Derivatives of Tetrahydroxyquinone

Tetrahydroxyquinone Esters

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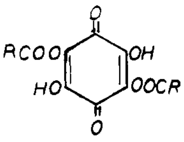
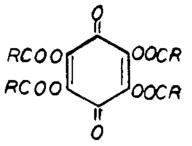
Several esters of tetrahydroxyquinone have been prepared and characterized. Esterification under mild conditions yielded tetrahydroxyquinone diesters; esterification under more vigorous (Spasov) conditions yielded tetrahydroxyquinone tetraesters.

PROPIONYL and *n*-butyryl esters of tetrahydroxyquinone first prepared by Hoglan and Bartow (*1*) were discussed previously (*4*). A conversion of tetrahydroxyquinone into diesters of general structure I and tetraesters of general structure II was described. This article outlines a preparation of other esters in the series. Melting points and properties of the compounds prepared show that all esters reported by Hoglan and Bartow (*1*) are diesters, except for the isobutyryl and benzoyl derivatives, which are tetraesters. Table I characterizes these compounds.



I



II

Using anhydrides larger than butyric anhydride in the esterification procedure described previously (*4*) produces no tetraester. Also, refluxing tetrahydroxyquinone with acid chlorides larger than butyryl chloride, according to the procedure of Hoglan and Bartow (*1*), produces only diester. This may be due to steric retardation of esterification by the larger alkyl groups. Either procedure yields tarry products. However, tetrahydroxyquinone can be smoothly converted to the diesters by heating with the acid chloride at moderate temperatures for several days. Brief reflux of the diester with acid chloride in the presence of magnesium, the Spasov method (*2*), readily converts diester to tetraester. Many hindered alcohols readily esterify under Spasov conditions (*2, 3*).

The methods described previously (*4*) and in this article fail when applied to the dibenzoylation of tetrahydroxyquinone. Esterification gives only tetrabenzoate.

EXPERIMENTAL

Melting points were determined on a Kofler micro hot stage and were corrected.

The esterifications described below for tetrahydroxyquinone diisovalerate and tetrahydroxyquinone tetraisovalerate typify the procedure employed. The diesters crystallized from benzene as orange platelets. Most tetraesters crystallize from pentane, except for tetrahydroxyquinone tetrabenzoate which crystallizes from diglyme. The tetraesters separated as pale yellow needles.

Tetrahydroxyquinone Diisovalerate. Tetrahydroxyquinone (1 gram) was heated with 5 ml. of isovaleryl chloride at 90° for 12 hours. The suspended tetrahydroxyquinone diisovalerate was collected and washed with pentane. The crude diester (451 mg., 23%) crystallized from benzene as orange platelets, m.p. 219° [lit. (*1*) m.p. 218°].

Tetrahydroxyquinone Tetraisovalerate. Tetrahydroxyquinone diisovalerate (153 mg.) was refluxed for 5 minutes with 3 ml. of isovaleryl chloride containing a chip of magnesium. The unreacted acid chloride was removed under reduced pressure, and the residue was washed with cold ethanol. The crude tetrahydroxyquinone tetraisovalerate thus obtained (121 mg., 53%) crystallized from pentane as pale yellow needles, m.p. 104°.

LITERATURE CITED

(1) Hoglan, F.A., Bartow, E., *J. Chem. Soc.* **62**, 2397 (1940).
(2) Spasov, A., *Ber.* **70B**, 1926 (1937).
(3) *Ibid.*, **75B**, 779 (1942).
(4) Verter, H.S., Frank, A., J. CHEM. ENG. DATA **9**, 383 (1964).

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Table I. Characterization of Tetrahydroxyquinone Esters

				Anal. Calcd.		Anal. Found		
Esters	No.	*R*=	M.P.	% C	% H	% C	% H	Yield, %
Diisobutyrate	I	$(CH_3)_2CH$—	208	53.8	5.17	53.9	5.27	38
Tetraisobutyrate	II	$(CH_3)_2)CH$—	127	58.4	6.24	58.2	6.22	71
Divalerate	I	n-C_5H_{11}—	236	56.5	5.92	56.4	5.97	28
Tetravalerate	II	n-C_5H_{11}—	61	61.4	7.14	61.4	7.27	61
Diisovalerate	I	$(CH_3)_2CHCH_2$—	219	56.5	5.92	56.3	6.08	23
Tetraisovalerate	II	$(CH_3)_2CHCH_2$—	104	61.4	7.14	61.7	7.24	53
Di-4-methylvalerate	I	$(CH_3)_2CHCH_2CH_2$—	210	58.7	6.57	58.5	6.52	60
Tetra-4-methylvalerate	II	$(CH_3)_2CHCH_2CH_2$—	84	63.8	7.85	63.9	7.97	49
Di-*n*-octanoate	I	n-C_8H_{17}—	228	62.3	7.60	62.5	7.61	43
Tetra-*n*-octanoate	II	n-C_8H_{17}—	64	67.4	8.93	67.4	8.74	33
Di-*n*-decanoate	I	n-$C_{10}H_{21}$—	215	65.0	8.39	64.9	8.45	39
Tetra-*n*-decanoate	II	n-$C_{10}H_{21}$—	71	70.0	9.71	70.2	9.97	88
Tetrabenzoate	II	C_6H_5—	275	69.4	3.43	69.3	3.68	51