was purified by chromatographic adsorption on activated alumina in petroleum ether solution. The yield was about 1.0 g. (13% based on phytol), of reddish-brown oil which strongly reduced an alcoholic silver nitrate solution in the cold.

Anal. Calcd. for $C_{31}H_{48}O_2$: C, 82.24, H, 10.70. Found: C, 82.48; H, 10.72.

Oxidation of Naphthotocopherol.—Two hundred milligrams of the above tocopherol was oxidized with ferric chloride in alcoholic solution. The reaction mixture was diluted with water, extracted with ether, and the ethereal solution washed, dried and concentrated. The residue was purified by chromatographing in petroleum ether solution on activated calcium sulfate. About 100 mg. (48%) of dark orange oil was obtained.

Anal. Calcd. for $C_{31}H_{48}O_3$: C, 79.43; H, 10.30. Found: C, 79.42; H, 10.03.

THE SQUIBB INSTITUTE FOR MEDICAL RESEARCH
DIVISION OF ORGANIC CHEMISTRY
NEW BRUNSWICK, N. J. RECEIVED APRIL 22, 1940

(5) Reported by the senior author in a lecture at Columbia University on December 4, 1939.

(6) Jacob, Sutcliffe and Todd, *J. Chem. Soc.*, 331 (1940), report an unsuccessful attempt to effect this condensation in boiling decalin. In our experience the tocopherol is destroyed at that temperature.

Collidine Treatment of 2-Bromocholestanone

BY ROBERT P. JACOBSEN

In the course of preparation of certain steroids for photochemical study, the author has had occasion to employ the collidine method of Butenandt, *et al.*,[1] for the splitting of hydrogen bromide from 2-bromocholestanone to form 1-cholestenone. On refluxing a collidine solution of the bromo compound for two hours, these workers obtained the α,β-unsaturated ketone (m. p. 95°, $[\alpha]_D$ + 64.5°) in 77% yield. Butenandt and Wolff[2] had earlier reported the preparation of 1-cholestenone (m. p. 111–112°, $[\alpha]_D$ −32.1°; oxime, m. p. 146–147°), in poor yield by the potassium acetate–acetic acid treatment of 2-bromocholestanone. This latter compound the German workers now call "hetero-Δ^1-cholestenone" and state that the "normal Δ^1-ketone" is the substance melting at 95°.

In the experience of the author, the collidine reaction appears to follow a less straightforward course than that indicated by Butenandt and his collaborators. 2-Bromocholestanone (m. p. 169°) was refluxed in collidine[3] for two, four, or six hours without effecting the complete fission of hydrogen bromide. After twelve hours of boiling, a non-homogeneous, crystalline, halogen-free product (m. p. 89–92° to a sludge which cleared at about 100°) was obtained in 74% yield. By repeated crystallization from methanol this gave a very small amount of material, m. p. 126–127.5° (nearly pure cholestanone), which showed no selective absorption[4] in the ultraviolet region between 2200 and 2600 Å. No pure 1-cholestenone could be obtained from the intermediate fractions by crystallization, although some sam-

(1) Butenandt, Mamoli, Dannenberg, Masch and Paland, *Ber.*, **72**, 1617 (1939).

(2) Butenandt and Wolff, *ibid.*, **68**, 2091 (1935).

(3) Obtained from the Research Department of the Barrett Company, 90% of the material boiling in the range 170.7–171.9°.

(4) Ultraviolet absorption measurements by Dr. P. A. Cole and Mr. C. Z. Nawrocki of this Laboratory.

ples[5] which melted at 93–96° showed an ultraviolet absorption maximum at 2275 Å. (log ϵ 4.07, cyclohexane). By brominating the combined intermediate fractions (0.5 g.) in cold acetic acid (5 cc.) there was obtained 0.20 g. of impure 1-cholestenone dibromide (effervesces at 85°). On allowing the filtrate to stand for a few minutes, hydrogen bromide was evolved and there separated 0.095 g. of needles, m. p. 152–156°. The dibromide liberated iodine on warming in an alcoholic sodium iodide solution but the needles did not. The latter on crystallization from methyl acetate melted at 169° and mixed with 2-bromocholestanone showed no depression. The crude dibromide was debrominated with sodium iodide or zinc dust in alcohol, or potassium iodide in 80% acetone, to give the corresponding unsaturated ketone, m. p. 102–104°. By repeating the purification through the dibromide, pure 1-cholestenone, crystallizing as a hydrate from 98% methanol or aqueous acetone, m. p. 107–108° ($[\alpha]^{24}D$ +65°).

These observations indicate that the collidine treatment of 2-bromocholestanone, under the conditions specified, gives principally a mixture of 1-cholestenone and cholestanone. The formation of the latter compound is not surprising in view of the work of Schwenk and Whitman,[6] who obtained cholestanone as the principal product of the treatment of 2-bromocholestanone with dimethylaniline.

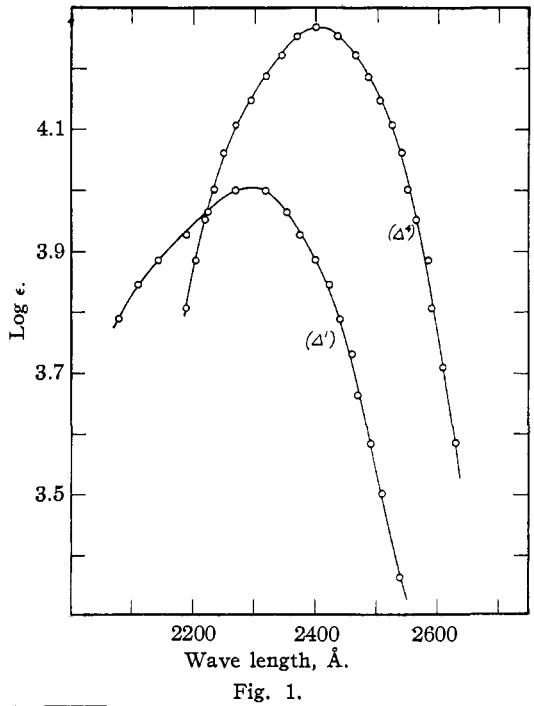

Fig. 1.

The ultraviolet absorption in alcohol of 1-cholestenone hydrate (calculated on the anhydrous basis) in the region of the maximum is compared with that of the Δ^4-isomer in Fig. 1.

The preparation of 1-cholestenone will be detailed later in connection with a report of photodehydrogenation studies now in progress.

(5) These properties correspond closely to those of the product (m. p. 95°) of Butenandt, *et al.*, who reported a maximum at 230 mμ (log ϵ 4.03).

(6) Schwenk and Whitman, THIS JOURNAL, **59**, 949 (1937).

WASHINGTON BIOPHYSICAL INSTITUTE
BETHESDA, MARYLAND RECEIVED APRIL 27, 1940

The Behavior of Certain Substituted Allenes toward the Meinel Color Test[1]

BY F. B. LAFORGE AND FRED ACREE, JR.

A method for the detection of conjugated double bonds has been proposed by Meinel[1a] based upon the treatment of the compound to be tested with one molecular equivalent of bromine in methanol solution. The isolated reaction product is then treated with a suspension of silver thiocyanate containing ammonium ferric sulfate. The formation of a red color of variable intensity depending upon the compound is indicative of the presence of a conjugated system of double bonds.

Conant and Jackson[2] have reported the formation of dibromo compounds along with the methyl hypobromite addition products when bromine in methanol solution is allowed to react on an unsaturated compound. Thus, while Meinel indicated that the methyl hypobromite addition product is responsible for the reaction with silver thiocyanate, there also is the possibility that the dibromo addition product might be the influencing factor in the reaction.

Meinel subjected a number of compounds to the test but did not include any that possessed a cumulated system of double bonds.

In studying the reaction of halogens[3] on compounds of this class it was of interest to determine whether or not they would also respond to the color test.

It was found that 1-phenyl-1,2-butadiene, 2,3-pentadiene, 1-cyclohexyl-2,3-pentadiene, and pyrethrone gave a positive reaction. When com-

(1) Not subject to copyright.

(1a) K. Meinel, *Ber.*, **70B**, 429 (1937).

(2) J. B. Conant and E. L. Jackson, THIS JOURNAL, **46**, 1727 (1924).

(3) Fred Acree, Jr., and F. B. LaForge, *J. Org. Chem.*, (in press).