Anodic Syntheses. Part XV.[1] Further Studies with Ethylenic Acids [2]

By **Robert F. Garwood, Naser-ud-Din, Claude J. Scott,** and **Basil C. L. Weedon,*** Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

Contrary to previous reports, $\beta\gamma$-ethylenic acids undergo the Kolbe electrolytic coupling reaction normally, giving a mixture of three products representing the three possible modes of dimerisation of the intermediate allylic radical. The non-terminal double bond in the products retains (ca. 90%) the stereochemistry of the starting materials. With hept-6-enoic acid the intermediate radical undergoes partial cyclisation to the cyclopentylmethyl radical. Electrolysis of terminally unsaturated acids results in some double bond migration unless conditions are used in which the electrolyte does not become alkaline in the course of the reaction.
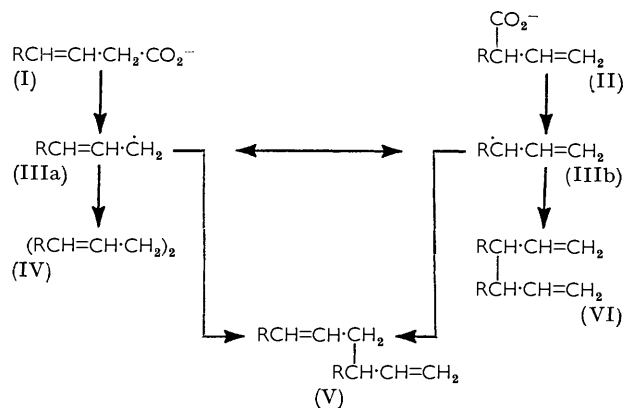
IT has been reported that $\beta\gamma$-unsaturated acids, like their $\alpha\beta$-analogues, fail to undergo the Kolbe anodic coupling, whereas acids in which the ethylenic bond is more remote than the carboxy-group couple normally with retention of stereochemistry at the double bond.[3] However, the conclusion drawn for $\beta\gamma$-unsaturated acids was based on experiments in aqueous solution. It was therefore decided to reinvestigate this type of reaction in methanol since it is known that the yields of coupled products in this solvent are usually better than in water. We have also investigated the electrolysis of a number of other ethylenic acids of different types and taken advantage of g.l.c. to submit the products to closer examination than was possible in the earlier studies.

(i) $\beta\gamma$-*Ethylenic Acids.*—Fichter and Holbro [4] studied the electrolysis of hex-3-enoic acid (presumably the *trans*-isomer) in aqueous solution. They were unable to isolate any coupled products; instead, small yields of pent-2-en-1-ol, penta-1,2-diene, and pent-2-enyl hex-3-enoate, were obtained. A possible interpretation of the formation of the oxygenated products is that, under these conditions, the intermediate resonance-stabilised allylic radical [(IIIa) ◀▶ (IIIb); R = Et] fails to dimerise but undergoes further oxidation to the corresponding carbonium ion which then attacks either the solvent or a carboxylate anion.[5]

We have confirmed that coupled products do not result in appreciable yield from the electrolysis of hex-*trans*-3-enoic acid in aqueous solution: mixed g.l.c. analysis of the products obtained with those from the electrolysis of the same acid in methanol (see later) indicated the absence of C_{12} hydrocarbons. Catalytic hydrogenation of the mixture gave some pentan-3-ol as well as pentan-1-ol, indicating that pent-1-en-3-ol is amongst the products of electrolysis.

When, however, the electrolysis was carried out in methanol, entirely different results were observed. The expected coupling products from a $\beta\gamma$-unsaturated acid (I) are the three dienes (IV)—(VI) resulting from the three possible modes of dimerisation of the mesomeric radical [(IIIa) ◀▶ (IIIb)], and these products were obtained from the *cis*- and *trans*-hex-3-enoic and oct-3-enoic acids in 35—40% yields. Hex-*trans*-3-enoic acid

(I; R = Et) afforded (35%) a mixture of hydrocarbons boiling in the range expected for decadienes (145—170°). The i.r. spectrum of the product indicated the presence of both $CH=CH_2$ and *trans*-$CH=CH$ systems, and this

$$RCH=CH \cdot CH_2 \cdot CO_2{}^- \quad (I)$$
$$RCH=CH \cdot \dot{C}H_2 \quad (IIIa)$$
$$(RCH=CH \cdot CH_2)_2 \quad (IV)$$
$$\overset{CO_2{}^-}{\underset{}{R\dot{C}H \cdot CH=CH_2}} \quad (II)$$
$$R\dot{C}H \cdot CH=CH_2 \quad (IIIb)$$
$$\overset{RCH \cdot CH=CH_2}{\underset{RCH \cdot CH=CH_2}{|}} \quad (VI)$$
$$\overset{RCH=CH \cdot CH_2}{\underset{RCH \cdot CH=CH_2}{|}} \quad (V)$$

was supported by the results of ozonolysis and esterification, which gave both dimethyl succinate [from (IV)] and dimethyl α-ethylsuccinate [from (V)]. G.l.c. analysis of the hydrocarbon product (squalane column) revealed the presence of three main components constituting respectively 13, 45, and 42% of the mixture. Catalytic hydrogenation resulted in the uptake of 2 mol. equiv. of hydrogen and g.l.c. analysis of the product again showed the presence of three main components in the same ratio. The hydrogenation products were identified as 3,4-diethylhexane, 3-ethyloctane, and n-decane, respectively, by comparison (mixed g.l.c.) with authentic specimens, and we conclude that the electrolysis product is a mixture of 3,4-diethylhexa-1,5-diene (VI; R = Et), 3-ethylocta-1,5-diene (V; R = Et), and deca-3,7-diene (IV; R = Et). The doubly branched hydrocarbon(VI) is present in the smallest proportion, dimerisation at the secondary centre being presumably sterically hindered. The formation of these three decadienes may be taken as additional confirmation that the Kolbe synthesis involves intermediate radicals. A similar mixture of three decadienes is formed by the action of magnesium on pent-2-enyl bromide.[6]

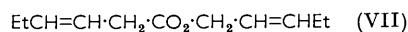Minor by-products of the electrolysis included a small

[1] Part XIV, B. W. Baker, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 1955, 2218.

[2] Preliminary publication, R. F. Garwood, C. J. Scott, and B. C. L. Weedon, *Chem. Comm.*, 1965, 14.

[3] B. C. L. Weedon, *Adv. Org. Chem.*, 1960, **1**, 1.

[4] F. Fichter, and T. Holbro, *Helv. Chim. Acta*, 1937, **20**, 1333.

[5] R. P. Linstead, B. R. Shepherd, and B. C. L. Weedon, *J. Chem. Soc.*, 1952, 3624; M. Finkelstein and R. C. Petersen, *J. Org. Chem.*, 1960, **25**, 136; B. Wladislaw and A. M. J. Ayres, *ibid.*, 1962, **27**, 281; B. Wladislaw and A. Giora, *J. Chem. Soc.*, 1964, 1037; B. Wladislaw and H. Viertler, *J. Chem. Soc. (B)*, 1968, 576.

[6] Ch. Prévost and G. Richard, *Bull. Soc. chim. France*, 1931, **49**, 1368.

low-boiling fraction (2%) showing evidence for the presence of an allene group (penta-1,2-diene?). Spectroscopic and g.l.c. evidence indicated the presence of methyl hex-*trans*-3-enoate (3%), and two unsaturated esters, believed to be (VII) and (VIII). n-Pentyl hex-

$$EtCH=CH\cdot CH_2\cdot CO_2\cdot CH_2\cdot CH=CHEt \quad (VII)$$
$$EtCH=CH\cdot CH_2\cdot CO_2\cdot CHEt\cdot CH=CH_2 \quad (VIII)$$

anoate [from (VII)] and 1-ethylpropyl hexanoate [from (VIII)] were identified in the hydrogenation product by mixed g.l.c. with authentic specimens.

There is evidence[7a] that allylic radicals can retain the *cis*- or *trans*-configuration at the double bond, and it was therefore of interest to study the stereochemistry of the Kolbe coupling of radicals of this type. Electrolysis of *cis*-hex-3-enoic acid gave a mixture of decadienes which on g.l.c. analysis (squalane column) gave three peaks in

having the same retention times as the corresponding two components of the product from the *trans*-acid. The two components are therefore *trans*- and *cis*-3-ethylocta-1,5-diene (V; R = Et), respectively. Similarly, the deca-3,7-diene (IV; R = Et) from hex-*trans*-3-enoic acid appeared, from its i.r. spectrum, to be mainly the *trans*,-*trans*-form, and was resolved by the silver nitrate column into two fractions (93 : 7), whereas that from *cis*-hex-3-enoic acid showed only weak absorption due to *trans*-CH=CH and was resolved by the silver nitrate column into two fractions (10 : 90). The minor decadiene from each of the two acids had the same retention time, and mixed g.l.c. analysis ($AgNO_3$) of the two decadiene fractions gave only three peaks, which therefore represent *trans*,*trans*-, *trans*,*cis*-, and *cis*,*cis*-deca-3,7-diene, respectively.

It is evident that there is very substantial retention of

TABLE 1

Composition of decadienes (%)

Source	(IV; R = Et)			(V; R = Et)		(VI; R = Et)
	cis,cis	*cis,trans*	*trans,trans*	*cis*	*trans*	
Hex-*cis*-3-enoic acid	40·0	4·5	0·0	38·6	2·4	14·5
Hex-*trans*-3-enoic acid	0·0	2·8	39·2	1·3	43·7	13·0
Acetic acid + Butadiene	0·0	2·9	40·9	1·2	42·6	12·4

TABLE 2

Composition of tetradecadienes (%)

Source	(IV; R = Bu)			(V; R = Bu)		(VI; R = Bu)
	cis,cis	*cis,trans*	*trans,trans*	*cis*	*trans*	
Oct-*cis*-3-enoic acid	34·5	5·3	1·1	44·3	2·8	12
Oct-*trans*-enoic acid	0·0	5·3	48·9	2·2	40·6	3
2-Vinylhexanoic acid	0·0	9·4	45·3	9·1	26·8	9·4

the ratio 14 : 41 : 45%. These peaks had the same retention times as the corresponding peaks from the hex-*trans*-3-enoic acid product, and mixed g.l.c. analysis of the two series of products gave only three peaks. The decadiene mixture from the *cis*-acid however showed i.r. bands indicating the presence of $CH=CH_2$ and *cis*-CH=CH systems, but only very weak absorption due to *trans*-CH=CH, and it was evident that the g.l.c. column used could not separate the geometrical isomers. We therefore separated the three structurally isomeric decadienes by preparative g.l.c. on a squalane column and re-chromatographed each fraction on a silver nitrate–poly-(ethylene glycol) column which successfully resolved the geometrical isomers.

The 3-ethylocta-1,5-diene fraction from hex-*trans*-3-enoic acid showed i.r. absorption due to *trans*-CH=CH but none due to *cis*-CH=CH, and was resolved by the silver nitrate column into two fractions in the ratio 97 : 3. The corresponding fraction from hex-*cis*-3-enoic acid showed i.r. absorption due to *cis*-CH=CH, but only very weak absorption due to *trans*-CH=CH, and was resolved by the silver nitrate column into two fractions (6 : 94).

the configuration at the olefinic bond during Kolbe coupling. Table 1 shows the composition of the products obtained from *cis*- and *trans*-hex-3-enoic acids, corrected for the presence of a small amount of *trans*-acid in the *cis*-acid used.

G.l.c. analysis of the 3,4-diethylhexa-1,5-diene (IV; R = Et) on the silver nitrate column also gave two peaks of approximately equal area; presumably these represent the (±)- and *meso*-forms. It has been shown that both *meso*- and (±)-1,2-dichlorosuccinic acids are obtained by dimerisation of the radical resulting from the action of benzoyl peroxide on chloroacetic acid.[7b]
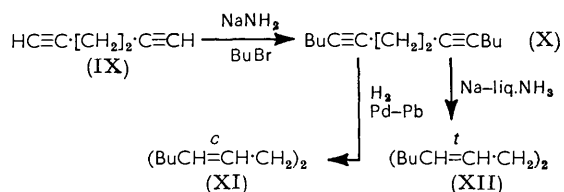
The mesomeric radical [(IIIa) ◄►► (IIIb); R = Et] also results from the addition of methyl radicals (from the electrolysis of acetic acid) to butadiene.[8] We have studied the decadiene fraction from this reaction and find that it closely resembles that resulting from the electrolysis of hex-*trans*-3-enoic acid, as would be expected in view of the greater thermodynamic stability of the *trans*-configuration.

Similar results were obtained on electrolysis of the *cis*- and *trans*-oct-3-enoic acids (I; R = Bu) (Table 2). In this case we confirmed the structure and stereochemistry

[7] (a) G. Walling and W. Thaler, *J. Amer. Chem. Soc.*, 1961, **83**, 3877; (b) M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Org. Chem.*, 1945, **10**, 386.

[8] R. V. Lindsey and M. L. Peterson, *J. Amer. Chem. Soc.*, 1959, **81**, 2073; W. B. Smith and H. G. Gilde, *ibid.*, p. 5325.
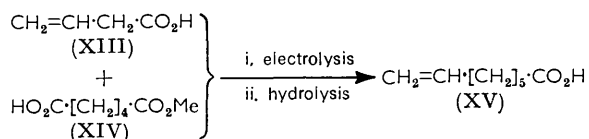
of the tetradeca-5,9-dienes (II; R = Bu) by direct comparison (mixed g.l.c.) with authentic specimens prepared by conventional routes from hexa-1,5-diyne (IX).

$$HC{\equiv}C{\cdot}[CH_2]_2{\cdot}C{\equiv}CH \xrightarrow[\text{BuBr}]{\text{NaNH}_2} BuC{\equiv}C{\cdot}[CH_2]_2{\cdot}C{\equiv}CBu \quad (X)$$
$$(IX)$$

$$\downarrow \substack{H_2 \\ Pd-Pb} \qquad \downarrow Na-liq.NH_3$$

$$\underset{(XI)}{\overset{c}{(BuCH{=}CH{\cdot}CH_2)_2}} \longleftarrow \underset{(XII)}{\overset{t}{(BuCH{=}CH{\cdot}CH_2)_2}}$$

The mesomeric radical [(IIIa) ←→ (IIIb); R = Bu] should also be produced by the electrolysis of 2-vinylhexanoic acid (II; R = Bu); Table 2 shows the composition of the tetradecadienes obtained from this acid. The products have, as would be expected, mainly the *trans*-configuration.
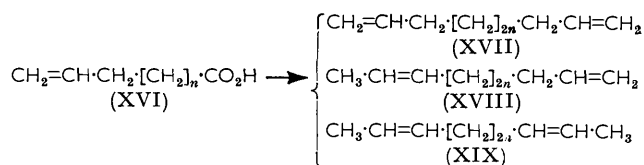
Retention of the stereochemistry of allylic radicals has been observed in the homolytic chlorination of olefins with t-butyl hypochlorite.[7a] In Kolbe electrolysis, in which the radical is generated under particularly mild conditions, there does not appear to be any increase in stereomutation as the size of the alkyl radical increases.

The simplest βγ-unsaturated acid, vinylacetic acid (XIII), can give only one Kolbe coupling product, biallyl (IV; R = H), which we obtained in poor yield. Cross coupling of vinylacetic acid with the half esters of dibasic acids, however, offers a route to terminally unsaturated acids, and we have successfully used this method in the synthesis of oct-7-enoic acid (XV) which we required in our work.

$$\left.\begin{array}{c} \underset{(XIII)}{CH_2{=}CH{\cdot}CH_2{\cdot}CO_2H} \\ + \\ \underset{(XIV)}{HO_2C{\cdot}[CH_2]_4{\cdot}CO_2Me} \end{array}\right\} \xrightarrow[\text{ii, hydrolysis}]{\text{i, electrolysis}} \underset{(XV)}{CH_2{=}CH{\cdot}[CH_2]_5{\cdot}CO_2H}$$

(ii) *Other Ethylenic Acids.*—Electrolysis of hex-*trans*-4-enoic and oct-*trans*-6-enoic acid in methanol gave (*ca.* 35%) the expected *trans,trans*-dienes, no isomers being detectable. However, with terminally unsaturated acids the products were found to depend on the conditions used. Electrolysis of hex-5-enoic acid (XVI; $n = 2$) in a Dinh-Nguyen cell[9] using a platinum anode and a mercury cathode, a procedure which prevents the electrolyte becoming alkaline, gave deca-1,9-diene (XVII; $n = 4$) in which no impurities were detected by either g.l.c. or i.r. When, however, the electrolysis was carried out using a platinum cathode, *i.e.* under conditions in which the electrolyte becomes alkaline towards the end of the reaction, the product on g.l.c. analysis gave three peaks, and its i.r. spectrum showed absorption due to *trans*-CH=CH. Catalytic hydrogenation of the mixture resulted in the uptake of 2 mol. equiv. of hydrogen, and only n-decane was detected in the product. It appears therefore that under these conditions some double-bond migration occurs, and the product is contaminated with deca-1,8-diene (XVIII; $n = 2$) and deca-2,8-diene (XIX; $n = 2$). We confirmed the presence of the latter by mixed g.l.c. with an authentic sample obtained by

electrolysis of hex-4-enoic acid. Ozonolysis supported these conclusions, for whereas the product from electrolysis in the Dinh-Nguyen cell gave a 68% yield of suberic acid accompanied by only 4·0% of pimelic acid and 1·7% of adipic acid (owing, presumably, to secondary oxidation), that from the electrolysis under alkaline conditions gave 55% of suberic acid, 12·3% of pimelic acid, and 3·4% of adipic acid under identical conditions.

$$\underset{(XVI)}{CH_2{=}CH{\cdot}CH_2{\cdot}[CH_2]_n{\cdot}CO_2H} \longrightarrow \left\{\begin{array}{l} \underset{(XVII)}{CH_2{=}CH{\cdot}CH_2{\cdot}[CH_2]_{2n}{\cdot}CH_2{\cdot}CH{=}CH_2} \\ \underset{(XVIII)}{CH_3{\cdot}CH{=}CH{\cdot}[CH_2]_{2n}{\cdot}CH_2{\cdot}CH{=}CH_2} \\ \underset{(XIX)}{CH_3{\cdot}CH{=}CH{\cdot}[CH_2]_{2n}{\cdot}CH{=}CH{\cdot}CH_3} \end{array}\right.$$

Similar results were noted in the electrolysis of undec-10-enoic acid (XVI; $n = 7$), which afforded only (XVII; $n = 7$) in the Dinh-Nguyen cell but gave (XVII), (XVIII), and (XIX) ($n = 7$) when the electrolyte was allowed to become alkaline. The mechanism of this type of rearrangement remains obscure. Eicosa-1,19-diene (XVII; $n = 7$) was unchanged after electrolysis in methanolic sodium methoxide, and undeca-10-enoic acid did not rearrange on heating with sodium methoxide in methanol.

Hept-6-enoic acid (XVI; $n = 3$) on electrolysis with either a platinum or a mercury cathode gave a mixture of hydrocarbons shown (g.l.c.) to contain three components. Catalytic hydrogenation of the mixture resulted in the uptake of only about two thirds of the volume of hydrogen expected for a dodecadiene, and the hydrogenation product also contained three components, one of which was identified (mixed g.l.c.) as n-dodecane. A second component had the same retention time as one of the original products, indicating that one of the latter is saturated. A saturated product could arise by union of two cyclopentylmethyl radicals, two cyclohexyl radicals, or one of each, these two radicals being possible cyclisation products of the hex-5-enyl radical (XX). Bicyclohexyl was shown to be absent from the electrolysis product by mixed g.l.c. with an authentic specimen. The electrolysis product was separated by preparative g.l.c. [poly(ethylene glycol)adipate] into three fractions, one of which was shown to be 1,2-dicyclopentylethane by direct comparison (mixed g.l.c.; i.r. and n.m.r. spectra) with an authentic specimen. Identification of the third component was more difficult, since the possible hydrogenation products, n-hexylcyclohexane and n-heptylcyclopentane, which were synthesised by standard methods, have the same retention time on the column used. However, ozonolysis of the mixed electrolysis product followed by oxidation with hydrogen peroxide and esterification gave dimethyl suberate [from (XXII)] and methyl 6-cyclopentylhexanoate [from (XXIV)]; the latter was conveniently synthesised via the crossed Kolbe coupling of cyclopentylacetic acid and methyl hydrogen adipate. Hence the third component must be (XXIV). The formation of (XXIV) and (XXIII) in-

[9] N. Dinh-Nguyen, *Acta Chem. Scand.*, 1958, **12,** 585.

volves cyclisation of (XX) to give the primary radical (XXI) rather than the (presumably more stable) secondary cyclohexyl radical. However it is at present difficult to rationalise the cyclisation of radicals of this type,
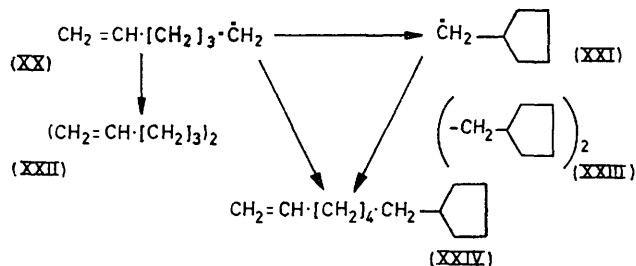
which may afford either five- or six-membered ring products;[10] in some cases[11] mixtures are obtained, the composition of which depends on the conditions used. It is interesting that five-membered ring compounds predominate in the products obtained by pyrolysis of hept-6-enoyl peroxide in toluene,[12] by reduction of hex-5-ene-1-thiol with triethyl phosphite,[13] by radical addition of hexafluoro-3-iodopropane to hepta-1,6-diene,[14] and by reaction of 6-phenylhex-1-ene with di-t-butyl peroxide.[15] Similarly the allyloxyethyl radical[16] cyclises giving, after hydrogen transfer, 3-methyltetrahydrofuran. Cyclisation of the corresponding acetylenic radicals affords both five- and six-membered rings.[17]

Electrolysis of oct-*trans*-6-enoic acid, in marked contrast to that of hept-6-enoic acid, gave no detectable cyclisation products; *trans,trans*-tetradeca-2,12-diene was the only hydrocarbon observed. Oct-7-enoic acid similarly afforded only tetradeca-1,13-diene when the electrolysis was carried out using a mercury cathode.

Cyclisation of the above type appears to be irreversible, for cyclopentylacetic and cyclohexylacetic acids underwent only normal coupling without detectable ring opening.

EXPERIMENTAL

Two types of electrolytic cell were used. Cell A was a simple cylindrical tube (20 × 4 cm) with a side arm for a reflux condenser and two bright platinum electrodes (3 × 2 cm); it was cooled in an ice-bath during electrolysis. Cell B was based on the design of Dinh-Nguyen[9] and had a rotating circular platinum anode (diam. 4·4 cm) and a mercury cathode; it was fitted with a water jacket for cooling. When cell A was used, 2—5% of the acid was neutralised with sodium methoxide in methanol and electrolysis was continued until the electrolyte became alkaline. When cell B was used, the acid was neutralised with the calculated amount of sodium methoxide in methanol, and electrolysis was continued until the current dropped from 1·6—1·8 to 0·2—0·4 A. G.l.c. analyses were carried out using a Pye Argon or a Perkin-Elmer Aerograph A90-P3 chromatograph. Columns used were (a) 10% poly(ethylene glycol)adipate

(PEGA) on 100—120 mesh Celite 545; (b) 10% squalane on Celite; (c) 10% Apiezon L on Celite; (d) 20% Carbowax M20 on Celite; (e) 25% solution of silver nitrate in poly(ethylene glycol) (PEG) 300 (35%) on 60—80 B.S. mesh firebrick. I.r. spectra were recorded on a Unicam SP 200 spectrophotometer. N.m.r. spectra were recorded on a Varian A60 spectrometer.

Electrolysis of Hex-3-enoic Acids.—(a) trans-*Hex-3-enoic acid.* The sample used (Light) contained 97·4% *trans*- and 2·6% *cis*-isomer (g.l.c. analysis of methyl ester). The acid (20·5 g) was added to sodium methoxide [from sodium (0·2 g)] in methanol (100 ml) and the mixture was electrolysed (cell A; 0·7—0·8 A; 10 h) until alkaline. The solution was diluted with water (3 l), acidified (HCl), and extracted with ether (3 × 150 ml), and the extract was washed with aqueous 2% potassium hydroxide (2 × 50 ml) and water (100 ml), and dried (Na_2SO_4). After removal of ether, distillation gave a decadiene fraction, b.p. 154—170° (2·9 g, 23%). G.l.c. analysis (squalane; 75°) showed three main peaks, ratio 13·0 : 45·0 : 42·0; $\nu_{max.}$ 915 and 995 ($CH=CH_2$), 970 (*trans*-CH=CH), and 1640 cm⁻¹ (C=C). On catalytic hydrogenation (Adams catalyst; ethanol) 1·9 mol. equiv. of hydrogen were absorbed and g.l.c. analysis of the product (squalane; 75°) showed three main peaks, ratio 13·8 : 44·2 : 42·0. These were identified by mixed g.l.c. with authentic specimens as 3,4-diethylhexane, 3-ethyloctane, and n-decane, respectively. Ozonolysis of the decadiene fraction (AcOH–AcOMe; 0°) followed by oxidative work up (H_2O_2) and esterification (MeOH–H_2SO_4) gave a mixture of esters shown to contain dimethyl succinate (from deca-3,7-diene) and dimethyl α-ethylsuccinate (from 3-ethylocta-1,5-diene) by mixed g.l.c. analysis (PEGA; 125°) with authentic specimens.

(b) cis-*Hex-3-enoic acid.* The acid (4·3 g) in methanolic sodium methoxide [from sodium (0·05 g) and methanol (100 ml)] was electrolysed (cell A) and the product was worked up as in (a). Distillation afforded a decadiene fraction, b.p. 140—160°, (1·1 g); $\nu_{max.}$ 920 and 1000 ($CH=CH_2$), 1640 (C=C), and 720 cm⁻¹ (*cis*-CH=CH); the band at 970 cm⁻¹ (*trans*-CH=CH) was very weak. G.l.c. analysis (squalane; 75°) showed three main peaks (ratio 14·5 : 41·0 : 44·5) which were inseparable from the corresponding peaks of the decadiene fraction from *trans*-hex-3-enoic acid. Catalytic hydrogenation (Adams catalyst; absolute ethanol) resulted in the absorption of 96% of the calculated amount of hydrogen, and mixed g.l.c. analysis of the products with authentic specimens identified them as 3,4-diethylhexane, 3-ethyloctane, and n-decane.

Separation of Decadienes.—Preparative g.l.c. (squalane; 75°) on the decadiene mixture from *trans*-hex-3-enoic acid gave: (a) 3,4-diethylhexa-1,5-diene, $\nu_{max.}$ 920 and 1000 ($CH=CH_2$), and 1640 cm⁻¹ (C=C); no band at 970 cm⁻¹ (*trans*-CH=CH); separable by g.l.c. analysis ($AgNO_3$–PEG; 50°) into two peaks, ratio 48 : 52, probably (±)- and *meso*-forms; (b) 3-ethylocta-1,5-diene, n_D^{20} 1·4340 (lit.,[18] 1·4324); $\nu_{max.}$ 920 and 1000 ($CH=CH_2$), 970 (*trans*-CH=CH), and 1640 cm⁻¹ (C=C); g.l.c. analysis ($AgNO_3$–PEG; 50°) showed two peaks, ratio 97·2 : 2·8 (*trans* : *cis*), the minor peak being

[10] For references see M. Julia, *Pure Appl. Chem.*, 1967, **15**, 167.

[11] M. Julia and M. Maumy, *Bull. Soc. chim. France*, 1969, 2415.

[12] R. C. Lamb, P. W. Ayers, and M. Toney, *J. Amer. Chem. Soc.*, 1963, **85**, 3483.

[13] C. Walling and M. S. Pearson, *J. Amer. Chem. Soc.*, 1964, **86**, 2262.

[14] N. O. Brace, *J. Amer. Chem. Soc.*, 1964, **86**, 523.

[15] H. Pines, N. C. Sih, and D. B. Rosenfeld, *J. Org. Chem.*, 1966, **31**, 2255.

[16] R. C. Lamb, J. G. Pacifico, and P. W. Ayres, *J. Org. Chem.*, 1966, **30**, 3099.

[17] W. H. Moore and D. G. Peters, *Tetrahedron Letters*, 1972, 453.

[18] Ch. Prévost and G. Richard, *Bull. Soc. chim. France*, 1931, **49**, 1368.

identical (mixed g.l.c.) with the corresponding major peak from the electrolysis of cis-hex-3-enoic acid; and (c) deca-3,7-diene, $\nu_{max.}$ 970 cm^{-1} (trans-CH=CH); no bands at 920 or 1000 cm^{-1}; g.l.c. analysis (AgNO$_3$–PEG; 50°) gave two peaks in the ratio 93·4 : 6·6 (trans,trans : trans,cis), the minor peak being identical (mixed g.l.c.) with the corresponding peak from the electrolysis of cis-hex-3-enoic acid.

Preparative g.l.c. on the decadiene fraction from cis-hex-3-enoic acid similarly gave: (a) 3,4-diethylhexa-1,5-diene; (b) 3-ethylocta-1,5-diene, $\nu_{max.}$ 920 and 1000 (CH=CH$_2$), 720 (cis-CH=CH), and 970 cm^{-1} (very weak; trans-CH–CH), separable by g.l.c. analysis (AgNO$_3$–PEG; 50°) into two fractions, ratio 6 : 94 (trans : cis), the minor peak being identical (mixed g.l.c.) with the major peak from the electrolysis of trans-hex-3-enoic acid; and (c) deca-3,7-diene, $\nu_{max.}$ 730 (cis-CH=CH), 1640 (C=C), and 970 cm^{-1} (very weak; trans-CH=CH), separable by g.l.c. analysis (AgNO$_3$–PEG; 50°) into two peaks, ratio 10 : 90 (trans,cis : cis,cis), the minor peak being identical (mixed g.l.c.) with the corresponding peak from the electrolysis of trans-hex-3-enoic acid.

Electrolysis of Acetic Acid in the Presence of Butadiene.—Glacial acetic acid (20 g) was added to methanolic sodium methoxide [from sodium (0·3 g) in methanol (120 ml)]; the solution was cooled to $-10°$ (Me$_2$CO–CO$_2$), and butadiene (20 g) was added. Electrolysis was carried out in cell A under a condenser (Me$_2$CO–CO$_2$) and the product was worked up as before, giving on distillation a decadiene fraction, b.p. 140—152° (1·4 g), $\nu_{max.}$ 915 and 995 (CH=CH$_2$), 970 (trans-CH=CH), and 1640 cm^{-1} (C=C), shown by mixed g.l.c. analysis (as above) to have nearly the same composition as the product from trans-hex-3-enoic acid (Table 1).

Electrolysis of Oct-3-enoic Acids.—(a) cis-Oct-3-enoic acid. cis-Oct-3-enoic acid [19] (2·2 g) in methanolic sodium methoxide [from sodium (0·02 g) and methanol (100 ml)] was electrolysed in cell A. Isolation of the product in the usual way gave a tetradecadiene fraction, b.p. 200—250° (0·95 g), $\nu_{max.}$ 720 (cis-CH=CH), 920 and 1000 (CH=CH$_2$), 1640 (C=C), and 1730 cm^{-1} (ester); there was a weak band at 970 cm^{-1} (trans-CH=CH). G.l.c. analysis (Carbowax, 170°) showed three main peaks (91%), ratio 12·0 : 47·1 : 40·9, together with minor peaks, one of which was identified as methyl cis-oct-3-enoate (mixed g.l.c.). The three main peaks were separated by preparative g.l.c. giving: (a) 5,6-divinyldecane, $\nu_{max.}$ 920 and 1000, (CH=CH$_2$) and 1640 (CH=CH); no bands at 720 (cis-CH=CH) or 970 cm^{-1} (trans-CH=CH); g.l.c. analysis (AgNO$_3$; 75°) gave two peaks, ratio 51 : 49; (b) cis-8-vinyldodec-5-ene, $\nu_{max.}$ 720 (cis-CH=CH) 920 and 1000 (CH=CH$_2$), and 1640 cm^{-1} (C=C), with a very weak band at 970 cm^{-1} (trans-CH=CH); g.l.c. analysis (AgNO$_3$; 75°) showed two peaks, ratio 6 : 94 (trans : cis), the minor peak having the same retention time as the corresponding major peak from the electrolysis of trans-oct-3-enoic acid; and (c) tetradeca-cis-5,cis-9-diene, $\nu_{max.}$ 720 cm^{-1} (cis-CH=CH), with a weak band at 970 cm^{-1} (trans-CH=CH); g.l.c. analysis (AgNO$_3$; 75°) gave three peaks in the ratio 2·6 : 13·0 : 84·3, the first and third of which were identified as tetradeca-trans-5,trans-9-diene and tetradeca-cis-5,cis-9-diene by mixed g.l.c. with authentic specimens; the remaining peak is presumably tetradeca-cis-5,trans-9-diene.

(b) trans-Oct-3-enoic acid. trans-Oct-3-enoic acid (2·7 g) in methanolic sodium methoxide [from sodium (0·03 g) and methanol (125 ml)] was electrolysed (cell A) and the product was worked up as usual. Distillation gave a fraction of b.p. 200—230° (1·0 g, 51%), $\nu_{max.}$ 915 and 1000 (CH=CH$_2$),

970 (trans-CH=CH) and 1640 cm^{-1} (C=C str.) with weak bands at 730 (cis-CH=CH) and 1730 cm^{-1} (ester); g.l.c. analysis (20% Carbowax M20; 170°) showed three main peaks, ratio 3 : 42·8 : 54·2, and several minor peaks, one of which was identified (mixed g.l.c.) as methyl trans-oct-3-enoate. The three main components were separated by preparative g.l.c. (Carbowax; 170°) as before and examined by g.l.c. (25% AgNO$_3$–PEG) in the same way as the products from the cis-acid; for the results see Table 2.

2-Vinylhexanoic Acid.—A mixture of hept-1-ene (65 g, 0·67 mol), carbon tetrachloride (180 ml), N-bromosuccinimide (100 g, 0·56 mol), and benzoyl peroxide (0·3 g) was heated (steam-bath) for 90 min under reflux. After cooling, the succinimide was filtered off, the solvent was removed, and the residue was distilled giving a mixture of bromoheptenes (42·5 g, 35·6%), b.p. 76—84° at 40 mmHg.

The bromoheptenes (42 g) in sodium-dried ether (40 ml) were slowly run onto magnesium turnings (12·0 g, 0·5 g atom) in ether (30 ml) with stirring (3 h). The Grignard reagent was added rapidly to a large excess of solid carbon dioxide, and, after the mixture had been kept for 30 min, crushed ice (500 g) and 10N-sulphuric acid (500 ml) were added. The organic layer was separated and the aqueous portion extracted with ether (3 $\times$ 100 ml). The combined ethereal layers were extracted with saturated sodium hydrogen carbonate (3 $\times$ 200 ml) and the aqueous layer was acidified (HCl) and extracted with ether (3 $\times$ 200 ml). The extracts were dried (MgSO$_4$) and evaporated. Distillation gave 2-vinylhexanoic acid, b.p. 62—63° at 0·1 mmHg (5·4 g, 16%), n_D^{20} 1·4370 (Found: C, 67·45; H, 9·85. C$_8$H$_{14}$O$_2$ requires C, 67·5; H, 9·9%). G.l.c. analysis (PEGA; 100°) of the methyl ester (prepared with MeOH–H$_2$SO$_4$) indicated 98·5% purity. The ester had $\nu_{max.}$ 920 and 1000 (CH=CH$_2$), 1640 (C=C), and 1735 cm^{-1} (ester); no band at 980 cm^{-1} (trans-CH=CH).

Electrolysis of 2-Vinylhexanoic Acid.—The acid (4·0 g) was added to methanolic sodium methoxide [from sodium (0·65 g) and methanol (100 ml)] and the solution was electrolysed (cell B). After work-up as usual distillation gave a tetradecadiene fraction, b.p. 180—220° (0·9 g, 33%), which was separated by preparative g.l.c. and examined by g.l.c. on a silver nitrate column as before; the results are given in Table 2.

Tetradeca-5,9-diyne (IX).—Hexa-1,5-diyne (10·0 g) in ether (50 ml) was added during 1·5 h to a stirred suspension of sodamide [from sodium (8 g) and liquid ammonia (500 ml)]. The mixture was stirred for a further 1 h and then 1-bromobutane (35 g) in ether (100 ml) was added gradually over 1 h. After further stirring (2 h) the mixture was decomposed with water (500 ml) and the product was extracted with ether (3 $\times$ 200 ml). The extracts were washed with 2N-sulphuric acid (3 $\times$ 50 ml), 5% sodium hydrogen carbonate solution (3 $\times$ 50 ml), and water (2 $\times$ 50 ml), and dried (MgSO$_4$). After removal of ether, distillation through a Vigreux column gave tetradeca-5,9-diyne, b.p. 132—134° at 12 mmHg, n_D^{21} 1·4649 (10 g, 41%) (Found: C, 88·45; H, 11·6. C$_{14}$H$_{22}$ requires C, 88·35; H, 11·65%). G.l.c. analysis (10% PEGA; 75°) showed only one peak.

Tetradeca-cis-5,cis-9-diene (XI).—Tetradeca-5,9-diyne (1·0 g), ethyl acetate (25 ml), Lindlar catalyst (0·4 g), and quinoline (0·04 g) were shaken under hydrogen at atmospheric pressure until absorption ceased (uptake 289 ml at S.T.P.; calc. 235 ml). After filtration and removal of solvent, distillation gave tetradeca-cis-5,cis-9-diene (0·5 g,

[19] J. A. Knight and H. Diamond, *J. Org. Chem.*, 1959, 400.

50%), b.p. 118° at 10 mmHg, n_D^{21} 1·4560; $\nu_{max.}$ 1650 (C=C) 1400, 970, and 720 cm^{-1} (cis-CH=CH) (Found: C, 86·45; H, 13·35%; M^+, 194·2034. $C_{14}H_{26}$ requires C, 86·5; H, 13·5%; M, 194·2034). G.l.c. analysis (AgNO$_3$; 75°) showed the presence of 2·9% of the cis-trans-stereoisomer.

Tetradeca-trans-5,trans-9-*diene* (XII).—Tetradeca-5,9-diyne (2·0 g) in ether (10 ml) was added during 4 h to a well stirred solution of sodium (10·0 g) in liquid ammonia (600 ml). Next day ammonium hydroxide (200 ml) and water (500 ml) were added, and the mixture was extracted with ether (3 × 200 ml). The extracts were washed successively with 2N-sulphuric acid (2 × 50 ml), 5% sodium hydrogen carbonate solution (2 × 50 ml), and water (50 ml), and dried (MgSO$_4$). Distillation gave *tetradeca*-trans-5,trans-9-*diene* (0·6 g, 30%), b.p. 120° at 11 mmHg, n_D^{21} 1·4480; $\nu_{max.}$ 970s (*trans*-CH=CH) (Found: C, 86·55; H, 13·65%; M^+, 194·203. $C_{14}H_{26}$ requires C, 86·5; H, 13·50%; M, 194·203).

Electrolysis of Vinylacetic Acid.—The acid (10·4 g) was added to a solution of sodium methoxide [from sodium (3·6 g) and methanol (100 ml)] and electrolysed (cell B) until the current dropped from 1·4 to 0·4 A (6 h). The solution was acidified, diluted with water (2 l), and extracted with toluene (3 × 75 ml), and the extracts were dried (MgSO$_4$). Distillation through an 18 in Dufton column gave a hexadiene fraction (3·4 g), b.p. 55—60°; $\nu_{max.}$ 1640 (C=C), 1820, 1000, and 920 cm^{-1} (CH=CH). Treatment of this fraction (3·0 g) in carbon tetrachloride (10 ml) with bromine (10 ml) gave 1,2,5,6-tetrabromohexane (4·2 g), m.p. and mixed m.p. 40—42° (from light petroleum). The yield of hexa-1,5-diene, based on isolated tetrabromide, was 13% of theory.

Electrolysis of trans-*Hex*-4-*enoic Acid.*—The acid (3·1 g) [20] was added to methanolic sodium methoxide [from sodium (0·05 g) in methanol (60 ml)] and the solution was electrolysed (cell A) until it became alkaline. After filtration to remove polymeric products, the product was worked up as usual giving a decadiene fraction (0·65 g, 36%), b.p. 160—170°, n_D^{20} 1·4394 (lit.,[4] b.p. 115—118° at 116 mmHg, n_D^{22} 1·4370 for deca-*trans*-2,*trans*-8-diene), $\nu_{max.}$ 975 cm^{-1} (*trans*-CH=CH); no appreciable absorption at 675—730 cm^{-1}; g.l.c. analysis (10% squalane; 75°, or 25% AgNO$_3$–PEG; 50°) showed only one main peak, indicating that the product was structurally and stereochemically homogeneous. Catalytic hydrogenation (Adams catalyst) resulted in the uptake of 108% of the hydrogen calculated for a decadiene; the reduction product was identified as n-decane by mixed g.l.c. analysis (10% squalane; 75%) with an authentic specimen.

*Electrolysis of Hept-*6-*enoic Acid* (XVI; $n = 3$).—The acid (5 g) [20] was added to methanolic sodium methoxide [from sodium (0·05 g) and methanol (100 ml)] and electrolysed (cell A) until the solution became alkaline. After work-up in the usual way, distillation afforded a main fraction, b.p. 99—104° at 16 mmHg (1·1 g, 35% of theory calculated as dodecadienes). G.l.c. analysis showed three peaks (ratio 42·7 : 37·0 : 20·7). On catalytic hydrogenation the uptake of hydrogen was only 67% of that expected for a dodeca-diene; g.l.c. analysis of the product (10% PEGA; 75%) again showed three peaks one of which had the same retention time as one of the peaks before hydrogenation. Two of the hydrogenation products were identified as n-dodecane (42·3%) and 1,2-dicyclopentylethane (37%), respectively, by mixed g.l.c., but the third had the same retention time as both n-heptylcyclopentane and n-hexylcyclohexane.

The three components of the original electrolysis mixture were separated by preparative g.l.c. (10% PEGA; 75°)

giving: (a) dodeca-1,11-diene, $\nu_{max.}$ 920 and 1000 (CH=CH$_2$), and 1640 cm^{-1} (C=C); (b) 1,2-dicyclopentylethane; no absorption at 920, 1000, or 1640 cm^{-1}, τ 8·1—9·2 (chain and ring protons, no absorption in the olefinic proton region); and (c) 7-cyclopentylhept-1-ene, $\nu_{max.}$ 920 and 1000 (CH=CH$_2$), and 1640 cm^{-1} (C=C). Ozonolysis of the crude electrolysis product followed by oxidative work-up and esterification (MeOH–H$_2$SO$_4$) afforded methyl 6-cyclopentylhexanoate and dimethyl sebacate (mixed g.l.c. with authentic specimens). Preparative g.l.c. of the products gave methyl 6-cyclopentylhexanoate (0·1 g), which was saponified by refluxing with potassium hydroxide (0·5 g) in water (5 ml) and ethanol (50 ml) for 4 h. After addition of water (1 l) and acidification (HCl), the mixture was extracted with ether (3 × 50 ml). The extract was dried (MgSO$_4$) and evaporated. To the residue was added benzylamine (0·3 g) and the mixture was heated at 200° for 30 min. The solid which separated on cooling was recrystallised from acetone; the product had m.p. and mixed m.p. 67—68° (with authentic *N*-benzyl-6-cyclopentylhexanamide; see later).

Electrolysis of hept-6-enoic acid in cell B gave the same products.

6-*Cyclopentylhexanoic Acid.*—Cyclopentylacetic acid was obtained by hydrogenation (Adams catalyst) of cyclopent-2-enylacetic acid (Light). The acid (7·6 g) and ethyl hydrogen adipate (16·0 g) were added to methanolic sodium methoxide [from sodium (3·4 g) in methanol (120 ml)] and the solution was electrolysed (cell B) until the current dropped from 1·6 to 0·1 A. The mixture was acidified (HCl), diluted with water (1·5 l), and extracted with ether (3 × 100 ml); the extract was well washed with 2% potassium hydroxide (2 × 100 ml) and the ether was distilled off. To the residue was added potassium hydroxide (10 g) in ethanol (100 ml) and water (100 ml) and the mixture was heated under reflux for 3 h. After dilution of the mixture with water (1 l) and acidification (HCl), the product was extracted with ether (3 × 100 ml); the extracts were washed with 10% potassium hydroxide (3 × 200 ml), and the aqueous extract was acidified (HCl) and extracted with light petroleum (b.p. 40—60°, 3 × 100 ml). Distillation of the extract gave 6-cyclopentylhexanoic acid, b.p. 104° at 0·1 mmHg (1·4 g, 13%), which solidified on cooling. The acid was converted into the methyl ester (MeOH–H$_2$SO$_4$) and the latter purified by preparative g.l.c. (10% PEGA; 150°). The product (0·96 g) was hydrolysed by boiling with potassium hydroxide (1 g) in water (5 ml) and methanol (50 ml) for 12 h. Addition of water (500 ml), acidification (HCl), extraction with ether (3 × 50 ml), and drying (MgSO$_4$), followed by removal of ether gave 6-cyclopentyl-hexanoic acid, m.p. 30—32·5° (lit.,[21] 33—33·5°). The acid (0·5 g) and freshly distilled benzylamine (2 ml) were heated at 200° for 30 min. The mixture was cooled and the product crystallised from acetone to give N-*benzyl*-6-*cyclopentylhexanamide*, m.p. 68—68·5° (Found: C, 79·25; H, 9·95; N, 5·05. $C_{18}H_{27}NO$ requires C, 79·1; H, 9·95; N, 5·15%).

Electrolysis of Cyclohexanecarboxylic Acid.—The acid (20·0 g) was added to methanolic sodium methoxide [from sodium (3·6 g) and methanol (120 ml)] and the solution was electrolysed (cell B; 1·7 A; 10 h). After work-up in the usual way distillation gave bicyclohexyl (0·75 g), b.p. 144—

[20] M. F. Ansell and S. S. Brown, *J. Chem. Soc.*, 1958, 2955.
[21] G. H. Yohl and R. Adams, *J. Amer. Chem. Soc.*, 1928, **50**, 1566.

148° at 40 mmHg, n_D^{20} 1·4772 (lit.,[22,23] b.p. 131—132° at 11 mmHg, n_D^{20} 1·4800). G.l.c. analysis (10% PEGA; 75°) gave only one peak.

Electrolysis of Cyclopentylacetic Acid.—The acid (20·4 g) was added to methanolic sodium methoxide [from sodium (0·2 g) and methanol (120 ml)] and the solution was electrolysed (cell A) until it became alkaline. After work-up in the usual way distillation gave the crude product (5·7 g, 43%), b.p. 120—122° at 18 mmHg, which on g.l.c. analysis (10% PEGA; 75°), showed only one main peak but whose i.r. spectrum showed a band at 1730 cm⁻¹ (ester). The product was added to potassium hydroxide (0·5 g) in water (5 ml) and methanol (30 ml) and the solution was boiled under reflux for 2 h. The mixture was then diluted with water (500 ml) and extracted with light petroleum (b.p. 40—60°). The extract was dried and evaporated. The residue was purified by preparative g.l.c. (10% PEGA; 75°) giving 1,2-dicyclopentylethane, n_D^{20} 1·4640 (lit.,[24] n_D^{20} 1·4657), $\nu_{max.}$ 860, 895, 940, 1455, 1480, 2840, and 2910 cm⁻¹ [no peaks at 920 or 1000 (CH=CH₂), 980 (*trans*-CH=CH), or 1620—1680 cm⁻¹ (C=C)] (Found: C, 86·5; H, 13·2. Calc. for C₁₂H₂₂: C, 86·65; H, 13·05%).

Electrolysis of Cyclohexylacetic Acid.—The acid was obtained by catalytic hydrogenation of methyl phenylacetate followed by saponification. The acid (10·0 g) was added to methanolic sodium methoxide [from sodium (0·05 g) and methanol (100 ml)] and the solution was electrolysed in cell A and worked up as usual giving the crude product (2·5 g, 33%), b.p. 79—81° at 10·4 mmHg, n_D^{20} 1·4760 (lit.,[25] b.p. 140° at 19 mmHg, n_D^{20} 1·4802). The product showed only one main peak on g.l.c. (10% PEGA; 100°) but the i.r. spectrum showed a weak band at 1735 cm⁻¹ (ester). The product (2·0 g) was therefore treated with a boiling solution of potassium hydroxide (0·5 g) in water (5 ml) and methanol (50 ml) for 4 h. The mixture was then diluted with water (1 l), acidified (HCl), and extracted with ether (3 × 50 ml). The ethereal solution was washed with 10% potassium hydroxide (50 ml), then with water (50 ml), and dried (MgSO₄). Distillation gave 1,2-dicyclohexylethane, b.p. 91—93° at 1·8 mmHg, n_D^{20} 1·4764; $\nu_{max.}$ 845, 895, 970, and 1445 cm⁻¹ [no bands at 920, 1000 (CH=CH₂), 980 (*trans*-CH=CH) or 1640 cm⁻¹ (C=C) or 1735 cm⁻¹ (ester)] (Found: C, 86·55; H, 13·15. Calc. for C₁₄H₂₆: C, 86·5; H, 13·5%).

Electrolysis of trans-Oct-6-enoic Acid.—The acid (2·0 g)[20] was added to methanolic sodium methoxide [from sodium (0·32 g) and methanol (80 ml)] and the solution was electrolysed (cell B; 1·5 A, 3 h). Isolation of the product in the usual way gave tetradeca-*trans*-2,*trans*-12-diene. G.l.c. analysis (10% PEGA; 100°) showed one main peak (95%); $\nu_{max.}$ 970 cm⁻¹ (*trans*-CH=CH) but no band at 730 cm⁻¹ (*cis*-CH=CH); there was a weak band at 1740 cm⁻¹ (ester). Catalytic hydrogenation resulted in the uptake of 89% of the amount of hydrogen calculated for a tetradecadiene; the product was identified as n-tetradecane by mixed g.l.c. with an authentic specimen.

Oct-7-enoic Acid (XV).—Ethyl hydrogen adipate (15 g, 0·08 mol) and vinylacetic acid (5·0 g, 0·05 mol) were dissolved in methanolic sodium methoxide [from sodium (3·3 g) in methanol (120 ml)] and the solution was electrolysed (cell B; 1·7 A; 6 h). The mixture was acidified (HCl), diluted with water (1·5 l), and extracted with ether (3 × 100 ml).

The extract was washed with 2% potassium hydroxide (2 × 50 ml), dried (MgSO₄), and evaporated. The residue was saponified by refluxing with potassium hydroxide (5 g) in methanol (50 ml) and water (10 ml) for 4 h. After addition of water (500 ml) and acidification (HCl), the solution was extracted with ether (3 × 75 ml); and ether was distilled off, and the residue was steam distilled. The distillate was extracted with ether (3 × 50 ml); the extract was dried (MgSO₄) and evaporated. The combined products from four runs gave, on distillation, oct-7-enoic acid (3·15 g, 10%), b.p. 80° at 9 mmHg, n_D^{20} 1·4422 (lit.,[25] b.p. 90—92° at 1 mmHg, n_D^{27} 1·4340; lit.,[26] n_D^{20} 1·4430). The amide, crystallised from water, had m.p. 80—81° (lit.,[26] 75—76°). G.l.c. analysis of the methyl ester (PEGA; 100°) indicated a purity of 98%.

Electrolysis of Oct-7-enoic Acid.—The acid (3·0 g) was added to methanolic sodium methoxide [from sodium (0·48 g) and methanol (120 ml)] and the solution was electrolysed (cell B) until the current dropped from 1·0 to 0·2 A. After work-up the product was purified by preparative g.l.c. (10% PEGA; 100°) giving tetradeca-1,13-diene (30%), $\nu_{max.}$ 910 and 990 (CH=CH₂), and 1640 cm⁻¹ (C=C). Hydrogenation (Adams catalyst) afforded n-tetradecane, identified by mixed g.l.c. (10% PEGA; 100°) with an authentic specimen. Two minor products of the electrolysis were identified as methyl oct-7-enoate (mixed g.l.c. with authentic specimen), and an unsaturated alcohol, probably hept-6-en-1-ol since on hydrogenation it afforded heptan-1-ol (mixed g.l.c.).

Electrolysis of Hex-5-enoic Acid (XVI; $n = 2$).—(a) The acid (5 g)[20] was added to methanolic sodium methoxide [from sodium (1·0 g) and methanol (70 ml)] and the solution was electrolysed (cell B; 1·4 A). After work-up in the usual way distillation gave a decadiene fraction (1·1 g, 37%), b.p. 165—170°, g.l.c. analysis of which (10% squalane; 75°) gave one main peak. Further purification by preparative g.l.c. (10% PEGA; 50°) gave deca-1,9-diene, n_D^{20} 1·4335 (lit.,[27] n_D^{25} 1·4316); $\nu_{max.}$ 910 and 1000 (CH=CH₂), and 1640 cm⁻¹ (C=C); no band at 980 cm⁻¹ (*trans*-CH=CH). Catalytic hydrogenation resulted in the uptake of 110% of the hydrogen calculated for a decadiene and gave a product identified as n-decane by mixed g.l.c. with an authentic specimen. Ozonolysis of the decadiene followed by oxidative work-up and esterification (MeOH–H₂SO₄) gave a dicarboxylic ester fraction found by mixed g.l.c. (10% PEGA; 150°) to contain methyl suberate (68%), methyl pimelate (4·0%), and methyl adipate (1·7%).

(b) The acid (15·0 g) was added to methanolic sodium methoxide [from sodium (0·1 g) and methanol (80 ml)] and the solution was electrolysed in cell A until it became alkaline. Work-up in the usual way followed by distillation gave a decadiene fraction (3·5 g, 39%), b.p. 164—170°. G.l.c. analysis (10% squalane; 75°) gave three peaks (ratio 57·1 : 33·2 : 9·7); the third was identified as deca-*trans*-2,*trans*-8-diene by mixed g.l.c. with an authentic specimen. The decadiene fraction had $\nu_{max.}$ 920 and 1000 (CH=CH₂), and 1640 (C=C) and a weak band at 975 cm⁻¹ (*trans*-CH=CH). Hydrogenation of the mixture gave n-decane (98%; mixed g.l.c.). Ozonolysis and oxidative work-up followed by esterification (MeOH–H₂SO₄) gave a dicarboxylic ester

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[26] V. P. Gol'mov and N. M. Afanas'ev, *Zhur. obshchei Khim.*, 1955, **23**, 1188.

[27] A. T. Blomquist and P. R. Taussig, *J. Amer. Chem. Soc.*, 1957, **79**, 3505.

fraction shown by mixed g.l.c. (10% PEGA; 150°) to contain methyl suberate (55%), methyl pimelate (12·3%), and methyl adipate (3·4%).

Electrolyses of Undec-10-enoic Acid (XVI; *n* = 7).— (*a*) The acid (7·85 g) was added to methanolic sodium methoxide [from sodium (0·95 g) and methanol (120 ml)] and the solution was electrolysed in cell B (1·5 A; 5½ h). After work-up as usual distillation gave an eicosadiene fraction (1·3 g, 25%), b.p. 152—154° at 11·4 mmHg. G.l.c. analysis (10% PEGA; 150°) showed only one main peak. Recrystallisation from ethanol gave eicosa-1,19-diene, m.p. 20—20·5° (lit.,[28] 19·5—20°), $v_{max.}$ 920 and 1000 (CH=CH$_2$), and 1640 cm^{-1} (C=C); no band at 980 cm^{-1} (*trans*-CH=CH). Catalytic hydrogenation resulted in the uptake of 110% of the hydrogen calculated for eicosadiene and gave n-eicosane (mixed g.l.c.).

(*b*) The acid (10 g) was added to methanolic sodium methoxide [from sodium (0·05 g) and methanol (70 ml)] and the solution was electrolysed until it became alkaline. Work-up in the usual way followed by distillation gave an eicosadiene fraction (32%), b.p. 136—140° at 0·4 mmHg, $v_{max.}$ 920 and 1000 (CH=CH$_2$), 1640 (C=C), and 980 (*trans*-CH=CH). G.l.c. analysis (10% PEGA, 150°) gave three peaks, ratio 59·7 : 29·8 : 10·5, the first of which was identified as eicosa-1,19-diene by mixed g.l.c. with an authentic specimen (previous experiment). Catalytic hydrogenation

of the mixture resulted in the uptake of 107% of the hydrogen calculated for an eicosadiene and gave only n-eicosane, identified by mixed g.l.c. with an authentic specimen.

Electrolysis of Cyclopent-2-enylacetic Acid.—The acid (Light; 10·5 g) was added to methanolic sodium methoxide [from sodium (1·6 g) and methanol (150 ml)] and the solution was electrolysed in cell B (16 h; 1·6 A). After work-up as usual the product had a strong band at $v_{max.}$ 1730 cm^{-1} (ester). It was therefore saponified and worked up as in the previous example, giving after distillation 1,2-*di*(*cyclopent-2-enyl*)*ethane* (1·05 g, 17%), b.p. 52—55° at 0·8 mmHg, $v_{max.}$ 720 (*cis*-CH=CH) and 1640 cm^{-1} (C=C), which on g.l.c. analysis (10% PEGA; 75°) showed only one main peak (95%). Hydrogenation (Adams catalyst) resulted in the uptake of 2·14 mol. equiv. of hydrogen, giving 1,2-dicyclopentylethane, identical (mixed g.l.c.) with that prepared by electrolysis of cyclopentylacetic acid.

[28] D. G. Bounds, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 1953, 2393.