Some Anodic Reactions of Furans

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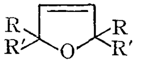
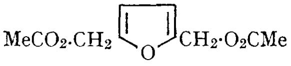
CONSIDERABLE interest has been shown recently in the anodic acetoxylation[1] and methoxylation[2] of organic compounds. We report results obtained when solutions of sodium acetate in acetic acid, and of sodium methoxide in methanol were electrolysed in the presence of furan and 2,5-dimethylfuran. With furan the products were the 2,5-dihydrofurans[3] (I; R = $MeCO_2$; R′ = H) and (I; R = MeO; R′ = H) previously obtained[4] by the action of lead tetra-acetate and by anodic oxidation in neutral or acidic methanol respectively. However, rather different results were obtained with 2,5-dimethylfuran. In the alkaline methanolic electrolyte a 2,5-dihydrofuran[3] was again obtained, but in the acetic acid system the product was 2,5-bisacetoxymethylfuran (II).[5] Neither of these compounds has hitherto been obtained electrolytically. Toluene is reported to undergo nuclear acetoxylation and side-chain methoxylation under similar conditions.



(I)



(II)

The observed substitution reaction must proceed through the abstraction of hydrogen atoms by anodically generated radicals. The acetoxy-group may be introduced by the combination of the resultant radicals with acetoxy-radicals present at the anode, but it is perhaps more likely that the initially formed radicals, which are benzylic in character, are oxidised at the anode to the corresponding carbonium ions, which then combine with acetate ions. In the other cases, where 1,4-addition across the diene system of a furan occurs, a mechanism analogous to either of those currently supported[1] for the anodic acetoxylation of aromatic compounds, *e.g.*, anisole, may be operating. That is, the reaction could involve the 1,4-addition of radicals across the diene system, or the anodic oxidation of the furan itself, followed by attack of the appropriate nucleophile.

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[1] *E.g.*, (a) D. R. Harvey and R. O. C. Norman, *J. Chem. Soc.*, 1964, 4860; (b) L. Eberson and K. Nyberg, *Acta Chem. Scand.*, 1964, **18**, 1568; (c) M. Leung, J. Herz, and H. W. Salzberg, *J. Org. Chem.*, 1965, **30**, 310.

[2] *E.g.*, (a) T. Inoue, K. Koyama, T. Matsuoka, K. Matsuoka, and S. Tsutsumi, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1963, **66**, 1659; (b) T. Inoue and S. Tsutsumi, *Bull. Chem. Soc. Japan*, 1965, **38**, 661.

[3] All 2,5-dihydrofurans were obtained as mixtures of *cis*- and *trans*-isomers.

[4] N. Emling, *Adv. Org. Chem.*, 1960, **2**, 67.

[5] Identified by its n.m.r. spectrum and a mixed m.p. determination.