Anodic Oxidation. Part XIII.[1] Products from Bicyclo[2.2.1]hept-2-ene, Bicyclo[2.2.1]hepta-2,5-diene, and Tetracyclo[3.2.0.0²,⁷.0⁴,⁶]heptane

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Conditions are described under which electrolysis of bicyclo[2.2.1]hept-2-ene in methanolic sodium methoxide gives methyl tricyclo[2.2.1.0²,⁶]heptan-3-yl carbonate, *exo*-2-methoxybicyclo[2.2.1]heptan-*syn*-7-yl methyl carbonate, its *anti*-isomer, and the corresponding 7-alcohols, and bicyclo[2.2.1]heptan-*exo*-2-yl methyl carbonate, in addition to the previously reported dimethoxylation products. Under the same conditions bicyclo[2.2.1]hepta-2,5-diene and tetracyclo[3.2.0.0²,⁷.0⁴,⁶]heptane each give as the major products *exo*-2,*syn*-7-dimethoxybicyclo-[2.2.1]hept-5-ene, *exo*-3,*endo*-5-dimethoxytricyclo[2.2.1.0²,⁶]heptane, and *exo*-3,*exo*-5-dimethoxytricyclo-[2.2.1.0²,⁶]heptane, but when bicyclo[2.2.1]hepta-2,5-diene is electrolysed in methanolic sodium methyl carbonate, methoxy-alcohols are again produced.

SOME years ago [2] we made a preliminary study of the products formed when bicyclo[2.2.1]hept-2-ene is electrolysed in methanolic sodium methoxide. As our results at that time indicated that more products were formed than have subsequently been reported in two accounts [3,4] of similar electrolyses we have recently undertaken a detailed analysis of the products formed under our electrolysis conditions, and now report our results.

Electrolysis of bicyclo[2.2.1]hept-2-ene in methanolic sodium methoxide, by use of an undivided cell, a platinum anode, and a mercury cathode at an uncontrolled potential with an initial current density of 0·3 A cm⁻¹ which dropped to 0·01 A cm⁻¹ during the 3·25 h duration of the electrolysis, gave an extremely complex product mixture with a low chemical conversion into products. The more abundant components of the mixture, ten in all, were separated by preparative g.l.c. and have been identified as the dimethoxybicyclo[2.2.1]heptanes (I), (II; R = Me), and (III; R = Me), the methoxybicyclo-[2.2.1]heptanols (II; R = H) and (III; R = H), the tricyclo[2.2.1.0²,⁶]heptanol (IV; R = H), and the methyl carbonate esters (II; R = CO₂Me), (III; R = CO₂Me), (IV; R = CO₂Me), and (V). The overall conversion into products was *ca.* 8% and none of the ten identified products was formed in more than *ca.* 1% yield. The structures and stereochemistries † were established by direct comparisons of the ¹H n.m.r. and i.r. spectra of the products with those of authentic samples, except in the case of compound (I) for which no authentic sample was available or readily accessible. The product assigned structure (I) was shown by high resolution mass spectrometry to have the molecular formula C₉H₁₆O₂ and its low resolution frag-

mentation pattern was in agreement with the published data [5] for the 2,3-dimethoxybicyclo[2.2.1]heptanes, which can be distinguished in this way from other dimethoxybicyclo[2.2.1]heptanes but not from each
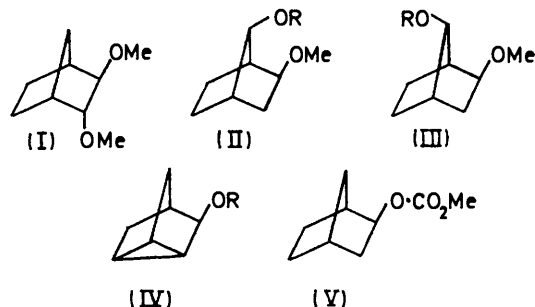
other.[5] Moreover, since the ¹H n.m.r. spectrum showed two separate signals at τ 6·71 and 6·73 attributable to methoxy-groups and signals near τ 6·7 and 7·1 attributable respectively to an *endo*- and an *exo*-hydrogen atom attached in each case to a carbon atom bearing a methoxy-group, the compound must be the *trans*-isomer.

Of the previously unreported compounds, *exo*-2-methoxybicyclo[2.2.1]heptan-*syn*-7-ol (II; R = H) and the corresponding *anti*-7-ol (III; R = H) were prepared by acid-catalysed methanolysis of *exo*-2,*exo*-3-epoxy-bicyclo[2.2.1]heptane. This reaction has recently been reported [6] as part of a route to *exo*-2-methoxybicyclo-[2.2.1]heptan-7-one, but the intermediate methoxy-alcohols were not isolated or characterised. We found that a minor product of this reaction was tricyclo-[2.2.1.0²,⁶]heptan-3-ol, known to be a minor product of the analogous hydrolysis of the epoxide, which gives as

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† In displayed formulae only one of a pair of enantiomeric structures is shown although in all cases both enantiomers were present, in equal amounts.

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[2] A. J. Baggaley, Ph.D. Thesis, Sheffield, 1967.

[3] T. Inoue, K. Koyama, T. Matsuoka, and S. Tsutsumi, *Bull. Chem. Soc. Japan*, 1967, **40**, 162.

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

[5] H. F. Gruetzmacher and K. H. Fechner, *Tetrahedron*, 1971, **27**, 5011.

[6] R. Siegfried, *Chem. Ber.*, 1974, **107**, 1472.

major products the *exo,anti-*, and *exo,syn*-bicyclo[2.2.1]-heptane-2,7-diols.[7] We assume that the methanolysis follows a reaction pathway analogous to that of the hydrolysis and thus formulate the major methanolysis products as the 2-methoxy-7-ols. Results described below fully confirm this orientation for the product (II; R = H). The two hydroxy-ethers (II and III; R = H) were separated by preparative g.l.c. and distinguished by their i.r. spectra in the 3700—3200 cm^{-1} region. The *syn,-exo*-isomer (II; R = H) exhibited a broad intramolecular O–H stretching band at 3520 cm^{-1} even at high dilution in carbon tetrachloride, whereas the *anti,exo*-isomer (III; R = H) showed only a sharp free O–H stretching band at 3625 cm^{-1} under the same conditions. Methylation of the hydroxy-ether (II; R = H) gave the diether (II; R = Me). The isomeric hydroxy-ether, *syn*-7-methoxybicyclo[2.2.1]heptan-*exo*-2-ol, was not present (g.l.c. retention time) amongst the products from our electrolysis. The four alkyl methyl carbonates (II, III, and IV; R = CO$_2$Me) and (V) were prepared from the corresponding alcohols by treatment with methyl chloroformate in the presence of pyridine.

The alkyl methyl carbonates were in fact the major products of our electrolysis, but neither they nor the alcohols had been reported earlier.[3,4] Tsutsumi and his co-workers[3] electrolysed bicyclo[2.2.1]hept-2-ene in methanolic sodium methoxide and reported as products only *exo*-2,*syn*-7-dimethoxybicyclo[2.2.1]heptane (II; R = Me), *exo*-2-methoxybicyclo[2.2.1]heptane, a compound tentatively assigned structure (I), and two unidentified compounds. Shono and Ikeda,[4] using a quaternary ammonium fluoroborate as supporting electrolyte, reported just three products, the *exo*-2,*syn*- and *anti*-7-dimethoxybicyclo[2.2.1]heptanes (II and III; R = Me) and 3-methoxytricyclo[2.2.1.0^{2,6}]heptane. Alkyl methyl carbonates were reported[8] amongst the very complex products from the electrolysis of 3,3-dimethylbut-1-ene in methanol containing acetic acid and potassium acetate. In that system carbon dioxide is being formed by the oxidative decarboxylation of acetate ion, but this is not the case in our system. However Szilard reported[9] in 1906 that the electrolysis of methanolic sodium methoxide at a current density sufficiently high to cause gas evolution at the anode led to the deposition of sodium methyl carbonate at the anode. We believe that a high concentration of methyl carbonate ions is produced at the anode during our electrolysis, in which gas evolution was observed at the anode, by the oxidation of the solvent and that the formation of the alkyl methyl carbonates can best be rationalised in terms of an initial oxidation of bicyclo[2.2.1]hept-2-ene to the cation radical[4] followed by further chemical and electro-

chemical steps including several of the well known rearrangements of cations in the bicyclo[2.2.1]heptane series, and with nucleophilic attack by the methyl carbonate ion occurring at any early stage in the product-forming pathway.[10] We further believe that the presence of alcohols (II, III, and IV; R = H) amongst our electrolysis products is the result of partial transesterification of the corresponding alkyl methyl carbonates (II, III, and IV; R = CO$_2$Me). We are aware of only two other cases[11,12] where hydroxy-groups are introduced during the electrolysis of an olefin in methanol. In both cases other explanations were put forward to explain their origin, but an analogous explanation now seems likely[10] at least for the production of cyclohex-2-enol from cyclohexene.[11] The anodic addition of two different nucleophiles to an olefin is uncommon so that it is of interest that the electrolysis of alka-1,3-dienes in methanolic potassium cyanate gives methoxy-substituted *N*-methoxycarbonyl amines[13] which are the nitrogen analogues of the methoxy-substituted alkyl methyl carbonates formed in our electrolysis.

We have extended our studies to include bicyclo-[2.2.1]hepta-2,5-diene and tetracyclo[3.2.0.0^{2,7}.0^{4,6}]-heptane (quadricyclane), which have not hitherto been functionalised electrochemically. Bicyclo[2.2.1]hepta-2,5-diene is reported as being electrochemically inert in acetonitrile containing lithium perchlorate.[14] When bicyclo[2.2.1]hepta-2,5-diene was electrolysed in methanol under the same conditions as for bicyclo[2.2.1]hept-2-ene only three major products were formed, *exo*-5,-*syn*-7-dimethoxybicyclo[2.2.1]hept-2-ene (VI), *exo*-3,-*endo*-5-dimethoxytricyclo[2.2.1.0^{2,6}]heptane * (VII; R^1 = R^2 = Me), and *exo*-3,*exo*-5-dimethoxytricyclo-[2.2.1.0^{2,6}]heptane * (VIII; R^1 = R^2 = Me). A 50% chemical conversion into products was achieved, much higher than for bicyclo[2.2.1]hept-2-ene. The structures were assigned on the basis of i.r. and ^{1}H n.m.r. spectra. In particular n.m.r. signals due to vinylic protons were present in the spectrum of (VI), but not in the spectra of its isomers, each of which, however, showed absorption at 3050 cm^{-1} characteristic[15] of the tricyclo[2.2.1.0^{2,6}]heptane system. The structure of (VI) was confirmed by its

(VI)   (VII)   (VIII)

hydrogenation to give the bicycloheptane (II; R = Me). The *exo,endo*-diether (VII; R^1 = R^2 = Me) showed two absorptions at τ 6·03 and 6·49 due to the protons at C-3 and C-5 showing the lack of symmetry about the plane containing C-1, C-4, and C-7. The other 3,5-diether,

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[13] E. T. Blues, B.P. 1,078,154/1967 (*Chem. Abs.*, 1969, **70**, 92,679).
[14] D. H. Geske, *J. Amer. Chem. Soc.*, 1959, **81**, 4145.
[15] J. D. Roberts, E. R. Trumball, jun., W. Bennett, and R. Armstrong, *J. Amer. Chem. Soc.*, 1950, **72**, 3116.

which therefore has to be symmetrical with respect to the C(1)C(4)C(7) plane, and which indeed showed a single absorption at τ 6·65 due to the C-3 and C-5 protons was tentatively assigned the *exo,exo*-stereochemistry from a consideration of the effect of the 3- and 5-methoxy-groups on the chemical shift of the 7-protons. The 7-protons are two carbon–carbon bonds removed from the oxygen substituents, whereas the 2- and 6-protons are only one bond removed. Thus in the absence of other effects the 7-protons should resonate at higher field than the 2- or 6-protons. This has been shown to be the case for the *endo*-3,*endo*-5-diacetates and dibenzoates.[16] However in the case of the *exo,exo*-diacetates and dibenzoates the 7-protons resonate at lower field than the 2- and 6-protons, owing to a through-space deshielding effect upon the 7-protons caused by the substituents at C-3 and C-5. In the case of our symmetrical 3,5-diether the 7-protons resonated at τ 8·30 whereas the 2- and 6-protons resonated at τ 8·55, so that we assign an *exo,exo*-stereochemistry to our product. 3,5-Dimethoxytricyclo[2.2.1.0^{2,6}]heptanes were isolated earlier from the reaction of bicyclo[2.2.1]-hepta-2,5-diene with lead tetra-acetate in methanol but no stereochemical assignments were made.[17]

The products from the electrolysis of tetracyclo-[3.2.0.0^{2,7}.0^{4,6}]heptane under the same conditions in methanolic sodium methoxide were the same compounds (VI, VII, and VIII; R^1 = R^2 = Me) as obtained from bicyclo[2.2.1]hepta-2,5-diene, formed in the same proportions with a 60% chemical conversion. A blank experiment showed that in the absence of a current no isomerisation of tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane to bicyclo-[2.2.1]hepta-2,5-diene occurred.[10] The formation of these products can be rationalised[10] in terms of the known anodic reactions of olefins[4] and cyclopropanes.[18]

Only methoxylation products are formed from bicyclo-[2.2.1]hepta-2,5-diene under conditions where alkyl methyl carbonates and the derived alcohols are also formed from bicyclo[2.2.1]hept-2-ene, but we have discovered that the electrolysis of bicyclo[2.2.1]hepta-2,5-diene in methanol in the presence of preformed sodium methyl carbonate, with a constant current density of 0·1 A cm^{-2}, leads to additional products. As well as the diethers (VI, VII, and VIII; R^1 = R^2 = Me) three new products, formed in equal proportions, were detected by analytical g.l.c. The new products could not be separated from each other by preparative g.l.c., but the i.r. spectrum of the mixture showed absorptions at 3500 and 1100 cm^{-1} characteristic of O–H and C–O–C groups, respectively. G.l.c.–mass spectrometry showed that all three compounds exhibited a molecular ion at m/e 140, corresponding to a molecular formula of C$_8$H$_{12}$O$_2$ (≡ C$_7$H$_8$ + OH + OMe). Methylation of the mixture gave only two products, but in a 2:1 ratio, identified (i.r., g.l.c.) as (major product) *exo*-3,*endo*-5-dimethoxytricyclo-

[2.2.1.0^{2,6}]heptane (VII; R^1 = R^2 = Me) and the *exo,-exo*-isomer (VIII; R^1 = R^2 = Me). These results show that the three new products must be *endo*-5-methoxytricyclo[2.2.1.0^{2,6}]heptan-*exo*-3-ol (VII; R^1 = H; R^2 = Me) and the isomeric *exo*-5-methoxy-*endo*-3-ol (VII; R^1 = Me; R^2 = H), which on methylation each give the *exo,endo*-3,5-dimethyl ether (VII; R^1 = R^2 = Me), together with *exo*-5-methoxytricyclo[2.2.1.0^{2,6}]heptan-*exo*-3-ol (VIII; R^1 = H, R^2 = Me) which on methylation gives the *exo,exo*-3,5-dimethyl ether (VIII; R^1 = R^2 = Me). The formation of methoxy-alcohols in this electrolysis is presumably the result of processes analogous to those occurring with bicyclo[2.2.1]hept-2-ene, leading initially to the alkyl methyl carbonates (VII; R^1 = CO$_2$Me, R^2 = Me) (VII; R^1 = Me, R^2 = CO$_2$Me), and (VIII; R^1 = CO$_2$Me, R^2 = Me) but with subsequent complete transesterification to the alcohols during the much longer duration (48 h) of the electrolysis.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on a Perkin-Elmer R12 A or Varian HA 100 instrument for solutions in CDCl$_3$ with tetramethylsilane as internal standard. I.r. spectra were measured on a Perkin-Elmer 137 or 457 instrument. Accurate mass measurements were made with an A.E.I. MS 9 instrument on pure samples isolated by preparative g.l.c. 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 210° and connected by a Biemann separator to an A.E.I. MS 12 spectrometer. Low resolution mass spectra were recorded on an A.E.I. MS 9 instrument.

Analytical g.l.c. was carried out on a Perkin-Elmer F 11 chromatograph with 6 ft glass columns containing either 5% FFAP or 2·5% OV 225 on 80—100 mesh Chromosorb G. Preparative g.l.c. was carried out on a Wilkins Aerograph A 700 instrument with 5 or 10 ft metal columns containing 30% Carbowax 20 M on 60—80 mesh Chromosorb W or on a Pye 105 instrument with glass columns containing either 7% FFAP on 60—80 mesh Chromosorb G (length 7 ft) or 30% Carbowax 20 M on 60—80 mesh Chromosorb W (length 10 ft). Semi-preparative g.l.c. was carried out on an F and M 720 instrument with a 6 ft metal column containing 10% Apiezon L on 60—80 mesh Chromosorb G at 128°. The F 11 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 A-700 and F and M instruments had thermal conductivity detectors and were operated at carrier gas (N$_2$–H$_2$; 4:1 and 9:1, respectively) flow rates of 250 and 40 ml min^{-1}, respectively.

Reference Compounds and Starting Materials.—Tricyclo-[2.2.1.0^{2,6}]heptan-3-ol (IV; R = H),[15] *exo*-2,*exo*-3-epoxy-bicyclo[2.2.1]heptane,[19,20] tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane,[21] and *exo*-2,*syn*-7-dimethoxybicyclo[2.2.1]heptane (II; R = Me)[20] were obtained by methods described in the literature. *exo*-2,*anti*-7-Dimethoxybicyclo[2.2.1]heptane (III; R = Me) was separated by semi-preparative g.l.c. from the products of the methylation[4,20] of a sample of bicyclo[2.2.1]heptane-*exo*-2,*anti*-7-diol contaminated with

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the exo-2,syn-7-diol.[7] syn-7-Methoxybicyclo[2.2.1]heptan-exo-2-ol,[17] $v_{max.}$ (film) 3490, 1460, 1410, 1360, 1200, 1105, 1080, 1050, and 1025 cm^{-1}, τ 6·23—6·43 (complex, CHOH and CHOMe), 6·68 (s, OMe), 7·67br and 7·81br (m, bridgeheads), and 8·0—9·0 (methylenes) was prepared by hydrolysis[17] of syn-7-methoxybicyclo[2.2.1]heptan-exo-2-yl acetate[22] and purified by preparative g.l.c. (A-700; 10 ft; 200°).

Methanolysis of exo-2,exo-3-Epoxybicyclo[2.2.1]heptane.[6]—The epoxide (5·5 g), methanol (25 ml), and 36N-sulphuric acid (4 drops) were refluxed together for 4 h. After cooling, the mixture was neutralised with barium carbonate and then filtered. Distillation of the filtrate gave material, b.p. 85—100° at 10 mmHg (4·45 g). Preparative g.l.c. (Pye 105; FFAP; 150°) gave tricyclo[2.2.1.0^{2,6}]heptan-3-ol (IV; R = H), m.p. 106—107° (lit.,[15] 108°) identified by comparison (^{1}H n.m.r. and i.r. spectra) with an authentic sample, exo-2-methoxybicyclo[2.2.1]heptan-syn-7-ol (II; R = H), $v_{max.}$ (film) 3480, 1090, and 1065 cm^{-1}, τ 6·05br (m, CHOH), 6·52 (d, J 9·5 Hz, OH), 6·43 (m, CHOMe), 6·62 (s, OMe), and 7·4—9·3 (complex, other protons) (Found: M^+, 142·0991. C$_8$H$_{14}$O$_2$ requires M, 142·0993), and exo-2-methoxybicyclo[2.2.1]heptan-anti-7-ol (III; R = H), $v_{max.}$ (film) 3620, 3420, 1100, 1070, and 1060 cm^{-1}, τ 5·75br (s, CHOH) 6·68 (s, OMe), 6·70 (m, CHOMe), 7·54br (s, OH), and 7·4—9·3 (complex, other protons) (Found: M^+, 142·0991). The peak areas for (IV), II, and III; R = H) were in the ratio 1 : 12 : 3 (cf. ref. 6).

Methylation of exo-2-Methoxybicyclo[2.2.1]heptan-syn-7-ol (II; R = H).—The methoxy-alcohol (0·48 g, 0·02 mol) in ether (25 ml) was added dropwise over 30 min to a vigorously stirred suspension of sodium hydride (0·48 g, 0·02 mol) in ether (25 ml). The mixture was stirred at room temperature for 9 h and then stirred and heated under reflux for 36 h. After cooling in ice, dimethyl sulphate (3·85 g, 0·0225 mol) was added dropwise over 5 min with stirring, which was then continued for 24 h at room temperature. The reaction was finally quenched by pouring the mixture into water (100 ml). The resultant solution was extracted with ether (3 × 50 ml), the combined ethereal extracts were dried, and the ether was evaporated off. The residue was refluxed for 1·5 h with aqueous 12N-sodium hydroxide (50 ml), and the solution was then extracted with ether (3 × 25 ml). The combined extracts were dried, and the ether was evaporated off. Analytical g.l.c. of the residue (2·1 g, 75%) (FFAP; 60—220° at 10° min^{-1}) showed that the material was essentially pure. Preparative g.l.c. (Pye 105; FFAP; 120°) gave exo-2,syn-7-dimethoxybicyclo[2.2.1]heptane (Found: M^+, 156·1160. Calc. for C$_9$H$_{16}$O$_2$: M,156·1150), identified by its ^{1}H n.m.r. and i.r. spectra.

Preparation of Alkyl Methyl Carbonates.—Methyl chloroformate (1·7 g) was added dropwise with cooling to tricyclo[2.2.1.0^{2,6}]heptan-3-ol (2·25 g) in pyridine (3·7 g). The mixture was stirred overnight at room temperature and then poured into acetic acid (5 ml) and water (15 ml). The solution was subsequently extracted with ether (3 × 15 ml) and the combined extracts were dried and evaporated, giving methyl tricyclo[2.2.1.0^{2,6}]heptan-3-yl carbonate (2·3 g, 66%), $v_{max.}$ (CCl$_4$) 1750, 1440, 1310, 1295, 1275, and 1000 cm^{-1}, τ 5·41br (s, CHOCO$_2$Me), 6·26 (s, CO$_2$Me), and 7·80—8·80 (complex, other protons). A sample isolated by preparative g.l.c. (A-700; 5 ft; 160°) had M^+, 168·0783 (C$_9$H$_{12}$O$_3$ requires 168·0786). Similarly prepared, and purified by preparative g.l.c., were bicyclo[2.2.1]heptan-exo-2-yl methyl carbonate (83%), $v_{max.}$ (CCl$_4$) 1745, 1440, 1305, 1270, 1060, and 975 cm^{-1}, τ 5·49 (m, CHOCO$_2$Me), 6·28 (s, CO$_2$Me), 7·50—7·80 (com-

plex, bridgeheads), and 8·0—9·0 (methylenes) (Found: M^+, 170·0945. C$_9$H$_{14}$O$_3$ requires M, 170·0943); exo-2-methoxybicyclo[2.2.1]heptan-anti-7-yl methyl carbonate, $v_{max.}$ (film) 1750 and 1270 cm^{-1}, τ 5·23br (s, CHOCO$_2$Me), 6·22 (s, CO$_2$Me), 6·72 (s, OMe), 6·70—6·74 (m, CHOMe), 7·54br and 7·67br (m, bridgeheads), and 8·0—9·0 (complex, methylenes) (Found: M^+, 200·1050. C$_{10}$H$_{16}$O$_4$ requires M, 200·1049); and exo-2-methoxybicyclo[2.2.1]heptan-syn-7-yl methyl carbonate, $v_{max.}$ (film) 1745 and 1270 cm^{-1}, τ 5·45 (m, CHOCO$_2$Me), 6·25 (s, CO$_2$Me), 6·50—6·65 (m, CHOMe), 6·73 (s, OMe), 7·37br and 7·65br (m, bridgeheads), and 8·0—9·0 (complex, methylenes) (Found: M^+, 200·1050).

Electrolysis of Bicyclo[2.2.1]hept-2-ene in Methanolic Sodium Methoxide.—Bicyclo[2.2.1]hept-2-ene (9·49 g, 0·1 mol) in methanolic 0·625M-sodium methoxide (400 ml) was electrolysed in the undivided cell having a platinum anode and a mercury cathode described previously[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 3·25 h. The methanolic solutions from three such electrolyses were combined, the methanol was distilled off, and water (50 ml) was added. The mixture was then extracted with ether (3 × 50 ml) and the combined extracts were dried. Distillation gave material, b.p. 24° at 11 mmHg to 140° at 0·3 mmHg (4·01 g), analytical g.l.c. (FFAP; 60—220° at 4° min^{-1}) of which gave a trace showing ten major peaks, t_R 9·5, 10, 11·5, 14, 14·5, 16·5, 18, 22, 24, and 25·5 min in the approximate ratios 1 : 4 : 4 : 4 : 1 : 1 : 1 : 4 : 1 : 4 (peak areas) together with a number of minor peaks. Samples of the products corresponding to each of the major peaks were obtained by preparative g.l.c. (Pye 105; Carbowax 20 M; 130—220° at 1·5° min^{-1}). Peak 1 (t_R 9·5 min) corresponded to exo-2,endo-3-dimethoxybicyclo[2.2.1]heptane (I), $v_{max.}$ (CDCl$_3$) 2960, 2940, 2900, 2870, 2820, 1450, 1370, 1350, 1190, 1125, 1105, 1090, 1050, and 985 cm^{-1}, τ 6·55—6·75 (m, CHOMe), 6·71 (s, OMe), 6·73 (s, OMe), 7·11br (t, J 2 Hz, CHOMe), 7·59br and 7·77br (m, bridgeheads), and 8·2—9·0 (complex, methylenes) (Found: M^+ 156·1152. C$_9$H$_{16}$O$_2$ requires M, 156·1150). The mass spectrum was in agreement with published data.[5] Peaks 2 and 3 (t_R 10 and 11·5 min) corresponded to exo-2,anti-7-dimethoxy- (III; R = Me) and exo-2,syn-7-dimethoxybicyclo[2.2.1]heptane (II; R = Me), identified by their i.r. and ^{1}H n.m.r. spectra. Peak 4(t_R 14 min) corresponded to a mixture from which the major component, tricyclo[2.2.1.-0^{2,6}]heptan-3-ol, m.p. 104—105° (lit.,[17] 108°), having i.r. and ^{1}H n.m.r. spectra identical with those of an authentic sample, was obtained by crystallisation from pentane. Peak 5 (t_R 14·5 min) corresponded to exo-2-methoxybicyclo-[2.2.1]heptan-syn-7-ol and had m/e 142 (2%), 124 (16), 110 (100), and 81 (100) and i.r. and ^{1}H n.m.r. spectra identical with those of an authentic sample. Peaks 6 and 7 (t_R 16·5 and 18 min) corresponded to bicyclo[2.2.1]heptan-exo-2-yl methyl carbonate, m/e 170 (2%), 154 (2), 141 (5), 124 (2), 111 (30), 95 (40), 94 (70), 79 (55), 67 (35), and 66 (100), and methyl tricyclo[2.2.1.0^{2,6}]heptan-3-yl carbonate, m/e 168 (11%), 141 (2), 109 (13), 94 (30), 93 (100), and 92 (60), respectively, and were identified by their i.r. and ^{1}H n.m.r. spectra. Peak 8 (t_R 22 min) was identified by its i.r. and ^{1}H n.m.r. spectra as corresponding to exo-2-methoxybicyclo[2.2.1]-heptan-anti-7-ol, m/e 142 (2%), 124 (54), 110 (100), 96 (100), and 81 (68). Peak 9 (t_R 24 min) corresponded to exo-2-methoxybicyclo[2.2.1]heptan-anti-7-yl methyl carbonate, m/e 200 (2%), 124 (100), and 92 (90), with i.r. and ^{1}H n.m.r.

[22] J. Kagan, Helv. Chim. Acta, 1972, 55, 2356.
[23] R. Brettle and D. Seddon, J. Chem. Soc. (C), 1970, 2175.

spectra identical with those of an authentic sample. Peak 10 (t_R 25·5) corresponded to a mixture with the same t_R as *exo*-2-methoxybicyclo[2.2.1]heptan-*syn*-7-yl methyl carbonate on analytical g.l.c. (FFAP; 60—220° at 4° min^{-1}). The sample showed all the absorptions in its i.r. and ^{1}H n.m.r. spectra present in the spectra of an authentic sample together with some extra absorptions due to an impurity.

Electrolysis of Bicyclo[2.2.1]*hepta-2,5-diene in Methanolic Sodium Methoxide.*—Bicyclo[2.2.1]hepta-2,5-diene (9·2 g, 0·1 mol) in methanolic 0·625M-sodium methoxide (400 ml) was electrolysed under conditions identical with those described for bicyclo[2.2.1]hept-2-ene. An identical work-up of a single such electrolysis gave a mixture (7·5 g) shown by analytical g.l.c. (FFAP; 110°) to contain three major components (t_R 9, 12·5, and 14·5 min) present in a 1 : 3·5 : 4 ratio (peak areas). Samples of each product were obtained by preparative g.l.c. (Pye 105; Carbowax 20M; 80—200° at 3° min^{-1}). The product having t_R 9 min was *exo*-5,*syn*-7-dimethoxybicyclo[2.2.1]hept-2-ene (VI) $\nu_{max.}$ (film) 2980, 2900, 2800, 1460, 1440, 1360, 1350, 1250, 1220, 1200, and 1100 cm^{-1}, τ 3·85—4·15 (m, C*H*=CH), 6·5—6·7 (m, C*H*OMe), 6·63 (s, OMe), 6·68 (s, OMe), 7·02br and 7·17br (m, bridgeheads), and 8·20—8·35 (complex, methylenes) (Found: C, 70·0; H, 9·3. $C_9H_{14}O_2$ requires C, 70·1; H, 9·1%). The product having t_R 12·5 min was exo-3,endo-5-*dimethoxytricyclo*[2.2.1.0^{2,6}]*heptane* (VII; $R^1 = R^2 = $ Me), $\nu_{max.}$ (film) 3050, 1120, and 1100 cm^{-1}, τ 6·05br (s, C*H*OMe), 6·49 (s, C*H*OMe), 6·71 (s, 2 × OMe), and 7·9—8·6 (complex, other protons) (Found: M^+, 154·0991. $C_9H_{14}O_2$ requires M, 154·0994). The product having t_R 14·5 min was exo-3,exo-5-*dimethoxytricyclo*[2.2.1.0^{2,6}]*heptane* (VIII; $R^1 = R^2 = $ Me), $\nu_{max.}$ (film) 3050, 1130, 1120, and 1095 cm^{-1}, τ 6·65br (s, 2 × C*H*OMe), 6·72 (s, 2 × OMe), 7·75br (s, H-4), 8·30br (s, 2 × H-7), and 8·55br (s, H-1, H-2, and H-6) (Found: M^+ 154·0991).

The unsaturated diether (VI) (150 mg) in ether (25 ml) and methanol (25 ml) was hydrogenated at atmospheric pressure over 5% palladium–charcoal (13 mg) until the theoretical amount of hydrogen had been absorbed. The mixture was then filtered through Celite and the residue washed with ether (25 ml). The solvents were removed from the combined filtrate and washings, giving *exo*-2,*syn*-7-dimethoxybicyclo[2.2.1]heptane (II; R = Me) (130 mg, 85%), identical (i.r. and ^{1}H n.m.r. spectra) with an authentic specimen.

Electrolysis of Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]*heptane in Methanolic Sodium Methoxide.*—Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (9·2 g, 0·1 mol) in methanolic 0·625M-sodium methoxide (400 ml) was electrolysed under conditions identical with those described above for bicyclo[2.2.1]hepta-2,5-diene. An identical work-up gave a mixture (9·1 g) shown by analytical g.l.c. (OV 225; 60—250° at 10° min^{-1}) to contain principally compounds (VI), (VII; $R^1 = R^2 = $ Me), and (VIII; $R^1 = $

$R^2 = $ Me), in a 1 : 3·5 : 4 ratio (peak areas). When a sample of tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane was dissolved in [${}^2H_4$]-methanol (0·5 ml) to which sodium hydride (60 mg) had previously been added, the ^{1}H n.m.r. spectrum of the solution remained unchanged over 3 days at 35°.

Electrolysis of Bicyclo[2.2.1]*hepta-2,5-diene in Methanolic Sodium Methyl Carbonate.*—Dry carbon dioxide was bubbled through methanolic sodium methoxide [from sodium (2·3 g, 0·1 g atom) in methanol (200 ml)] for 15 min. Bicyclo-[2.2.1]hepta-2,5-diene (9·2 g, 0·1 mol) was then added to the suspension and the mixture was electrolysed in a simple undivided cell fitted with an internal cooling coil and a magnetic stirrer. Both the anode and the cathode were rectangular platinum plates (2 × 3 cm). A constant current density of 0·1 A cm^{-2} was maintained at 45 V for 48 h corresponding to the passage of 9 F mol^{-1}. The usual work-up gave a residue (7·5 g) which was shown by analytical g.l.c. (FFAP; 80—160° at 3° min^{-1}) to contain compounds (VI), (VII; $R^1 = R^2 = $ Me), and (VIII; $R^1 = R^2 = $ Me) and three new components (t_R 20, 21·25, and 22·5 min) present in a 1 : 1 : 1 ratio (peak areas). G.l.c–mass spectrometry showed a molecular ion for each new component at m/e 140. The product mixture was distilled to give three fractions: (i) b.p. 40—60° at 20 mmHg (3·4 g); (ii) b.p. 78—80° at 17 mmHg; and (iii) b.p. 110—115° at 17 mmHg (1·7 g). Analysis of these fractions by g.l.c. (FFAP; 80—180°; at 3° min^{-1}) showed that fraction (iii) contained only the three new components.

Fraction (iii) (0·35 g) in dry ether (10 ml) was added dropwise to a vigorously stirred suspension of sodium hydride (0·1 g) in dry ether (10 ml). The mixture was stirred at room temperature for 9 h and was then heated under reflux with stirring for a further 36 h. The mixture was then cooled and dimethyl sulphate (0·5 g) was added over 5 min. After stirring at room temperature for a further 24 h the mixture was poured into water. The aqueous phase was extracted with ether (3 × 15 ml) and the combined extracts were dried and evaporated. The residue was heated under reflux for 1·5 h with 12N-sodium hydroxide (59 ml) and the mixture was then extracted with ether (3 × 25 ml). The combined extracts were dried and evaporated. Analytical g.l.c. (FFAP; 80—180° at 3° min^{-1}) of the residue (0·27 g) showed the presence of only two major components in a 2 : 1 ratio (peak areas), identified by peak enhancement studies as *exo*-3,*endo*-5-dimethoxytricyclo[2.2.1.0^{2,6}]heptane (VII; $R^1 = R^2 = $ Me) (t_R 12·5 min, major component) and *exo*-3,*exo*-5-dimethoxytricyclo[2.2.1.0^{2,6}]heptane (VIII; $R^1 = R^2 = $ Me) (t_R 14·5 min).