dition of ether the bulk of the saponin present in the extract was removed. The filtrate was concentrated with removal of ether and, after standing a few days in the ice-box, crystals appeared. These were filtered off and recrystallized from methyl alcohol, forming colorless plates, melting at 142–143°; $[\alpha]^{21}D$ +42.0° (H_2O, c = 1.8).

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.89; H, 7.37. Found: C, 43.95; H, 7.44.

Tetramethylpolygalitol.—Ten grams of polygalitol was methylated according to the method of West and Holden. The product obtained was a limpid, colorless sirup which distilled at a bath temperature of 80° under 2 mm. pressure; $[\alpha]^{23}D$ +67.67° (no solvent); n^{22} 1.4444, d. 1.0571.

Anal. Calcd. for $C_{10}H_{20}O_5$: C, 54.54; H, 9.13; CH_3O, 56.31. Found: C, 54.54; H, 9.10; CH_3O, 56.55.

Tetramethylmannitol.—A solution of 30 g. of tetramethylmannose in 75 cc. of water and 15 cc. of alcohol was reduced for seven hours at 135° under a pressure of 1300 pounds (85 atm.) of hydrogen in the presence of Raney nickel. The filtered solution was evaporated *in vacuo* to a clear, thick sirup which did not reduce Fehling's solution. The sirup was purified by distillation at a bath temperature of 150° under 2 mm. pressure; $[\alpha]^{21}D$ +20.7° (EtOH, c = 10.15), $[\alpha]^{21}D$ +17.5° ($CHCl_3$, c = 10.6), n^{24} 1.4605.

Anal. Calcd. for $C_{10}H_{22}O_6$: C, 50.40; H, 9.32; CH_3O, 52.03. Found: C, 50.34; H, 9.27; CH_3O, 52.38.

Tetramethyl-1,5-anhydromannitol.—Fifteen grams of tetramethylsorbitol and 2 cc. of 13% sulfuric acid solution were heated *in vacuo* for a half hour at 140°. The solution was neutralized with 0.4 g. of anhydrous sodium carbonate, after which a small amount of decolorizing charcoal and 50 cc. of ether were added. The solution was filtered and dried over anhydrous sodium sulfate. After filtering off the sodium sulfate, the ether was removed leaving a limpid sirup which distilled colorless at a bath temperature of 95° under 2 mm. pressure; $[\alpha]^{22}D$ +30.6° (no solvent), n^{22} 1.4479, density 1.0435.

Anal. Calcd. for $C_{10}H_{20}O_5$: C, 54.54; H, 9.13; CH_3O, 56.31. Found: C, 54.21; H, 9.03; CH_3O, 56.24.

Hexamethylmannitol.—Ten grams of tetramethylmannitol was methylated according to the method of West and Holden. The product obtained was a colorless sirup which distilled at a bath temperature of 95° under 2 mm. pressure; $[\alpha]^{22}D$ +12.53° (no solvent), $n^{21}D$ 1.4403, density 1.0458. For comparison 10 g. of isolated mannitol was methylated in the above fashion. The resulting product was found to distil at 97° under 2 mm. pressure; $[\alpha]^{22}D$ +12.46° (no solvent), $n^{21}D$ 1.4400, d. 1.0410.

Anal. Calcd. for $C_{12}H_{26}O_6$: C, 54.14; H, 9.77; CH_3O, 69.92. Found: C, 54.28; H, 9.58; CH_3O, 69.90 (product from tetramethylmannitol); C, 54.28; H, 9.79; CH_3O, 70.07 (product from mannitol).

Acknowledgments.—The authors wish to express their thanks to Dr. P. A. Levene for permission to carry out the high pressure reductions in his laboratory, to Prof. S. Takei for the styrax used, and to the Atlas Powder Co. for a sample of natural mannitol. The microanalyses were made by J. F. Alicino of this Laboratory.

Summary

Styracitol has been proved to be 1,5-anhydro-*d*-sorbitol by the synthesis of its tetramethyl derivative.

Polygalitol has been shown not to be 1,5-anhydro-*d*-mannitol.

A new method is described for establishing the presence of furanose and pyranose rings by preparing the corresponding methylated anhydro sugar alcohols.

NEW YORK, N. Y. RECEIVED DECEMBER 20, 1939

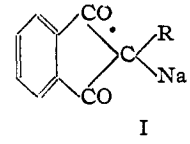
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

A Synthesis of Substituted α-Naphthoquinones

BY C. F. KOELSCH AND D. J. BYERS

The recent discovery that vitamin K is a substituted α-naphthoquinone adds importance to all reactions leading to substances of this class. The research described in the present paper is an investigation of a series of reactions by means of which 2-alkyl, 2-alkyl-3-hydroxy-, and 2-alkyl-3-carbalkoxy-α-naphthoquinones and hydroquinones can be prepared. The reactions may be formulated as

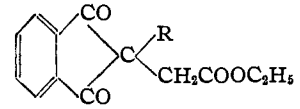
$$o\text{-}C_6H_4(COOC_2H_5)_2 + RCH_2COOC_2H_5 \xrightarrow{Na}$$



I

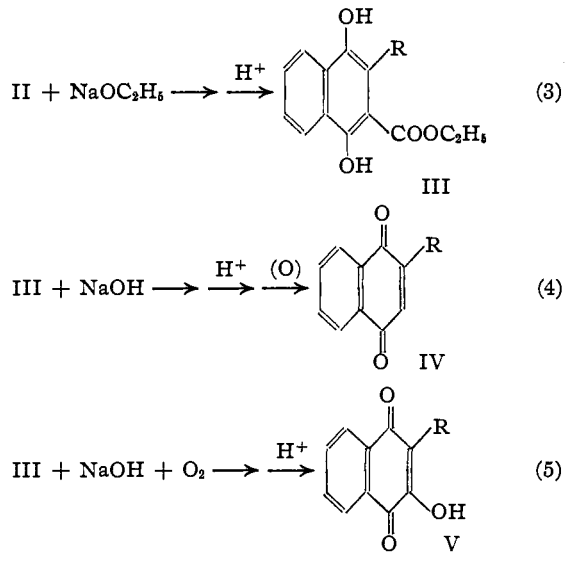
(1)

$$I + BrCH_2COO_2H_5 \longrightarrow$$



II

(2)



Reaction (1) has been carried out previously by Wislicenus and Kötzle[1] for the case where R was methyl. In the present investigation it was carried out for the cases where R was methyl, ethyl, *n*-propyl and *n*-butyl.

Reaction (2) has been studied by Nathanson,[2] by Radulescu and Gheorgiu[3] and by Gheorgiu[4] for the cases where R was phenyl and methyl. In the present investigation the reaction was carried out for the cases where R was methyl, ethyl, *n*-propyl and *n*-butyl; the products in the latter two cases were not purified, but were used directly in reaction (3).

Reaction (3) was found to take place when R was phenyl by Radulescu and Gheorgiu,[3] and was later studied for the case where R was methyl by Gheorgiu.[5] The yield and the quality of the methyl quinone so obtained were reported to be inferior to those of the phenyl quinone prepared previously by the analogous method. The reaction was applied in the present research to the cases where R was methyl, ethyl, *n*-propyl and *n*-butyl, the expected hydroquinones being formed in fair yields.

The combination of reactions represented in (4) was believed feasible by analogy with the results of Nef[6] who showed that quinone acids lose carbon dioxide readily. It was carried out only in the case where R was ethyl, and yielded 77% of the theoretical amount of 2-ethylnaphthoquinone.

(1) Wislicenus and Kötzle, *Ann.*, **252**, 80 (1889).
(2) Nathanson, *Ber.*, **26**, 2577 (1893).
(3) Radulescu and Gheorgiu, *ibid.*, **60**, 186 (1927).
(4) Gheorgiu, *J. prakt. Chem.*, **146**, 193 (1936).
(5) Gheorgiu, *Compt. rend.*, **198**, 755 (1934).
(6) Nef, *Ber.*, **18**, 3496 (1885).

The reactions formulated in (5) were carried out in the cases where R was ethyl and *n*-butyl. They find an analogy in the work of Radulescu and Gheorgiu,[3] who discovered that when air was not excluded in the rearrangement of II (R = phenyl) to III, the product contained some 2-phenyl-3-hydroxynaphthoquinone.

Experimental

Since corresponding experiments involving compounds differing only in the size of the alkyl group R were quite similar, details are given for those only in which R was ethyl. Analytical data, yields, and melting points are given in Table I.

2-Ethylindanedione-1,3.—To a hot (115°) mixture of ethyl phthalate (55 g.) and sodium wire (10.5 g.) was added 30 g. of ethyl butyrate. Heating was continued for four hours; the mixture was then cooled and triturated with moist ether. The acidic products were removed by solution in dilute aqueous alkali. The quantity of dilute sulfuric acid necessary to precipitate all of the organic material was added in three portions, the mixture being extracted with ether after each addition. The third extract contained phthalic acid, while the diketone was in the first two. It distilled at 135–140° (7 mm.), and was recrystallized from benzene.

Ethyl 2-Ethylindanedionyl-2-acetate.—To a solution of the above diketone (13.6 g.) in absolute alcohol (25 ml.) was added a solution of potassium hydroxide (4.4 g.) in absolute alcohol (50 ml.) and then 13.0 g. of ethyl bromoacetate. The resulting mixture was boiled for two and one-half hours, distilled to a volume of 40 ml. and poured into water. The precipitated oil soon solidified and was then recrystallized from alcohol.

2 - Ethyl - 3 - carbethoxy - 1,4 - naphthohydroquinone.—The above diketo-ester (13.8 g.) was added to a solution of sodium (3 g.) in absolute alcohol (40 ml.) under a hydrogen atmosphere. The resulting reddish-brown solution was boiled for two hours, and then air-free water (50 ml.) was added through the condenser. The whole was poured into 600 ml. of air-free cold dilute sulfuric acid, and the precipitated pale yellow product was crystallized from alcohol.

2 - Ethyl - 3 - carbethoxy - 1,4 - naphthoquinone.—2-Ethyl-3-carbethoxynaphthohydroquinone was oxidized with chromic acid in cold acetic acid. The resulting yellow quinone was crystallized from a mixture of ether and petroleum ether.

2-Ethyl-3-hydroxy-1,4-naphthoquinone.—Sodium hydroxide (20 ml. of 1%) was added to 2-ethyl-3-carbethoxynaphthohydroquinone (1 g.) in warm alcohol (5 ml.). Air was bubbled through the solution at 50° for ten minutes, and then heating was continued for ten minutes without the air stream. The water solution was decanted from the yellow oil into cold dilute acetic acid, and the yellow product which separated was crystallized twice from alcohol.

2-Ethylnaphthoquinone.—A solution of 2-ethyl-3-carbethoxynaphthohydroquinone (1 g.) in 12 ml. of 5% sodium hydroxide containing 5 drops of alcohol was boiled under hydrogen for two hours. Acidification under hydrogen

TABLE I

MELTING POINTS, YIELDS AND ANALYSES

Compound	M. p., °C.	Yield, %	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
2-Methylindanedione	83–85[a]	31	$C_{10}H_8O_2$				
2-Ethylindanedione	53–55[b]	32	$C_{11}H_{10}O_2$				
2-*n*-Propylindanedione	48–49.5[c]	17	$C_{12}H_{12}O_2$				
2-*n*-Butylindanedione	35[d,e]	18	$C_{13}H_{14}O_2$				
Ethyl 2-methylindanedionyl-2-acetate	91–92[f]	62	$C_{14}H_{14}O_4$	68.3	5.7	68.5	6.0
Ethyl 2-ethylindanedionyl-2-acetate	77–78.5	68	$C_{15}H_{16}O_4$	69.2	6.2	69.3	6.3
Ethyl 2-*n*-propylindanedionyl-2-acetate	Oil	[g]	$C_{10}H_{18}O_4$				
Ethyl 2-*n*-butylindanedionyl-2-acetate	Oil	[g]	$C_{17}H_{20}O_4$				
2-Methyl-3-carbethoxynaphthohydroquinone	100–101	44	$C_{14}H_{14}O_4$	68.3	5.7	68.3	5.7
2-Ethyl-3-carbethoxynaphthohydroquinone	110.5–111	68	$C_{15}H_{16}O_4$	69.2	6.2	69.5	6.2
2-*n*-Propyl-3-carbethoxynaphthohydroquinone	125–126.5	14[h]	$C_{16}H_{18}O_4$	70.0	6.6	69.9	6.8
2-*n*-Butyl-3-carbethoxynaphthohydroquinone	98.5–100	24[h]	$C_{17}H_{20}O_4$	70.8	7.0	70.7	7.1
2-Methyl-3-carbethoxynaphthoquinone	99–100	92	$C_{14}H_{12}O_4$	68.8	5.0	69.0	5.2
2-Ethyl-3-carbethoxynaphthoquinone	47.5–48	88	$C_{15}H_{14}O_4$	69.7	5.5	69.6	5.3
2-Ethyl-3-hydroxynaphthoquinone	137.5–138.5[i]	36	$C_{12}H_{10}O_3$	71.3	5.0	71.5	5.4
2-*n*-Butyl-3-hydroxynaphthoquinone	100–101[j]	55	$C_{14}H_{14}O_3$				

[a] Reported [Wojack, *Ber.*, **71**, 1102 (1938)] m. p. 84–85°. [b] Reported (ref. *a*) m. p. 55.5°. [c] Reported (ref. *a*) m. p. 50.5°. [d] B. p. 155–160° at 1 mm. [e] Reported (ref. *a*) m. p. 33°. [f] Reported[4] m. p. 161–162°. Possibly Gheorgiu had a hydrolysis product rather than ester. [g] Not purified. [h] Over-all, including preceding step. [i] Reported [Hooker, THIS JOURNAL, **58**, 1178 (1936)] m. p. 138.2–138.5°. [j] Reported [Hooker, *ibid.*, **58**, 1167 (1936)] m. p. 101–101.5°.

gave a solid which was removed, dissolved in acetic acid (10 ml.) and treated with a solution of chromic acid (0.5 g.) in water. This mixture was heated on a water-bath for fifteen minutes and then diluted with water. The resulting precipitate was obtained in the form of yellow needles (0.55 g., 77%) that melted at 87–88° (literature[7] 88°) by crystallization from acetic acid.

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.4; H, 5.4. Found: C, 76.9; H, 5.5.

We thank the Graduate School of the University of Minnesota for a grant from the Fluid Research Fund.

(7) Kruber and Schade, *Ber.*, **69**, 1722 (1936).

Summary

A series of reactions has been described which appears to constitute a general method for the preparation of 1,4-naphthoquinones and hydroquinones which contain a hydrocarbon residue in position 2 and which bear a hydrogen, a hydroxyl or a carbethoxyl in position 3.

MINNEAPOLIS, MINN. RECEIVED DECEMBER 22, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

p-Cymene Studies. IV. Mononitration of 2-Amino-*p*-cymene. Preparation of 3-Amino-*p*-cymene and *o*- and *p*-Cymylenediamine

BY THOMAS F. DOUMANI AND KENNETH A. KOBE

Of the three possible nitro-2-amino-*p*-cymenes, only one has been reported formed in the nitration of 2-amino-*p*-cymene liquid isomer obtained by Wheeler and Brooks.[1,2] We now find that the large amount of tarry by-product in this reaction consists almost exclusively of a solid isomer. Wheeler and Brooks claimed their liquid product to be 2-amino-5-nitro-*p*-cymene, which would make the solid product the 2-amino-3-nitro-*p*-cymene. In our investigation of these compounds the following proof is given that the liquid isomer (I) is 2-amino-3-nitro-*p*-cymene and the solid isomer (II) is 2-amino-5-nitro-*p*-cymene. Product I on reduction gave an unknown diamine in which the *ortho* position of the amino groups is proved by their ready condensation with benzil and phenanthraquinone, and by its conversion to a benzimidazole on heating with glacial acetic acid or atmospheric distillation of its diacetyl derivative. Product II when reduced to the diamine could be oxidized to thymoquinone.

The 2-acetamino-*p*-cymene is extremely diffi-

(1) Wheeler and Brooks, THIS JOURNAL, **49**, 2832–2834 (1927).
(2) Wheeler and Cutlar, *ibid.*, **49**, 2819–2822 (1927).