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AUTOXIDATION OF MONO-t-ALKYLDERIVATIVES OF PYROCATECHOL AND HYDROQUINONE

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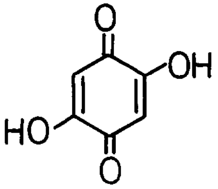
In connection with the study of the oxidation transformations of dihydric phenols in alkaline medium that followed our previous work when one of us had prepared 2,5-dihydroxy-1,4-benzoquinone (I) from pyrocatechol (1) and, under the same conditions, 2-hydroxy-5-t-octyl-1,4-benzoquinone (IIc, R = 1,1,3,3-tetramethylbutyl, R^1=H) from 4-t-octylpyrocatechol (2), we elucidated the products of oxidation of other 4-t-alkylpyrocatechols containing alkyls C_4, C_5 and C_{12}.



I

We isolated hydroxy-1,4-benzoquinones IIa (R = t-butyl, R^1= H), m.p.101-103°. Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.84; H, 6.71 IR spectrum: Fig.1a; IIb (R = 1,1-dimethylpropyl, R^1= H), m.p. 55-58°. Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.81; H, 7.25; and IId (R = 1,1,3,3,5,5-hexamethylhexyl, R^1 = H), m.p. 94-98°. Anal. Calcd. for

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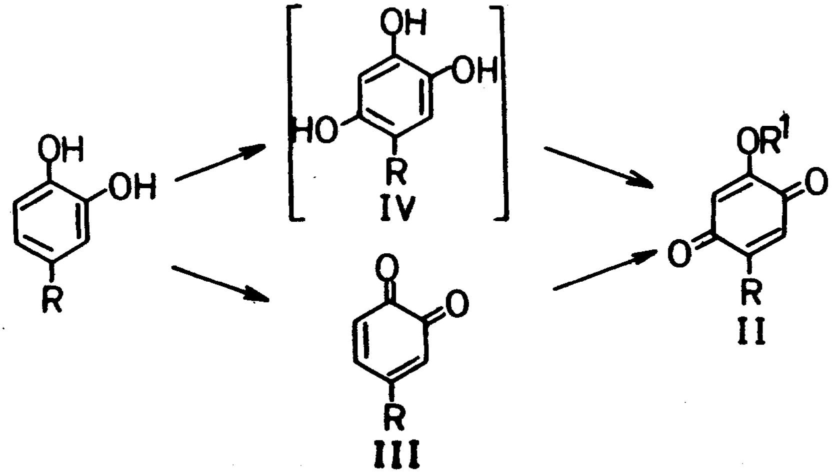
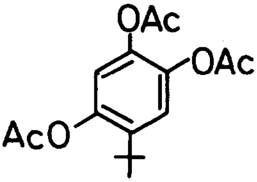
$C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found: C, 73.90; H, 9.80. The same compounds are formed in alkaline medium from 4-t-alkyl-1,2-benzoquinones (III) under conditions quite analogous for the oxidation of t-alkyl pyrocatechols.

Two compounds can be taken in account as intermediates in the mechanism of autoxidation changes of 4-t-alkylpyrocatechols; there can be assumed either primary attack of the free ortho position to the alkyl group in 4-t-alkylpyrocatechol and intermediary formation of 1,2,4-trihydroxy-5-t-alkylbenzene (IV) or formation of 4-t-alkyl-1,2-benzoquinone (III). In the next steps of the reaction both substances can be transformed into hydroxyquinones II (R = t-alkyl, R^1= H). The course of the reaction according to the first alternative can be supported by the result obtained by Flaig et al. (3), who isolated hydroxyquinone of the same properties as the substance IIa during autoxidation of 1,2,4-trihydroxy-5-t-butylbenzene. The possibilities of transforming o-quinones III into hydroxyquinones II (R^1= H) are confirmed in our work.

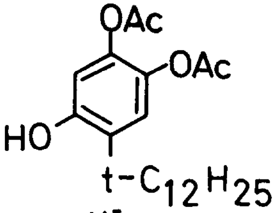


SCHEME 1.

Using the acetylation reaction of hydroxy-1,4-benzoquinones II (R^1= H) we prepared 2-acetoxy-5-t-alkyl-1,4-benzoquinones IIe (R = t-butyl, R^1= Ac), m.p. 91-94°, IIf (R = 1,1-dimethylpropyl, R^1= Ac), m.p. 76-79°, and IIg (R = = 1,1,3,3,5,5-hexamethylhexyl, R^1= Ac), m.p. 69.5 - 73.5°. 1,2,4-Triacetoxy-5-t-butylbenzene (V), m.p. 110-111° was formed by the reductive acetylation reaction of hydroxybenzoquinone IIa. Up to now we have not been successful in preparing a uniform product from the reaction mixture after reductive acetylation of hydroxyquinone IIb. Under the same conditions a diacetate, i.e. 2-(1,1,3,3,5,5-hexamethylhexyl)-4,5-diacetoxyphenol (VI), m.p. 112-114° was formed from hydroxyquinone IId due to steric hindrance of the position 4 by a bulky t-alkyl C_{12}.



V



VI

The yields of hydroxyquinones II (R^1= H) were found considerably dependent on the composition of the reaction medium. As in the case of the oxidation of 4-t-octylpyrocatechol (2), the highest yields of hydroxyquinones IIa, b,d were also reached in oxidizing 4-t-butyl-, 4-t-pentyl-, and 4-t-dodecyl- (i.e. 1,1,3,3,5,5-hexamethylhexyl) pyrocatechols in 75 % aqueous methanol, containing 22,5% KOH. The dependence of the yield of hydroxyquinone IIa on the content of methanol in the mixture water-methanol serves as an example:

Methanol (% vol.)	0	25	50	75
Yield of IIa, %	7,5	24	43	49

The yield of other derivatives is subjected to a similar effect as well. At the same time also the character of the t-alkyl group asserts itself; e.g. the yield of hydroxyquinones increases almost twofold with the size of the alkyl group in the series from t-C_4H_9 to t-$C_{12}H_{25}$.

Under conditions analogous to those of the autoxidation of pyrocatechol derivatives we oxidized even 2-t-alkylderivatives of hydroquinone and 1,4-benzoquinone and found that in addition to some other as yet undefined substances, mono-t-alkylmonohydroxybenzoquinones are formed. These are isomeric to the products of the oxidation of alkylpyrocatechols, from which they differ by chromatographic behavior and spectral properties.

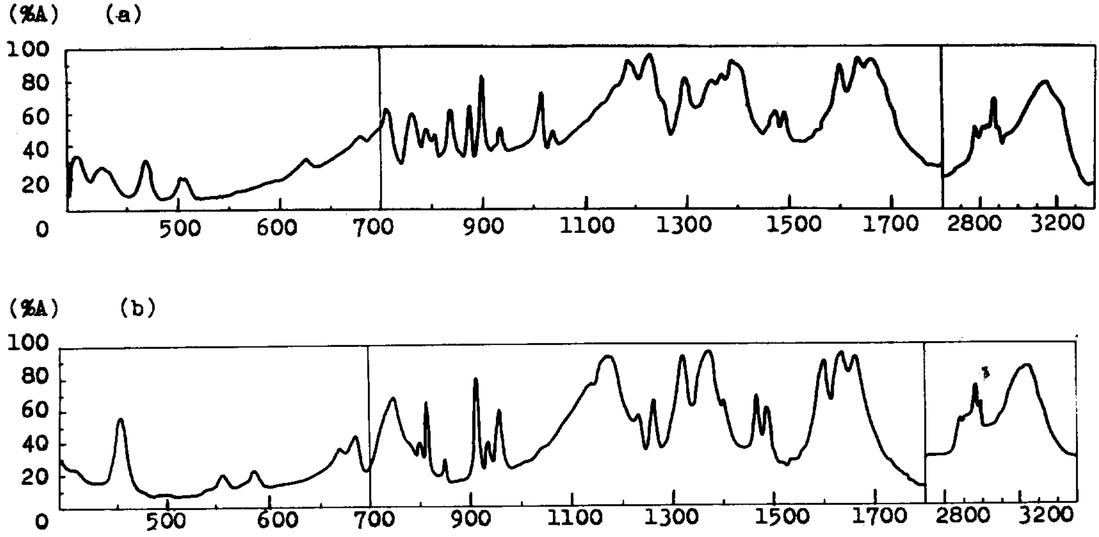
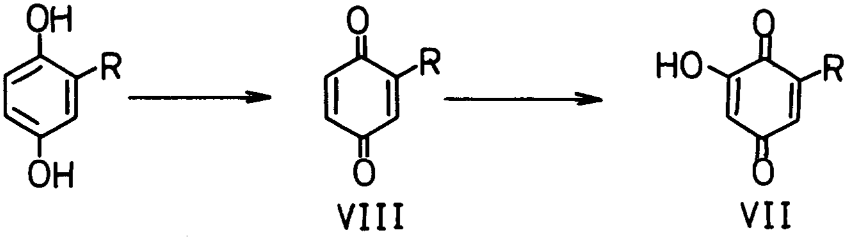


FIG. 1. IR Spectra: a) 2-Hydroxy-5-t-butyl-1,4-benzoquinone (IIa); b) 2-Hydroxy-6-t-butyl-1,4-benzoquinone (VII).

The formation of hydroxyquinones will the structure II was not observed in this case. E.g. a substance with m.p. 124-128° was formed from 2-t-butylhydroquinone. Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.55; H, 6.94. Its IR spectrum (FIG.1b) as well as the IR spectrum, m.p. and mixed m.p. of the triacetate obtained from it by reductive acetylation reaction (m.p. 91-94°) is identical with those of 2-hydroxy-6-t-butyl-1,4-benzoquinone (VII) and 1,2,4-triacetoxy-6-t-butylbenzene resp. prepared according to Flaig et al. (3) as model substances for the purpose of comparison.

Thus, hydroxyquinone VII (R = t-butyl) is the product of the oxidation of 2-t-butylhydroquinone. A substance of the same structure was formed in methanolic KOH in the presence of oxygen even from 2-t-butyl-1,4-benzoquinone (VIII, R= t-butyl). Accordingly, the course of oxidation can be demonstrated in a scheme as follows:



SCHEME 2.

The results of this study point to a difference in the courses of the oxidation of 2-t-alkylhydroquinones and 4-t-alkylpyrocatechols in alkaline medium. A detailed study of these oxidation changes is in progress and the results will be published in full details later.

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