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Electrochemical Behaviour of 3,3-Sigmatropic Systems - Anodic Oxidation of Aryl Allyl Ethers and Aryl Propargyl Ethers

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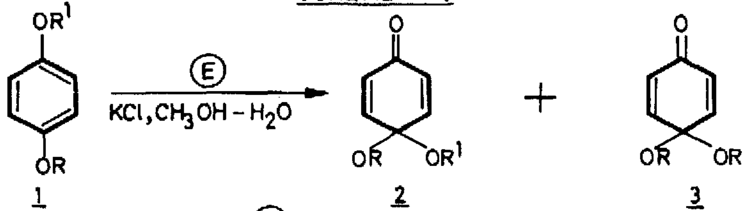
Abstract : The electrochemical oxidation of a few methoxy substituted aromatic 3,3-sigmatropic systems yielded mixed quinone monoketals in aqueous methanol and dimerised products in anhydrous acetonitrile.

In recent years, a lot of interest has been evinced in studies involving cation radicals as pericyclic reaction partners[1]. We have investigated the behaviour of cation radical species generated from aromatic 3,3-sigmatropic oxy-Claisen systems[2]. In the present communication, we report the electrochemical behaviour of a few aryl allyl, aryl propargyl and aryl allenic ethers under the anodic oxidation condition which has been used for the generation of cation radicals[1].

Anodic oxidation of the ethers, 1a-1f, (2.5-3 mmol) in 60% aqueous methanol using a platinum foil electrode (1.5 cm^2 area) at room temperature furnished directly the mixed quinone monoketals, 2 as the major product alongwith a small amount of dimethyl quinone monoketal, 3 (Table 1, Scheme I)[3]. In the case of the ether, 1f,

SCHEME - I



(E) = Applied potential

Table 1

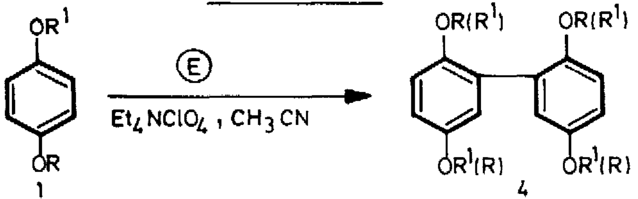
Entry	Compound No.	R	R^1	E_p^a	Yield[b] 2	3
1	1a[c]	CH_3	$CH\equiv C-CH_2$	1.30	65	28
2	1b	CH_3	$CH_2=CH-CH_2$	1.20	70	20
3	1c	CH_3	$CH_2=C=CH-CH_2$	1.25	72	21
4	1d	CH_3	$PhCH=CH-CH_2$	1.26	48	--
5	1e	CH_3	$PhCH_2$	1.15	71	19
6	1f	$CH\equiv C-CH_2$	$CH\equiv C-CH_2$	1.30	78[d]	--

(a) Peak potentials versus SCE in cyclic voltammetry at a platinum microelectrode; (b) yield based on HPLC analysis of crude material; (c) structures are confirmed by spectral data and comparison with authentic samples[5]; (d) in 2f, R=CH_3 and R^1 = $CH\equiv C-CH_2$.

the product isolated was exclusively the mixed quinone monoketal, 2f. Even the more reactive allenic ether, 1c afforded only the ketal 2c[4].

The oxidation of ethers, 1a and 1f in anhydrous acetonitrile afforded mainly the dimerised compounds, 4 in 55-60% yield (Scheme II). In none of these reactions (exhibiting a characteristic deep red colour) were there any evidence for the occurrence of cation radical mediated Claisen rearrangement or cyclisation[6].

SCHEME - II



1

4

(1a) R = CH_3
R^1=CH≡C−CH_2
(1f) R = R^1= CH≡C−CH_2

(4a) R= CH_3
R^1= CH≡C−CH_2
(4f) R = R^1=CH≡C−CH_2

Quinone monoketals are valuable synthons in organic synthesis[7]. Some recent reports describe the formation of quinone ketals from the anodic oxidation of aromatic ethers[8]. To our knowledge, this is the first detailed study on the behaviour of aromatic 3,3-sigmatropic oxy-Claisen systems under anodic oxidation conditions[9]. Our method provides a convenient direct entry to mixed quinone monoketals without involving the hydrolysis of bisketals.

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