BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 659—660 (1973)

# Preparation of Hydroquinone Derivatives

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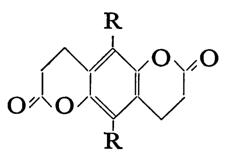
(Received July 6, 1972)

Nakabayashi and Cassidy prepared hydroquinone-bis-$\delta$-lactone (Ia) by heating 2,5-bis(2′-carbethoxy)-hydroquinone.[1] We previously reported on the preparation of 2,5-dimethylhydroquinone-bis-$\delta$-lactone (Ib).[2] In the course of our studies on redox polymers containing hydroquinone or benzoquinone units in polymer chains,[3,4] we prepared some hydroquinone derivatives including 2,3,5-trimethylhydroquinone-$\delta$-lactone (II). In this paper, we describe the preparation of the lactone (II), 2-(3′-hydroxypropyl)-3,5,6-trimethylhydroquinone (III), and 2-(3′-hydroxypropyl)-3,5,6-trimethylbenzoquinone (IV).



Ia: R=H
Ib: R=$CH_3$

I

We attempted to synthesize hydroquinone alcohol (III) from the malonic ester (V) *via* the carboxylic acid (VI) and its ester (VII). When V was heated in hydrobromic acid at 140—160°C for 15 hr, the lactone (II), 6-hydroxy-5,7,8-trimethyl-3*H*,4*H*-dihydrocoumarin, was obtained in a good yield instead of VI. The IR spectrum (KBr disk) of II showed characteristic absorption bands at 3482 and 1740 $cm^{-1}$, assignable to hydroxyl and lactone carbonyl groups, respectively. The NMR spectrum in acetone-$d_6$ gave signals at $\delta$ (ppm) 2.20 (s, 9H, $CH_3$) and 2.73 (m, 4H, $CH_2$). These spectral data and elemental analysis verify the formation of II.

When the bis-malonic ester (VIII) was subjected to the same treatment, the carboxylic acid IXa was formed from VIIIa after 3 hr,[1] while the bis-lactone (Ib) was obtained from VIIIb as in the case of V.

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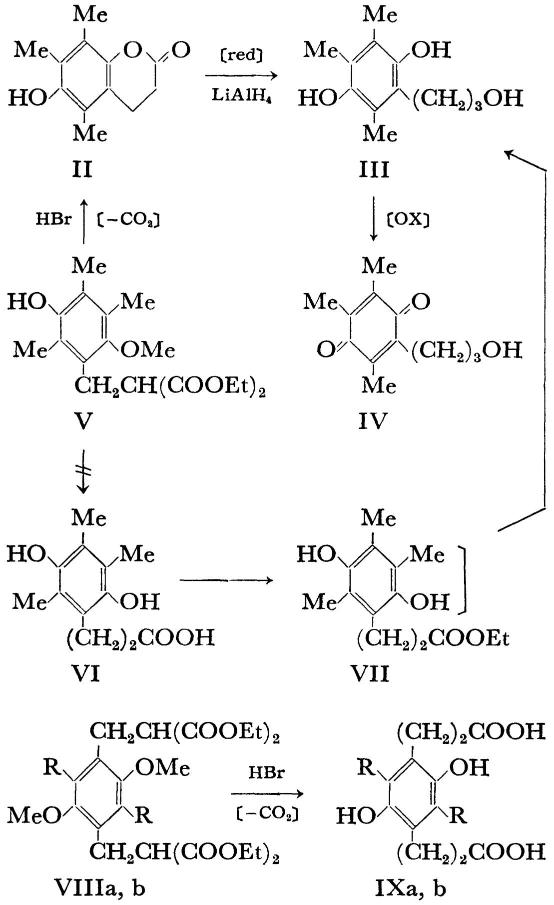
[1] N. Nakabayashi and H. G. Cassidy, *J. Polym. Sci.*, *A-1*, **7**, 1275 (1969).

[2] S. Iwabuchi, M. Ueda, and K. Kojima, *ibid.*, *A-1*, **9**, 3405 (1971).

[3] M. Ueda, S. Iwabuchi, and K. Kojima, *ibid.*, *B*, **9**, 367 (1971).

[4] S. Iwabuchi, M. Ueda, T. Shioda, H. Suda, and K. Kojima, *Kobunshi Kagaku*, in press.



(Suffixes denote a: R=H and b: R=$CH_3$)

Reduction of II with lithium aluminum hydride yielded 2-(3'-hydroxypropyl)-3,5,6-trimethylhydroquinone (III). The IR spectrum (KBr) showed characteristic bands at 3420 and 3150 $cm^{-1}$, assignable to hydroxyl groups, but not to carbonyl or ester groups. The NMR spectrum in acetone-$d_6$ showed signals at $\delta$(ppm) 1.37 (qui, 2H, $CH_2$), 1.75 (s, 9H, $CH_3$), 2.40 (tr, 2H, $CH_2$), 3.16 (tr, 2H, $CH_2O$), 5.95 (s, 1H, OH), and 6.75 (s, 1H, OH).

Hydroquinone alcohol (III) was oxidized with lead tetracetate to yield 0.95 g (53%) of benzoquinone alcohol (IV); mp 42—43°C. The IR spectrum showed characteristic bands at 3210 $cm^{-1}$ (OH) and 1645 $cm^{-1}$ (quinone C=O). The NMR spectrum in $CDCl_3$ showed signals at $\delta$(ppm) 1.73 (m, 2H, $CH_2$), 2.05 (s, 9H, $CH_3$), 2.50 (s, 1H, OH), 2.63 (tr, 2H, $CH_2$), and 3.63 (tr, 2H, $CH_2O$).

## Experimental

*Preparation of II.* 22 g (0.063 mol) of V[5] was heated in 440 ml of 48% HBr solution up to 120°C (bath temp.) and for 2 hr to remove ethyl bromide. The tempetature was then raised to 140°C (3 hr) and finally to 160°C (15 hr). The raw product crystallized from the solution upon cooling in an ice bath. It was filtered, washed with water and dried. Recrystallization from *p*-xylene gave 8.7 g of II as pale yellow needles (yield: 68%); mp 172—173°C (lit,[6] 173—174°C). Found: C, 69.73; H, 6.79%. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84%.

*Preparation of III.* The method of Karret and Banerjed for the reduction of coumarin[7] was applied to II with the following modification. To a stirred suspension of 3.0 g (0.08 mol) of $LiAlH_4$ in 150 ml dry THF cooled with ice was added dropwise 100 ml THF containing 10.3 g (0.05 mol) of II. After the vigorous reaction had subsided, the mixture was refluxed for 2 hr. Excess hydride was decomposed by careful addition of water, and the mixture was neutralized with acetic acid. To this was added 50 ml of saturated aq. $NH_4Cl$ soln. The upper, organic layer was decanted and the lower extracted with four 150 ml portions of THF. The combined THF layers were dried over magnesium sulfate. After the solvent was removed by evaporation from the dried mixture, the residue was recrystallized from chloroform to give 6.58 g (64%) of III as white crystals; mp 135—136°C. Found: C, 68.35; H, 8.62%. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63%.

*Preparation of IV.* To a solution of 1.82 g (8.7 mmol) of III in 70 ml THF were added 70 ml of water under stirring and then 4.43 g (10 mmol) of lead tetracetate. The mixture was refluxed for 30 min. After addition of aqueous NaOH, the mixture was extracted with ether. Red-yellow oil obtained on removal of ether was recrystallized from THF-*n*-heptane to yield 0.95 g (53%) of IV as yellow crystals; mp 42—43°C. Found: C, 69.19; H, 7.80%. Calcd for $C_{12}H_{16}O_3$: C, 69.20; H, 7.74%.

*Solvents and Reagents.* Solvents were purified in the usual way just before use. Commercial $LiAlH_4$ and lead tetracetate were used without further treatment.

*Spectral Measurements.* IR data were obtained with a Perkin-Elmer Model 421 spectrophotometer and NMR data with a Varian Associates Model A-60 spectrometer.

We wish to thank Professor H. G. Cassidy for his continuous encouragement throughout this research. One of us (S.I.) is indebted to The United States Public Health Service for postdoctoral support at Yale University. Thanks are also due to Dr. Akira Terahara for the measurement and interpretation of the spectral data.

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