

## Anodic Oxidation. Part XV.<sup>1</sup> Electrochemical Functionalisation of Phenylcyclopropane and 2-Isobutenyl-1,1-dimethylcyclopropane in Methanol<sup>2</sup>

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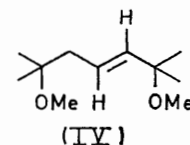
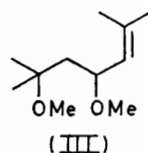
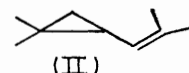
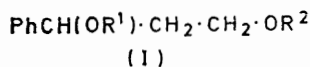
Electrolysis of phenylcyclopropane in methanolic sodium methoxide gives 1,3-dimethoxy-1-phenylpropane, which is also formed together with 3-methoxy-3-phenylpropan-1-ol and 3-methoxy-1-phenylpropan-1-ol in methanolic sodium methyl carbonate. Electrolysis of 2-isobutenyl-1,1-dimethylcyclopropane in either system gives 4,6-dimethoxy-2,6-dimethylhept-2-ene and (*E*)-2,6-dimethoxy-2,6-dimethylhept-3-ene.

THE anodic oxidation of hydrocarbons containing a cyclopropane ring has been studied by Shono and his co-workers.<sup>3,4</sup> Electrolysis of phenylcyclopropane in methanolic ammonium toluene-*p*-sulphonate at a carbon anode with a high and uncontrolled potential gave a single product, 1,3-dimethoxy-1-phenylpropane (I; R<sup>1</sup> = R<sup>2</sup> = Me). As we have recently shown<sup>1,5</sup> that when olefins are electrolysed in methanolic sodium methoxide at a high current density (method A)<sup>1</sup> or methanolic sodium methyl carbonate at a low, constant current density (method B)<sup>1</sup> the products may include hydroxy-methoxy-compounds or methoxy-substituted alkyl methyl carbonates, in addition to dimethoxy-compounds, we have now investigated the behaviour of phenylcyclopropane by these methods.

When phenylcyclopropane was electrolysed in methanolic sodium methoxide at a platinum anode using a high, uncontrolled potential and a high current density the sole product was 1,3-dimethoxy-1-phenylpropane (I; R<sup>1</sup> = R<sup>2</sup> = Me). However, when phenylcyclopropane was electrolysed in methanolic sodium methyl carbonate at a low current density for 48 h there were three products, 1,3-dimethoxy-1-phenylpropane (I; R<sup>1</sup> = R<sup>2</sup> = Me), 3-methoxy-3-phenylpropan-1-ol (I; R<sup>1</sup> = Me, R<sup>2</sup> = H), and 3-methoxy-1-phenylpropan-1-ol (I; R<sup>1</sup> = H, R<sup>2</sup> = Me) formed in 42, 16.5, and 6.5% yield,† respectively. The products were identified from the <sup>1</sup>H n.m.r. spectra of samples of each, isolated by preparative g.l.c., which were in agreement with published data.<sup>3,6</sup> We believe that the alcohols (I; R<sup>1</sup> = Me, R<sup>2</sup> = H and R<sup>1</sup> = H, R<sup>2</sup> = Me) are formed by the transesterification of the corresponding methyl carbonates (I; R<sup>1</sup> = Me, R<sup>2</sup> = CO<sub>2</sub>Me and R<sup>1</sup> = CO<sub>2</sub>Me, R<sup>2</sup> = Me) and that all three products arise by EC<sub>N</sub>EC<sub>N</sub> processes related to the one proposed earlier<sup>3</sup> to explain the formation of (I; R<sup>1</sup> = R<sup>2</sup> = Me) by electrochemical methoxylation of phenylcyclopropane but in which the first two steps (EC<sub>N</sub>) are probably concerted.

We have also investigated the electrochemical behaviour of a vinylcyclopropane by these methods to compare the effect of a double bond in conjugation with a cyclopropane ring with that of a phenyl group. The compound chosen was 1-isobutenyl-2,2-dimethylcyclopropane (II), which is readily available from phorone.<sup>7</sup>

When (II) was electrolysed by either of the methods used with phenylcyclopropane or earlier<sup>1,5</sup> with a variety of olefins, only two major products, both dimethoxy-compounds, and a number of very minor products, were



formed. The major products were 4,6-dimethoxy-2,6-dimethylhept-2-ene (III) and (*E*)-2,6-dimethoxy-2,6-dimethylhept-3-ene (IV) which were formed in 12 and 61% yields, respectively, by method A, and which could be separated by preparative g.l.c. Compounds (III) and (IV) were assigned their constitutions on the basis of microanalytical data and of their i.r. and <sup>1</sup>H n.m.r. spectra. The configuration of the double bond in (IV) was established by a <sup>1</sup>H n.m.r. method. Under ordinary conditions in carbon tetrachloride solution the vinyl protons H-3 and -4 had the same chemical shift, but by the addition of a lanthanide shift reagent and then spin-spin decoupling it was possible to establish that the value of *J*<sub>3,4</sub> was 16 Hz, corresponding to a *trans*-relationship between H-3 and -4. We assume that the dimethoxy-compounds (III) and (IV) are formed from a common allylic cation produced from (II) by an EC<sub>N</sub>E process.

Compound (II) is the only olefin or cyclopropane we have so far investigated which undergoes exclusively methoxylation by either method A or B; phenylcyclopropane, like bicyclo[2.2.1]heptadiene,<sup>5</sup> undergoes exclusively methoxylation by method A. The reasons for these gradations in behaviour are not yet clear but the overall chemical conversions are notably greater for those cases where only methoxylation is observed than for the majority of cases, in which other oxygenated products are also formed.

<sup>4</sup> T. Shono, Y. Matsumara, and Y. Nakagawa, *J. Org. Chem.*, 1971, **36**, 1771.

<sup>5</sup> A. J. Baggaley, R. Brettle, and J. R. Sutton, *J.C.S. Perkin I*, 1975, 1055.

<sup>6</sup> P. O. I. Virtanen and K. Manninen, *Suomen Kem. (B)*, 1967, **40**, 341 (*Chem. Abs.*, 1968, **69**, 18,951).

<sup>7</sup> E. R. Nelson, M. Maienthal, L. A. Lane, and A. A. Benderley, *J. Amer. Chem. Soc.*, 1957, **79**, 3467.

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

<sup>1</sup> Part XIV, R. Brettle and J. R. Sutton, preceding paper.

<sup>2</sup> Preliminary report, R. Brettle and J. R. Sutton, *J.C.S. Chem. Comm.*, 1974, 449.

<sup>3</sup> T. Shono and Y. Matsumara, *J. Org. Chem.*, 1970, **35**, 4158.

## EXPERIMENTAL

For general instructions, details of the instruments used for g.l.c., and details of the electrolysis procedures (methods A and B), see the preceding paper.<sup>1</sup>

*Starting Materials.*—Phenylcyclopropane, b.p. 69° at 25 mmHg (lit.,<sup>8</sup> 60° at 13 mmHg), was prepared from cinnamaldehyde<sup>8</sup> in 29% yield. 2-Isobutenyl-1,1-dimethylcyclopropane, 99% pure by g.l.c. (F 11; 6 ft  $\beta$ -oxydi-propionitrile; 50 °C;  $t_R$  5.5 min), b.p. 130–132° at 750 mmHg (lit.,<sup>7</sup> 130–132°) was prepared from phorone<sup>7</sup> in 32% yield.

*Electrolysis Products from Phenylcyclopropane.*—(i) When phenylcyclopropane was electrolysed by method A<sup>1</sup> (cf. ref. 3) the sole product, isolated by semi-preparative g.l.c. (F and M; 720 °C; 6 ft Carbowax 20M; 100–200 °C at 10° min<sup>-1</sup>;  $t_R$  15 min), was 1,3-dimethoxy-1-phenylpropane (I; R<sup>1</sup> = R<sup>2</sup> = Me), identified through its <sup>1</sup>H n.m.r. spectrum.<sup>3</sup>

(ii) When phenylcyclopropane (11.8 g) was electrolysed by method B,<sup>1</sup> the products were isolated as an oil, b.p. 40° at 14 mmHg to 110° at 0.6 mmHg (10.05 g), shown by analytical g.l.c. (F 11; 6 ft FFAP; 100–220 °C at 6° min<sup>-1</sup>) to contain three components ( $t_R$  11.5, 18.5, and 19 min; peak areas 7.5 : 2.5 : 1). Preparative g.l.c. (Pye 105; 10 ft Carbowax 20M; 210 °C) gave 1,3-dimethoxy-1-phenylpropane (I; R<sup>1</sup> = R<sup>2</sup> = Me) ( $t_R$  11.5 min), 3-methoxy-3-phenylpropan-1-ol (I; R<sup>1</sup> = Me, R<sup>2</sup> = H) ( $t_R$  18.5 min), and 3-methoxy-1-phenylpropan-1-ol (I; R<sup>1</sup> = H, R<sup>2</sup> = Me) ( $t_R$  19 min), identified through their <sup>1</sup>H n.m.r. spectra, which were in agreement with published data.<sup>3,6</sup>

*Electrolysis Products from 1-Isobutenyl-2,2-dimethylcyclopropane.*—(i) The electrolysis of 1-isobutenyl-2,2-dimethyl-

cyclopropane (II) (12.4 g) by method A<sup>1</sup> gave an oil (13.6 g) shown by analytical g.l.c. (F 11; 6 ft FFAP; 60–220 °C at 6° min<sup>-1</sup>) to contain two components ( $t_R$  9 and 10.5 min; peak areas 1 : 5). Preparative g.l.c. (Wilkins Aerograph A 700; 30 ft Carbowax 20M on 60–80 mesh Chromosorb W; 120 °C) gave 4,6-dimethoxy-2,6-dimethylhept-2-ene (III) ( $t_R$  9 min),  $\tau_{\max}$  (CCl<sub>4</sub>) 1 670, 1 100, and 1 080 cm<sup>-1</sup>,  $\tau$ (CCl<sub>4</sub>) 5.03br (d,  $J$  10 Hz, C=CH), 6.04 (m, CH·OMe), 6.93 (s, 2 × OMe), 8.28br and 8.33br (2 × s, Me<sub>2</sub>C=), 8.3–8.6 (m, CH<sub>2</sub>), and 8.89 and 8.95 (2 × s, Me<sub>2</sub>C·OMe) (Found: C, 70.8; H, 11.8. C<sub>11</sub>H<sub>22</sub>O<sub>2</sub> requires C, 71.0; H, 11.8%), and (E)-2,6-dimethoxy-2,6-dimethylhept-3-ene (IV) ( $t_R$  10.5 min),  $\nu_{\max}$  (CCl<sub>4</sub>) 1 660, 1 375, 1 360, 1 250, 1 225, 1 210, 1 170, 1 145, 1 120, 1 075, 970, and 840 cm<sup>-1</sup>,  $\tau$  (CCl<sub>4</sub>; no shift reagent) 4.32–4.80 (m, CH=CH), 6.89 and 6.97 (2 × s, 2 × OMe), 7.88 (d,  $J$  5 Hz, CH<sub>2</sub>), and 8.83 and 8.94 (2 × s, 4 × Me) (Found: C, 70.8; H, 11.6%); the addition of Eu(fod)<sub>3</sub> followed by irradiation at the frequency of the doublet due to the protons at C-5 caused the protons H-3 and -4 to give rise to an AB system,  $J_{3,4}$  16 Hz.

(ii) The electrolysis of 1-isobutenyl-2,2-dimethylcyclopropane (II) (12.4 g) by method B<sup>1</sup> gave an oil (9.0 g), b.p. 50–120° at 15 mmHg, shown by analytical g.l.c. (F 11; 6 ft OV 17; 60–250 °C at 6° min<sup>-1</sup>) to contain 4,6-dimethoxy-2,6-dimethylhept-2-ene and (E)-2,6-dimethoxy-2,6-dimethylhept-3-ene in the same proportions by direct comparison with the products from (i).

We thank the S.R.C. for an award (to J. R. S.).

[5/753 Received, 21st April, 1975]

<sup>8</sup> R. J. Petersen and P. S. Skell, *Org. Synth.*, 1967, **49**, 98.