

Reactions of Alkenes with Unstable Cations Electrogenerated from Phenols

Yoshikazu Shizuri, Kensuke Nakamura, and Shosuke Yamamura*

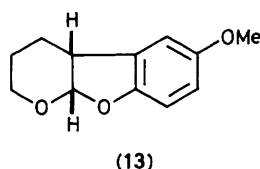
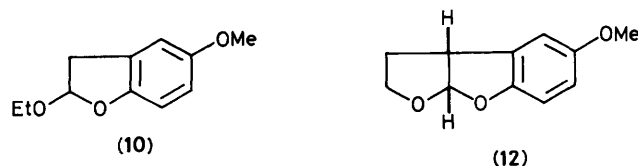
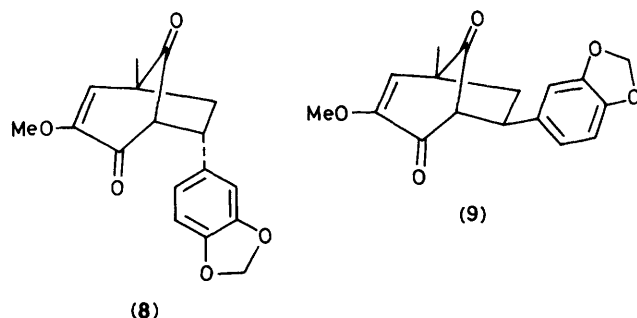
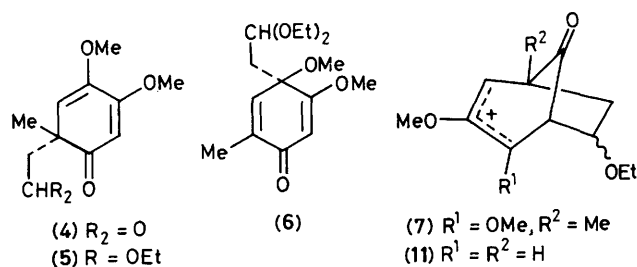
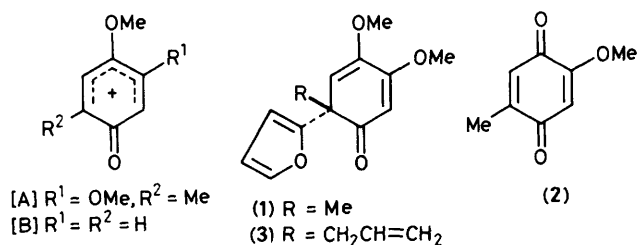
Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Yokohama, Japan

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, H₂O, 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



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 $\text{AcOH}-\text{Ac}_2\text{O}$ (3:2) (25 ml) containing excess of furan (10 mM) and Bu^nNBF_4 as a supporting electrolyte under Ar atmosphere, the electrogenerated cation [A] reacted with furan to afford the

† The electrolyses of the phenols (0.5 mM) were carried out at a constant current of 0.27 mA/cm² and quenched after ca. 2 F/mol; the isolated yields are given.

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^nNBF_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^nNBF_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-methylenedioxybenzene 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^nNBF_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

References

- M. M. Baizer in 'Organic Electrochemistry,' Marcel Dekker, New York, 1973; see also 'Organic Electrochemistry, 2nd edn.,' eds. M. M. Baizer and H. Lund, Marcel Dekker, New York, 1983; 'Technique of Electroorganic Synthesis,' Vols. 1–3, ed. N. L. Weinberger, Wiley, New York, 1974–1983.
- Y. Shizuri and S. Yamamura, *Tetrahedron Lett.*, 1983, **24**, 5011.

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