Anomalous Course of Electrochemical Oxidation of Furans caused by Aromaticity of the Substituent

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Summary Furans with aromatic or potentially conjugated 2-substituents are electrochemically transformed into 5-methoxyfurans upon anodic oxidation; the results can be explained in terms of the *ECEC* mechanism.

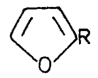
Electrochemical oxidation of furans is known to yield the unsaturated five-membered acetals of general formula (*A*), $\overline{\mathrm{O{\cdot}C(OMe)R^1CR^2 = CR^3C(OMe)R^4}}$, [1,2]. The anomalous oxidation of 2,5-dialkylfurans in acetic acid, using sodium acetate as electrolyte, has been published recently,[3] but these compounds yielded the acetals (*A*) upon anodic oxidation in methanol.

Table. Electrochemical oxidations of furans

Starting compounds	Product[a]	Yield (%)	B.p./°C (Torr)
(I)	(VI)	42	132 (0·6)
(II)	(VII)	68	115 (0·6)
(III)	(VIII)	55	100 (0·9)
(IV)	(IX)	72	120 (0·5)
(V)	(X)	76	75 (12)

[a] All products gave satisfactory elemental analyses and n.m.r. spectra, except the product from (I). In this case the n.m.r. spectrum of the partially crystallised product could not be completely analysed in terms of an ABX system. However, structure (VI) corresponds reasonably with the spectrum and the elemental analysis is satisfactory.

We report a new course of this reaction caused by the aromaticity of a substituent in the 2-position of the furan ring. We have studied this reaction using 2,2′-bifuryl (I)[4] and 2-(2-thienyl)furan (II).[5] Compound (II) gave the anomalous product (VII). In order to investigate the formation of this product we studied the analogous reaction with the substituted furans (III),[6] (IV),[6] and (V).[7] Compound (V) was included in order to elucidate the possible rôle of steric effects of the substituent.[8] Anomalous products were isolated from (III) and (IV). The results are in the Table. In a typical experiment, a constant current of 4 A was passed through a solution, at −25 °C under inert atmosphere, of the furan (0·1 mol) and NH_4Br (4 g) in MeOH (200 ml) in a glass cell[9] with a carbon anode and a nickel cathode, until 4 F/mol had passed. The products were isolated as described previously.[10]

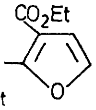


(I) R = 2-furyl

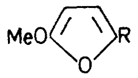
(II) R = 2-thienyl

(III) R = Ph

(IV) R =

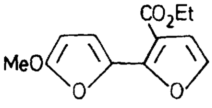


(V) R = Bu^t

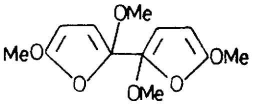


(VII) R = 2-thienyl

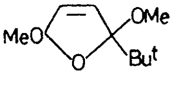
(VIII) R = Ph



(IX)



(VI)



(X)

In our opinion, the anomalous course of the electrochemical reaction could be explained by the *ECEC* mechanism, the last step probably being elimination in the anomalous cases. This mechanism could be denoted as EC_NEC_B. The fact that compound (I) gave no anomalous product could be explained in terms of the aromaticity of the furan, thiophen, and benzene rings, (*ca.* 100 : 75 : 46, respectively).

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