Electrochemical Production of Alkyl Methyl Carbonates. A Source of Hydroxy-compounds

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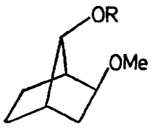
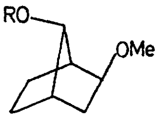
Summary An electrochemical functionalisation of olefins and cyclopropanes involving the introduction of hydroxy-groups *via* alkyl methyl carbonates is described.

Electrolysis of bicyclo[2,2,1]heptene in methanolic sodium methoxide at a platinum anode with a current density of 0·3 A cm^{-2} for 3 h with the passage of 3 F mol^{-1} (method A) gave the carbonates (I, II, and III; R = CO_2Me) as the major products[†] together with the corresponding alcohols (I, II, and III; R = H) and the previously reported[1] methoxylation products (*e.g.* I, II, and III; R = Me). Cyclohexene[2] and 2,3-dimethylbut-2-ene behaved similarly. Hydroxy-ethers were only obtained from styrene[3] and bicyclo[2,2,1]heptadiene when methyl sodium carbonate was substituted for sodium methoxide. Electrolysis of 3,3-dimethylbut-1-ene (IV) (method A) gave only the carbonates (V, VI, and VII; R = CO_2Me). At a current density of 0·1 A cm^{-2} for 48 h with the passage of 9 F mol^{-1} and with methyl sodium carbonate in place of sodium methoxide (method B) the corresponding alcohols (V, VI, and VII; R = H) were formed in yields[‡] of 16, 18, and 1·5% respectively. The one-step routes to (V) and (VI) are of preparative significance.



(I)



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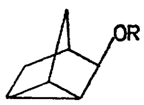

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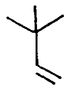

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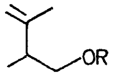

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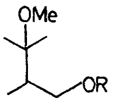
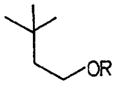
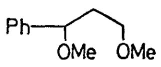


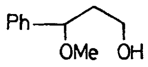
(VI)



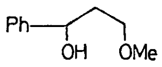
(VII)



(VIII)



(IX)



(X)

We believe that the hydroxy-compounds arise in these essentially non-aqueous systems by transesterification of the corresponding alkyl methyl carbonates during the electrolyses. Compounds (I, II, III, V, VI, and VII; R = CO_2Me) are completely transesterified by methanolic sodium methoxide at room temperature in 48 h and di-

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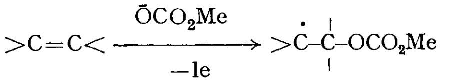
[†] All compounds described in this communication are racemic; only one configuration is shown in displayed formulae. All new compounds have been adequately characterised and structures and stereochemistry have been established by spectroscopic methods, by chemical correlations, and in most cases by direct comparison with samples prepared by rational syntheses.

[‡] Isolated yields; no other products are formed but complete conversion into products was not achieved.

methyl carbonate is present in the product mixture containing (V, VI, and VII; R = H). All the products can be rationalised in terms of an initial electrochemical step of the type in reaction (1). The production of methyl sodium carbonate during the electrolysis of methanolic sodium methoxide was noted many years ago.§[4]



$$>C=C< \xrightarrow[-1e]{\bar{O}CO_2Me} >\dot{C}-\overset{|}{\underset{|}{C}}-OCO_2Me \qquad (1)$$

The procedure can also be applied to cyclopropanes. For example phenylcyclopropane[5] (method B) gives compounds (VIII), (IX), and (X) in 42, 16·5, and 6·5% yield‡ respectively.

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§ W. B. Smith and Y. H. Yuh, *Tetrahedron*, 1968, **24**, 1163 reported the presence of alkyl methyl carbonates amongst the very complex products from the electrolysis of (IV) in methanol containing potassium acetate.

[1] T. Inoue, K. Koyama, T. Matsuoka, and S. Tsutsumi, *Bull. Chem. Soc. Japan*, 1967, **40**, 162; T. Shono and A. Ikeda, *J. Amer. Chem. Soc.*, 1972, **94**, 7892.

[2] A. J. Baggaley and R. Brettle, *J. Chem. Soc.* (*C*), 1968, 2055. The formation of cyclohex-2-en-1-ol and an unidentified methyl ester, now shown to be an alkyl methyl carbonate, was reported in this paper.

[3] T. Inoue and S. Tsutsumi, *Bull. Chem. Soc. Japan*, 1965, **38**, 661.

[4] B. Szilard, *Z. Elektrochem.*, 1906, **12**, 393.

[5] T. Shono and Y. Matsumura, *J. Org. Chem.*, 1970, **35**, 4158.