Electro-organic Reactions. Part 11.† Mechanism of the Kolbe Reaction; the Stereochemistry of Reaction of Anodically Generated Cyclohex-2-enyl Radicals and Cations

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Cyclohex-2-enecarboxylate and *cis*-4-phenylcyclohex-2-enecarboxylate ions have been oxidised in methanol at a platinum anode. The products are markedly dependent on carboxylate concentration; at 0.4—1.0M two-electron oxidation and substitution to cyclohexenyl methyl ethers prevails whereas at higher concentrations substantial amounts of Kolbe dimers are formed (one-electron oxidation). For the *cis*-4-phenyl compound regio- and stereo-isomeric products are formed by one- and two-electron oxidation. For one-electron oxidation (Kolbe) a comparison of the measured with the statistically predicted proportions of isomers leads to the conclusion that the intermediate cyclohex-2-enyl radical is stabilised by adsorption at the anode.

THE significance for the Kolbe reaction of interactions between radical intermediates and the anode has long been in doubt.[1] Analysis of the stereochemistry of radical dimerisation in terms of the probable stereochemical fates of the adsorbed or desorbed chiral radicals formed in the Kolbe reaction cannot provide an answer.[2] The observed racemisation may be explained by the combination of solution free radicals or by the combination of adsorbed radicals involved in a dynamic adsorption–desorption equilibrium. However, the random distribution of stereoisomeric bicyclohexyls produced [3] in Kolbe electrolysis of substituted cyclohexanecarboxylates is strong evidence for radical combination in bulk solution, at least for saturated radicals. In the same investigation [3] it was apparent that phenyl substitution in the cyclohexane ring was associated with non-random radical combination and it also encouraged 2e oxidation to cyclohexyl cations. This was attributed to a surface effect involving the unsaturated, phenyl ring. In this paper we report fully on a detailed investigation of the Kolbe electrolysis of cyclohex-2-enylcarboxylate and *cis*-4-phenylcyclohex-2-enylcarboxylate ions. Preliminary experiments have been described.[4]

It was long believed that, because stabilised allylic cations are formed by 2e oxidation, αβ-unsaturated carboxylates were unpromising substrates for 1e Kolbe coupling. Weedon and his co-workers [5] showed this not to be the case by their successful preparation of dimers from *cis*- and *trans*-hex-3-enoic acids. In the present study coupling of 4-phenylcyclohex-2-enyl radicals [*i.e.* (1) in Scheme 2] was carried out. This allylic radical can combine at two positions and together with diastereoisomeric and enantioisomeric possibilities a total of 64 isomers may be expected. Analysis of their distribution provides compelling evidence against or for adsorption at the anode depending on whether or not random coupling of the unsaturated radicals is observed.

RESULTS AND DISCUSSION

Preparation and Stereochemistry of cis-4-*Phenylcyclohex-2-enecarboxylic Acid.*—Cyclohex-2-enecarboxylic (2) and *cis*-4-phenylcyclohex-2-enecarboxylic acid (3) were prepared according to Scheme 1. Previously described

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† Part 10, R. Lines and J. H. P. Utley, *J.C.S. Perkin II*, 1977, 803.

[1] B. E. Conway and A. K. Vijh, *Chem. Rev.*, 1967, **67**, 623; J. H. P. Utley in 'Technique of Electro-organic Synthesis, ed. N. L. Weinberg, Wiley, New York, 1974, ch. 6.

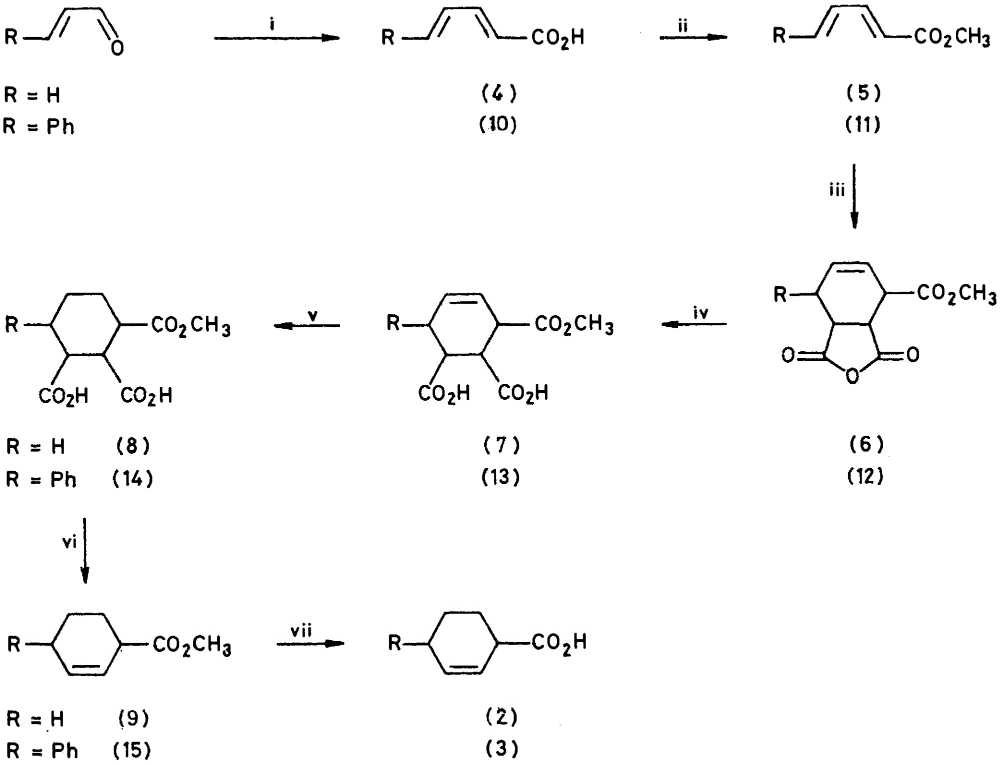
[2] E. S. Wallis and F. H. Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 3838; L. Eberson and G. Ryde-Petterson, *Acta Chem. Scand.*, 1973, **27**, 1159; L. Eberson, K. Nyberg, R. Servin, and I Wennerbeck, *ibid.*, 1976, **30**, 186.

[3] G. E. Hawkes, J. H. P. Utley, and G. B. Yates, *J.C.S. Perkin II*, 1976, 1709.

[4] G. E. Hawkes, J. H. P. Utley, and G. B. Yates, *J.C.S. Chem. Comm.*, 1973, 305.

[5] R. F. Garwood, Naser-ud-Din, C. J. Scott, and B. C. L. Weedon, *J.C.S. Perkin I*, 1973, 2714.

syntheses of cyclohex-2-enecarboxylic acid involve dissolving metal reduction of benzoic acid or an ester.[6] This method could not be applied with a phenyl substituent present; the substituent itself would be vulnerable to attack and the position of the double bond would be influenced by the ring substituent. The method chosen gives unambiguous synthesis of *cis*-4-phenylcyclohex-2-enecarboxylic acid, the stereochemistry and position of the double bond being, respectively, guaranteed by the Diels–Alder step and anodic bisdecarboxylation. The stereochemistry was confirmed by catalytic hydrogenation of methyl 4-phenylcyclohex-2-enecarboxylate the product of which was identical with an authentic sample of methyl *cis*-4-phenylcyclohexanecarboxylate.



SCHEME 1 Reagents: i, $CH_2(CO_2H)_2$; ii, MeOH–H^+; iii, maleic anhydride–benzene; iv, H_2O; v, H_2–PtO_2; vi, Pt anode–pyridine–H_2O–Et_3N; vii, H_2O–H^+

Anodic Oxidation.—Cyclohex-2-enecarboxylate. As in the previous work [3] oxidation of methanol solutions of the partly neutralised acid was at a platinum anode, and at constant current density. The results for cyclohex-2-enecarboxylate (Table 1) show that at relatively low concentrations of carboxylate the sole product is 3-methoxycyclohexene, formed by overall 2e oxidation (Scheme 2, R = H). There is some evidence for the cyclohex-2-enyl cation escaping into the bulk solution; because ester formation is insignificant methanol clearly competes more effectively for the cation than does the unreacted carboxylate. If reaction were predominantly at the anode, where carboxylate concentrations are high,[7] the formation of ester would be expected. Trapping of the cation by carboxylate is observed for electrolysis at the higher concentration and current density. Electrolysis at the higher concentration also produced a moderate amount of bicyclohex-2-enyl. The formation, by bimolecular combination, of the Kolbe dimer is expected to be favoured by higher current density and hence higher radical concentration. The absence at either concentration of products which could arise from abstraction or disproportionation (*e.g.* cyclohexene, cyclohexadiene, benzene) is consistent with the greater stability of allylic radicals *vis à vis* saturated radicals.

TABLE 1

Kolbe electrolysis of cyclohex-2-enecarboxylic acid [a]

Concentration (M) [b]	Current density (A cm^{-2})	Ether [c] (%)	Dimer [d] (%)	Ester [e] (%)	Others (%)
0.4	0.2	100			
2.0	0.3	51.2	38.9	6.9	2.0

[a] In dry MeOH, constant current. [b] 25% neutralised with NaOMe. [c] 3-Methoxycyclohexene. [d] Bicyclohex-2-enyl. [e] Cyclohex-2-enyl cyclohex-2-enecarboxylate.

cis-4-*Phenylcyclohex-2-enecarboxylate. Dimers.* Combination of the radical produced anodically from this carboxylate can in principle give rise to 64 isomers 20 of which should be physically distinguishable.

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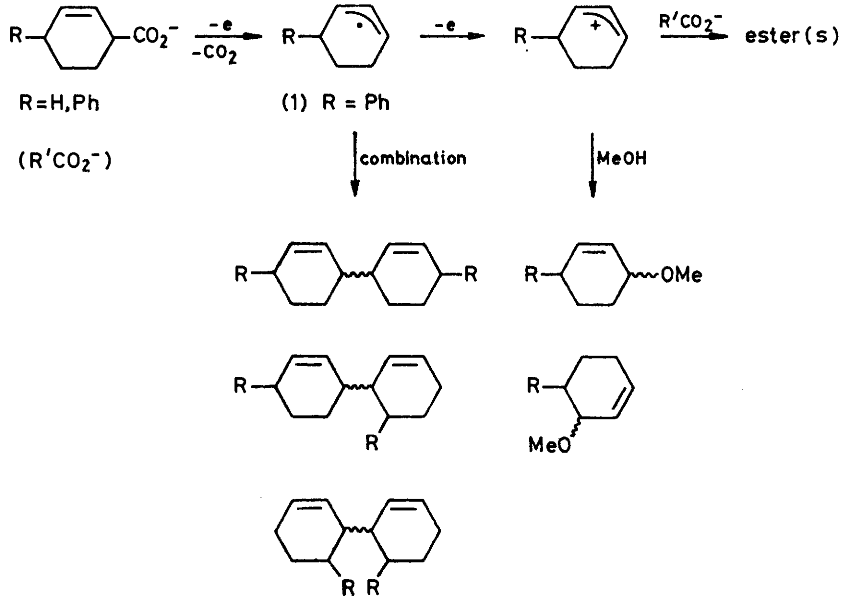
[6] (*a*) E. J. Boorman and R. P. Linstead, *J. Chem. Soc.*, 1935, 258; (*b*) P. Markov and C. Ivanoff, *Tetrahedron Letters*, 1962, 1139.

[7] T. Dickinson and W. F. K. Wyne-Jones, *Trans. Faraday Soc.*, 1962, **58**, 382, 388, 400.

Coupling of (1) at the 4,4′ positions will give 16 isomers, 6 of which are distinguishable; 2,2′ coupling will similarly give 16 with 6 distinguishable; and the 2,4′ and 2′,4 combinations gives 32 with 8 distinguishable. The situation, together with the proportions of isomers predicted for random combination of (1), is summarised in Table 2 which indicates in detail for 4,4′-coupling the analysis required for the predictions.



Scheme 2

The analytical problem is severe but using g.l.c. with careful temperature programming it was possible to separate the isomeric products of radical combination into three groups according to the position of coupling. Each group contained isomers defined by the relative stereochemistry of the 4,4′-phenyl groups and the bond linking the cyclohexenyl rings, *i.e. cis,cis*, *cis,trans*, and *trans,trans*. The positional isomers were characterised by isolation using preparative scale g.l.c. followed by hydrogenation and g.l.c. comparison of the bicyclohexyls so produced with authentic specimens. The authentic samples of 4,4′-, 2,2′-, and 2,4-diphenylbicyclohexyls were produced by Kolbe coupling and cross-coupling of *trans*-4-phenyl- and *cis*-2-phenyl-cyclohexanecarboxylate.[3] Only partial separation was achieved for stereoisomers within each group of positional isomers; each positional isomer gave a large and a small peak on g.l.c. with relative areas *ca.* 3 : 1 and in each case the smaller component appeared at longer retention time. This chromatographic behaviour is similar to that observed[3] for the isomers of 4,4′- and 2,2′-diphenylbicyclohexyls and 4,4′-di-t-butylbicyclohexyl. Furthermore hydrogenation of isolated positional isomers gave mixtures of stereoisomeric bicyclohexyls which according to g.l.c. corresponded to authentic samples of the stereoisomers of, respectively, 4,4′-, 2,2′-, and 2,4-diphenylbicyclohexyl. Further details are given in the Experimental section (Table 5). The results of these experiments, including the distributions of both 1e and 2e products, are summarised in Table 3. For the formation of hydrocarbon dimers the distribution of stereoisomers for each positional isomer is in the ratio of 3 : 1 [(*a,a* + *a,e*) : *e,e*] as expected for random coupling. However, the positional isomers are not in the expected 1 : 2 : 1 ratio (*cf.* Table 2); the 2,2′ : 2,4 : 4,4′ ratio is 0.4 : 2 : 1.

Table 2

Stereoisomers of dimers from coupling of phenylcyclohex-2-enyl radical

4,4′-Coupling; configuration in sequence C(1), C(4); C(4′), C(1′)

Isomer	Enantiomer	Number	Ring junction[a]
S,S; *S,S*	*R,R*; *R,R*	2	*a,a*
S,S; *S,R*	*R,R*; *R,S*	4	*a,e*
R,S; *S,S*	*S,R*; *R,R*		
S,S; *R,S*	*R,R*; *S,R*	4	*a,e*
S,R; *S,S*	*R,S*; *R,R*		
R,S; *S,R*	*S,R*; *R,S*	2	*e,e*
S,S; *R,R*	*R,R*; *S,S* (*meso*)	2	*a,a*
R,S; *R,S*	*S,R*; *S,R* (*meso*)	2	*e,e*

a,a : *a,e* : *e,e* = 4 : 8 : 4

2,2′-Coupling 16 isomers, *a,a* : *a,e* : *e,e* = 4 : 8 : 4

2,4′-; 4,2′-Coupling 32 isomers, *a,a* : *a,e* : *e,e* = 8 : 16 : 8

[a] For the conformation with both phenyl groups equatorial.

Two explanations are offered for the relatively low yield of the 2,2′-isomer. Should the combination of the allylic radicals require an energy of activation significantly above that associated with diffusion, bond formation would be well advanced in the transition state and it is likely that combination at the 2-position would be hindered by the phenyl substituent. This explanation also demands some steric hindrance to formation of the 2,4-isomer; the 2,4′ : 4,4′ ratio is however 2 : 1 as expected for random coupling.

An alternative explanation involves the coupling of radicals whilst they are adsorbed on the anode. It has been pointed out[3] that when radicals are stabilised by adsorption the energy of activation for combination is increased; the argument is similar to that commonly used to explain the rate-decreasing effect of polar solvents on reactions in which charge is dispersed or destroyed. Adsorption would therefore result in a more product-like transition state for combination which would be susceptible to steric effects. We may assume that polar effects are small in these reactions.

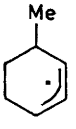
Table 3

Kolbe electrolysis of 4-phenylcyclohex-2-enecarboxylic acid[a]

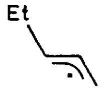
			Ethers (%)				Dimers (%)			
	Sodium	Current	1,2-		1,4-					
Concentration (*M*)	salt (%)[b]	density (A cm^{-2})	*cis*	*trans*	*cis*	*trans*	2,2′	2,4′	4,4′	Others (%)
1.0	50	0.49	7.2	18.6	29.8	19.4	Total 11.2			13.4[c]
2.3	10	0.26	6.4	17.1	27.0	17.5	Total 13.8			18.2[d]
1.8	25	0.47	3.5	9.4	14.8	9.6	5.4[e]	26.4[f]	13.1[g]	17.8[h]

[a] In dry MeOH, constant current. [b] Partly neutralised with NaOMe. [c] Phenylcyclohexenes (5.9%), biphenyl (2.9%), unidentified (4.6%). [d] Phenylcyclohexenes (8.3%), biphenyl (4.1%), unidentified (5.8%). [e] Two components on g.l.c., ratio 3.03 : 1. [f] Three components on g.l.c., ratio (I + II : III) 3.16 : 1. [g] Two components on g.l.c., ratio 2.88 : 1. [h] Phenylcyclohexenes (5.2%), biphenyl (2.4%), unidentified (10.2%).

Comparison with the results of two other investigations of the reactions of anodically generated allylic radicals leads us to prefer the explanation involving adsorption. The addition of Kolbe generated methyl radicals to cyclohexa-1,3-diene gave[8] equal amounts of the 1,2- and 1,4-dimethyl products which arise from addition of a second methyl radical to the first-formed intermediate (16). We have concluded previously[3] that saturated radicals, such as methyl, react away from the surface; the result described above suggests therefore that in bulk solution steric effects are small for combination with cyclohexylallylic radicals. In another study the allylic radical (17) is formed in the Kolbe reaction[5] of *trans*-hex-3-enoic acid. For Kolbe dimerisation there are three possibilities for coupling; γ,γ, α,γ, and α,α; the respective dimers are formed in the ratio 0.3 : 1.1 : 1.0 (*cf.* 1 : 2 : 1 expected for random coupling). This implies that formation of the γ,γ and α,γ dimers is inhibited by steric hindrance. It appears therefore that the allylic radicals (1) and (17) which are formed at an anode combine with a significant energy of activation whereas the allylic radical (16), which is formed in solution, reacts very rapidly with methyl radicals. On balance we believe that the anodically generated allylic radicals are stabilised by adsorption. Because, for each positional isomer, the stereoisomers are formed in the statistical ratio, it must further be concluded that in the transition state carbon–carbon bond formation is only advanced sufficiently to be influenced by the most severe steric interaction, *i.e.* that involved in formation of the 2,2′-diphenyl isomer. The major effect of adsorption is to encourage two-electron oxidation; a similar effect was observed[3] for the anodic oxidation of *trans*-4-phenyl- and *cis*-2-phenyl-cyclohexanecarboxylate.

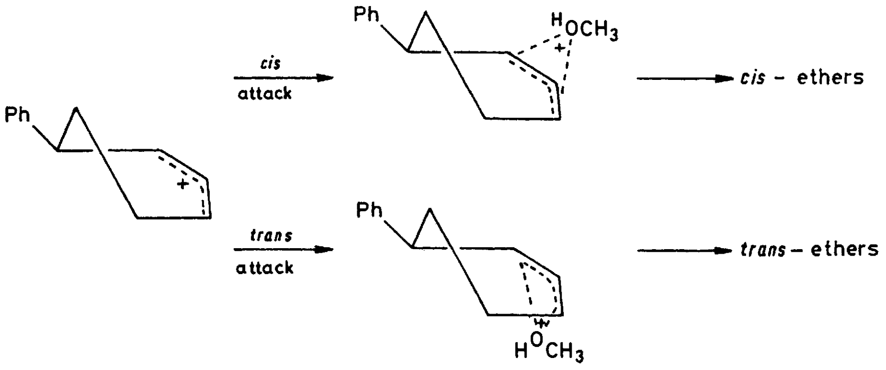


(16)



(17)

Two-electron oxidation of cis-4-*phenylcyclohex*-2-*enecarboxylate*. Four isomeric methyl ethers are produced as a consequence of the anodic production of the allylic 4-phenylcyclohexenyl cation in methanol (Table 3). For each of the experiments carried out the major ether product was *cis*-3-phenyl-6-methoxycyclohexene; this compound is almost certainly less stable than the corresponding *trans*-isomer. This result contrasts with that for the anodic 2e oxidation in methanol of sub-



Scheme 3

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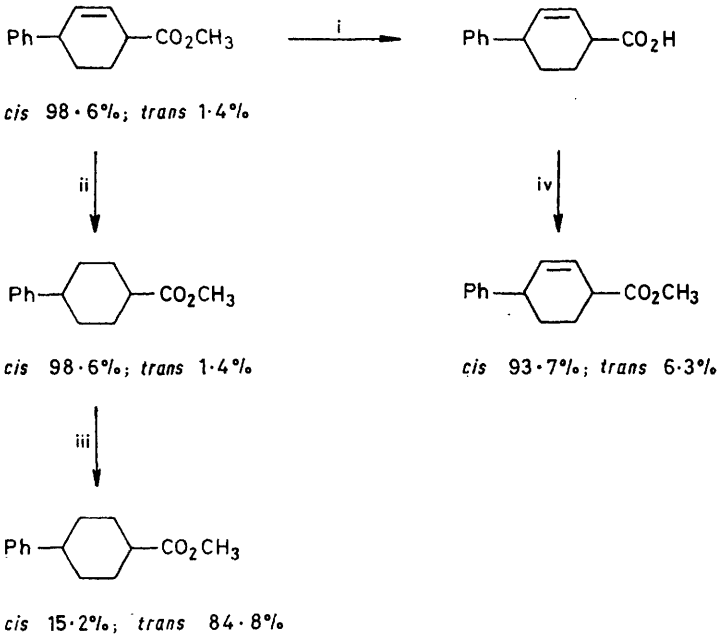
[8] W. B. Smith and H. G. Gilde, *J. Amer. Chem. Soc.*, 1961, **83**, 1355.

stituted cyclohexanecarboxylates in which case the *trans*-methoxy isomers predominate and the reaction appears to be thermodynamically-controlled.[3]

An attractive rationalisation of the product distribution is based on the observation that the sum of *cis*-1,2 and -1,4 ether formation equals the sum of *trans*-1,2 and -1,4 ether formation. Such a distribution is well explained by the formation in the rate-limiting step and with equal probability of two bridged intermediates involving the nucleophile and allylic cation (Scheme 3). The remote phenyl group would not be expected greatly to influence *cis versus trans* attack. Subsequent rapid breakdown of the intermediates to products would be prone to steric influences; consequently the *cis*-intermediate would partition in favour of the *cis*-1,4-isomer rather than the least stable *cis*-1,2-isomer.



SCHEME 4 Reagents: i, H_2O-H^+; ii, H_2-PtO_2; iii, NaOMe–MeOH; iv, CH_2N_2

EXPERIMENTAL

Cyclohex-2-enecarboxylic Acid and cis-*4-Phenylcyclohex-2-enecarboxylic Acid.*—The reactions outlined in Scheme 1 were used for these compounds. The following intermediates were prepared by reported methods: penta-2,4-dienoic acid[9] (4), 5-phenylpenta-2,4-dienoic acid[10] (10), cyclohex-4-ene-1,2,3-tricarboxylic acid 1,2-anhydride 3-methyl ester[11] (6), and 6-phenylcyclohex-4-ene-1,2,3-tricarboxylic acid 1,2-anhydride 3-methyl ester[12] (12). The anhydride (6) was hydrolysed in boiling water for *ca.* 30 min to give the known acid[11] (7). The anhydride (12) was only sparingly soluble in hot water but after hydrolysis at 80° for 30 h the solid recovered showed no absorption in the i.r. due to anhydride carbonyl groups. The dicarboxylic acid (13) was formed in 73% yield, m.p. 195—196° (decomp.); $\nu_{max.}$(Nujol) 1 700, 1 715 (carbonyl), and 2 400—3 200 (OH) cm^{-1}; δ_H[$(CD_3)_2CO$] 7.25 (5 H, m, aromatic), 5.67—6.60 (2 H, m, vinylic), 4.52 (2 H, s, OH), 3.61 (3 H, s, CO_2CH_3), and 3.47—4.57 (4 H, m, $CHCO_2R$ and benzylic). The substituted cyclohexenes (7) and (13) were hydrogenated at atmospheric pressure in a conventional glass apparatus in acetic acid solution in the presence of Adam's catalyst.

Methyl 4-Phenylcyclohex-2-enecarboxylate (15).—The dicarboxylic acid (14) (9.5 g, 0.03 mol) was dissolved in 90% pyridine–water (130 cm³), neutralised with triethylamine (9 cm³, 0.03 mol) and placed in a cell equipped with platinum foil electrodes (26 × 32 mm) spaced 3 mm apart. The cell was kept at 5—10° and efficient stirring was maintained throughout the electrolysis. Electrolysis was carried out at constant current (1 A, 0.12 A cm^{-2}) for 6 h (*ca.* 6 F mol^{-1}).

The pyridine solution was poured onto ice (400 g), acidified (H_2SO_4), and shaken with dichloromethane (4 × 60 cm³). The combined extracts were washed well and dried. Evaporation gave a brown residue from which the product was obtained by trituration with dry ether and subsequent short path distillation under reduced pressure, yield 1.01 g (15%), b.p. (hot box temperature) 90—100° at 0.2 mmHg; $\nu_{max.}$ (film) 1 737 (C=O), 1 650 (C=C), 1 604, 1 585, 1 490 (aromatic C=C), 754 (5 adjacent aromatic CH), and 697 (alkene CH) cm^{-1}; δ_H(CCl_4) 7.16 (5 H, m, aromatic), 5.87 (2 H, m, vinylic), 3.68 (3 H, s, CO_2CH_3), 2.90—3.53 (2 H, m, $CHCO_2R$ and benzylic), 1.52—2.18 (4 H, m, ring protons); *m/e* 216.1146 (M^+, $C_{14}H_{16}O_2$ requires *m/e* 216.1150).

Methyl cyclohex-2-enecarboxylate[13] (9) was similarly

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[9] R. G. Glushkov and O. Yu. Magidson, *Med. Prom. S.S.S.R.*, 1962, **16**, No. 3, 27 (*Chem. Abs.*, 1963, **58**, 442).

[10] G. S. Gill, H. K. Gakhar, N. K. Ralhan, and K. S. Narang, *Indian J. Chem.*, 1965, **3**, 323.

[11] M. Lora-Tamayo, G. G. Munoz, and R. Madronero, *Bull. Soc. chim. France*, 1958, 1331.

[12] K. V. Alder and M. Schumaker, *Annalen*, 1951, **571**, 108.

[13] O. Aschan, *Annalen*, 1892, **271**, 234.

prepared by anodic decarboxylation in 35% yield. It was hydrolysed under reflux in 2.5 : 1 aqueous sulphuric acid (6% v/v)–dioxan to give the corresponding acid (2) which was purified by short path distillation, yield 67%; b.p. (hot box temperature) 110—115° at 5 mmHg (lit.,[6a] 120° at 10 mmHg); $\nu_{max.}$ (film) 1 705 (C=O), 730 (alkene CH), and 2 400—3 800 (OH) cm^{-1}.

Similar hydrolysis of methyl 4-phenylcyclohex-2-enecarboxylate gave *cis*-4-phenylcyclohex-2-enecarboxylic acid (3), yield 71%; b.p. (hot box temperature) 140—150° at 0.2 mmHg; $\nu_{max.}$ (film) 3 400—3 800 (OH), 1 703 (C=O), 1 605, 1 500 (aromatic C=C), 763 (5 adjacent aromatic CH), and 703 (alkene CH) cm^{-1}; $\delta_H(CCl_4)$ 10.75—11.08 (1 H, m, OH), 7.18 (5 H, m, aromatic), 5.95 (2 H, m, vinylic), 2.98—3.46 (2 H, m, benzylic and $CHCO_2H$), and 1.70—2.32 (4 H, m, ring protons).

Confirmation of Stereochemistry of cis-4-*Phenylcyclohex-2-enecarboxylic Acid*.—The sequence of reactions described in Scheme 4 support the assignment of stereochemistry. Hydrolysis and re-esterification showed that little epimerisation occurred during hydrolysis so that the acid (3) used for electrolysis had the same configuration as the ester. The isomer compositions were measured by g.l.c. analysis on 2.5% SE30 at 160°. An authentic sample of methyl *trans*-4-phenylcyclohexanecarboxylate was available from previous work.[3]

Electrolysis of Substituted Cyclohex-2-enecarboxylates in Dry Methanol.—The relevant apparatus, cells, and general procedure for electrolysis and analysis have been described.[3]

Run 1: *cyclohex-2-enecarboxylic acid*. A solution of the acid (0.5 g) (25% as its sodium salt [3]) in dry methanol (total volume 2 cm^3) was electrolysed between platinum electrodes at 0.3 A cm^{-2} for 2 F mol^{-1}. After work-up [3] 0.09 g of acid was recovered. The major components of the product mixture and the methods used to identify them are given in Table 4.

TABLE 4

Analysis of the products of electrolysis of cyclohex-2-enecarboxylic acid [a]

Component	Retention time (min)	Assignment	Method
1	11	3-Methoxycyclohexene	*cf.* authentic [b]
2	20	Bicyclohex-2-enyl	*cf.* authentic [c]
3	26	Cyclohex-2-enyl cyclohex-2-enecarboxylate	*d*

[a] G.l.c. analysis after addition of known weight of internal standard (cyclohexanone) using Perkin-Elmer F11 instrument, column DE207, linearly at 10° min^{-1} to 200°. [b] Also g.l.c. peak enhancement using 15% PEG S column (60°). [c] Also g.l.c. peak enhancement using 15% PEG S column (160°). [d] After hydrogenation, g.l.c. comparison with ester product from electrolysis of cyclohexanecarboxylate.[3]

Run 2: cis-4-*phenylcyclohex-2-enecarboxylic acid* (1M). Acid (0.3 g) in methanol (total volume 1.5 cm^3), 50% as sodium salt; current density 0.49 A cm^{-2}; 1.2 F mol^{-1}.

Run 3: (2.3M). Acid (0.46 g) in methanol (total volume 1 cm^3), 10% as sodium salt; current density 0.26 A cm^{-2}; 2 F mol^{-1}.

Run 4: (1.8M). Acid (0.44 g) in methanol (total volume 1 cm^3), 25% as sodium salt; current density, 0.475 A cm^{-2}; 1.5 F mol^{-1}.

Run 5: (0.08M). Acid (0.236 g) in methanol (9 cm^3), 50% as sodium salt; current density, 0.1 A cm^{-2}; 4.8 F mol^{-1}.

The range of products identified in these experiments, and their characterisation, are given in Table 5. The results of quantitative g.l.c. analysis using appropriate internal standards [3] are summarised in Tables 1 and 3.

TABLE 5

Analysis of the products of electrolysis of *cis*-4-phenylcyclohex-2-enecarboxylic acid [a]

Component	Retention time (min)	Assignment	Method
1	8—10	Phenylcyclohexenes and phenylcyclohexadienes	retention time
2	12	Biphenyl	isolation,[b,c] *cf.* authentic [d]
3	18	*cis*-4-Phenyl-3-methoxycyclohexene	isolation,[e,f] *cf.* authentic [g]
4	19	*trans*-4-Phenyl-3-methoxycyclohexene	isolation,[b,h] *cf.* authentic [g]
5	22	*cis*-3-Phenyl-6-methoxycyclohexene	isolation,[b,i] *cf.* authentic [g]
6	24	*trans*-3-phenyl-6-methoxycyclohexene	isolation,[b,j] *cf.* authentic [g]
7	53	6,6′-diphenylbicyclohex-2-enyl	isolation,[k,l] *cf.* authentic [r]
8	55		isolation,[k,m] *cf.* authentic [r]
9	60	4,6′-diphenylbicyclohex-2-enyl	isolation,[k,n] *cf.* authentic [r]
10	61		*cf.* authentic [r]
11	63		isolation,[k,o] *cf.* authentic [r]
12	67	4,4′-diphenylbicyclohex-2-enyl	isolation,[k,p] *cf.* authentic [r]
13	69		isolation,[k,q] *cf.* authentic [r]

[a] Perkin-Elmer F11, 2.5% SE30, 120° for 30 min., rising linearly at 5° min^{-1} to 240°, N_2 pressure 20 lb in^{-2}. [b] G.l.c. Varian-Aerograph A90P, 10% Apiezon grease, 155°, He, 60 cm^3 min^{-1}. [c] Found: M^+, 154.078 3. Calc. for $C_{12}H_{10}$: M, 154.078 25. [d] G.l.c. peak enhancement, column DE207, 145°, nitrogen pressure 20 lb in^{-2}, and 20% DEGS, 140°, nitrogen pressure 20 lb in^{-2}. [e] Varian-Aerograph A90P, 5 ft 20% DEGS, 145°, He, 60 cm^3 min^{-1}. [f] Found: M^+, 188.119 8. Calc. for $C_{13}H_{16}O$: M, 188.120 11. [g] Small samples of the individual ethers, collected by preparative scale, g.l.c.[e] from the electrolysis mixture, were hydrogenated, using a Brown hydrogenator and Adam's catalyst, to the corresponding methoxycyclohexanes, which were identified by g.l.c. comparison with authentic samples (F11, 20% DEGS, 140°, nitrogen pressure 20 lb in^{-2} and 2.5% SE30, 120°, nitrogen pressure 20 lb in^{-2}). [h] M^+, 188.119 8. [i] M^+, 188.120 2; δ_H, (CCl_4) 3.30 (3 H, s, OCH_3), 7.15 (5 H, m, aromatic), 5.84 (2 H, m, vinylic), 3.15—3.50 (1 H, m, benzylic), 3.65 (1 H, m, OCH, and 1.75—2.00 (4 H, m, ring protons). [j] M^+, 188.119 8; $\delta_H(CCl_4)$ 3.29 (3 H, s, OCH_3), 7.11 (5 H, m, aromatic), 5.80 (2 H, m, vinylic), 3.25—3.60 (1 H, m, benzylic), 3.65—3.90 (1 H, m, OCH), and 1.40—2.20 (4 H, 2 × m, ring protons). [k] Varian-Aerograph A90P, 5 ft 10% SE30, 230°, He, 60 cm^3 min^{-1}. [l] Found: M^+, 314.202 5. Calc. for $C_{24}H_{26}$: M, 314.203 45. [m] M^+, 314.202 5. [n] M^+, 314.202 8. [o] M^+, 314.202 8. [p] M^+, 314.202 5. [q] M^+, 314.202 5. [r] Samples of the dimers, which were eluted in three groups (7, 8; 9—11; 12, 13), were collected by preparative scale g.l.c.[k] The individual groups of dimers were hydrogenated [g] to give the corresponding phenylcyclohexyl compounds which were identified by g.l.c. (F11, 2.5% OV17, 260°, nitrogen pressure 25 lb in^{-2}), comparison being with the dimeric products from electrolyses of *trans*-4-phenyl- and *cis*-2-phenyl-cyclohexanecarboxylate and from the mixed electrolysis of 4-phenyl- and 2-phenyl-cyclohexanecarboxylates in methanol.

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