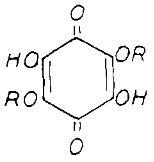
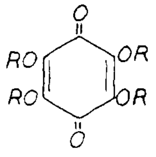
# Derivatives of Tetrahydroxyquinone. Tetrahydroxyquinone Esters

HERBERT S. VERTER and ANDRE FRANK
Central Michigan University, Mount Pleasant, Mich.

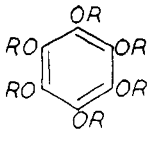
WHEN *n*-BUTYRYL CHLORIDE was refluxed with tetrahydroxyquinone (Ia) under conditions similar to those reported by Hoglan and Bartow (*3*), the major product was a compound which melted 160° lower than the *n*-butyryl derivative previously prepared but not described by analysis (*3*). This indicated that further investigation was in order. Thus far, the investigation has been limited to the propionyl and *n*-butyryl esters of tetrahydroxyquinone.



I



II



III

a. R = H
b. R = $CH_3CH_2CO$—
c. R = $CH_3CH_2CH_2CO$—

When tetrahydroxyquinone was refluxed with propionic anhydride, the black quinone slowly dissolved to form a pale yellow solution from which three compounds were isolated: tetrahydroxyquinone dipropionate (Ib), tetrahydroxyquinone tetrapropionate (IIb), and a trace of hexahydroxybenzene hexapropionate (IIIb). The structure assignments of dipropionate Ib and tetrapropionate IIb are based on elemental and infrared analyses. The infrared spectrum of dipropionate Ib shows characteristic —OH absorption at 3$\mu$ which is absent in the infrared spectrum of tetrapropionate IIb and hexapropionate IIIb. The infrared spectra of dipropionate Ib and tetrapropionate IIb both show strong absorption at approximately 5.65, 5.95, and 6.05$\mu$, which we have assigned to the ester carbonyl, quinone carbonyl and carbon-carbon double bond, respectively. Hexahydroxybenzene hexapropionate (IIIb) was identified with an authentic sample (1) by mixture melting point determination and comparison of the infrared spectra. The 2,5-relationship of the ester groups in dipropionate Ib is not regarded as being established, but by analogy with studies on the basic hydrolysis of tetrahydroxyquinone tetramethylether (*2*), it would appear that the 3,6-dianion produced by hydrolysis of tetraester IIb would be the most stable.

When tetrahydroxyquinone was treated with *n*-butyric anhydride under conditions similar to those used to prepare the propionyl derivatives, a mixture of tetrahydroxyquinone di-*n*-butyrate (Ic) and tetrahydroxyquinone tetra-*n*-butyrate (IIc) was obtained. In this case, no hexahydroxybenzene hexa-*n*-butyrate (IIIc) could be isolated. The melting points of dipropionate Ib and di-*n*-butyrate Ic agree well with the melting points of the propionyl and *n*-butyryl esters reported by Hoglan and Bartow (*3*). Preliminary results from this laboratory suggest that the esters reported by Hoglan and Bartow (*3*) are diesters of general structure I, except for the benzoate, the properties of which seem to correspond with those of the known tetrahydroxyquinone tetrabenzoate (*4*).

## EXPERIMENTAL

Melting points were determined on a Kofler micro hot stage and are corrected. The infrared spectra were obtained in Nujol mulls on a Perkin-Elmer Infracord, Model 137.

**Propionyl esters.** Tetrahydroxyquinone (2 grams) was refluxed for 15 min. with 8 ml. of propionic anhydride containing one drop of sulfuric acid. The reaction mixture was cooled, poured into 40 ml. of benzene, and extracted with several portions of cold sodium bicarbonate solution. The Burgundy-red bicarbonate extract was acidified with concentrated hydrochloric acid and the orange precipitate filtered off. The crude tetrahydroxyquinone dipropionate thus obtained (600 mg., 18%) crystallized from dioxane-cyclohexane as orange platelets, m.p. 231–233° [lit. (*3*) m.p. 231°]. *Anal.* Calcd. for $C_{12}H_{12}O_8$: C, 50.7; H, 4.26. Found: C, 51.0; H, 4.34. The benzene solution was evaporated to dryness and the residue dissolved in 6 ml. of cold benzene. A trace of hexahydroxybenzene hexapropionate was removed by filtration, and the clear filtrate evaporated once again. The crude tetrahydroxyquinone tetrapropionate thus obtained (1 gram, 22%) crystallized from cyclohexane as pale yellow needles, m.p. 104–105°. *Anal.* Calcd. for $C_{18}H_{20}O_{10}$: C, 54.5; H, 5.09. Found: C, 54.7; H, 5.25.

**N-butyryl esters.** The *n*-butyryl esters were prepared by a method similar to that used to prepare the propionyl esters.

Tetrahydroxyquinone di-*n*-butyrate, m.p. 237–238° (dioxane-cyclohexane) [lit. (*3*) m.p. 237°]. Yield: 18%. *Anal.* Calcd. for $C_{14}H_{16}O_8$: C, 53.8; H, 5.17. Found: C, 53.8; H, 5.31.

Tetrahydroxyquinone tetra-*n*-butyrate, m.p. 76–77° (cyclohexane). Yield: 32%. *Anal.* Calcd. for $C_{12}H_{28}O_{10}$: C, 58.4; H, 6.24. Found: C, 58.6; H, 6.19.

## LITERATURE CITED

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