Electro-organic Reactions. Part IX.† Mechanism of the Kolbe Reaction; Stereochemistry of Reaction of Anodically Generated Cyclohexyl Radicals and Cations

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The products of anodic oxidation, under comparable conditions in methanol, have been characterised and identified for a series of 4-substituted cyclohexanecarboxylates (substituents *cis*- and *trans*-t-butyl and *trans*-phenyl) and *cis*-2-phenylcyclohexanecarboxylate. The stereoisomeric bicyclohexyls (one-electron oxidation) from the 4-*cis*- and -*trans*-t-butyl- and -*trans*-phenyl compounds, and *cis*- and *trans*-1-methyl-4-t-butylcyclohexane (from cross coupling with acetate) are formed in the statistically expected proportions. This is compelling evidence that cyclohexyl radicals are not strongly adsorbed at the anode. The stereoisomeric dimers from *cis*-2-phenylcyclohexylcarboxylate are formed in non-random proportions, which supports the view that substitution by aromatic species encourages adsorption. Further oxidation to cyclohexyl cations is also encouraged by 2- and 4-phenyl substitution, and comparison with the results of solvolysis experiments shows that this is also a surface effect.

It is widely accepted that the many products [1] obtained from Kolbe electrolyses are explained by the mechanistic pathways outlined in Scheme 1. Much discussion has, however, centred on whether or not there is a significant stabilising effect of the solid anode (usually an ill-defined oxide of platinum) [2] on the reactive species (carboxylate anions, radicals, or carbenium ions).

SCHEME

It is highly probable that carboxylate anions are significantly adsorbed at the anode, because the product distribution from the anodic oxidation [3] of substituted phenylacetate ions is profoundly altered by addition of other, electrochemically inert, anions. The nature of the effect of added anions is best rationalised in terms of competitive and important adsorption at the anode.

It is unlikely that cations are involved in significant attractive interactions at the anode because of coulombic interactions and the energy of solvation to be gained following desorption.

Extreme views have, however, been expressed about the likelihood and significance of interactions between radical intermediates and the anode. The results of

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† Part VIII, J. H. P. Utley and R. J. Holman, *Electrochim. Acta*, 1976, in the press.

[1] J. H. P. Utley in ' Technique of Electroorganic Synthesis,' ed. N. L. Weinberg, Wiley, New York, 1974, ch. 6; L. Eberson, ' Chemistry of the Carboxylic Acid Group,' ed. S. Patai, Interscience, London, 1970.

[2] T. Biegler and R. Woods, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1968, **20**, 73.

[3] J. P. Coleman, R. Lines, B. C. L. Weedon, and J. H. P. Utley, *J.C.S. Perkin II*, 1974, 1064.

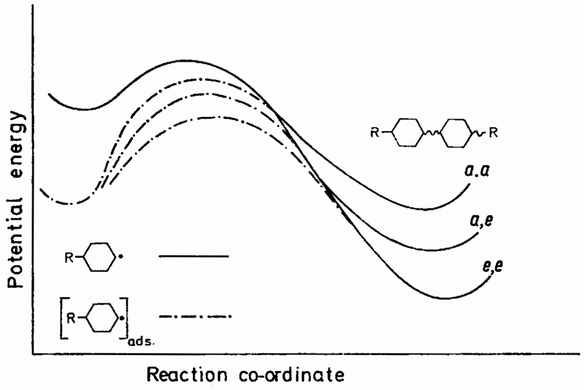
purely electrochemical experiments have been adduced[4] in favour of strong adsorption of radicals with subsequent rapid dimerisation at the surface. Certainly the work of Fleischmann and Goodridge and their co-workers,[5] whereby the products of acetate oxidation were determined as a function of the duration of anodic pulses, may be taken as strong evidence that the initial electron transfer is slow and is followed by rapid decarboxylation and combination. A related study[6] of oxide formation at platinum strongly suggests that at the high anode potentials[7] associated with Kolbe oxidation ($\geqslant$ 2.2 V *vs.* n.h.e.) the reaction is proceeding at an oxide film which is established in *ca.* 10^{-3} s. The electrochemical methods do not, however, distinguish between two possible causes of rapid radical dimerisation, *i.e.* strong and essential adsorption or the establishment near to the anode of high local concentrations of radicals.

Experiments on the stereochemistry of the Kolbe reaction also failed to provide an unambiguous result concerning the interaction of radical intermediates with the anode. In an early experiment[8] the anodic oxidation of 2-methylbutyrate gave an optically inactive product. The result was unsatisfactory because the *meso* : (±) ratio for the dimer was not known and, in any case, the maximum possible optical activity was small. A better designed experiment has been described[9] which involves a Kolbe crossed coupling reaction from ethyl hydrogen (+)-ethylmethylmalonate and isovalerate. The product was at least 99.98% racemic so it can safely be assumed that anodically generated chiral radicals have an opportunity to racemise before combination.[*] Unfortunately such experiments cannot prove whether combination occurs at the surface or in bulk solution, because racemisation of the radical would result whatever the position of a dynamic adsorption–desorption equilibrium and the anode cannot discriminate between enantiomeric adsorbed radicals.

In principle the question can be answered from a study, not of optical activity, but of the relative proportions of diastereoisomeric dimers formed. If combination occurs in bulk solution, and is essentially diffusion controlled, the statistically expected ratio of diastereoisomers will be observed. If the radicals are significantly stabilised at the surface an energy of activation for combination will result and because of the possibility of diastereoisomeric transition states, a deviation from random coupling will be expected. This principle is illustrated in terms of a potential energy–reaction co-ordinate diagram (Figure). Preliminary experiments based on this principle, and using *cis*- and *trans*-substituted cyclohexanecarboxylates, have been described.[10] We herein report fully on those experiments and others aimed at elucidating the stereochemistry of one- and two-electron oxidation of stereoisomers of substituted cyclohexanecarboxylates.

RESULTS AND DISCUSSION

Choice of Reaction Conditions.—A major aim of the present study was to examine the stereochemistry of substituted bicyclohexyls formed from the corresponding cyclohexanecarboxylates. Accordingly conditions for electrolysis were sought which optimised the yields of bicyclohexyls. Non-aqueous solvents generally promote dimer formation in the Kolbe reaction. Methanol is commonly used but it has been reported[11] that for the one-electron oxidation of diphenylacetate ion to tetraphenylethane the competing two-electron oxidation is inhibited in dimethylformamide. Acetonitrile has also been used[12] successfully for Kolbe coupling but no sys-



Combination of 4-substituted cyclohexyl radicals

TABLE 1

Kolbe electrolysis[a] of cyclohexanecarboxylic acid in various solvents

Solvent	% Bicyclohexyl/ % Substitution[b]
H_2O–MeOH (30% v/v)[c]	0.97
MeOH[c]	1.76
MeCN[d]	2.26
HCO·NMe_2[d]	4.32

[a] Acid (0.78M) neutralised 25%; Pt anode, 0.25 A cm^{-2}. [b] Alcohol, ester, ether, and acetamide according to solvent. [c] Sodium salt. [d] Tetra-n-butylammonium salt.

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[*] A possible objection to this system is that the spin on the chiral centre is delocalised over the ethoxycarbonyl group. However complete racemisation is also found for the s-butyl radicals involved in cross coupling of (+)-2-methylbutanoic acid and methyl hydrogen malonate (L. Eberson, *Acta Chem. Scand.*, in the press).

[4] B. E. Conway and A. K. Vijh, *Chem. Rev.*, 1967, **67**, 623.

[5] M. Fleischmann, J. R. Mansfield, and Lord Wynne-Jones, *J. Electroanalyt. Chem.*, 1965, **10**, 522; M. Fleischmann and F. Goodridge, *Discuss. Faraday Soc.*, 1968, **45**, 254.

[6] M. Fleischmann, J. R. Mansfield, and Lord Wynne-Jones, *J. Electroanalyt. Chem.*, 1965, **10**, 511.

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

[8] E. S. Wallis and F. H. Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 3838.

[9] L. Eberson and G. Ryde-Petterson, *Acta Chem. Scand.*, 1973, **27**, 1159.

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

[11] L. Rand and A. F. Mohar, *J. Org. Chem.*, 1965, **30**, 3156; 3885.

[12] C. D. Russell and F. C. Anson, *Analyt. Chem.*, 1961, **33**, 1282; L. Eberson and K. Nyberg, *Acta Chem. Scand.*, 1964, **18**, 1567.

tematic comparison of the solvents has been reported. Table 1 summarises the results of a comparison of the usefulness of these common solvents in promoting the formation of bicyclohexyl from cyclohexanecarboxylate ion. The highest relative yields of dimer are obtained from dimethylformamide and acetonitrile. However, methanol was chosen as solvent for the remaining experiments because it has the advantages of being easily removed and in it are produced low boiling, low molecular weight substitution products (from two-electron oxidation).

Product Distribution from Cyclohexanecarboxylates.—The results of amperostatic electrolyses at a platinum anode of several substituted cyclohexanecarboxylates are summarised in Table 2. The alkanes and dimers are derived from the corresponding radical (one-electron oxidation) whereas the methyl ethers are formed *via* the carbenium ion (two-electron oxidation). Alkenes may be formed from the radical (by disproportionation) or from the carbenium ion (by elimination). This point is dealt with later in the discussion. The mechanistic implications of the results are conveniently discussed by detailed, separate, consideration of the products of one- and two-electron oxidation.

TABLE 2

Kolbe electrolysis [a] of cyclohexanecarboxylic acids in methanol

Carboxylate	Alkane (%)	Alkenes (%)	Ethers (%) cis	Ethers (%) trans	Bicyclohexyls (%)	Others (%) [b]
Cyclohexane	10.7	39.1	20.5		19.2	11.5 [c]
trans-4-t-Butylcyclohexane	19.3	32.1 [d]	3.0	7.5	25.1	12.8
trans-4-Phenylcyclohexane	19.4	44.0 [e]	4.2	9.0	12.3	11.2
cis-2-Phenylcyclohexane	6.3	12.5 [f]	72.0 [f]			8.1

[a] Pt anode, 0.4 A cm^{-2}; acid 18% neutralised with NaOMe. [b] Includes variety of alcohols and ketones, individually in low yield. [c] Includes cyclohexyl cyclohexanecarboxylate (1.7%). [d] Includes some 3-t-butylcyclohexene (5%). [e] 4-Phenylcyclohexene (36%), 3-phenylcyclohexene (8%). [f] See Table 4 for detailed analysis.

One-electron Oxidation (*Radical-derived Products*).—(a) *Combination of the* 4-*t-butylcyclohexyl radical.* Three stereoisomeric dimers were expected corresponding to linkage of the rings in e,e, e,a, and a,a modes. G.l.c. separated the dimer mixture cleanly into two components. Component 1 (of lower retention time) was partially further resolved on the chromatogram into a peak with a prominent shoulder. The combined peak area corresponding to component 1 was three times that of the peak at higher retention time. Preparative scale g.l.c. allowed the collection of small samples of components 1 and 2. The high resolution mass spectra of the components showed virtually identical fragmentation and in each case the peak at highest mass gave m/e 278.296 ($C_{20}H_{30}$ requires 278.297). The purity of the samples was also confirmed by satisfactory microanalyses for carbon and hydrogen. An initial assignment of stereochemistry followed from inspection of the t-butyl signals in the ^1H n.m.r. spectra (CCl_4; 220 MHz). From component 2 a sharp singlet at δ 0.82 ($W_{\frac{1}{2}}$ 10 Hz) is obtained, whereas from component 1 three signals of equal intensity are found, centred at δ 0.83 with total $W_{\frac{1}{2}}$ 4.1 Hz. This is consistent with component 2 being either of the isomers in which the t-butyl groups are equivalent (e,e or a,a) and component 1 being a mixture of the a,e isomer with one of the symmetrical isomers. This assignment was confirmed and the e,e, and a,a isomers were distinguished by the epimerisation and synthesis experiments summarised in Scheme 2.

Friedel–Crafts alkylation of t-butylbenzene with 4-t-butylcyclohexyl chloride (*trans*-rich mixture) gave a complex mixture of products (see Experimental section) from which, by preparative scale g.l.c., was isolated 1-t-butyl-4-(4-t-butylcyclohexyl)benzene. The ^1H n.m.r. spectrum of the compound contained a broad multiplet (1 H) at δ 2.20—2.53 attributed to the benzylic proton; the broadness arises from axial–axial coupling and hence the product is the *trans*-isomer. This is the more stable isomer so its formation is to be expected from a reaction under thermodynamic control (scrambling of alkyl groups was observed).

Hydrogenation of *trans*-1-t-butyl-4-(4-t-butylcyclohexyl)benzene (Adams catalyst; room temperature) gave a product which, according to g.l.c., contained the major isomer (a,e) and the isomer of highest retention time in the ratio 1.8 : 1. Because the starting material contains a *trans*-linkage (equatorial) it follows that the two dimers formed are the a,e and e,e isomers. The a,a isomer must therefore be responsible for the shoulder in the chromatogram of component 1.

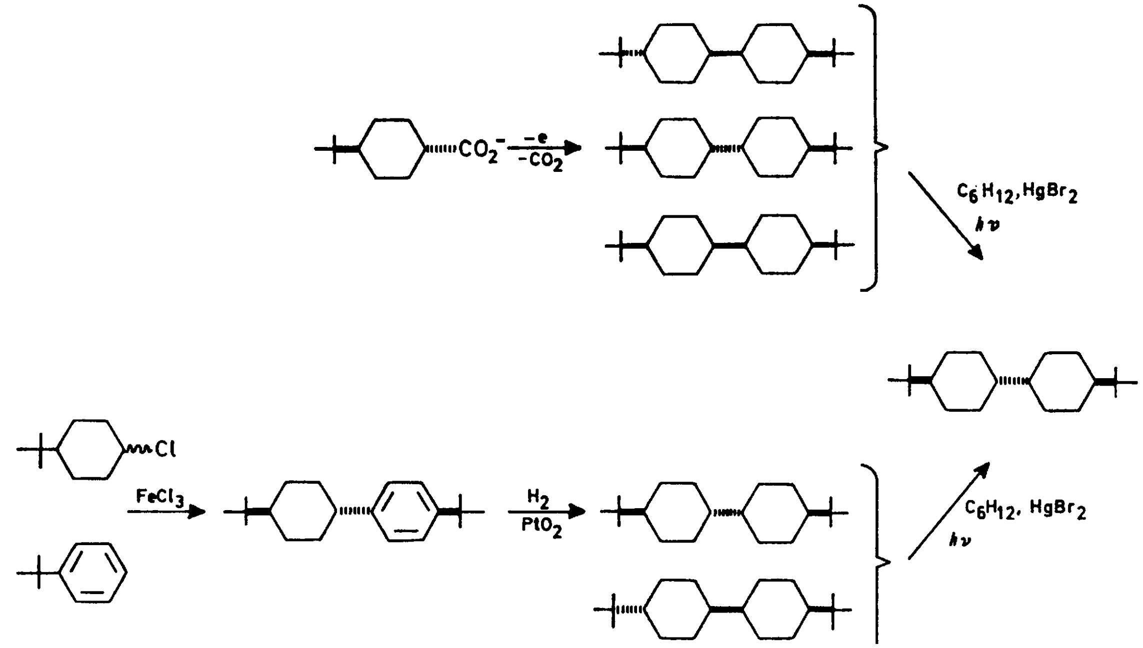
Samples of the dimers formed by electrolysis and those produced by hydrogenation of *trans*-1-t-butyl-4-(4-t-butylcyclohexyl)benzene were separately epimerised by u.v. irradiation in the presence of mercury(II) bromide. By this method [13] abstraction of tertiary hydrogen atoms in saturated molecules allows inversion, with hydrogen abstraction from the solvent (cyclohexane) completing the reaction. In each case g.l.c. showed that after 67 h the two isomers of lowest retention time were converted almost entirely into that of longest retention time. This confirms that the dimer of longest retention time is the e,e isomer, *i.e.* the most stable.

From the integrated areas of the t-butyl signals in the n.m.r. spectra and from the partial resolution in g.l.c. analysis the ratios of isomers (a,a : a,e : e,e) are 1 : 2 : 1, as expected for statistical combination of the 4-t-butylcyclohexyl radical. The ratio would be disturbed if there were substantial stabilisation at the anode (see Figure). It is concluded, therefore, that in this case the

[13] D. Kogan and Y. Mazur, *Tetrahedron Letters*, 1971, 2401.

anodically generated 4-t-butylcyclohexyl radical is essentially a 'free' radical

(b) *Cross-coupling of methyl and* 4-*t-butylcyclohexyl.* Co-electrolysis of *cis*- or *trans*-4-t-butylcyclohexanecarboxylate and acetate gave in each case a 1 : 1 mixture of *cis*- and *trans*-1-methyl-4-t-butylcyclohexane (Table 3). Again, the products of combination are not of equal stability and their formation in the statistical ratio implies a reaction of very low energy of activation and consequently little stabilisation of the initial state (radicals).



SCHEME 2

(c) *Combination of* 4-*phenylcyclohexyl.* There is much evidence from adsorption studies, albeit at relatively low potentials, that π-systems interact with metal anodes. In particular aromatic hydrocarbons adsorb [14] at gold and platinum from solution with energies of adsorption of the order of 40 kJ mol^{-1}. Consequently phenyl substitution of cyclohexanecarboxylate might be expected to provide stabilisation of a radical produced at the anode by encouraging adsorption.

TABLE 3

Kolbe cross coupling [a]

Carboxylate	Alkane (%)	Alkene (%)	Ethers (%) [b] *cis*	Ethers (%) [b] *trans*	Bicyclohexyls (%) [c]	1-Methyl-4-t-butylcyclohexane (%) *cis*	1-Methyl-4-t-butylcyclohexane (%) *trans*
trans-4-t-Butylcyclohexane	6.5	<1.0	6.5	19.6	7.6	*ca.* 11.0	*ca.* 11.0
cis-4-t-Butylcyclohexane	7.1	<1.0	7.0	23.8	8.3	*ca.* 7.0	*ca.* 7.0

[a] Pt anode, methanol, 0.03 A cm^{-2}; 4-t-butylcyclohexanecarboxylic acid (0.14M) and acetic acid (0.14M) *ca.* 20% neutralized with NaOMe. [b] Water present, therefore alcohols and ketone also present (*ca.* 33%). [c] Stereoisomers (a,a, a,e, and e,e) in 1 : 2 : 1 ratios.

The electrolysis of *trans*-4-phenylcyclohexanecarboxylate in methanol (Table 2) gave the isomeric 4,4'-diphenylbicyclohexyls (M^+ 318.2353; $C_{24}H_{30}$ requires 318.2348). G.l.c. gave two peaks (the first partially resolved), in the ratio 3 : 1 (the minor component being that of longest retention time). By analogy with the 4-t-butyl case this is interpreted as a 1 : 2 : 1 ratio of a,a, a,e, and e,e isomers, which suggests that if the 4-phenylcyclohexyl radical is adsorbed the effect is not great enough to disturb the essentially random coupling. The behaviour of the 4-phenylcyclohexanecarboxylate is, however, significantly different from the 4-t-butyl case in that, for identical conditions, the proportion of dimer from the 4-phenyl compound is less and that of alkene more (*via* two-electron oxidation). Substitution by 2-phenyl causes even larger changes in favour of two-electron oxidation and both cases are discussed below in detail.

(d) *Combination of* 2-*phenylcyclohexyl.* Under conditions which produce significant amounts of bicyclohexyls from the *cis*- and *trans*-4-t-butyl- and *trans*-4-

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[14] (*a*) H. Dahms and M. Green, *J. Electrochem. Soc.*, 1963, **110**, 1075; J. O'M. Bockris, M. Green and D. A. J. Swinkels, *ibid.*, 1964, **111**, 743; X. de Hemptinne, *Ann. Soc. sci. Bruxelles, Ser. 9*, 1966, **80**, 140; (*b*) L. Eberson and R. G. Wilkinson, *Acta Chem. Scand.*, 1972, **26**, 1671; L. Eberson and H. Sternerup, *ibid.*, p. 1431.

phenyl-cyclohexanecarboxylates no dimer is formed from the *cis*-2-phenyl compound (Table 2). A five-fold increase in carboxylate concentration results in the production on electrolysis (Table 4) of a low yield of the isomeric dimers, which were isolated by g.l.c. and identified by high resolution mass spectrometry.

The dimers may be analysed by g.l.c.; again two peaks are obtained, the first being partially resolved. The ratio of peak areas is 0.8 : 1 with, in this case, the slightly larger component appearing at the longer retention time. For the non-polar dimers it is reasonable to assume a relationship between g.l.c. retention time and shape. Consequently, by analogy with the previous results, the peak at longest retention time is attributed to ***trans*,*trans***-2,2′-diphenylbicyclohexyl in which the linkage is e,e when the phenyl groups are equatorial. For the 2,2′-disubstituted dimers there are six stereoisomers (Table 5) but for the random combination, and assuming that the preferred conformations have both phenyl groups equatorial, the (a,a + a,e) and e,e isomers would be formed in the ratio 3 : 1. The observed ratio is 0.8 : 1, which suggests that the 2-phenylcyclohexyl radical is sufficiently strongly adsorbed at the anode to cause a departure from random combination in favour of the most stable product (*trans,trans*). This is consistent with the hypothesis contained in the Figure, *i.e.* as one moves from the diffusion-controlled situation the relative stabilities of the transition states for production of the stereoisomeric dimers will reflect product stabilities, thus favouring production of the e,e isomer.

TABLE 4

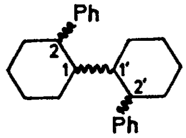
Kolbe electrolysis [a] of *cis*-2-phenylcyclohexanecarboxylic acid in methanol

Conc. (M)	Products (%) Ph-cyclohexane	3-Ph-cyclohexene	[PhC(OMe)]cyclopentane	1-MeO-1-Ph-cyclohexane	*cis*- and *trans*-1-MeO-2-Ph-cyclohexane	Bicyclohexyls [b]	Others
0.33	6.3	12.5	41.1	25.0	6.9		8.1
1.63	11.2	14.0	31.6	20.4	5.6	7.2	10.0

[a] Acid neutralised to 25% with NaOMe; Pt anode, 0.4 A cm^{-2}. [b] See text for stereoisomer distribution.

TABLE 5

Stereoisomers of bicyclohexyls from coupling of 2-phenylcyclohexyl radical



Isomer C(2), C(1); C(1′), C(2′)	Enantiomer	Number	Ring junction [a]
R,R; *S,S*	*S,S*; *R,R* (*meso*)	2	*a,a*
R,R; *S,R*	*S,S*; *R,S*	4	*e,a*
R,S; *R,R*	*S,R*; *S,S*		
R,R; *R,S*	*S,S*; *S,R*	4	*a,e*
R,S; *S,S*	*S,R*; *R,R*		
R,R; *R,R*	*S,S*; *S,S*	2	*a,a*
R,S; *S,R*	*S,R*; *R,S*	2	*e,e*
R,S; *R,S*	*S,R*; *S,R* (*meso*)	2	*e,e*

[a] When Ph groups are equatorial.

Two-electron Oxidation (*Carbenium Ion-derived Products*).—We are here concerned with alkenes and methyl ethers. Some of the alkene may be formed *via* radical disproportionation but it is safe to assume that at least the amount formed in excess of the corresponding alkane is derived from the carbenium ion.

From Table 2 it is evident that oxidation of the phenyl-substituted carboxylates gives proportionally more two-electron products than oxidation of the 4-t-butylcyclohexanecarboxylate. For electrolysis of 0.33M-solutions 4-phenyl substitution is associated with a diversion of products from dimers to alkene and, more strikingly, 2-phenyl substitution is associated with almost complete diversion to two-electron products. In this latter case substitution to give ethers predominates over elimination (to alkene) and only the small amount of alkane (6%) can be attributed to one-electron oxidation.

As the amount of alkane formed is similar for the 4-t-butyl and 4-phenyl cases the excess of alkene formed from 4-phenylcyclohexanecarboxylate is carbenium ion-derived and suggests that the 4-phenylcyclohexyl radical is more readily oxidised than the 4-t-butylcyclohexyl radical. To establish whether or not a hitherto unrecognised feature can stabilise, in bulk solution, the 4-phenylcyclohexyl cation *vis à vis* the 4-t-butylcyclohexyl cation the solvolysis experiments summarised in Table 6 were carried out. It is well established[15] that methanolysis of the type described in Table 6 proceeds *via* an ion-paired intermediate (hence inversion during substitution). The *trans*-4-t-butyl- and *trans*-4-phenyl-cyclohexyl brosylates gave in methanol virtually identical elimination : substitution ratios indicating that, in homogeneous reaction, the 4-substituent has little influence on the reactivity of the carbenium ion. The difference in the products of electrolysis may therefore be ascribed to a surface effect, *i.e.* greater adsorption of the 4-phenyl substituted radical favouring further electron-transfer. This conclusion has also been reached[14b] following experiments on the competitive anodic

TABLE 6

Methanolysis of *trans*-4-substituted cyclohexyl brosylates [a]

Substituent	Alkenes (%)	Ethers (%) [b]
4-t-Butyl	59.7	40.3
4-Phenyl	57.2	42.8

[a] At 338 K; see text for experimental details. [b] Mainly *cis*-isomer; *trans* <1%.

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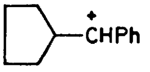
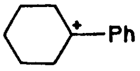
[15] N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc.* (*B*), 1968, 355.

acetoxylation of hydrocarbons and the distribution of products from anodic acetoxylation of 2-substituted indanes. Such an explanation requires that the ease of further oxidation of the radical is more sensitive to adsorption than discrimination between coupling reactions leading to stereoisomeric dimers. Support for this view comes from consideration of the products from electrolysis of *cis*-2-phenylcyclohexanecarboxylate (Tables 2 and 4). The proportions of the stereoisomeric dimers indicate adsorption of the 2-phenylcyclohexyl radical, and this is also the case in which, at 0.33M, almost complete two-electron oxidation is found.

The presence of the methyl ethers, formed *via* the 2-phenylcyclohexyl cation, shows that extensive rearrangement has occurred. The driving force for rearrangement is formation of a benzylic cation. It is not, however, clear why the major substitution product arises from a benzylic secondary cation (1) rather than from a benzylic tertiary cation (2).



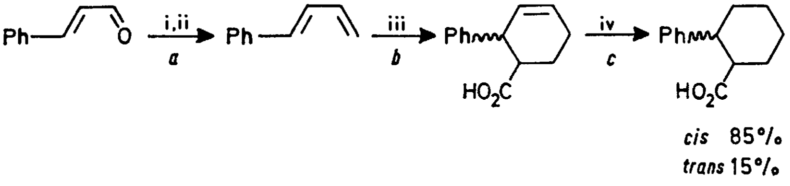
(1)



(2)

EXPERIMENTAL

Substituted cyclohexanecarboxylic Acids.—*cis*- and *trans*-4-t-Butylcyclohexane carboxylic acid were prepared and purified by the method previously described.[16] *trans*-4-Phenylcyclohexanecarboxylic acid was prepared by slight modication of a literature method.[17] *cis*-2-Phenylcyclohexane carboxylic acid was prepared according to Scheme 3, which includes references pertaining to the key steps.



SCHEME 3 Reagents: i, MeMgI; ii, aq.H_2SO_4; iii, $HO_2C{\cdot}CH{:}CH_2$; iv, H_2–PtO_2

References: (*a*) O. Grummit and E. Becker, *J. Amer. Chem. Soc.*, 1948, **70**, 149; (*b*) J. S. Meek, F. J. Lorenzi, and S. J. Cristol, *J. Amer. Chem. Soc.*, 1949, **71**, 1830; (*c*) H. W. Zimmerman and T. W. Cutshall, *J. Amer. Chem. Soc.*, 1958, **80**, 2893; 1959, **81**, 4305.

In the final, hydrogenation, step 2-phenylcyclohex-3-enecarboxylic acid (10 g) was dissolved in ethyl acetate (40 cm^3) and hydrogenated at room temperature over Adams catalyst (0.1 g) in a conventional glass apparatus. Part of the mixture of acids thus obtained (total 9.8 g; m.p. 57—90°) was converted into the corresponding methyl esters with ethereal diazomethane. G.l.c. analysis (Perkin-Elmer F11; 2½% SE30 at 160 °C) showed the mixture to be 85% *cis* and 15% *trans*. The pure *cis*-acid (m.p. 76—77°) was obtained by careful and repeated crystallisation of the crude mixture from aqueous acetic acid.

Electrolyses.—*Apparatus*. Simple undivided and water-jacketed cells were used, fitted with horizontally mounted parallel platinum plate electrodes (1.1 cm^2) separated by *ca*. 3 mm. Current densities were calculated according to the assumption that all the reaction takes place at the opposing faces of the electrodes. A stabilised d.c. power supply was used (Coutant Electronics Ltd., model LA 200) which allowed electrolysis at a pre-set current for the duration of the run or until the required cell voltage exceeded 50 V.

Procedure. Electrolysis of cyclohexanecarboxylic acid in various solvents (*Table* 1). Cyclohexanecarboxylic acid (4 g, 0.031 2 mol) was converted into a mixture containing *ca*. 25% of the tetra-n-butylammonium salt by addition of the appropriate amount of aqueous tetra-n-butylammonium hydroxide (40% w/w), followed by evaporation and removal of water by repeated azeotropic distillation. The residue was dried *in vacuo* (P_2O_5). The mixture of the acid and its salt was dissolved in the required solvent (40 cm^3) and electrolysed at constant current (0.4 A; 0.24 A cm^{-2}) for 4.2 h (2 F mol^{-1}).

The work-up varied according to the solvent; each procedure is summarised below. In each case the product mixture was analysed by g.l.c. (Perkin-Elmer F11; DE 207; 60 °C for 12 min rising to 160 °C at 10° min^{-1}). The products were identified by g.l.c. comparison with authentic samples.

Work up from: (a) *methanol*. The methanol was removed by distillation. Water (40 cm^3) was added to the residue and the mixture shaken with ether (2 × 20 cm^3). The combined ethereal extracts were washed successively with saturated aqueous sodium hydrogen carbonate and water, then dried ($MgSO_4$).

(b) NN-*dimethylformamide*. The electrolyte was poured into water (60 cm^3) and shaken with ether (3 × 20 cm^3). The combined extracts were washed successively with saturated aqueous sodium hydrogen carbonate, dilute hydrochloric acid, and water, then dried ($MgSO_4$).

(c) *Acetonitrile*. Acetonitrile was removed by distillation under reduced pressure and the residue dissolved in ether (40 cm^3). The ethereal solution was washed and dried as in (b).

Electrolysis of substituted cyclohexanecarboxylates in dry methanol. Methanol was dried by distillation from magnesium methoxide and stored over molecular sieves (4 A). A solution of the acid, *ca*. 18% of which was converted into its sodium salt, was prepared by addition of the acid to a solution of sodium methoxide in methanol. The solution was electrolysed at constant current density until 1.5 F mol^{-1} had passed. It was necessary occasionally to reverse the polarity of the two platinum electrodes to remove a film formed at the anode. The electrolyte was poured into water and shaken with ether. Sodium chloride was sometimes added to aid separation. The combined ethereal extracts were washed with saturated sodium hydrogen carbonate solution and water, and dried ($MgSO_4$). After

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[16] G. E. Hawkes and J. H. P. Utley, *J.C.S. Perkin II*, 1973, 128.

[17] W. S. Johnson and R. D. Offenhauer, *J. Amer. Chem. Soc.*, 1945, **67**, 1045.

reduction in volume the ethereal extract was analysed by g.l.c. Acidification of the combined aqueous layers and extraction with ether allowed recovery of unchanged acid.

Product Analysis, Identification, and Characterisation of Stereoisomers.—(a) *G.l.c. analysis*. A Perkin-Elmer F11 machine was used with, if necessary, linear temperature programming. The columns were stainless steel (2 m × $\frac{1}{8}$ in o.d.) with standard commercial packings. G.l.c. peaks were identified by comparison of retention times or peak enhancement with authentic samples on, where possible, two columns. For quantitative work peak areas were compared with those of suitable internal standards, a known weight of which was added to the product mixture. Detector response factors (for weights) were determined by using authentic specimens of the expected products. Where authentic specimens were not separately prepared they were isolated by preparative scale g.l.c. (Varian Aerograph A90 P with thermal conductivity detector, and 5ft × $\frac{1}{4}$ in stainless steel columns with standard packings).

(b) *Preparation of authentic samples of expected products. Alcohols*. Isomeric mixtures of *cis*- and *trans*-2- and -4-phenylcyclohexanols were prepared from either *o*- or *p*-phenylphenol by hydrogenation[18] over Raney nickel in methanol containing a small amount of sodium methoxide at 160 atm. and 160 °C. Samples of the *trans*-isomers were obtained for 4-Bu^t, 2-Ph, and 4-Ph by reduction of the appropriate cyclohexanones with sodium in ethanol.[19] 1-Phenylcyclohexanol was prepared by addition of phenylmagnesium bromide to cyclohexanone. Cyclopentyl(phenyl)methanol was prepared by reduction of cyclopentyl phenyl ketone with lithium aluminium hydride.[20]

Methyl ethers. General method. Potassium (0.39 g, 0.01 mol) was added to a solution of the alcohol (0.01 mol) in dry ether (25 cm^3). When the reaction was complete methyl iodide (2.84 g, 0.02 mol) was added and the mixture stirred at room temperature for 2 days. Potassium iodide was filtered off and the ether solution used directly for g.l.c. characterisation of the ethers. 3-Methoxycyclohexene was prepared by the amperostatic electrolysis (2.3 F mol^{-1} at 1.1 A cm^{-2}; graphite anode) of cyclohexene (5 g) in dry methanol (20 cm^3) containing tetra-n-butylammonium perchlorate (2 g). According to g.l.c. there were two major products—that of lowest retention time was collected (Aerograph A90P; 20% DEGS; 12 ft × $\frac{1}{4}$ in column; 90 °C) and identified as 3-methoxycyclohexene by comparison of its ^{1}H n.m.r. spectrum with that published.[21]

Alkenes. 3-Phenylcyclohexene[22] was obtained by the reaction in ether between 3-bromocyclohexene and phenylmagnesium bromide. 1-Phenylcyclohexene and 4-phenylcyclohexene[23] were prepared by sulphuric acid-catalysed dehydration of the corresponding alcohols. 4-t-Butylcyclohexene[24] was obtained from a mixture of *cis*- and *trans*-4-t-butylcyclohexyl tosylates by elimination at 80 °C with lithium chloride dissolved in dimethylformamide.

Alkanes. t-Butylcyclohexane[25] was prepared by conventional hydrogenation of 4-t-butylcyclohexene over Adams catalyst. Phenylcyclohexane[26] was prepared by the reaction between cyclohexyl bromide and refluxing benzene over aluminium.

Bicyclohexyl. Cyclohexylmagnesium bromide [from cyclohexyl bromide (30 g, 0.184 mol)] in dry ether, was added to a vigorously stirred suspension of silver bromide (35 g, 0.186 mol) in dry ether. The mixture was stirred at room temperature for 0.5 h then heated under reflux for 1 h. Dilute hydrochloric acid was added and the solution filtered. The ether layer was separated and after washing (H_2O), drying ($MgSO_4$), and distillation under reduced pressure a crude product was obtained which was heated under reflux with sodium (1 g) prior to final fractional distillation; yield 3.3 g (20%); b.p. 99—100° at 9 mmHg; $\nu_{max.}$ (film), 855, 890 995, 1262, and 1356 cm^{-1}; δ_H (60 MHz; CCl_4) 1.8—2.0 (m); M^+ 166.172 ($C_{12}H_{22}$).

(c) *Dimers from electrolyses*. The isolation and characterisation of the isomeric 4,4′-di-t-butylbicyclohexyls are adequately described in the main text. A mixture of isomeric 4,4′-diphenyl bicyclohexyls was isolated as a white solid (m.p. 203—206°) from the relevant electrolysis product by preparative scale g.l.c. (Aerograph A90P; 10% SE30; 6 ft × $\frac{1}{4}$ in column; 230 °C); M^+ 318.235 ($C_{24}H_{30}$). Following electrolysis of 2-phenylcyclohexanecarboxylate at relatively high concentration (1.63M) a mixture of isomeric 2,2′-diphenylbicyclohexyls was similarly obtained (10% SE30; 5 ft × $\frac{1}{4}$ in column; 220 °C); M^+ 318.235 ($C_{24}H_{30}$). In each case best resolution for analytical g.l.c. (F11 instrument) was obtained by using $2\frac{1}{2}$% SE30 columns with linear temperature programming.

(d) *Non-electrochemical preparation of dimers. 1-t-Butyl 4-(4-t-Butylcyclohexyl)benzene*. 4-t-Butylcyclohexyl chloride (4 g) was slowly added to a mixture of t-butylbenzene (16 g) and anhydrous iron(III) chloride (2 g) at 10 °C. The mixture was allowed to warm to 25 °C and left until evolution of hydrogen chloride was complete. After conventional work-up a fraction of b.p. 155—180° at 0.1 mmHg was collected (2 g). G.l.c. analysis (F11; 15% SE30; 220 °C) showed the fraction to contain four components. The three of highest retention time were in the ratio 2.1 : 2.8 : 1: component (1), t_R 6 min, M^+ 216, tentative assignment 1-phenyl-4-t-butylcyclohexane; component (2), t_R 12 min, M^+ 272, $\nu_{max.}$ (film) 1 393, 1 365 (Bu^t), 1 450—1 480 (CH), 788, and 703 (ArH) cm^{-1}, δ_H (CCl_4) 7.06 (4H, m, aromatic), 2.10—2.60 (1 H, m, benzylic), 1.33 (9 H, s, ArBu^t), 0.9 (9 H, s, cyclohexyl Bu^t), and 0.8—2.6 (9 H, m, cyclohexyl), tentative assignment 1-t-butyl-2-(4-t-butylcyclohexyl)benzene; component (3), t_R time 14 min, M^+ 272, $\nu_{max.}$ (film) 1 392, 1 363, 1 450—1 480, 825, and 780 cm^{-1}, δ_H (CCl_4) 6.87—7.27 (4 H, m), 2.10—2.60 (1 H, m), 1.26 (9 H, s,) and 0.85 (9 H, s), tentative assignment, 1-t-butyl-3-(4-t-butylcyclohexyl)-benzene; component (4), t_R 16 min, M^+ 272.250 ($C_{20}H_{32}$); $\nu_{max.}$ (Nujol) 830 cm^{-1} (2 adjacent aromatic CH), δ_H (CCl_4) 6.86—7.25 (4 H, AA′BB′q, *J* 8.5 Hz, *p*-disubstituted benzene), 2.20—2.53 (1 H, m), 1.30 (9 H, s), 0.90 (9 H, s), and 0.90—2.10 (9 H, m), assignment *trans*-1-t-butyl -4-(4-t-butylcyclohexyl)benzene.

trans,trans-4,4′-Di-t-butylbicyclohexyl and the *trans,cis*-isomer were obtained by hydrogenation of 1-t-butyl-4-(4-t-butylcyclohexyl)benzene at atmospheric pressure and room temperature over Adams catalyst with carefully purified

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acetic acid as solvent. G.l.c. analysis (F11; $2\frac{1}{2}$% SE30; 165 °C) gave the ratio of isomers as 1 : 1.6, the minor component being subsequently confirmed as the *trans,trans*-isomer (e,e).

(d) *Epimerisation experiments.*[13] Cyclohexane (B.D.H. spectroscopic grade) was further purified by washing with a 1 : 1 mixture of concentrated sulphuric and nitric acids and water (× 3). After drying ($CaCl_2$) it was carefully distilled through an efficient column. Reagent grade mercury(II) bromide was recrystallised from water and dried *in vacuo* (P_2O_5). The reaction tube was a quartz–Pyrex graded seal (*ca.* 60 mm; 10 mm bore) which was permanently sealed at the quartz end. The tube containing the relevant mixture of isomeric bicyclohexyls (0.04 mmol), mercury(II) bromide (0.013 g, 0.04 mmol), and cyclohexane (2 cm^3) was evacuated, flushed repeatedly with nitrogen, and then sealed under vacuum. The mixture was irradiated for 67 h (Hanovia type 509/10 50 W lamp, medium-pressure) and then the contents were analysed by g.l.c. (F11; $2\frac{1}{2}$% SE30; 165 °C).

Methanolysis of p-*Bromobenzenesulphonates.*—*p*-Bromobenzenesulphonates (brosylates) were prepared by Schleyer's method.[27] A solution of the brosylate (0.06 mol) in dry methanol was heated under reflux. Samples (*ca.* 0.5 cm^3) were removed at intervals during several days and analysed by g.l.c. The products were identified by g.l.c. peak enhancement with authentic samples. Samples were taken until the alkene : methyl ether ratio was constant (*ca.* 6 : 1 during 60 h). This was necessary because direct injection of the brosylate into the g.l.c. machine resulted in decomposition into the alkene. Hence unchanged brosylate could, in principle, give a misleading elimination : substitution ratio.

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