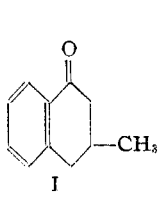
NOTES

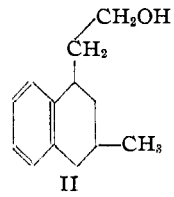
The Preparation of 3-Methyl-1-tetralone and β-[1-(3-Methyl-1,2,3,4-tetrahydronaphthyl)]-ethyl Alcohol

By W. E. Bachmann and W. S. Struve

In the course of an investigation β-[1-(3-methyl-1,2,3,4-tetrahydronaphthyl)] - ethyl alcohol (II) was required. The starting material for the preparation was γ-phenyl-β-methylbutyric acid, which was prepared from 1-allylbenzene according to the procedure of Carter.[1] Cyclization of the acid through its acid chloride by means of aluminum chloride gave 3-methyl-1-tetralone (I), whose structure was established by its conversion to β-methylnaphthalene by Clemmensen reduction and subsequent dehydrogenation of the product. By means of the Reformatsky reaction with methyl bromoacetate and subsequent dehydration of the resulting hydroxy ester, the ketone was converted into what is probably the methyl ester of 1-(3-methyl-3,4-dihydronaphthyl)-acetic acid, although the position of the double bond was not established. Reduction of the ester by means of sodium and alcohol yielded the desired alcohol (II). The alcohol reacted with phosphorus tribromide to give the corresponding bromide.



I



II

Experimental

3-Methyl-1-tetralone.—A mixture of 25.5 g. of γ-phenyl-β-methylbutyric acid, 20 cc. of thionyl chloride, and 5 drops of pyridine was allowed to stand at room temperature for a half hour. The thionyl chloride was evaporated under reduced pressure, 150 cc. of carbon disulfide was added and the solution was cooled in an ice–salt mixture. Twenty-two grams of aluminum chloride was added in portions and the mixture was refluxed for ten minutes. After hydrolysis of the complex with ice and hydrochloric acid, the organic layer was separated, the carbon disulfide was evaporated, and the residue was dissolved in benzene. The benzene solution was washed with dilute ammonium hydroxide and with water and the benzene was evaporated. The 3-methyltetralone distilled under reduced pressure as a colorless liquid at 94–96° at 0.3 mm.; weight, 16.7 g. (73%).

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.5; H, 7.5. Found: C, 82.4; H, 7.4.

The **oxime** crystallizes from dilute alcohol as colorless needles; m. p. 122.5–123.5°.

Anal. Calcd. for $C_{11}H_{13}NO$: N, 8.0. Found: N, 7.8.

A mixture of 5 g. of the above ketone, 25 g. of amalgamated zinc, 50 cc. of concentrated hydrochloric acid, 25 cc. of water, and 2.5 cc. of acetic acid was refluxed for twenty-four hours, an additional 50 cc. of concentrated hydrochloric acid being added in portions over this time. The oil was extracted with ether, the ether extract was dried with anhydrous sodium sulfate, and the residue obtained by evaporation of the ether was distilled at 12 mm. pressure. The colorless distillate was heated for four hours at 200–220° with 2.3 g. of powdered sulfur. A small amount of copper bronze was then added and the heating was continued for ten minutes more. The mixture was extracted with ether, the filtered ether solution, after having been dried with anhydrous sodium sulfate, was evaporated, and the residue was distilled at 10 mm., giving 2.0 g. of colorless distillate which solidified on cooling to room temperature; m. p. 29–30.5°. After being purified through the picrate, the hydrocarbon melted at 34–35°. The mixed melting point with authentic β-methylnaphthalene gave no depression. The picrate melted at 115–116.5° and the mixed melting point with authentic β-methylnaphthalene picrate gave no depression.

Methyl 1-(3-Methyl-3,4-dihydronaphthyl)-acetate.—A mixture of 20 g. of 3-methyl-1-tetralone, 14.4 cc. of methyl bromoacetate, 48 g. of zinc, 480 cc. of dry ether, 480 cc. of dry benzene, and a small amount of iodine was refluxed for four hours, additional zinc and iodine being added at the end of each hour and an additional 14.4 cc. of methyl bromoacetate being added at the end of the second hour. The complex was decomposed with ice and hydrochloric acid, the organic layer was washed with ammonium hydroxide and then with water, and the benzene and ether were evaporated. The hydroxy ester was dehydrated by heating with 100 cc. of anhydrous formic acid on a steam-bath for fifteen minutes; water was added and the ester was extracted several times with benzene. The benzene extract was washed with dilute sodium carbonate solution and then with water, the benzene was evaporated, and the residue was distilled under reduced pressure, the yellowish liquid distilling at 130–133° at 0.4 mm. being collected; weight, 23 g. (85%).

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.8; H, 7.4. Found: C, 77.6; H, 7.6.

β - [1 - (3 - Methyl - 1,2,3,4 - tetrahydronaphthyl)]-ethyl Alcohol.—To a boiling solution of 25 g. of the above ester in 125 cc. of absolute methanol was added 21.3 g. of sodium metal over a period of fifteen minutes. After the vigorous reaction had subsided, another 50 cc. of methanol was added. When all of the sodium had reacted, 100 cc.

(1) Carter, *J. Biol. Chem.*, **108**, 622 (1935).

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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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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(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).