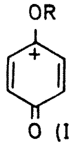
Anodic Acyl and Methyl Transfers from Derivatives of Durohydroquinone

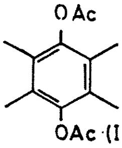
By VERNON D. PARKER

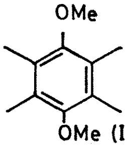
(*Division of Organic Chemistry, University of Lund, Chemical Center, P.O.B. 740, S-22007 Lund, Sweden*)

Summary The diacetyl and dimethyl derivatives of durohydroquinone undergo anodic oxidation accompanied by acyl and methyl transfer, respectively, and the quantitative generation of duroquinone.

CHEMICAL oxidation of hydroquinone monoesters[1] and monoethers[2] results in transfer of the acyl or alkyl group and generation of the quinone. Hydroquinone diesters are resistant to oxidation and acyl transfer has not been observed.[1] The diethers of hydroquinone, for example 1,4-dimethoxybenzene, have been shown to produce relative stable cation-radicals.[3] The ease of acyl and alkyl transfer from the monoesters or ethers of hydroquinone is presumably due to the formation of the intermediate (I). The driving force of the reaction then is the generation of the quinone.


(I)


(II)

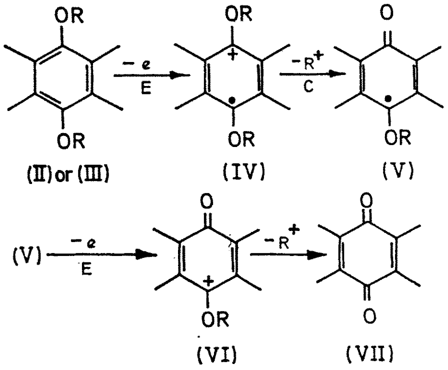

(III)

I now report two new reactions, anodic deacylation and demethylation of a hydroquinone diacetate and dimethyl ether.

The cyclic voltammogram of (II) was recorded in acetonitrile containing lithium perchlorate as supporting electrolyte. On the first anodic sweep, an oxidation peak, O_1, is observed at $+1{\cdot}90$ v.† On reversing the direction of the scan, two cathodic peaks, R_2 ($-0{\cdot}15$ v) and R_3 ($-0{\cdot}56$ v) are observed and on the second anodic scan a new oxidation peak, O_3 ($-0{\cdot}35$ v), appears. The oxidation–reduction couple (O_3–R_3) was enhanced by the addition of duroquinone to the solution. The cathodic peak, R_2, is possibly due to the reduction of the protonated form of the quinone.[4] Controlled-potential coulometry of (I) in the same medium resulted in the consumption of two Faradays per mole of substrate. Voltammetric analysis of the coulometric solution indicated that duroquinone was produced in quantitative yield. The product isolated from controlled-potential electrolysis of (I) was identical with authentic duroquinone.

The oxidation of (II) appears to occur by a 2*e* transfer by the voltammetric techniques employed, however it is very likely that the reaction proceeds by an ECE mechanism (Scheme) in which the initial intermediate is the cation-radical (IV) which undergoes rapid deacylation to the radical (V), followed by a second electron transfer to the cation (VI) and finally, loss of the second acyl group.

The peak potential for the voltammetric oxidation of dimethoxydurene (III) appears at $+1{\cdot}28$ v. The cyclic voltammetry of (III) parallels that of (II) and need not be repeated. Controlled-potential coulometry results in the consumption of two Faradays per mole of substrate and duroquinone was isolated in quantitative yield. The results available at this time do not distinguish between the ECE mechanism (Scheme) and one involving decomposition of an anodically generated dication.



SCHEME. R = Me or Ac.

The occurrence of the deacylation and dealkylation reactions is indeed surprising in view of the availability of methyl groups on the durohydroquinone derivatives. *p*-Methoxytoluene undergoes almost exclusive side-chain anodic oxidation in acetic acid[5] or acetonitrile.[6] Pentamethylanisole undergoes initial one electron oxidation followed by rapid proton loss and in the presence of water, further oxidation to form the corresponding benzyl alcohol.[6]

Anodic acyl and alkyl transfers appear to be general reactions. Preliminary results show that they occur with several mono- and poly-nuclear compounds.

This work was supported by the Swedish Natural Science Research Council. I thank Docent Lennart Eberson for helpful discussions and for providing facilities for this investigation.

(*Received, April* 21*st*, 1969; *Com.* 554.

---

† All potentials referred to in this communication are *versus* the saturated calomel reference electrode.

[1] V. M. Clark, M. R. Eraut, and D. W. Hutchinson, *J. Chem. Soc.* (*C*), 1969, 79.
[2] E. Adler and R. Magnuson, *Acta Chem. Scand.*, 1959, **13**, 505.
[3] A. Zweig, W. G. Hodgson, and W. H. Jura, *J. Amer. Chem. Soc.*, 1964, **86**, 4124.
[4] B. R. Eggins and J. Q. Chambers, *Chem. Comm.*, 1969, 232.
[5] L. Eberson, *J. Amer. Chem. Soc.*, 1967, **89**, 4669.
[6] V. D. Parker and R. N. Adams, submitted for publication.