Anodic Oxidation. Part XIV.[1] Products from the Electrochemical Functionalisation of Olefins in Methanol[2]

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The products formed when 3,3-dimethylbut-1-ene, 2,3-dimethylbut-2-ene, cyclohexene, and styrene are electrolysed in methanol (A) containing methoxide ion, at a high current density, and (B) containing the methyl carbonate ion, at a constant low current density, have been investigated.

We recently reported[1] that electrolysis of bicyclo[2.2.1]heptene in methanolic sodium methoxide at a high current density (method A) gives very low chemical yields of a variety of oxygenated products, including hydroxy-methoxy-compounds and methoxy-substituted alkyl methyl carbonates. We also reported[1] that similar compounds can be obtained from bicyclo[2.2.1]heptadiene if the electrolysis is carried out using a suspension of methyl sodium carbonate in methanol and a constant and relatively low current density (method B). These methods appeared to be potentially useful for the functionalisation of olefins.[2] We now report the extent to which they are of preparative significance for some representative olefins.

The electrolysis of 3,3-dimethylbut-1-ene (I) and potassium acetate in methanol gives twelve products,

$\mathrm{CMe_3{\cdot}CH{:}CH_2}$ (I)

$\mathrm{CH_2{:}CMe{\cdot}CHMe{\cdot}CH_2{\cdot}OR}$ (II)

$\mathrm{Me_2C(OMe){\cdot}CHMe{\cdot}CH_2{\cdot}OR}$ (III)

$\mathrm{CMe_3{\cdot}CH_2{\cdot}CH_2{\cdot}OR}$ (IV)

which include alkyl and alkenyl methyl carbonates.[3] Each of our methods led to a much simpler product spectrum. When (I) was electrolysed by method A only two major products, 2,2-dimethylbut-3-enyl methyl carbonate (II; R = CO_2Me) and 2,3-dimethyl-3-methoxybutyl methyl carbonate (III; R = CO_2Me) were formed, in 2.6 and 1.7% yield,† respectively, after passage of 3 F mol^{-1}. One of the minor products had a g.l.c. retention time identical with that of 3,3-dimethylbutyl methyl carbonate (IV; R = CO_2Me). When (I) was electrolysed by method B, three major products, 2,3-dimethylbut-3-en-1-ol (II; R = H), 2,3-dimethyl-3-methoxybutan-1-ol (III; R = H), and 3,3-dimethylbutan-1-ol (IV; R = H) were formed in 16, 18, and 1.6% yield,† respectively, after passage of 9 F mol^{-1}; the two major components could be obtained by simple fractional distillation. Dimethyl carbonate was also shown to be a product of this electrolysis by analytical g.l.c. The identities of the products (II—IV; R = H or CO_2Me) from these two electrolyses were established by comparisons with authentic samples.[3-5] 2,3-Dimethyl-3-methoxybutan-1-ol (III; R = H) was synthesised as follows. Methoxymercuration of a mixture[6] of ethyl 2,3-dimethylbut-2-enoate and ethyl 2,3-dimethylbut-3-enoate, followed by reduction with sodium borohydride, gave ethyl 2,3-dimethyl-3-methoxybutanoate. Reduction with lithium aluminium hydride then gave (III; R = H), which was converted into the methyl carbonate derivative with methyl chloroformate–pyridine.[3] The one-step electrochemical route to (III; R = H) from the commercially available olefin (I) is more convenient.

The initial step in the formation of the alkyl methyl carbonates from (I) can be regarded[1] as a one-electron oxidation of the olefin with nucleophilic attack by a methyl carbonate anion either present from the start of the electrolysis (method B) or generated by oxidation of methoxide ion at a high current density (method A) to give an intermediate radical. The product (IV) with an unrearranged carbon skeleton then arises by hydrogen abstractions from the solvent by this radical, whereas the other products arise by a further one-electron oxidation to a cation which rearranges to a tertiary cation. This is then either solvolysed [to give (III; R = CO_2Me)] or loses a proton [to give (II; R = CO_2Me)]. At the much longer electrolysis time (48 h) obtaining in method B transesterification of the alkyl methyl carbonates occurs to give the corresponding alcohols (II—IV; R = H) and dimethyl carbonate. We have shown that when a mixture of the electrolysis products (II—IV; R =

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† Chemical yield, based on g.l.c. analysis of the product mixture and not taking into account unchanged starting material.

[1] Part XIII, A. J. Baggaley, R. Brettle, and J. R. Sutton, *J.C.S. Perkin I*, 1975, 1055.

[2] Preliminary account, R. Brettle, and J. R. Sutton *J.C.S. Chem. Comm.*, 1974, 449.

[3] W. B. Smith and Y. H. Yuh, *Tetrahedron*, 1968, **24**, 1163.

[4] N. C. Yang, D. H. Yang, and C. B. Ross, *J. Amer. Chem. Soc.*, 1959, **81**, 135.

[5] H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, 1959, **81**, 6428.

[6] R. C. Huston and G. L. Goerner, *J. Amer. Chem. Soc.*, 1946, **68**, 2504.

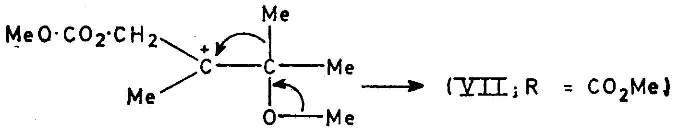
CO_2Me) obtained in 3 h by method A is treated with methanolic sodium methoxide at room temperature for 48 h, complete transesterification to (II—IV; R = H) and dimethyl carbonate occurs.

The electrolysis of the isomeric and more symmetrical olefin 2,3-dimethylbut-2-ene proved to be less useful synthetically. When 2,3-dimethylbut-2-ene was electrolysed by method A five major products, 2,3-dimethoxy-2,3-dimethylbutane (V; $R^1 = R^2 =$ Me), 2,3-dimethylbut-3-en-2-ol (VI), 3-methoxy-2,3-dimethylbutan-2-ol (V; $R^1 =$ H, $R^2 =$ Me), 2-hydroxy-1,1,2-trimethylpropyl formate (V; $R^1 =$ H, $R^2 =$ CHO), and the cyclic carbonate of 2,3-dimethylbutane-2,3-diol (V; $R^1R^2 =$ CO) were formed in 4.8, 3.6, 2.7, 2.4, and 1.9% yield,† respectively. The products were identified spectroscopically (samples separated by preparative g.l.c.), but the unexpected production of the hydroxy-formate (V; $R^1 =$ H, $R^2 =$ CHO) led us to prepare an authentic sample by the method of Hickinbottom and his co-workers;[7] it proved identical (i.r. and ^1H n.m.r.) with the material from the electrolysis. The production of sodium formate on electrolysis of methanolic sodium methoxide has been reported[8] by Giacomello and Mayer; it is thus possible that in this electrolysis formate ion is produced and competes successfully with methoxide and methyl carbonate ions in the formation of products by the solvolysis of cationic intermediates. This is the only example of the production of a formate ester that we have encountered in our recent fairly extensive studies on the electrolysis of olefins in methanol. It is possible that there is a connection between the formation of the hydroxy-formate (V; $R^1 =$ H, $R^2 =$ CHO) and the cyclic carbonate (V; $R^1R^2 =$ CO), since the formation of a cyclic carbonate in the oxidation of an olefin by performic acid has in one case been envisaged as proceeding *via* a hydroxy-formate.[9] However we also encountered a cyclic carbonate in the electrolysis of cyclohexene (see below) where no hydroxy-formate co-occurred so that the rationalisation given below for the formation of that cyclic carbonate may also be correct for the formation of (V; $R^1R^2 =$ CO).

$Me_2C(OR^1){\cdot}Me_2C(OR^2)$ (V)

$CH_2{:}CMe{\cdot}Me_2C{\cdot}OH$ (VI)

$MeCO{\cdot}CMe_2{\cdot}CH_2{\cdot}OR$ (VII)



(VIII)

(VII; R = CO_2Me) (i)

Different results were obtained when 2,3-dimethylbut-2-ene was electrolysed by method B. From a complex mixture of products we separated by preparative g.l.c. and identified four major products, the cyclic carbonate (V; $R^1R^2 =$ CO), 4-hydroxy-3,3-dimethylbutan-2-one (VII; R = H), the corresponding 4-methyl carbonate (XII; R = CO_2Me), and 2-methoxy-3-methoxymethoxy-2,3-dimethylbutane (V; $R^1 =$ Me, $R^2 = MeO{\cdot}CH_2$), formed in 13, 3.8, 3.5, and 1.3% yield,† respectively. Several minor products could not be separated in a pure state or identified but 2,3-dimethoxy-2,3-dimethylbutane (V; $R^1 = R^2 =$ Me) and 3-methoxy-2,3-dimethylbutan-2-ol (V; $R^1 =$ H, $R^2 =$ Me) were shown to be present by analytical g.l.c. The major products were initially identified by their spectroscopic (i.r. and ^1H n.m.r.) properties which were subsequently shown to be identical with those of authentic samples. Compound (V; $R^1 =$ Me, $R^2 = MeO{\cdot}CH_2$) was prepared by partial etherification of 2,3-dimethylbutane-2,3-diol (V; $R^1 = R^2 =$ H) with chloromethyl methyl ether followed by methylation of the intermediate. In our hands a previously reported[10] synthesis of (VII; R = H) proved unsatisfactory; another published method[11] required an inaccessible starting material. Accordingly we prepared (VII; R = H) by reduction of the ethylene acetal of methyl αα-dimethylacetoacetate, followed by deacetalisation. The carbonate (VII; R = CO_2Me) was prepared by using methyl chloroformate–pyridine.[3] Most of these products are clearly secondary, but it is noteworthy that analogous secondary products have not been observed in any of the other olefinic systems which we have recently investigated. The conversion of methoxy-compounds into methoxymethoxy-compounds by electrolysis in methanol has been reported previously[12] and a process of this sort may account for the formation of (V; $R^1 =$ Me, $R^2 = MeO{\cdot}CH_2$) by a secondary reaction involving (V; $R^1 = R^2 =$ Me). However other routes to (V; $R^1 =$ Me, $R^2 = MeO{\cdot}CH_2$) based on another known[13] electrochemical synthesis of acetals can also be envisaged. We have previously noted ketones as secondary products in electrochemical oxidations in methanol. 4-Methoxy-3,4-dimethylpentan-2-one is a product from 2,2,3,3-tetramethylcyclopropanecarboxylic acid.[14] As in that case we believe that the ketone (VII; R = CO_2Me) arises from a methoxy-substituted carbocation [in this case (VIII)] by a process of the type shown in (i). The formation of the cation (VIII) can be rationalised in terms of well known electrochemical reactions of olefins.

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[7] W. J. Hickinbottom, D. R. Hogg, D. Peters, and D. G. M. Wood, *J. Chem. Soc.*, 1954, 4400.

[8] G. Giacomello and A. Mayer, *Gazzetta*, 1935, **65**, 546.

[9] D. F. Kleinfelter and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1961, **83**, 2329.

[10] R. Longeray and J. Dreux, *Bull. Soc. chim. France*, 1964, 2849.

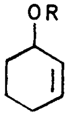
[11] R. A. Schneider and J. Meinwald, *J. Amer. Chem. Soc.*, 1967, **89**, 2023.

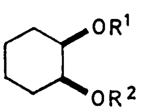
[12] T. Shono and Y. Matsumura, *J. Amer. Chem. Soc.*, 1969, **91**, 2803.

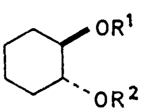
[13] S. D. Ross, J. E. Barry, M. Finkelstein, and E. J. Rudd, *J. Amer. Chem. Soc.*, 1973, **95**, 2193.

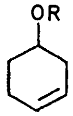
[14] R. Brettle and G. B. Cox, *J. Chem. Soc.* (*C*), 1969, 1227.

We have also reinvestigated the electrolysis of cyclohexene in methanol, since we have earlier reported[15] the formation of cyclohex-2-enol (IX; R = H) and of material which seemed to be a mixture but which showed the spectroscopic properties [$\nu_{max.}$ 1 740 cm^{-1}, τ 6.23(s)] of a methyl ester, along with other products, when cyclohexene was electrolysed in methanolic sodium methoxide. The formation of an unidentified methyl ester in the electrolysis of cyclohexene in methanolic sodium malonate has also been reported.[16] The co-occurrence of an alcohol and a methyl ester in our earlier work led us to suspect that the unidentified methyl ester might be an alkyl methyl carbonate and that the alcohol (IX; R = H) might be produced in a secondary reaction from the corresponding alkyl methyl carbonate (IX; R = CO_2Me), since we have now observed the co-formation of hydroxy-compounds and the corresponding alkyl methyl carbonates during electrolysis of several olefins in methanol.[1,2] When cyclohexene was electrolysed by method A (*cf.* ref. 15) the products included 3-methoxycyclohexene (IX; R = Me), dimethoxymethylcyclopentane, cyclohex-2-enol (IX; R = H), cyclohex-3-enyl methyl carbonate (XII; R = CO_2Me), cyclohex-2-enyl methyl carbonate (IX; R = CO_2Me), and the previously reported 'ester' mixture, each formed in yields † in the range 0.5—1.0%, together with some compounds having a longer retention time on g.l.c. which were not investigated. Smaller amounts of products corresponding in retention time to both *cis*- and *trans*-1,2-dimethoxycyclohexane (X and XI *; $R^1 = R^2$ = Me) were detected by g.l.c.–mass spectrometry. The two cyclohexenyl methyl carbonates (IX and XII; R = CO_2Me) were isolated by preparative g.l.c. and identified by comparison (g.l.c., i.r., and ^1H n.m.r.) with authentic samples prepared by standard methods. The previously reported 'ester' mixture was separated from the other products by preparative g.l.c. and had spectroscopic properties (i.r. and ^1H n.m.r.) consistent with it being a mixture of cyclohexyl methyl carbonate and *trans*-2-methoxycyclohexanol (XI*; R^1 = Me; R^2 = H). Analytical g.l.c. (capillary column) showed that the mixture contained two components (peak areas 4 : 1) having retention times identical with those of the above-named pair of compounds. Similar results were obtained when cyclohexene was electrolysed by method B except that the cyclohexenyl methyl carbonates (IX and XII; R = CO_2Me) were not present, but both cyclohex-3-enol (XII; R = H) and cyclohex-2-enol (IX; R = H) were ; dimethyl carbonate was also detected by analytical g.l.c. The ratio of (XII; R = CO_2Me or H) to (IX; R = CO_2Me and/or H) was essentially the same for the two electrolyses. *trans*-2-Hydroxycyclohexyl methyl carbonate (XI *; $R^1 = CO_2Me$, R^2 = H) and the cyclic carbonate from *trans*-cyclohexane-1,2-diol (XI *; R^1R^2 = CO) were identified amongst the higher boiling products from the second electrolysis by comparison (g.l.c., i.r., and ^1H n.m.r.) of samples isolated by preparative g.l.c. with authentic samples prepared by standard methods, and *cis*-2-hydroxycyclohexyl methyl carbonate (X; $R^1 = CO_2Me$, R^2 = H) was also detected by analytical g.l.c. Pure samples of the remaining high-boiling products could not be obtained by preparative g.l.c. Compounds (XI *; $R^1 = CO_2Me$, R^2 = H) and (XI *; R^1R^2 = CO) were formed in 5.4 and 2.2% yields,† respectively.


(IX)


(X)


(XI)


(XII)

We have previously reported[15] the formation of 3-methoxycyclohexene (IX; R = Me), dimethoxymethylcyclopentane, and *cis*- and *trans*-1,2-dimethoxycyclohexane (X and XI; $R^1 = R^2$ = Me) in the electrolysis of cyclohexene in methanolic sodium methoxide. In a more recent report of the electrolysis of cyclohexene in methanol containing a quaternary ammonium salt the products are given[17] as (IX; R = Me), dimethoxymethylcyclopentane, and just the *trans*-1,2-dimethoxycyclohexane (XI; $R^1 = R^2$ = Me). Our present results confirm that both the *cis*- and *trans*-forms of 1,2-dimethoxycyclohexane are minor products of the electrolysis by method A, which corresponds to the method used previously,[15] although there is a preponderance of the *trans*-form. By method B the amount of the *trans*-1,2-dimethoxycyclohexane produced was very small, and the *cis*-form was not detected by g.l.c. The *trans*-forms also preponderate in the cases of the diol monoethers (X and XI; R^1 = Me, R^2 = H) and mono(methyl carbonate) derivatives (X and XI; $R^1 = CO_2Me$, R^2 = H).

The mechanism of the electrochemical allylic substitution of cyclohexene has been discussed recently.[17] We now believe that the allylic alcohol (IX; R = H) arises by transesterification of the corresponding methyl carbonate (IX; R = CO_2Me) which is formed in an electrochemical substitution reaction involving the methyl carbonate ion. The production of cyclohex-3-enyl methyl carbonate (XII; R = CO_2Me), the presumed precursor of the corresponding alcohol (XII; R = H), seems to be the first example of electrochemical homoallylic substitution. This surprising result can in principle be rationalised in terms of a 1,2-hydride shift in an intermediate cation. Such rearrangements are well documented for the unsubstituted cyclohexane ring[18] but in this case the positive charge would be adjacent to the oxygen substituent, so that ring contraction to give an oxygen-stabilised cation, which is analogous to the precursor of dimethoxymethylcyclopentane, seems more likely. Dimethoxymethylcyclopentane and cyclohex-3-enyl methyl carbonate (XII;

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* Only one enantiomer of the racemic product is shown in the displayed formula.

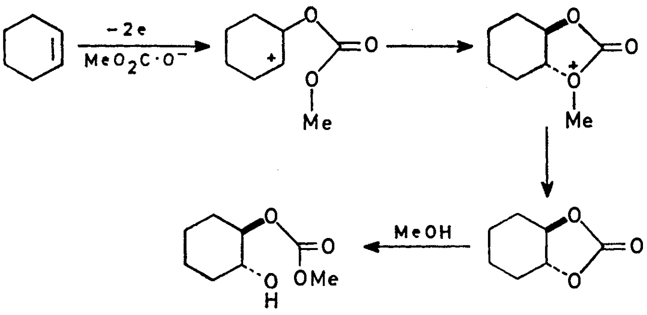
[15] A. J. Baggaley and R. Brettle, *J. Chem. Soc.* (*C*), 1968, 2055.

[16] E. K. Spicer and H. G. Gilde, *Chem. Comm.*, 1967, 373.

[17] T. Shono and A. Ikeda, *J. Amer. Chem. Soc.*, 1972, **94**, 7892.

[18] J. L. Fry and G. J. Karabatsos, 'Carbonium Ions' Wiley–Interscience, New York, 1969, p. 553.

R = CO_2Me) were formed in roughly equal amounts in our first electrolysis. We suggest that the cyclic carbonate (XI; R^1R^2 = CO) may arise by the process shown in the Scheme and that it is the precursor of the diol mono(methyl carbonate) (XI; R^1 = CO_2Me, R_2 = H) (*cf.* ref. 19). The cyclic carbonate (V; R^1R^2 = CO) produced in the electrolysis of 2,3-dimethylbut-2-ene (see above) may arise by a pathway analogous to that shown in the Scheme.



SCHEME *

We have also investigated the low-boiling products from the electrolysis of styrene in methanol containing the methyl carbonate ion. It had earlier been reported [20] that the electrolysis of styrene in methanolic sodium methoxide gave 1,2-dimethoxy-1-phenylethane (XIII; X = Y = OMe), 1-methoxy-1-phenylethane (XIII; X = OMe, Y = H), and 1-methoxy-2-phenylethane (XIII; X = H, Y = OMe), together with the higher

$PhCHX{\cdot}CH_2Y$

(XIII)

boiling *meso*-1,4-dimethoxy-2,3-diphenylbutane. When styrene was electrolysed by method B the two most abundant low-boiling products were 1,2-dimethoxy-1-phenylethane (XIII; X = Y = OMe) [20] and 2-methoxy-2-phenylethanol (XIII; X = OMe, Y = OH).[21] Method B involves the use of sodium methyl carbonate, which is only sparingly soluble in methanol and so we have also made a brief study of the low-boiling products from the electrolysis of styrene in the presence of lithium methyl carbonate, which is much more soluble in methanol.[22] When styrene was electrolysed in methanolic lithium methyl carbonate the major low boiling products were 1,2-dimethoxy-1-phenylethane (XIII; X = Y = OMe),[20] 2-methoxy-2-phenylethanol (XIII; X = OMe, Y = OH),[21] and 2-methoxy-1-phenylethanol (XIII; X = OH, Y = OMe),[21] formed in 5.6, 3, and 1% yield,† respectively. 2-Phenylethanol (XIII; X = H, Y = OH) was also detected amongst the minor products by g.l.c., but the two ethers reported in the earlier work [20] were not detected. We presume that (XIII; X = OMe, Y = OH or *vice versa*), like other hydroxy-methoxy-compounds encountered in our recent work,[1,2] arise by transesterification of the corresponding alkyl methyl carbonates (XIII; X = OMe, Y = $O{\cdot}CO_2Me$ or *vice versa*) which themselves arise by an EC_NEC_N process in which the initial nucleophilic attack is by the methyl carbonate ion. The orientation in the initial attack, which also competes with attack by methanol leading to (XIII; X = Y = OMe), takes place, as expected, predominantly at the terminal carbon atom to give an intermediate benzylic radical. The production of (XIII; X = H, Y = OH) from styrene is analogous to the production of (IV; R = H) from (I) described above.

EXPERIMENTAL

^1H n.m.r. spectra were recorded on a Perkin-Elmer R12A or Varian HA-100 instrument for solutions in $CDCl_3$ or CCl_4 with Me_4Si as internal standard. In all cases integration agreed with the proton assignments. I.r. spectra were measured on a Perkin-Elmer 137 or 457 instrument. G.l.c.–mass spectrometry was performed on a Pye 104 chromatograph with a 6 ft glass column packed with 5% FFAP on 80—100 mesh Chromosorb G operating at 60—220 °C (programmed at 6° min^{-1}) with a carrier gas (He) flow rate of 60—40 ml min^{-1} and connected by a Biemann separator to an A.E.I. MS 12 mass spectrometer.

Analytical g.l.c. was carried out on a Perkin-Elmer F11 chromatograph (6 ft glass columns containing 5% FFAP or 2.5% OV 17 on 80—100 mesh Chromosorb G, 15% hexadecane on 60—80 mesh Chromosorb P, or 80—100 mesh Porapak Q, or a 50 m × 25 mm stainless steel capillary column containing Carbowax 20M). Preparative g.l.c. was carried out on a Pye 105 instrument [glass columns containing 7% FFAP or 10% OV 17 on 60—80 mesh Chromosorb G, 30% Harflex 370 on 80—100 mesh Chromosorb W (all 7 ft columns), or 30% Carbowax 20M on 60—80 mesh Chromosorb W (10 ft column)]. Semipreparative g.l.c. was carried out on an F and M 720 instrument [6 ft metal columns containing 10% polyphenyl ether (5 ring polymer) or Carbowax 20M on 60—80 mesh Chromosorb W]. The F11 and Pye 105 instruments had flame ionisation detectors and were operated at carrier gas (N_2) flow rates of 40 and 105 ml min^{-1}, respectively. The F and M instrument had a thermal conductivity detector and was operated at a carrier gas (N_2–H_2, 9 : 1) flow rate 40 ml $min.^{-1}$

General Procedures for Electrolyses.—(i) *Method A.* The olefin (0.1 mol) in methanolic 0.625M-sodium methoxide (400 ml) was electrolysed in the individual cell having a platinum anode and a mercury cathode described previously [1,23] with the passage of 3 F mol^{-1}. The current density of initially 0.3 A cm^{-2} at 12 V fell to 0.01 A cm^{-2} at 100 V in *ca.* 3 h. The methanol was then distilled off and water (50 ml) was added. The mixture was then extracted with ether (3 × 50 ml), the combined extracts were dried, and the ether was removed to give the crude electrolysis products.

(ii) *Method B.* Dry carbon dioxide was passed through methanolic 0.5M-sodium methoxide (200 ml) for 15 min. The olefin (0.1 mol) was then added to the suspension and the mixture was electrolysed in the simple undivided cell with platinum electrodes described previously.[1] A constant current density of 0.1 A cm^{-2} was maintained at *ca.* 45 V for

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[19] E. I. Stout, W. M. Doane, B. S. Shasha, C. R. Russell, and C. E. Rist, *Tetrahedron Letters*, 1967, 4481.

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

[21] W. Reeve and I. Christoffel, *J. Amer. Chem. Soc.*, 1950, **72**, 1480; S. Winstein and L. L. Ingraham, *ibid*, 1955, **77**, 1738.

[22] W. Behrendt, G. Gattow, and M. Drager, *Z. anorg. Chem.*, 1973, **397**, 237.

[23] R. Brettle and D. Seddon, *J. Chem. Soc.* (*C*), 1970, 2175.

48 h, corresponding to the passage of 9 F mol^{-1}. The crude product was isolated as in the previous method.

Starting Materials and Reference Compounds.—2,3-Dimethylbut-2-ene was prepared from 2,3-dimethylbutane-2,3-diol [24] and purified by distillation; it had b.p. 70—72° (lit.,[24] 72—73°) and was pure by g.l.c. (6 ft hexadecane; 40 °C; t_R 20.25 min). 2-Methylbut-2-ene, b.p. 37.5° (lit.,[25] 37.5°) was prepared by dehydration of 2-methylbutan-2-ol [25] and separated for the 2-methylbut-1-ene, also formed, by distillation through a 1 m spinning-band column. It was converted into 2,3-dimethylbut-3-en-1-ol (II; R = H), b.p. 133—135° at 755 mmHg (lit.,[4] 132—133° at 749 mmHg) by a Prins reaction; [4] the methyl carbonate derivative [3] (II; R = CO_2Me) was prepared with methyl chloroformate and was purified by preparative g.l.c. (Carbowax 20 M; 120 °C), $\nu_{\text{max.}}$ (CCl_4) 1 750, 1 650, 1 440, 1 265, 965, and 890 cm^{-1}, τ (CCl_4) 5.26 (m, $CH_2{=}C$), 5.8—6.2 (m, $C\mathit{H}_2O{\cdot}CO_2Me$), 6.32 (s, $O{\cdot}CO_2\mathit{Me}$), 7.3—7.7 (m, $C\mathit{H}CH_3$), 8.26 (s, $={C}{\cdot}CH_3$), and 8.92 (d, *J* 7 Hz, $CH{\cdot}C\mathit{H}_3$). A mixture of ethyl 2,3-dimethylbut-2-enoate and ethyl 2,3-dimethylbut-3-enoate (peak areas 5 : 8, t_R 6.5 and 8.5 min on FFAP; 60—160 °C at 5° min^{-1}) was prepared by the method [6] of Huston and Goerner (dehydration of ethyl 3-hydroxy-2,3-dimethylbutanoate prepared by a Reformatskii reaction between acetone and ethyl α-bromopropionate [26]). 2-Hydroxy-1,1,2-trimethylpropyl formate (V; R^1 = CHO, R^2 = H) was prepared from 2,3-dimethylbut-2-ene [7] and purified by preparative g.l.c. (Carbowax 20 M; 130 °C); $\nu_{\text{max.}}$ (CCl_4) 3 600, 3 460, 1 725, 1 195, 1 160, 1 140, and 1 100 cm^{-1}, τ (CCl_4) 2.03 (s, $O{\cdot}CHO$), 7.43 (s, OH), and 8.50 and 8.83 (2 × s, 2 × Me). 2,3-Dimethylbutane-2,3-diyl carbonate (V; R^1R^2 = CO) was prepared from the diol [27] and had m.p. 180° (lit.,[28] 180—181°), $\nu_{\text{max.}}$ 1 805, 1 265, and 1 020 cm^{-1}. Cyclohex-2-enol [15] (IX; R = H), cyclohex-3-enol [29] (XII; R = H), b.p. 66—68° at 15 mmHg (lit.,[29] 164—165° at 760 mmHg), $\nu_{\text{max.}}$ (film) 3 330, 3 020, 1 645, 1 065, 1 645, and 1 035 cm^{-1}, τ ($CDCl_3$) 4.40 (m, CH=CH), 5.90—6.30 (m, $C\mathit{H}{\cdot}OH$), 7.45 (s, OH, exchangeable), and 7.65—8.65 (complex, methylenes), cyclohexyl methyl carbonate,[30] $\nu_{\text{max.}}$ (CCl_4) 1 745, 1 440, 1 275, and 1 255 cm^{-1}, τ (CCl_4) 5.35—5.63 (m, $C\mathit{H}{\cdot}O{\cdot}CO_2Me$), 6.34 (s, $O{\cdot}CO_2Me$), and 7.9—8.75 (complex, methylenes), and *trans*-cyclohexane-1,2-diyl carbonate [31] (XI; R^1R^2 = CO), m.p. 42—43° (lit.,[31] 47°), $\nu_{\text{max.}}$ (CCl_4) 1 795, 1 350, 1 160, 1 140, and 1 030 cm^{-1}, τ (CCl_4) 5.15—5.45 (m, 2 × $CH{\cdot}O{\cdot}CO$) and 7.9—8.75 (complex, methylenes), were prepared by literature methods. Reaction of methanolic sodium methoxide with styrene oxide [21] (XIII; XY = O) gave a mixture of 2-methoxy-1-phenylethanol (XIII; X = OH, Y = OMe) and 2-methoxy-2-phenylethanol (XIII; X = OMe; Y = OH) (peak areas 2 : 1 on FFAP; 60—220° at 5° min^{-1}, t_R 25.5 and 24 min, respectively) from which samples of (XIII; X = OH, Y = OMe), $\nu_{\text{max.}}$ (CCl_4) 3 600, 3 475, 2 915, 2 895, 2 820, 1 445, 1 190, and 1 120 cm^{-1}, and (XIII; X = OMe, Y = OH), $\nu_{\text{max.}}$ (CCl_4) 3 600, 3 475, 2 915, 2 870, 2 815, 1 455, 1 110, 1 060, and 1 040 cm^{-1}, τ (CCl_4) 2.77 (s, Ph), 5.80 (dd, $PhC\mathit{H}{\cdot}OMe$), 6.38—6.62 (m, $C\mathit{H}_2{\cdot}OH$), 6.74 (s, OMe), and 7.40 (s, OH, exchangeable), were isolated by preparative g.l.c. (Carbowax 20M, 200 °C). 2-Phenylethanol (XIII; X = H, Y = OH), b.p. 100—103° at 15 mmHg (lit.,[31] 116—118° at 25 mmHg), 1-methoxy-1-phenylethane (XIII; X = OMe, Y = H), b.p. 58° at 15 mmHg (lit.,[20] 74—75° at 30—32 mmHg), and 1-methoxy-2-phenylethane, b.p. 68—74° at 15 mmHg (lit.,[20] b.p. 46—47° at 3—4 mmHg), were prepared by literature methods.

3-*Methoxy*-2,3-*dimethylbutan*-1-*ol* (III; R = H).—A mixture (4.4 g, 0.03 mol) of ethyl 2,3-dimethylbut-2-enoate and ethyl 2,3-dimethylbut-3-enoate was added in one portion to a stirred suspension of mercury(II) acetate (10.3 g, 0.03 mol) in methanol (35 ml). The mixture was stirred for 24 h at room temperature, and then 3M-sodium hydroxide (35 ml) was added, followed by sodium borohydride (1.3 g) in 3M-sodium hydroxide (35 ml). The solution was stirred for a further 30 min at room temperature and then extracted with ether (3 × 30 ml). The combined extracts were dried and the ether was removed to give an oil (3.5 g), τ ($CDCl_3$) 6.85 (s, OMe), part of which (2.8 g) in dry ether (10 ml) was then added with vigorous stirring to lithium aluminium hydride 0.92 g) in dry ether (15 ml) at such a rate that the ether maintained a gentle reflux. The mixture was stirred and refluxed for a further 30 min and then cooled in ice. Water (3 ml) was added, followed by 10N-hydrochloric acid (9 ml), and the mixture was cooled and stirred for 30 min. The inorganic residue was filtered off and washed with 10N-hydrochloric acid (2 ml), and the combined filtrate and washings were extracted with ether (3 × 10 ml). The combined extracts were dried and evaporated to give an oil (1.1 g) which was shown to contain only one major component (t_R 13.75 min) by analytical g.l.c. (FFAP; 80—180 °C at 4° min^{-1}). Preparative g.l.c. (Carbowax 20M; 135 °C) gave 3-*methoxy*-2,3-*dimethylbutan*-1-*ol* (III; R = H), $\nu_{\text{max.}}$ (film) 3 400 and 1 020 cm^{-1}, τ ($CDCl_3$) 6.3—6.7 (m, $C\mathit{H}_2{\cdot}OH$), 6.78 (s, OMe), 8.0—8.5 (m, $CH\mathit{Me}$), 8.27 (s, OH), 8.82 and 8.87 (2 × s, Me_2C), and 9.14 (d, $CH\mathit{Me}$) (Found: C, 63.4; H, 12.0. $C_7H_{16}O_2$ requires C, 63.6; H, 12.1%). The *methyl carbonate derivative* (III; R = CO_2Me), prepared by the standard method [3] and purified by preparative g.l.c. (Carbowax 20 M; 190 °C), had $\nu_{\text{max.}}$ (CCl_4) 1 748, 1 440, 1 380, 1 365, 1 270, 1 080, and 970 cm^{-1}, τ (CCl_4) 5.65—6.3 (m, $C\mathit{H}_2{\cdot}O{\cdot}CO_2Me$), 6.32 (s, $O{\cdot}CO_2Me$), 6.87 (s, OMe), 8.05 (m, $C\mathit{H}Me$), 8.89 and 8.92 (2 × s, Me_2C), and 9.06 (d, $CH\mathit{Me}$) (Found: C, 56.5; H, 9.3. $C_9H_{18}O_4$ requires C, 56.8; H, 9.5%).

3,3-*Dimethylbutyl Methyl Carbonate* (IV; R = CO_2Me).—This was prepared from 3,3-dimethylbutan-1-ol (IV; R = H) [5] by the standard method [3] and purified by preparative g.l.c. (Carbowax 20 M; 195 °C). It had $\nu_{\text{max.}}$ (CCl_4) 1 745, 1 440, 1 365, 1 310, 1 270, and 950 cm^{-1}, τ (CCl_4) 5.91 (t, $C\mathit{H}_2{\cdot}O{\cdot}CO_2Me$), 6.32 (s, $O{\cdot}CO_2Me$), 8.43 (t, $C\mathit{H}_2{\cdot}CH_2$), and 9.04 (s, 3 × *Me*) (Found: C, 60.1; H, 10.3. $C_8H_{16}O_3$ requires C, 60.0; H, 10.0%).

Methoxymethylation of 2,3-*Dimethylbutane*-2,3-*diol*.—Chloromethyl methyl ether [32] (23.7 g), dimethylaniline

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(37 g), and 2,3-dimethylbutane-2,3-diol (52 g) in benzene (100 ml) were stirred together for 7 h at 20—23 °C. The mixture was washed with N-hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and water and then dried. Distillation gave two fractions: (i) b.p. 60—64° at 10 mmHg (12.4 g) and (ii) b.p. 70—80° at 10 mmHg (4.8 g). G.l.c. (FFAP; 60—220 °C at 6° min^{-1}) showed that fraction (i) contained two major components (t_R 9.25 and 11 min, peak areas 9 : 1) and that fraction (ii) contained the same two components (peak areas 9 : 4). Samples of the two components were isolated by preparative g.l.c. (Carbowax 20 M; 180 °C). The first peak (t_R 9.25 min) was 3-*methoxymethoxy*-2,3-*dimethylbutan*-2-*ol* (V; $R^1 = CH_2 \cdot OMe$, $R^2 = H$), $\nu_{max.}$ (CCl_4) 3 580, 1 375, 1 365, 1 160, 1 140, 1 110, 5.34 (s, $OCH_2 \cdot OMe$), 6·68, 1 080, and 1 030 cm^{-1}, τ (CCl_4) (s, OMe), 7.50 (s, OH) and 8.81 and 8.88 (2 × s, 4 × Me). (Found: C, 59.1; H, 10.9. $C_8H_{18}O_3$ requires C, 59.3; H, 11.1%). The second peak (t_R 11 min) was 2,3-*bis*(*methoxymethoxy*)-2,3-*dimethylbutane* (V; $R^1 = R^2 = CH_2 \cdot OMe$), $\nu_{max.}$ (CCl_4) 1 370, 1 360, 1 210, 1 125, 1 080, 1 030, and 915 cm^{-1}, τ (CCl_4) 5.35 (s, 2 × $CH_2 \cdot OMe$), 6.72 (s, 2 × OMe), and 8.79 (s, 4 × Me) (Found: C, 58.3; H, 10.5. $C_{10}H_{22}O$ requires C, 58.3; H, 10.7%).

2-*Methoxy*-3-*methoxymethoxy*-2,3-*dimethylbutane* (V; $R^1 = CH_2 \cdot OMe$, $R^2 = Me$).—3-Methoxymethoxy-2,3-dimethylbutan-2-ol (3.9 g, 0.024 mol) in 1,2-dimethoxyethane (30 ml) was added to a refluxing mixture of sodium (1.32 g, 0.057 g atom) in 1,2-dimethoxyethane (60 ml). After a further reflux of 1 h, dimethyl sulphate (6 g, 0.048 mol) in 1,2-dimethoxyethane (15 ml) was added dropwise over 5 min. The mixture was cooled and treated with 1.75M-ammonium hydroxide (30 ml) and then water (30 ml). Ether (60 ml) was added and the organic layer was separated. The aqueous layer was extracted with ether (3 × 60 ml) and the combined extracts were dried and evaporated. Analysis of the residual oil (1.5 g) by g.l.c. (FFAP; 60—220 °C at 6° min^{-1}) showed the presence of two components (t_R5 and 6.5 min) in equal amounts. Samples of these were isolated by semipreparative g.l.c. (Carbowax 20M; 80 °C). The first peak (t_R 5 min) was identical (i.r. and ^1H n.m.r.) with 3-methoxy-2,3-dimethylbutan-1-ol (see below). The second peak (t_R 6.5 min) was 2-*methoxy*-3-*methoxymethoxy*-2,3-*dimethylbutane* (V; $R^1 = CH_2 \cdot OMe$, $R^2 = Me$), $\nu_{max.}$ (CCl_4) 1 370, 1 360, 1 160, 1 150, 1 090, 1 070, and 1 040 cm^{-1}, τ (CCl_4) 5.38 (s, $O \cdot CH_2 \cdot OMe$), 6.74 (s, $O \cdot CH_2 \cdot OMe$), 6.85 (s, OMe), and 8.84 and 8.89 (2 × s, 4 × Me) (Found: C, 61.6; H, 11.5. $C_9H_{20}O_3$ requires C, 61.4; H, 11.4%).

Methyl αα-*Dimethylacetoacetate Ethylene Acetal*.—Methyl αα-dimethylacetoacetate (22.8 g) and ethane-1,2-diol (11.5 g) were heated overnight in refluxing benzene (50 ml) containing toluene-*p*-sulphonic acid (50 mg) in an apparatus fitted with a water-separator. The excess of solvent was evaporated off and the residue was taken up in ether. The ethereal solution was washed with aqueous sodium hydrogen carbonate, and water, and dried. Distillation gave *the acetal* (19.9 g, 66%), b.p. 90—92° at 15 mmHg, $\nu_{max.}$ (CCl_4) 1 375, 1 270, 1 175, 1 130, 1 095, and 1 045 cm^{-1}, τ (CCl_4) 6.14 (s, $CH_2 \cdot CH_2$), 6.40 (s, CO_2Me), 8.74 [s, MeC(·O)·O] and 8.83 (s, 2 × Me) (Found: C, 57.5; H, 8.6. $C_9H_{16}O_4$ requires C, 57.4; H, 8.5%).

4-*Hydroxy*-3,3-*dimethylbutan*-2-*one* (VII; R = H).—The above acetal (18.8 g, 0.1 mol) in ether (25 ml) was added to lithium aluminium hydride (2 g, 0.56 mol) in ether (40 ml). The mixture was then stirred and refluxed for 30 min and quenched by addition of water and then 2N-hydrochloric acid. The solution was extracted with ether (3 × 40 ml) and the combined extracts were dried and distilled to give 4-hydroxy-3,3-dimethylbutan-2-one (VII; R = H) (7.2 g, 62%), b.p. 77—79° at 10 mmHg (lit.,[11] 75° at 8 mmHg). Preparative g.l.c. (FFAP; 150 °C) gave a sample showing $\nu_{max.}$ (CCl_4) 3 530, 1 700, 1 350, 1 120, and 1 050 cm^{-1}, τ (CCl_4) 6.58 (s, $CH_2 \cdot OH$), 7.91 (s, MeCO), 7.91 (s, OH, exchangeable), and 8.88 (s, 2 × Me). The methyl carbonate derivative, prepared by the standard method [3] and purified by preparative g.l.c. (Carbowax 20M; 190 °C), had $\nu_{max.}$ (CCl_4) 1 750, 1 715, 1 440, 1 365, 1 355, and 1 265 cm^{-1}, τ (CCl_4) 5.94 (s, $CH_2 \cdot O \cdot CO_2Me$), 6.29 (s, $O \cdot CO_2Me$), 7.89 (s, MeCO), and 8.85 (s, 2 × Me) (Found: C, 55.2; H, 8.3. $C_8H_{14}O_4$ requires C, 55.2; H, 8.1%).

Cyclohexenyl Methyl Carbonates.—Cyclohex-2-enol and cyclohex-3-enol were converted in *ca.* 65% yield by the standard method [3] into their methyl carbonate derivatives which were purified by preparative g.l.c. (Carbowax 20M; 80—180 °C at 2° min^{-1}; and FFAP; 130 °C). *Cyclohex-2-enyl methyl carbonate* (IX; $R = CO_2Me$) had $\nu_{max.}$ (CCl_4) 3 040, 1 745, 1 440, 1 270, 1 250, 1 005, and 920 cm^{-1}, τ τ (CCl_4) 4.0—4.4 (m, $CH{=}CH$), 5.03 (m, $CH \cdot O \cdot CO_2Me$), 6.33 (s, $O \cdot CO_2Me$), and 7.90—8.45 (complex, methylenes) (Found: C, 61.4; H, 7.5. $C_8H_{12}O_3$ requires C, 61.6; H, 7.7%). *Cyclohex-3-enyl methyl carbonate* (XII; $R = CO_2Me$) had $\nu_{max.}$ (CCl_4) 3 025, 1 745, 1 650, 1 440, and 1 270 cm^{-1}, τ (CCl_4) 4.44 (m, $CH{=}CH$), 5.1—5.4 (m, $CH \cdot O \cdot CO_2Me$), 6.32 (s, $O \cdot CO_2Me$), and 7.50—8.50 (complex, methylenes) (Found: C, 61.7; H, 7.6%).

Methylation of Cyclohexane-1,2-*diols* (cf. *ref.* 33).—(i) Silver oxide (12.5 g, 0.55 mol) was added in small portions to a refluxing mixture of *cis*-cyclohexane-1,2-diol [34] (10 g, 0.09 mol) in iodomethane (35 g, 0.25 mol). The mixture was refluxed for a further 18 h and then cooled and filtered. The filtrate was extracted with ether (3 × 20 ml) and the combined extracts were dried and evaporated. Analytical g.l.c. (FFAP; 60—220 °C at 5° min^{-1}) of the resultant oil (1.6 g) showed the presence of two major components (t_R 10.5 and 14.5 min), samples of which were isolated by preparative g.l.c. (FFAP; 80—220° at 4° min^{-1}), giving *cis*-1,2-dimethoxycyclohexane [15] (X; $R^1 = R^2 = Me$) (t_R 10.5 min) and *cis*-2-methoxycyclohexan-1-ol [35] (X; $R^1 = Me$, $R^2 = H$) (t_R 14.5 min), identified by their i.r. and ^1H n.m.r. spectra.

(ii) Similar treatment of *trans*-cyclohexane-1,2-diol [36] gave mainly *trans*-2-methoxycyclohexanol [37] (XI; $R^1 = Me$, $R^2 = H$), a pure sample of which was isolated by preparative g.l.c. (FFAP; 130 °C) and identified by its i.r. and ^1H n.m.r. spectra.

Reaction of Cyclohexane-1,2-*diols with Methyl Chloroformate*.—(i) Methyl chloroformate (4.5 g) was added dropwise to a stirred cooled solution of *trans*-cyclohexane-1,2-diol [36] (2.4 g) and pyridine. Stirring was continued for 24 h at room temperature and the mixture was then poured into a solution of acetic acid (5 ml) in water (15 ml). An oily layer formed which was separated and dried. A solid (0.4 g) crystallised from the oil and was collected. Re-

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crystallisation from light petroleum (b.p. 60—80°) gave trans-*cyclohexane*-1,2-*diyl bis*(*methyl carbonate*) (XI; $R^1 = R^2 = CO_2Me$), m.p. 73—74°, $\nu_{\text{max.}}$ (CCl_4) 1 750, 1 440, and 1 270 cm^{-1}, τ ($CDCl_3$), 5.2—5,5 (m, 2 × C*H*·O·CO_2Me), 6.26 (s, 2 × O·CO_2Me), and 7.7—8.6 (complex, methylenes) (Found: C, 51.9; H, 6.8. $C_{10}H_{10}O_6$ requires C, 51.7; H, 6.9%). Preparative g.l.c. (FFAP; 180 °C) of the liquid portion gave trans-2-*hydroxycyclohexyl methyl carbonate* (XI; $R^1 = CO_2Me$, $R^2 = H$), m.p. 42—43°, $\nu_{\text{max.}}$ (CCl_4) 3 605, 3 480, 1 750, 1 440, and 1 265 cm^{-1}, τ (CCl_4) 5.56—5.86 (m, C*H*·O·CO_2Me), 6.30 (s, OCO_2Me), 6.36—6.68 (m, C*H*·OH), 7.31 (s, OH, exchangeable), and 7.85—8.90 (complex, methylenes) (Found: C, 55.0; H, 8.1. $C_8H_{14}O_4$ requires C, 55.2; H, 8.1%).

(ii) Similar treatment of *cis*-cyclohexane-1,2-diol [34] gave two liquid products, separated by preparative g.l.c. (OV 17; 200 °C) and identified as cis-2-*hydroxycyclohexyl methyl carbonate* (X; $R^1 = CO_2Me$, $R^2 = H$), $\nu_{\text{max.}}$ (CCl_4) 3 600, 3 480, 1 750, 1 440, and 1 265 cm^{-1}, τ (CCl_4) 5.28—5.48 (m, C*H*·O·CO_2Me), 6.05—6.30 (m, C*H*·OH), 6.29 (s, O·CO_2Me), 8.09 (s, OH, exchangeable), and 7.90—8.80 (complex, methylenes) (Found: C, 54.9; H, 8.1%), and cis-*cyclohexane*-1,2-*diyl bis*(*methyl carbonate*) (X; $R^1 = R^2 = CO_2Me$), $\nu_{\text{max.}}$ (CCl_4) 1 750, 1 440, 1 310, 1 285, 1 260, 1 250, and 1 210 cm^{-1}, τ (CCl_4) 5.1—5.3 (m, 2 × C*H*·O·CO_2Me), 6.29 (s, 2 × O·CO_2Me), and 7.9—8.75 (complex, methylenes) (Found: C, 51.6; H, 6.8%).

Electrolysis Products from 3,3-*Dimethylbut*-1-*ene* (I).—(i) Analytical g.l.c. (FFAP; 60—220 °C at 8° min^{-1}) of the products (0.75 g) from the electrolysis of 3,3-dimethylbut-1-ene (8.4 g) by method A showed the presence of two major components (t_{R} 8.5 and 12.5 min, peak areas 5 : 4) and several minor components. Preparative g.l.c. (Carbowax 20M; 195 °C) gave 2,3-dimethylbut-3-enyl methyl carbonate (II; $R = CO_2Me$) (t_{R} 8.5 min) and 3-methoxy-2,3-dimethylbutyl methyl carbonate (III; $R = CO_2Me$) (t_{R} 12.5 min), identified by comparison (g.l.c., i.r., and ^{1}H n.m.r.) with authentic samples. 3,3-Dimethylbutyl methyl carbonate (IV; $R = CO_2Me$) had the same t_{R} (7 min) as one of the minor components.

(ii) The material from the electrolysis of 3,3-dimethylbut-1-ene (8.4 g) by method B was distilled to give four fractions: (i) b.p. <75° at 750 mmHg, (ii) b.p. 40—50° at 20 mmHg (1.4 g), (iii) b.p. 58° at 20 mmHg (1.1 g), and (iv) b.p. 60° at 20 mmHg (1.6 g). Analytical g.l.c. (Porapak Q; 170 °C) of fraction (i) (mostly methanol) showed the presence of a compound having the same t_{R} (7.5 min) as dimethyl carbonate. Analytical g.l.c. (FFAP; 60—220 °C at 8° min^{-1}) of the other three fractions showed the presence of three components (t_{R} 5.5, 6.25, and 10.5 min). Samples of each of these were collected by preparative g.l.c. (Carbowax 20M; 130 °C) and identified by comparison (i.r., ^{1}H n.m.r., and g.l.c.) with authentic samples as 3,3-dimethylbutan-1-ol (IV; $R = H$) (t_{R} 5.5 min), 2,3-dimethylbut-3-en-1-ol (II; $R = H$); (t_{R} 6.25 min), and 3-methoxy-2,3-dimethylbutan-1-ol (III; $R = H$) (t_{R} 10.5 min).

Part of the products (0.27 g) from the electrolysis of (I) by method A [containing (II—IV; $R = CO_2Me$)] was treated with methanolic 0.25M-sodium methoxide (100 ml) at room temperature for 48 h. Material of b.p. <75° was distilled and then examined by analytical g.l.c., which showed the presence of dimethyl carbonate. The residue was treated with water (20 ml) and the mixture was extracted with ether (3 × 20 ml). The combined extracts were dried and evaporated, leaving an oil (0.20 g), shown by analytical g.l.c. to contain the hydroxy-compounds (II—IV; $R = H$).

Electrolysis Products from 2,3-*Dimethylbut*-2-*ene*.—(i) A white solid (0.1 g) crystallised from the oily products (1.9 g) from the electrolysis of 2,3-dimethylbut-2-ene (8.2 g) by method A and was identified (m.p., mixed m.p., i.r., and ^{1}H n.m.r.) as 2,3-dimethylbutane-2,3-diyl carbonate (V; $R^1R^2 = CO$). The liquid portion was examined by analytical g.l.c. (50 m Carbowax 20M capillary; 60—180 °C at 3° min^{-1}) and found to contain five major components (t_{R} 8, 10, 12, 27, and 28 min; peak areas 4 : 2 : 2 : 2 : 1). Preparative g.l.c. (Carbowax 20M; 60—220 °C at 4° min^{-1}) gave 2,3-dimethoxy-2,3-dimethylbutane (V; $R^1 = R^2 = Me$), $\nu_{\text{max.}}$ (CCl_4) 1 465, 1 365, 1 355, 1 100, and 1 065 cm^{-1}, τ (CCl_4) 6.85 (s, 2 × OMe) and 8.92 (s, 4 × Me) (t_{R} 8 min), 2,3-dimethylbut-3-en-2-ol (VI; $R = H$), $\nu_{\text{max.}}$ (CCl_4) 3 600, 3 480, 1 640, 1 370, 1 360, 1 160, 1 105, and 900 cm^{-1}, τ (CCl_4) 5.1br and 5.35br (2 × s, CH_2=C), 8.23br (s, =CMe), 8.72 (s, 2 × Me), and 8.74 (s, OH) (t_{R} 10 min), 3-methoxy-2,3-dimethylbutan-2-ol (V; $R^1 = Me$, $R^2 = H$), $\nu_{\text{max.}}$ (CCl_4) 3 570, 1 370, 1 360, 1 150, 1 115, and 1 065 cm^{-1}, τ (CCl_4) 6.87 (s, OMe), 7.85 (s, OH) and 8.90 (s, 4 × Me) (t_{R} 12 min), 2-hydroxy-1,1,2-trimethylpropyl formate (V; $R^1 = CHO$, $R^2 = H$) (t_{R} 27 min), and 2,3-dimethylbutane-2,3-diyl carbonate (V; $R^1R^2 = CO$) (t_{R} 38 min), identical (g.l.c., i.r., and ^{1}H n.m.r.) with authentic samples.

(ii) 2,3-Dimethylbutane-2,3-diyl carbonate (V; $R^1R^2 = CO$) (1.5 g), m.p. and mixed m.p. 180°, crystallised from the oily mixture of products from electrolysis of 2,3-dimethylbut-2-ene (7.5 g) by method B. The liquid portion was distilled to give two fractions: (i) b.p. 40° at 15 mmHg (0.6 g) and (ii) b.p. 50—120° at 15 mmHg (1.8 g). Analytical g.l.c. (FFAP; 60—220 °C at 5° min^{-1}) of fraction (ii) apparently showed the presence of two major components (t_{R} 6.25 and 6.5 min) and two minor components (t_{R} 3.5 and 5.5 min) having retention times identical with those of 2,3-dimethoxy-2,3-dimethylbutane (V; $R^1 = R^2 = Me$) and 3-methoxy-2,3-dimethylbutan-2-ol (V; $R^1 = Me$, $R^2 = H$) (see above). Material corresponding to the two apparent major components was collected by preparative g.l.c. (Carbowax 20M; 60—200 °C at 3° min^{-1}) of fraction (i). The material having t_{R} 6.25 min was identified as 2-methoxy-3-methoxymethoxy-2,3-dimethylbutane (V; $R^1 = Me$, $R^2 = CH_2$·OMe) by comparison (g.l.c., i.r., and ^{1}H n.m.r.) with an authentic sample; the other material (t_{R} 6.5 min) was shown by analytical g.l.c. (50 m Carbowax 20M capillary; 80 °C) to be a mixture of two components (t_{R} 13.75 and 14.25 min), which were not further investigated. Analytical g.l.c. (FFAP; 60—220 °C at 5° min^{-1}) of fraction (ii) apparently showed the presence of four major components (t_{R} 8.75, 9.0, 12.0, and 15.5 min). However preparative g.l.c. (Carbowax 20M; 100—220 °C at 4° min^{-1}) only led to the isolation of two pure (analytical g.l.c.) compounds, 2,2-dimethyl-3-oxobutyl methyl carbonate (VII; $R = CO_2Me$) (t_{R} 12 min) and 2,3-dimethylbutane-2,3-diyl carbonate (V; $R^1R^2 = CO$), identified by comparison (g.l.c., i.r., and ^{1}H n.m.r.) with authentic samples. The material with t_{R} 9 min was further purified by preparative g.l.c. under different conditions (Harflex 370; 75—190 °C at 3° min^{-1}) to give 4-hydroxy-3,3-dimethylbutan-2-one (VII; $R = H$), identified by comparison (i.r. and ^{1}H n.m.r.) with an authentic sample.

Electrolysis Products from Cyclohexene.—(i) Analytical g.l.c. (FFAP; 60—220 °C at 8° min^{-1}) of the products

(1.1 g) from the electrolysis of cyclohexene (10 g) by method A showed the presence of six major components (t_R 5, 6.75, 10.5, 11.5, 12.75, and 13 min; peak areas 1 : 2 : 2 : 2 : 2 : 4) together with many minor components. G.l.c.–mass spectrometry of the more volatile components confirmed the presence of 3-methoxycyclohexene (IX; R = Me), *m/e* 112 (t_R 5 min), 1,1-dimethoxymethylcyclopentane, *m/e* 144 (t_R 6.75 min), and *cis*- and *trans*-1,2-dimethoxycyclohexane (X and XI; $R^1 = R^2 =$ Me), each *m/e* 144, previously identified from a similar electrolysis,[15] and the presence of *cis*-1,2-dimethoxycyclohexane was confirmed by peak enhancement with an authentic sample. Samples of the other four major components were isolated by preparative g.l.c. (Carbowax 20M; 130 °C) and identified as cyclohex-2-enol (IX; R = H) (t_R 10.5 min), cyclohex-3-enyl methyl carbonate (XII; R = CO_2Me) (t_R 12.75 min), cyclohex-2-enyl methyl carbonate (IX; R = CO_2Me, t_R 13 min), and the previously reported [15] 'ester' mixture (t_R 11.5 min) through their i.r. and ^1H n.m.r. spectra. The 'ester' mixture was shown by analytical g.l.c. (50 m Carbowax 20M capillary; 100 °C) to be a mixture of two components (t_R 17 and 18 min; peak areas 1 : 4).

(ii) Dimethyl carbonate was detected by analytical g.l.c. (Porapak Q; 170 °C) in the material of b.p. $<75°$ distilled during the isolation of the products from the electrolysis of cyclohexene (8.2 g) by method B. Distillation of the products gave three fractions; (i) b.p. 40—50° at 16 mmHg (0.6 g), (ii) 50—60° at 15 mmHg (1.3 g), and (iii) b.p. 80—140° at 15 mmHg (2.2 g). Analytical g.l.c. (FFAP; 60—200 °C at 8° min^{-1}) showed that fractions (i) and (ii) contained four major components (t_R 5.25, 6, 6.1, and 7 min) and a number of minor components. A comparison (g.l.c.) with authentic samples showed that the compounds with t_R 5.25, 6, and 6.1 min were 1,1-dimethoxymethylcyclopentane, cyclohex-2-enol (IX; R = H), and cyclohex-3-enol (XII; R = H), respectively, and that *cis*-1,2-dimethoxycyclohexane was not present. A sample of the material having t_R 7 min was shown by analytical g.l.c. (50 m Carbowax 20M capillary; 100 °C) to be a mixture of the two compounds (t_R 17 and 18 min) detected in the 'ester' mixture from the previous electrolysis, but now present in the inverse ratio (peak areas 4 : 1). Peak enhancement using the capillary conditions showed that the two compounds had the same t_R values as *trans*-2-methoxycyclohexanol (XI; R^1 = Me, R^2 = H) (t_R 17 min) and cyclohexyl methyl carbonate (t_R 18 min); the spectral (i.r. and ^1H n.m.r.) properties of the 'ester' mixture were shown to be consistent with it being a mixture of these two compounds by comparison with the spectra of the pure compounds. *cis*-2-Methoxycyclohexanol (X; R^1 = Me, R^2 = H) and *trans*-1,2-dimethoxycyclohexane (XI; $R^1 = R^2$ = Me) were shown by peak enhancement using the capillary conditions to be minor components of fractions (i) and (ii). Analytical g.l.c. (FFAP; 60—200 °C at 8° min^{-1}) of fraction (iii) revealed four major components (t_R 16.5, 17.75, 18.25, and 21 min; peak areas 1 : 3 : 2 : 1) and a number of minor components. The component having t_R 16.5 min had the same t_R as *cis*-2-hydroxycyclohexyl methyl carbonate (X; $R^1 = CO_2Me$, R^2 = H). The component having t_R 17.75 min was isolated by preparative g.l.c. (FFAP; 160 °C) and identified as *trans*-2-hydroxycyclohexyl methyl carbonate (XI; $R^1 = CO_2Me$, R^2 = H) by comparison (i.r. and ^1H n.m.r.) with an authentic sample. The other two major components were apparently mixtures. A sample of the material having t_R 21 min collected by preparative g.l.c. (FFAP; 160 °C) was shown by its i.r. and ^1H n.m.r. spectra to consist mainly of *trans*-cyclohexane-1,2-diyl carbonate (XI; R^1R^2 = CO) contaminated with an unidentified alkyl methyl carbonate, $\nu_{max.}$ ($CHCl_3$) 1 740 cm^{-1}, τ (CCl_4) 6.27 (s).

Electrolysis Products from Styrene.—(i) The products from the electrolysis of styrene (10.4 g) by method B were distilled and the lower boiling material was collected as two fractions: (i) b.p. 108—122° at 15 mmHg (2.6 g) and (ii) b.p. 60—100° at 0.1 mmHg (2.3 g). Analytical g.l.c. (OV 17; 100—320 °C at 10° min^{-1}) showed the presence of three major components (t_R 5.5, 6.0, and 10 min; peak areas 5 : 10 : 1). Preparative g.l.c. (Carbowax 20M; 200 °C) gave 1,2-dimethoxy-1-phenylethane (XIII; X = Y = OMe) (t_R 5.5 min), $\nu_{max.}$ (CCl_4) 3 060, 3 020, 1 600, 1 190, 1 130, 1 100, 870, and 700 cm^{-1}, τ (CCl_4) 2.80 (s, Ph), 5.80 (dd, $PhCH\cdot OMe$), 6.63 (m, $CH_2\cdot OMe$), and 6.73 and 6.78 (2 × s, 2 × OMe), and 2-methoxy-2-phenylethanol (XIII; X = OMe, Y = OH), identified by comparison (g.l.c., i.r. and ^1H n.m.r.) with an authentic sample.

(ii) (with N. BRAMALL). Lithium (0.9 g) was dissolved in dry methanol (210 ml) under an argon atmosphere. Dry carbon dioxide was then bubbled through the solution for 1 h. Styrene (10.4 g) was added and the solution was electrolysed at a constant current of 0.4 A cm^{-2} for 3.5 h with the passage of 2.6 F mol^{-1}. The cell used and the procedure employed for the isolation of the products (4.2 g) were as described for method B. Distillation of the products gave two fractions: (i) b.p. 75—80° at 12 mmHg (0.75 g) and (ii) b.p. 130—150° at 0.5 mmHg (0.80 g). Analytical g.l.c. (OV 17; 100—300 °C at 10° min^{-1}) showed that fraction (i) contained one major (t_R 5.5 min) and one minor component (t_R 6.0 min) and that fraction (ii) contained the component having t_R 6.0 min as the major component together with the component having t_R 5.5 min, an additional component having t_R 7.25 min, and other minor components and components of longer retention time. The component having t_R 5.5 min was isolated from fraction (i) by preparative g.l.c. (OV 17; 80 °C) and identified (i.r. and ^1H n.m.r.) as 1,2-dimethoxy-1-phenylethane (XIII; X = Y = OMe). The components having t_R 6.0 and 7.25 were collected in an impure state from fraction (ii) by preparative g.l.c. (OV 17; 100—280 °C at 4° min^{-1}), purified by further preparative g.l.c. under different conditions (Carbowax 20M; 200 °C), and identified (g.l.c. and i.r.) as 2-methoxy-2-phenylethanol (XIII; X = OMe, Y = OH) and 2-methoxy-1-phenylethanol (XIII; X = OH, Y = OMe), respectively, by comparison with authentic samples. Analytical g.l.c. (Carbowax 20M; 60—220 °C at 5° min^{-1}) showed the presence of 2-phenylethanol (XIII; X = H Y = OH) (t_R 26 min) amongst the minor components.

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