Electro-organic Reactions. Part 12.† The Anodic Oxidation of Alicyclic Unsaturated Carboxylic Acids

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For 1,2,4-trimethylcyclohexene-4-carboxylic acid voltammetric experiments and controlled potential electrolysis are used to show that the carbon–carbon double bond is more readily oxidised than the carboxylate function. Electro-oxidation in aqueous acetonitrile gives high yields of lactones. These products have been characterised and their formation rationalised. Chlorolactonisation may be achieved by anodic oxidation of chloride in the presence of the acid.

1,2-Dimethylcyclopentene-4-carboxylic acid does not lactonise under any of the above conditions. The stereochemical reasons for the difference in behaviour of the two acids is discussed.

UNSATURATED alkanoates usually undergo normal Kolbe dimerisation [1] but where stereochemistry permits cyclic products may be obtained.[2] Hept-6-enoate gives cyclopentyl derivatives *via* cyclisation of an intermediate alkenyl radical [2a] and the anodic oxidation of certain unsaturated carboxylic acids gives lactones as a major product. In particular the electro-oxidation [2b] of sodium (*E*)-5-phenylpent-4-enoate (1) in methanol gives the lactone (2) in high yield; from *exo*- and *endo*-norborn-5-ene-2-carboxylic acid (3) the lactone (4) is

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† Part 11, J. H. P. Utley and G. B. Yates, *J.C.S. Perkin II*, 1978, 395.

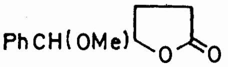
[1] J. H. P. Utley in 'Technique of Electroorganic Synthesis,' ed. N. L. Weinberg, John Wiley and Sons, New York, 1974, ch. 6.

[2] (*a*) R. F. Garwood, Naser-ud-din, C. J. Scott, and B. C. L. Weedon, *J.C.S. Perkin I*, 1973, 2714; (*b*) F. M. Banda and R. Brettle, *J.C.S. Perkin I*, 1974, 1907; (*c*) A. Laurent, E. Laurent, and M. Thomalla, *Compt. rend.*, 1972, *C*274, 1537.

obtained[2c] in 20% yield by anodic oxidation in acetonitrile. The carbenium ions (5) and (6) are implicated as intermediates but so far no clear evidence has been presented which distinguishes between the possible routes to such species (Scheme 1).

$PhCH{:}CH(CH_2)_2CO_2Na$

(1)



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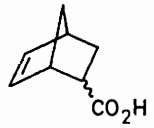

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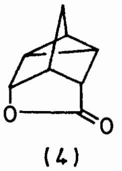

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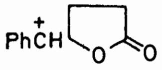

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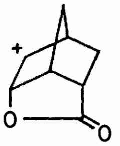

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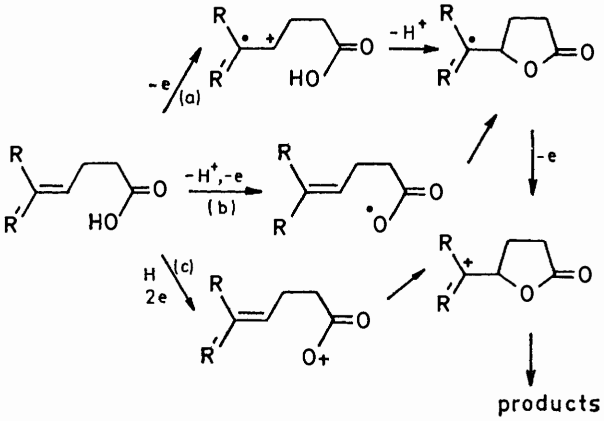
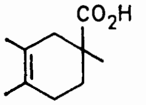


Scheme 1

Here we report the results of: (i) voltammetric experiments on a range of derivatives of alicyclic carboxylic acids; (ii) preparative scale electrolyses involving the acids (7) and (8); and (iii) a comparison between attempted halogenolactonisation of the same acids using chemical and electrochemical methods. The only mechanism consistent with all of the results is that depicted in path (a) of Scheme 1.



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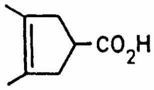
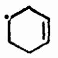
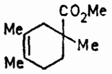
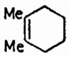
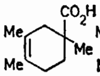
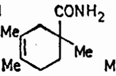
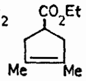
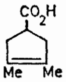
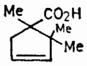
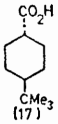


(8)

Cyclic voltammetry;[a] oxidation of derivatives of unsaturated carboxylic acids

Compound	 (9)	 (10)	 (11)	 (12)	 (7)	 (13)	 (14)	 (8)	 (15)	 (16)	 (17)
$E_p/2$ (V *vs.* Ag wire)	1.70	1.49	1.49	1.05 (1.06)[b]	1.07 (1.13)[b]	0.92 (1.05)[b]	1.72	1.55 (1.42)[b]	1.52	1.49	>2.4
($E_p - E_p/2$)		0.14			0.03	0.06	0.22	0.16			

[a] Solutions were *ca.* 1 mM in CH_2Cl_2–Bu_4NClO_4 (0.1 M); Pt bead anode, scan rate 0.2 V s^{-1}. [b] Solution in MeCN.

RESULTS AND DISCUSSION

Voltammetric Experiments.—Single sweep cyclic voltammetry gave for each compound studied an irreversible oxidation peak. The peak width varied from compound to compound (see Table, E_p–$E_p/2$ values). However the results are generally characteristic for ECEC processes in which initial electron transfer is followed by rapid chemical reaction.[3] Consequently the measured $E_p/2$ values (see Table) depend not only on the ease of oxidation but also on the rapidity of follow-up reactions.[4] Despite this qualification and uncertainties arising from the variable peak widths trends can be discerned from the results given in the table. From the large differences in $E_p/2$ values for the cycloalkenes (9), (10), and (12) it is clear that electro-oxidation is made easier by steric constraint [as in (10)] and by alkyl substitution at the double bond [as in (12)]. Furthermore the similarity of $E_p/2$ values for the substrates (12), (7), and (13) argues for the prior oxidation of the double bond being a common factor. The closeness of the $E_p/2$ values for the unsaturated five-membered cyclic compounds (8), (15), (16) may be similarly interpreted. It is clear that under the conditions of the voltammetric experiments the carboxylic acid function is not oxidised; the saturated acid, *trans*-4-t-butylcyclohexanecarboxylic acid (17), did not give an oxidation peak prior to the potential at which the electrolyte is oxidised. Remote ester group substitution apparently makes oxidation of the double bond more difficult as is evident from a comparison of the $E_p/2$ values for compounds (11) *vs.* (7) and compounds (14) *vs.* (8). The oxidation peak for (14) was, however, broad (E_p–$E_p/2$ = 220 mV) and consequently comparison with the sharper peaks for the other compounds may not be reliable.

Preparative Scale Controlled Potential Electrolyses.—1,2,4-*Trimethylcyclohexene*-4-*carboxylic acid* (7).

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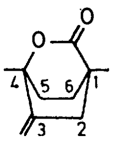
[3] S. Piekarski and R. N. Adams, 'Physical Methods of Chemistry,' Interscience, New York, 1971, Vol. 1, Part IIA, ch. VII.

[4] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.

Attempts at the electrolysis of (7) at a platinum gauze anode in methylene chloride or acetonitrile failed because of the early onset of severe electrode fouling. The film on the anode could not be removed sufficiently by the application of cathodic pulses to the electrode.

The best conditions involved the use of aqueous acetonitrile (10% v/v H_2O). Using this solvent with lithium perchlorate (0.1 M) good currents were obtained at 1.65 V (*vs.* Ag wire). With the carboxylic acid at 0.38 M initial current densities were of the order of 0.02 A cm^{-2} and electrolyses proceeded to 2 F mol^{-1}. After aqueous work-up and extraction into methylene chloride the major products were isolated by preparative g.l.c.; four isomeric unsaturated lactones were present of which two (20) and (19) were obtained as pure samples. They were identified according to their mass, ^1H n.m.r., and i.r. spectra (see Experimental section). Lactones (18) and (21) were obtained as a mixture and assignment of structure is in this case tentative. G.l.c. analysis using an internal standard gave the yields as 38% (20), 44% (19), and 12% (18) and (21).



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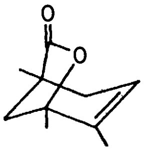

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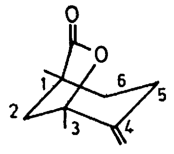

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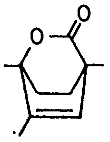
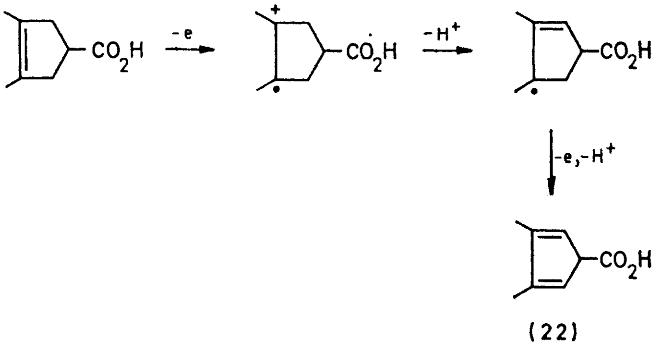


(21)

1,2-*Dimethylcyclopentene*-4-*carboxylic acid* (8). Because several products of intramolecular attack may be formed from the cyclohexene derivative (7), the behaviour of the symmetrical cyclopentene carboxylic acid (8) was studied. Alkyl substitution at the double bond ensures that as with compound (7) oxidation takes place at an accessible potential.

Electrode fouling inhibited electrolysis in water-free solvents. By the application of periodic cathodic pulses to the anode a current could be maintained allowing electrolysis in CH_2Cl_2–Bu_4NClO_4 (0.1 M) to *ca.* 2F mol^{-1}. Analysis of the product mixture by g.c.–m.s. revealed that no lactones were formed and the only significant product was the dimethylcyclopentadienecarboxylic acid (22). This must arise by the sequence in Scheme 2. It is clear that, even though carbenium ion intermediates are formed, intramolecular attack by the carboxylate function is precluded in this substrate. Electrolysis in aqueous acetonitrile (10% v/v H_2O)–$LiClO_4$ (0.1 M) proceeded smoothly and was halted at 2 F mol^{-1}. The product mixture was complex and consisted mainly of polymeric material. The characteristic lactone carbonyl band was absent in the i.r. spectrum of the crude product.



(22)

SCHEME 2

Halogenolactonisation.—In an attempt to trap the intermediate cation (23) with acetate, compound (7) was electro-oxidised in CH_2Cl_2–Bu_4NClO_4 (0.5 M) solution in the presence of the salt $Bu_4NOAc{\cdot}HOAc$ [1.5 molar equivalent with respect to (7)]. Electrolysis at 1.65 V (*vs.* Ag wire) gave a complex mixture of products from which the chloro-lactone (24) was isolated in low yield. This result is rationalised in terms of an indirect reaction. Chloride ion is produced by a nucleophilic substitution reaction between the tetrabutylammonium acetate ion-pair and methylene chloride;[5] anodic oxidation of chloride produces chlorine which induces the well known halogenolactonisation reaction.[6,7] This interpretation is confirmed by the results of similar electrolyses of (7) in the presence of Bu_4NCl (2 equivalents) rather than $Bu_4NOAc{\cdot}HOAc$ at a potential (1.14 V) at which chloride is oxidised but the double bond is electrochemically inert. For this reaction the chloro-lactone is produced in 75% yield. The chloro-lactone (24) and the bromo-lactone (25) are also produced in high yield by the treatment of (7) with the halogen dissolved in chloroform (no added base was necessary for these reactions).

Halogenolactonisation of the cyclopentene carboxylic acid (8) could not be achieved either by the indirect electrochemical method or by direct treatment with halogen with or without treatment with base.

Mechanism and Stereochemistry.—The ready lactonisation of (7) and the failure to lactonise of (8) may be explained by reference to their geometry. Inspection of Dreiding models shows that in the conformation required for cyclisation the closest distance of approach between the relevant ring carbon atom and the carboxylate oxygen is for (7) *ca.* 2.5 Å and for (8) *ca.* 3.5 Å. It is also clear from models of the lactone products that, if formed, the lactone derived from (8) would be highly strained.

It is noteworthy that application of Baldwin's rules[8]

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[5] K. Holmberg and B. Hansen, *Tetrahedron Letters*, 1975, 2303.

[6] E. E. van Tamelen and M. Shamma, *J. Amer. Chem. Soc.*, 1954, **76**, 2315.

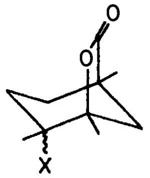
[7] V. I. Staninets and E. A. Shilov, *Russ. Chem. Rev.*, 1971, **40**, 272.

[8] J. E. Baldwin, *J.C.S. Chem. Comm.*, 1976, 734.

also predicts the ready cyclisation of the radical-cation of (7) preferably by attack at C-3; the relevant oxygen atom of the carboxylate group lies on the line of approach (to the trigonal cationic centre at, say, C-3) subtending the favoured 'magic-angle' of 109.5°. This is not the case for the C-3 atom of the cyclopentene derivative.

The reluctance of (8) to lactonise is not a simple function of the acid's ring size; Torssell and his co-workers[9] report the bromolactonisation of 1,2,2-trimethylcyclopent-3-ene-1-carboxylic acid. A possible difference in their case is that, as they propose, the corresponding dibromo-acid is first formed with subsequent internal S_N2 displacement of bromide by carboxylate (treatment with base on work-up is required to complete the reaction). For compounds (7) and (8) initial addition of halogen is to a tetrasubstituted alkene and for these cases intramolecular attack on the stabilised halogenonium ion becomes more likely. Even if the dibromo-acid were an intermediate in these cases subsequent S_N2 attack would be at a hindered (tertiary) centre. We prefer to believe that lactonisation proceeds *via* the planar halogenonium ions; in the case of (7) Baldwin's rules predict cyclisation whereas for (8) one can apply the argument outlined above for the corresponding radical-cation.

The stereochemistry of the halogenolactones (24) and (25) cannot be determined with the information to hand. Intramolecular attack by carboxylate on the intermediate bridged halogenonium ions would result in a *trans*-arrangement of oxygen and halogen whereas a *cis*-arrangement is predicted for intramolecular S_N2 attack. Unfortunately there seems to be little difference in chemical shift to be expected between axial and equatorial methyl groups at C(4); chemical shifts are very similar[10] for axial and equatorial methyl groups in the diastereoisomers of 1-methyl-1-X-4-t-butylcyclohexane where X = Cl and NH_3^+. The stereochemistry of (24) and (25) is, therefore, not established.

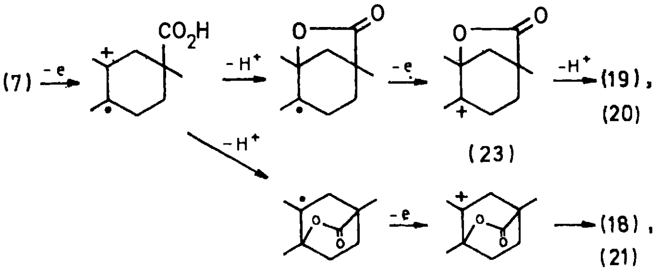


(24) X = Cl
(25) X = Br

In summary, the unsaturated acid (7) is oxidised anodically with intramolecular cyclisation according to Scheme 3.

EXPERIMENTAL

Materials.—1,2-Dimethylcyclopentene-4-carboxylic acid (8) and its ethyl ester (14) were prepared as previously described.[11,12] 1,2-Dimethylcyclohexene (12) was prepared by a modification of literature method.[13] This method gave an isomeric mixture from which the pure 1,2-dimethylcyclohexene was obtained after removal of other isomers by treatment with mercuric acetate in methanol, followed by ether extraction and final distillation (b.p. 135—136 °C).



SCHEME 3

1,2,4-Trimethylcyclohexene-4-carboxylic acid (7) was prepared by modification of a literature method.[14] The amide (13) was prepared by refluxing (7) (3.36 g, 0.02 mol) with thionyl chloride (12 cm^3) for 0.5 h, after which the excess of thionyl chloride was distilled off and the residue was added to concentrated ammonia (10 cm^3) at −40 °C. The mixture was heated to reflux, cooled, and extracted with ether. The ether phase was dried, evaporated, and the residue recrystallised from cyclohexane to afford pure carboxamide (1.48 g; m.p. 105—106 °C).

Dichloromethane was purified by fractional distillation over calcium hydride. Methanol (B.D.H. AnalaR grade) and lithium perchlorate (B.D.H. reagent grade) were used without further purification. Tetra-n-butylammonium perchlorate was prepared from the corresponding bromide[15] and dried at 100 °C under reduced pressure immediately before use.

Acetonitrile was purified by stirring over calcium hydride for 24 h, and distilled. It was further purified by successive fractional distillations over phosphorus pentaoxide and calcium hydride.

Electrolyses Apparatus.—Standard H-type cells with sintered glass separators were used. For cyclic voltammetry the cells were equipped with a platinum bead anode. Electrode potentials were measured against a silver wire reference, the wire being immersed in the electrolyte and in contact with the working electrode *via* a Luggin capillary. Preparative-scale electrolyses were carried out at a cylindrical platinum gauze anode, using a Chemical Electronics Ltd. TR70/2A potentiostat combined with a waveform generator type RB1 and an electronic integrator. Current densities were calculated on the assumption that all the reaction occurred at the outer surface of the anode. Voltammograms were recorded using a Hewlett-Packard 17035B X–Y recorder.

Constant Potential Electrolyses.—*In aqueous acetonitrile.* In a typical experiment 1,2,4-trimethylcyclohexene-4-

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[9] J. Goldman, N. Jacobsen, and K. Torssell, *Acta. Chem. Scand.* (*B*), 1974, **28**, 492.

[10] D. N. Kirk and P. M. Shaw, *J. Chem. Soc.* (*C*), 1970, 183; J. C. Richer and R. Bisson, *Canad. J. Chem.*, 1969, **47**, 2488.

[11] P. D. Bartlett and G. D. Sargeant, *J. Amer. Chem. Soc.*, 1965, **87**, 1297.

[12] H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, 1970, **92**, 6259.

[13] F. K. Signaigo and P. L. Cramer, *J. Amer. Chem. Soc.*, 1933, **55**, 3326.

[14] A. A. Petrov and N. P. Sopov, *Zhur. obshchei. Khim.*, 1948, **18**, 1781.

[15] H. O. House, E. Feng, and N. P. Reet, *J. Org. Chem.*, 1971, **36**, 2371.

carboxylic acid (7) (0.51 g, 0.003 mol) in acetonitrile–water (8 cm^3, 10% v/v water) containing lithium perchlorate (0.1M) was electrolysed at a constant potential of 1.65 V. Periodic brief cathodic pulsing to 0 V was used to minimise fouling of the platinum surface. The reaction was stopped at 2 F mol^{-1}. The electrolysed solution was poured into saturated salt solution (40 cm^3) and shaken with dichloromethane (10 cm^3). The dichloromethane extract was dried ($MgSO_4$) and evaporated to afford the product mixture (0.47 g, yield 92%). Samples were dissolved in ether for g.l.c. analysis.

In dichloromethane. The unsaturated acid was dissolved in dichloromethane containing tetra-n-butylammonium perchlorate (0.1M). After electrolysis the solvent was evaporated and the residue was extracted with ether several times. The ether layer was washed with sodium hydrogen carbonate solution (10%, 3 × 25 cm^3) and water, and then dried (Na_2SO_4) and evaporated.

Analysis and Identification of Products.—G.l.c. analysis. For quantitative work a Perkin-Elmer F11 machine was used, and peak areas were compared with those of a suitable internal standard, a known weight of which was added to the product mixture. The products derived from compound (7) were separated by preparative g.l.c. (Varian Aerograph A90P).

G.l.c. analysis (F11; 15% Carbowax, 120 °C) of the product mixture from electrolysis of compound (7) in aqueous acetonitrile showed four components of which two were major. Quantitative yields were determined using ethyl benzoate as an internal standard. The major components were separated by preparative g.l.c. (Varian, 20% Carbowax, 150 °C) and the two minor components of longest retention time were collected together owing to their inadequate separation. The products may be distinguished by the spectroscopic data given below. The n.m.r. spectrum and attempted characterisation of component A is discussed separately.

Component A, 38.2% of the mixture, $\nu_{max.}(CHCl_3)$ 1 760 cm^{-1} (lactone); $\delta_H(CDCl_3)$ 4.85br (1 H, s, C:CH$_2$), 4.90br (1 H, s, C:CH$_2$), 2.40—2.56 [2 H, m, C(2)H$_2$], centred at 2.12 (slightly split 1 : 1 d, J = 12 Hz), centred at 1.84 (slightly split 1 : 1 d, J = 12 Hz) (the signals 2.12 and 1.84 protrude from a broad envelope, 2.20—1.78, total 4 H), 1.60 [3 H, s, C(4)CH$_3$], 1.25 [3 H, s, C(1)CH$_3$]; M^+, m/e 166 (<1%), 122 (54.5), 107 (100), 94 (36), 93 (26), 91 (27), 79 (29), and 77 (15). The carbonyl i.r. absorption (1 760 cm^{-1}) is not helpful in this case; of the four isomeric lactones, two of which must be γ- and two δ-lactones, carbonyl stretching frequencies of 1 760 (×2), 1 765, and 1 725 cm^{-1} are found. Thus it is only possible to use the 1 725 cm^{-1} in support of structure, in this case of the δ-lactone (21).

Attempted analysis of n.m.r. spectrum of component A. The 2 H multiplet at δ 4.85—4.90 is essentially two broad signals, the downfield one being the broader. This is commonly found for *exo*-methylene protons and is attributed to part of an AB system in which the outer lines are not seen; the result is consistent with a small chemical shift difference for the protons.[16a] Also there is little allylic coupling. Component A is therefore either the lactone (18) or (20). An important difference between these structures is that lactone (18) has a rigid conformation whereas lactone (20) does not. Apart from the methyl group signals the remaining features of the spectrum are the 2 H multiplet at δ 2.40—2.56 and a 4 H multiplet at δ 2.20—1.78 which appears as two pairs of lines, centred respectively at δ 2.12 and δ 1.84, superimposed upon a broad envelope. The lower field pair are further split by *ca.* 2 Hz.

The δ 2.40—2.56 multiplet is assigned to allylic methylene protons and these could be the C(2) protons of (18) or the C(5) protons of (20). In the latter case the multiple splitting could come from the vicinal C(6) protons with conformational mobility at C(4), C(5), and C(6) further accounting for the complicated and relatively narrow signal. The C(6) methylene signals would in this case be contained in the 4 H multiplet at δ 2.20—1.78. Alternatively, in terms of structure (18), the 2.40—2.56 multiplet may be attributed to the C(2) methylene protons with the assumption that they have similar chemical shifts and a small geminal coupling constant. The splitting could be further complicated in this rigid system by coupling to one of the C(6) protons which lies on a W connecting path. Since lactone (18) has a rigid conformation, the hydrogens at C(2) would be expected to show an AB pattern, modified by long-range coupling, and the observed multiplet does not have a symmetrical appearance.

The 4 H multiplet (δ 2.20—1.78) may also be rationalised in terms of both structures. For structure (20) a case can be made for the signal being an AB quartet from the C(2) protons superimposed on the absorptions due to the C(6) protons. The AB quartet stands out sharply from the broad envelope and it has the anticipated intensity ratios due to second-order effects. An attractive feature of this explanation is that the lowfield (equatorial) component of the C(2) AB quartet is connected with the C(6) equatorial proton by a W-path which would account for the observed secondary splitting of *ca.* 2 Hz. It is difficult to rationalise this broad envelope with superimposed AB quartet in terms of structure (18). The resonance must be due to the protons at C(5) and C(6) and they would be expected to show more sharply defined coupling constants than appear in the spectrum.

Although the n.m.r. spectrum does not allow a completely clear choice between (18) and (20) it is much better rationalised in terms of structure (20).

Component B, 44% of the mixture identified as (19): $\nu_{max.}(CHCl_3)$ 1 760 cm^{-1} (lactone); $\delta_H(CDCl_3)$, 5.46 [1 H, m, C(5)H (vinylic)], 2.2 [2 H, m, C(6)H$_2$], 2.04 [1 H, d, A part of AB quartet, J = 4 Hz, C(2)H$_2$], 1.76 [3 H, m, C(4)CH$_3$], 1.48 [3 H, s, C(3)CH$_3$], and 1.28 [3 H, s, C(1)CH$_3$]; M^+ m/e, 166 (26%), 122 (47), 107 (100), 105 (19), 91 (33), 79 (16), and 77 (14). The n.m.r. spectrum confirms the identification of (19); in particular the splitting of the C(4)CH$_3$ by allylic coupling to C(5)H and homoallylic coupling to C(6)H is characteristic of this type of structure.[16b]

Components C and D, total 12% of the mixture (*ca.* 1 : 1), identified tentatively as a mixture of (20 or 18) and (21): $\nu_{max.}(CHCl_3)$ 1 765 cm^{-1} [γ-lactone (20 or 18)] and 1 725 cm^{-1} [δ-lactone (21)]; $\delta_H(CDCl_3)$, 5.46br [s, vinyl H(21)], 5.06br [s, C:CH$_2$ (20) or (18)], 4.88br [s, C:CH$_2$ (20) or (18)], 2.42 [m, C(5)H$_2$ (20) or (18)], 1.76 [m, C(3)CH$_3$ (21)], 1.50 [s, C(4)CH$_3$ (21)], 1.25 [s, C(1)CH$_3$, (20) or (18) and (21)]; M^+ m/e, 166 (25%), 122 (48), 107 (100), 98 (23), 93 (20), and 91 (30). Identification can only be tentative in this case. The expectation on mechanistic grounds is that (20) or (18) and (21) would be formed; the mass spectrum of the mixture confirms that at least one component has the correct molecular weight (M^+, m/e 166) and that no saturated or sub-

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[16] (*a*) L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, London, 1969, p. 130; (*b*) p. 317.

stituted lactone is present. The i.r. spectrum supports the suggestion that a γ- and a δ-lactone are present. The n.m.r. spectrum is consistent with the mixture containing (20) or (18) and (21) but, unfortunately, integration is meaningless in this context and some signals must be overlaid by the intense multiplet centred at δ 1.76.

Following treatment with an ethereal solution of diazomethane the g.l.c. and g.c.–m.s. analyses of electrolysis mixtures derived from compound (8) indicated the presence of a complex mixture of esters. I.r. analysis of the crude product did not show any peak in the region 1 760—1 780 cm^{-1}, which suggests that no lactones were present.

Halogenolactonisation.—(i) *Chemical*. In a typical experiment bromine (2.30 g, 0.029 mol) was added to a solution of 1,2,4-trimethylcyclohexene-4-carboxylic acid (7) (2.18 g, 0.013 mol) in chloroform (6 cm^3) at 10 °C during 15 min. The mixture was left at room temperature for 30 min, after which the chloroform was evaporated. (The residue showed strong i.r. absorption at 1 780 cm^{-1}; lactonisation is therefore complete before the ensuing treatment with base.) Sodium carbonate solution (10%) was added and the product was extracted from the aqueous layer with dichloromethane, dried (Na_2SO_4), and the solution evaporated to yield an oily colourless liquid (3.3 g) which was recrystallised from hexane to yield pure lactone (2.51 g, 78% yield). The bromo-lactone (25) was characterised as follows: m.p. 44.5—45.0 °C; $\nu_{max.}$($CHCl_3$) 1 780 cm^{-1} (γ-lactone); δ_H($CDCl_3$), 2.74 [1 H, 1 : 1 d,[*] J = 12 Hz, C(2)CH_2], 1.81 [3 H, s, C(4)CH_3], 1.54 [3 H, s, C(3)CH_3], 1.17 [3 H, s, C(1)CH_3]; M^+ *m/e*, 246.026 ($C_{10}H_{15}BrO_2$ requires *m/e*, 246.0247) (9.6%), 202 (2), 167 (50.0), 139 (15.4), 123 (100), 122 (40.4), 111 (73.1), 107 (36.5), and 81 (26.9) (Found: C, 49.2; H, 6.2. $C_{10}H_{15}BrO_2$ requires C, 48.6; H, 6.1%).

(ii) *Electrochemical*. Electrolysis of 1,2,4-trimethylcyclohexene-4-carboxylic acid (7) (0.17 g, 0.001 mol) in dichloromethane containing 0.25M-tetra-n-butylammonium perchlorate and 1.5 equivalents of tetra-n-butylammonium acetate ($Bu_4NOAc\cdot HOAc$) gave the chloro-lactone as the major product. The lactone (24) was isolated from the mixture in 11% yield by t.l.c. on Merck silica-gel plates (20 cm × 20 cm) with carbon tetrachloride–methanol (5%) as eluant, m.p. 66—67 °C, $\nu_{max.}$($CHCl_3$) 1 778 cm^{-1} (γ-lactone); δ_H($CDCl_3$), 2.61 [1 H, d, J = 12 Hz, A part of AB quartet, C(2)CH_2], 1.60 [3 H, s, C(4)CH_3], 1.48 [3 H, s, C(3)CH_3], and 1.16 [3 H, s, C(1)CH_3]; M^+ *m/e* 202.076 ($C_{10}H_{15}ClO_2$ requires *m/e*, 202.0761) (6.4%), 167 (27.7), 145 (17.0), 123 (44.7), 122 (40.5), 112 (32.0), 111 (100), 107 (61.8), 105 (25.6), 98 (21.3), 91 (27.7), 83 (23.4), 82 (40.5), 81 (19.2), and 78 (21.3) (Found: C, 59.7; H, 7.5. $C_{10}H_{15}ClO_2$ requires C, 59.2; H, 7.5%).

We are grateful to London University (Central Research Fund) for a grant towards the purchase of g.c.–m.s. equipment and to S.R.C. for a fellowship (to C. A.).

[7/1890 *Received, 28th October*, 1977]

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[*] The other half of this AB system may just be discerned under the strong absorption at δ 1.81; from the relative intensities of the visible part it may be estimated that the B proton pair is centred at *ca.* δ 1.90.