Reactions of Alkenes with Unstable Cations Electrogenerated from Phenols

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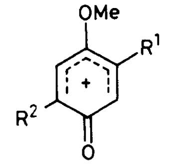
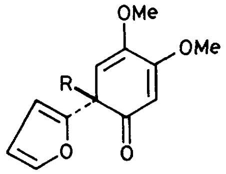
Reactions of several alkenes with the unstable cations electrogenerated from 3,4-dimethoxy-6-methylphenol as well as from *p*-methoxyphenol have been carried out, resulting in C–C bond formation to give the corresponding 1 : 1 adducts.

As seen in many examples of anodic oxidation of phenols, the cations electrogenerated from phenols are readily attacked by solvent molecules (MeOH, H_2O, AcOH, MeCN, *etc.*), while inter- or intra-molecular C–C and C–O coupling reactions take place in the case of the corresponding cation radicals or radicals.[1] For electrogenerated cations C–C bond formation is normally rare except for cyanation using CN^- as a nucleophile. In connection with our synthetic study on *Aniba* neolignans,[2] we have studied the reactions of several alkenes with the cations electrogenerated from 3,4-dimethoxy-6-methylphenol as well as from *p*-methoxyphenol, as follows.

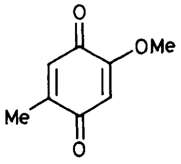
A 30 ml glassy carbon (GC-20) beaker and a platinum wire



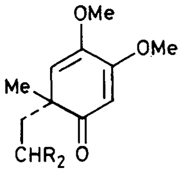
[A] R^1 = OMe, R^2 = Me
[B] R^1 = R^2 = H



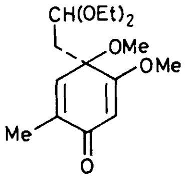
(1) R = Me
(3) R = $CH_2CH{=}CH_2$



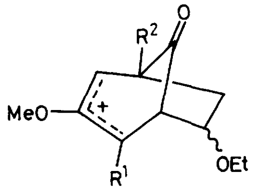
(2)



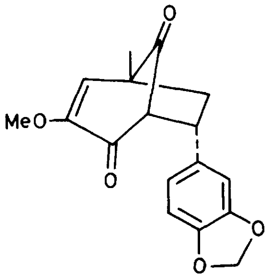
(4) R_2 = O
(5) R = OEt



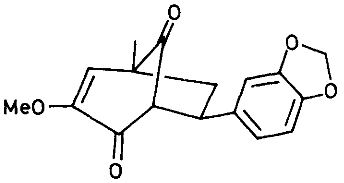
(6)



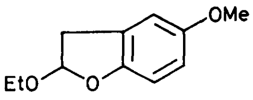
(7) R^1 = OMe, R^2 = Me
(11) R^1 = R^2 = H



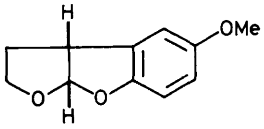
(8)



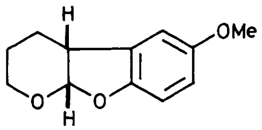
(9)



(10)



(12)



(13)

tip were used as the anode and cathode, respectively, without separating the two electrodes. On electrolysis† of 3,4-dimethoxy-6-methylphenol (0.5 mM) [+780—800 mV *vs.* saturated calomel electrode (S.C.E.)] in AcOH–Ac_2O (3 : 2) (25 ml) containing excess of furan (10 mM) and $Bu^n_4NBF_4$ as a supporting electrolyte under Ar atmosphere, the electrogenerated cation [A] reacted with furan to afford the corresponding 1 : 1 adduct (**1**),‡ although in low yield (6%), in addition to the known quinone (**2**) in 75% yield. However, on electrolysis (+160—220 mV *vs.* S.C.E.)† of the same phenol in Ac_2O alone containing furan and $Bu^n_4NBF_4$, the adduct (**1**) was obtained in 32% yield. In the case of 6-allyl-3,4-dimethoxyphenol, the corresponding adduct (**3**)‡ was obtained in 30% yield. Electrolysis under similar conditions (+180—600 mV *vs.* S.C.E.)† of 3,4-dimethoxy-6-methylphenol in Ac_2O containing ethyl vinyl ether (*ca.* 10 mM) and $Bu^n_4NBF_4$ afforded three dienones (**4**), (**5**), and (**6**)‡ in 29, 18, and 8% yields, respectively;§ the acetal (**5**) was readily converted into (**4**) on acid treatment. Interestingly, the alkene reacts with the electrogenerated cation [A] at C-4 and C-6, while methoxylation of the cation [A] in MeOH takes place regioselectively at C-4.[2] Compounds (**4**) and (**5**) may be formed *via* the intermediate (**7**), although we have no evidence for this. When 3,4-methylenedioxystyrene was used instead of ethyl vinyl ether, both *endo* and *exo* adducts (**8**) and (**9**)‡ were obtained in 47 and 17% yields, respectively.

We also studied the anodic oxidation of *p*-methoxyphenol, providing the corresponding cation [B] which should react with alkenes. Thus, when electrolysed† (+400—800 mV *vs.* S.C.E.) in Ac_2O containing ethyl vinyl ether (*ca.* 10 mM)¶ and excess of $Bu^n_4NBF_4$, *p*-methoxyphenol was converted into the dihydrobenzofuran (**10**)‡ in 33% yield,§ possibly *via* the intermediate (**11**). Use of dihydrofuran and tetrahydropyran instead of ethyl vinyl ether gave the corresponding dihydrobenzofurans (**12**) and (**13**)‡ in 11 and 33% yields, respectively. Although the reaction conditions have not been optimized and satisfactory yields have not yet been obtained, the reactions of the electrogenerated cations with alkenes in Ac_2O result in C–C bond formation giving the corresponding 1 : 1 adducts, which may be difficult to obtain by other methods.||

This research has been supported in part by grants from the Ministry of Education, Science and Culture (Japan), to which grateful acknowledgement is made.

Received, 4th December 1984; Com. 1712

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2 Y. Shizuri and S. Yamamura, *Tetrahedron Lett.*, 1983, **24**, 5011.

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† The electrolyses of the phenols (0.5 mM) were carred out at a constant current of 0.27 mA/cm^2 and quenched after *ca.* 2 F/mol; the isolated yields are given.

‡ The i.r., n.m.r., and high resolution mass spectral data for the new compound(s) were in accord with the stucture(s) assigned.

§ When a mixed solvent of AcOH and Ac_2O was used, the corresponding quinone was mainly obtained rather than adducts.

¶ As the half-wave potential of the alkene is +1.3 V *vs.* S.C.E., the corresponding cation radical will not be formed from it.

|| The authors are indebted to one of the referees for the following comments. In protic media, phenol radical-cations are very acidic and completely ionised to proton and radical except at very negative pH's. This point probably has a bearing on choice of suitable solvents for these reactions.