of water was added and the mixture was refluxed for three hours. The mixture was cooled, acidified with dilute sulfuric acid, and extracted several times with benzene. The benzene extracts were extracted with 2 *N* sodium carbonate solution and with water, the benzene was evaporated, and the residue was distilled under reduced pressure, the colorless viscous liquid distilling at 134–137° at 0.4 mm. being collected; weight, 12.4 g. (57%).

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.5. Found: C, 81.8; H, 9.4.

The acid obtained by acidification of the alkaline washings was esterified with methanolic hydrochloric acid, purified by distillation (7 g., b. p. 128–133° at 0.4 mm.), and this recovered ester could be used in subsequent reductions.

β - [1 - (3 - Methyl - 1,2,3,4 - tetrahydronaphthyl)]-ethyl Bromide.—A mixture of 5.0 g. of the above alcohol and 2 cc. of phosphorus tribromide was heated on a steam-bath for two hours. The mixture was taken up in benzene and washed with 2 *N* sodium carbonate solution and then with water. The residue obtained by evaporation of the benzene was distilled, the colorless liquid distilling at 137–140° at 0.4 mm. being collected; weight, 5.2 g. (75%).

Anal. Calcd. for $C_{13}H_{17}Br$: Br, 31.6. Found: Br, 31.8.

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RECEIVED APRIL 6, 1940

The Preparation of Pentaacetyl-*d*-gluconyl Chloride

BY CHARLES E. BRAUN, S. H. NICHOLS, JR., J. L. COHEN AND THEIS E. AITKEN

In the course of work being carried out in these laboratories a method has been developed for the preparation of pentaacetyl-*d*-gluconyl chloride in quantity. This new procedure, based upon that of Major and Cook,[1] involves much less manipulation and gives consistently good results. The details are presented here for those interested.

Anhydrous pentaacetylgluconic acid[2] (25 g. or 0.062 mole) was dissolved in 185 cc. of anhydrous ethyl ether and an excess of phosphorus pentachloride (15 g. or 0.072 mole) was added without cooling. The reactants were allowed to stand at room temperature from four to twelve hours (usually overnight). The excess phosphorus pentachloride was then filtered off on a sintered glass funnel, and the ethereal filtrate concentrated to about one-half of its volume *in vacuo* at room temperature. The concentrated solution was kept at zero degrees or below[3] for fifteen to twenty-four hours. The mother liquor was then decanted, *care being taken not to break up or disturb the crystals which had formed on the bottom of the flask.* The crystalline mass was next broken up, mechanically removed and filtered on a sintered glass funnel. After thorough washing with petroleum ether (Eastman Kodak Company, practical, b. p. 35–55°), the crystalline acid chloride was preserved *in vacuo* over calcium chloride and potassium hydroxide at room temperature.

The decanted mother liquor, after being concentrated *in vacuo* at room temperature to one-half of its volume, was allowed to stand at zero degrees or below for another twenty-four hours. The second crop of crystals thus obtained was treated as described above. The concentrated mother liquor which contained all of the phosphorus oxychloride was usually discarded. By this procedure pentaacetyl-*d*-gluconyl chloride was produced as large colorless crystals; m. p. 68–71°; $[\alpha]^{21}D$ +1.71° (alcohol-free chloroform, *c*, 4.38).

Anal. Calcd. for $C_{16}H_{21}O_{11}Cl$: Cl, 8.35. Found: Cl, 8.20.

The yields obtained in five typical preparations were 83%, 86%, 92%, 88% and 93%, or an average yield of 88.4%.

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RECEIVED MARCH 25, 1940

(1) Major and Cook, THIS JOURNAL, **58**, 2477 (1936).

(2) Major and Cook, *ibid.*, **58**, 2475 (1936).

(3) At higher temperatures the yields are decreased appreciably due to the increase in solubility of the acid chloride in the anhydrous ether.

Additional Observations on the Vitamin K Activity of Quinones

BY ERHARD FERNHOLZ, H. B. MACPHILLAMY AND S. ANSBACHER

Several months ago we reported that phlorone (2,5-dimethyl-1,4-benzoquinone) has vitamin K activity,[1] an observation recently confirmed by H. J. Almquist.[2] In this connection it seemed of interest to investigate whether 2-methyl-5,6,7,8-tetrahydro-1,4-naphthoquinone possesses the great potency of the parent substance. The hydrogenated quinone, first synthesized by Chuang and Han,[3] was prepared by catalytic hydrogenation of 2-methyl-1,4-naphthoquinone. It was found to be active at 1 mg., a degree of activity which should be considered practically negligible, since it is common to a great number of quinones.

We have also studied the analogous hydrogenation product of vitamin K_1 (β,γ,5,6,7,8-hexahydrovitamin K_1). It showed no vitamin K activity, not even in a dose of 2 mg. In contrast to this, Fieser, Tishler, and Sampson[4] reported it to have slight activity, although the dosage is not indicated.

We wish to point out that we have prepared and assayed the naphthotocopherol and its quin-

(1) Ansbacher and Fernholz, *J. Biol. Chem.*, **131**, 399 (1939).

(2) 52nd Annual Meeting, Am. Physiol. Soc., New Orleans, May 16 (1940).

(3) Chuang and Han, *Ber.*, **68**, 876 (1935).

(4) Fieser, Tishler and Sampson, THIS JOURNAL, **62**, 996 (1940).