

Electro-organic Reactions. Part VI.† Stereoselective Cathodic Reduction of Unhindered Cyclic Ketones

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The cathodic reduction to alcohol of the conformationally rigid ketones 4-t-butylcyclohexanone, dihydroisophorone, *trans*-decalin-2-one, and *trans*-4a-methyldecalin-2-one has been investigated with particular reference to factors influencing the ratio of axial:equatorial alcohol. The parameters which have been varied include cathode material, solvent, proton donor, cathode potential, current density, and supporting electrolyte. The highest stereoselectivity in favour of the axial alcohols (kinetic control) is obtained using small or doubly charged electrolyte cations in ethanol. From 4-t-butylcyclohexanone the corresponding *cis*-alcohol is thereby obtained in 98% purity and 84% current efficiency. The control of stereochemistry is explained in terms of ion-pairing of key carbanionic intermediates.

THE stereoselective chemical reduction of cyclic ketones has been much studied and there is considerable knowledge of the factors controlling the stereochemistry of

† Part V, R. E. Sioda, B. Terem, J. H. P. Utley, and B. C. L. Weedon, *J.C.S. Perkin I*, 1976, 561.

¹ (a) E. L. Eliel and R. S. Ro, *J. Amer. Chem. Soc.*, 1961, **83**, 606; (b) D. H. R. Barton, *J. Chem. Soc.*, 1953, 1027, footnote 23.

catalytic hydrogenation,¹ reduction by hydride reagents,² and hydrogenation through homogeneous catalysis.³ For unhindered, conformationally biased, cyclic ketones

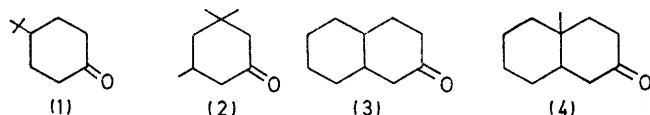
² J. D. Morrison and H. S. Mosher, 'Asymmetric Organic Reactions,' Prentice-Hall, New Jersey, 1971, pp. 84—132.

³ H. B. Henbest and T. R. B. Mitchell, *J. Chem. Soc. (C)*, 1970, 785.

chemical reduction usually gives, as the major product, the more stable of the epimeric alcohols. For homogeneous reactions, high degrees of stereoselectivity in favour of the less stable epimer require highly substituted hydride reagents⁴ or expensive homogeneous catalysts.³

The cathodic reduction of saturated aldehydes and ketones to give alcohols, pinacols, and hydrocarbons has also been much studied.⁵ The stereochemistry of cathodic pinacolisation⁶ and asymmetric induction in the reduction of, *e.g.*, acetophenone⁷ have received attention but there has been little systematic investigation of the control of the stereochemistry of reduction of conformationally biased cyclic ketones. We here present a full report on such an investigation.^{8,9}

The bulk of the systematic study is concerned with 4-*t*-butylcyclohexanone (1). It has been found that the stereochemistry of reduction of this substrate is controlled by the nature of cations present in the electrolyte. This conclusion is confirmed by the results of similar reductions using dihydroisophorone (2) and the bicyclic ketones (3) and (4).



RESULTS

Voltammetry.—Cyclohexanones are not easily reduced at the cathode. In ethanol solution at the dropping mercury cathode, single 2e polarographic waves at $E_{\frac{1}{2}}$ *ca.* -2.5 V [*vs.* saturated calomel electrode (s.c.e.)] have been reported¹⁰ for cyclohexanone and some steroidal ketones. In dimethylformamide (DMF) solution $E_{\frac{1}{2}}$ -2.79 V (*vs.* s.c.e.) has been reported¹¹ for cyclohexanone. Addition to DMF of small amounts of a proton donor, phenol, moved the $E_{\frac{1}{2}}$ value anodically (to -2.70 V).

In the present work cyclic voltammetric experiments using 4-*t*-butylcyclohexanone (8mM) showed that in acetonitrile-tetra-*n*-butylammonium perchlorate (0.3M) and a sweep speed of 0.3 V s⁻¹ a single irreversible reduction peak was observed at -2.65 V (*vs.* Ag wire) on both a hanging mercury drop and vitreous carbon cathodes. In this system addition of proton donor (quinol or acetic acid) led to preferential hydrogen-ion discharge which precluded observation of the ketone reduction peak.

Because the stereochemistry of reduction was found to be strongly dependent on cations present in the electrolyte it was also necessary to assess the likely electrochemical behaviour of the cations under the conditions for ketone reduction. Accordingly polarisation curves were recorded for DMF solutions containing a variety of cations.

Extrapolation of the curves to zero current gave cathode potentials for each cation which may be used to judge the

⁴ H. C. Brown and S. Krishnamarthy, *J. Amer. Chem. Soc.*, 1972, **94**, 7159; J. Hooz, S. Akiyama, F. J. Cedar, M. J. Bennett, and R. M. Tuggle, *ibid.*, 1974, **96**, 274.

⁵ 'Organic Electrochemistry,' ed. M. M. Baizer, Dekker, New York, 1973, pp. 347 *et seq.*

⁶ J. H. Stocker and R. M. Jenevein, *J. Org. Chem.*, 1968, **33**, 2145.

⁷ (a) L. Horner, *et al.*, *Chem. Eng. Tech.*, 1972, **44**, 209; *Tetrahedron Letters*, 1971, 1241, 1245; 1970, 1103, 2803, 2679; 1968, 5889; (b) E. Kariv, H. A. Terni, and E. Gileadi, *Electrochim. Acta*, 1973, **18**, 433.

relative deposition potentials (Table 1). The significant point is that apart from the tetra-*n*-butylammonium case, reduction of the metal cations is preferred to reduction of 4-*t*-butylcyclohexanone. At mercury this would presumably lead to the formation of amalgamated electrodes. However, control experiments showed that the stereochemical course of the reaction was dictated by the cations in solution and not by the nature of the electrode.

TABLE 1
Electrolyte cation deposition potentials

Electrolyte ^a	Working electrode	Deposition potential (V) ^b (<i>vs.</i> Ag wire)
LiCl	Hg drop	-1.68
MgCl ₂	Hg drop	-1.49
Zn(ClO ₄) ₂	Hg drop	-0.96
	Vitreous carbon	-1.26
Bu ₄ N ⁺ I ⁻	Hg drop	-2.8 ^c

^a Solution 0.1M in redistilled, dry DMF. ^b See text for definition; measured with a recorder sensitivity of 4 μ A cm⁻¹, sweep speed 0.3 V s⁻¹. ^c *vs.* S.c.e.

Cathodic Reduction of 4-*t*-Butylcyclohexanone.—Products. In protic solvents (MeOH or EtOH) and in DMF with added proton donor the major products of reduction are the isomeric *cis*- and *trans*-4-*t*-butylcyclohexanols. In some experiments significant amounts (*ca.* 10%) of the 4e reduction product, 4-*t*-butylcyclohexane, were obtained. No pinacols were formed in any experiment. They could easily have been detected because 4-*t*-butylcyclohexanone was pinacolised chemically (see Experimental section) and analysed by g.l.c. under the conditions used for analysis of the cathodic reduction products.

Stereoselectivity in alcohol formation. Methanol proved to be a convenient solvent for the systematic investigation of the effects on the ratio of axial : equatorial alcohols of varying cathode material, cathode potential, and current density. The relevant results are summarised in Table 2. The only change which produces a significant alteration of the axial : equatorial isomer distribution is the change of supporting electrolyte from NaOAc to Bu₄N⁺OAc; in the presence of the larger cation the axial : equatorial ratio (12 : 88) approaches the equilibrium ratio. A change of cathode material produces little change in the isomer ratio which suggests that adsorption effects are unlikely to be important.

Effect of cations, solvents, and proton donors. Subsequent experiments designed to reveal any effect on stereoselectivity of changes in cations and solvents used divided cells with amperostatic reduction at a mercury pool. We here define stereoselectivity as selectivity in favour of the less stable (axial) epimer. For a given pair of cations (Li⁺ and Bu₄N⁺) the effects of changing solvents are summarised in Table 3. Again it is evident that the greatest stereoselectivity is obtained with the smaller cation and the effect is most marked in ethanol. There is no obvious relationship with dielectric constant, *e.g.* in BuⁿOH and BuⁿO(CH₂)₂OH, solvents of relatively low dielectric constant, axial : equatorial ratios tend to the equilibrium value.

⁸ Preliminary communication, J. P. Coleman, R. J. Kobylecki, and J. H. P. Utley, *Chem. Comm.*, 1971, 104.

⁹ Preliminary communication, R. J. Holman and J. H. P. Utley, *Tetrahedron Letters*, 1974, 1553.

¹⁰ P. Kabasakalian and J. McGlotten, *Analyt. Chem.*, 1959, **31**, 1091.

¹¹ A. Albinsson, G. Mousset, and J. Simonet, *Compt. rend.*, 1971, **272**, 646.

The reaction most likely to reduce the current efficiency for reduction of the saturated cyclic ketones is competitive evolution of hydrogen from the proton donor. Accordingly several sets of protic conditions were assessed for reduction under given conditions and the results are given in Table 4.

ΔG) is obtained with the cations of high ratios of charge : ionic radius. The degree of stereoselectivity obtained using zinc or magnesium salts as electrolytes (>98% axial OH) compares very favourably with the most stereoselective chemical methods of reduction. Furthermore the cathodic

TABLE 2

Cathodic reduction of 4-t-butylcyclohexanone at constant potential or constant current density and with a variety of cathode materials

Electrolyte ^a	Electrode material	Current density (mA cm ⁻²)	Cathode potential (V) (<i>vs. s.c.e.</i>)	% <i>ax</i> -ROH	% <i>eq</i> -ROH	<i>eq</i> -ROH/ <i>ax</i> -ROH	$-\Delta G_{25}/$ kJ mol ⁻¹ ^b	% RH	% Total current efficiency (%)
A ^c	Lead	124—154	-2.5	33	62	1.9	1.53	5	15.7
A ^c	Lead	77—124	-2.1	25	65	2.6	2.33	10	7
A ^c	Lead	30—84	-1.85	22	65	2.9	2.63	13	3
A ^c	Lead	18—34	-1.5	28.5	61.5	2.2	1.9	10	1
B ^c	Lead	44—78	-2.4	12	88	7.3	4.90		66
A ^c	Lead	210	-1.5 to -2.4	38	56	1.5	0.94	6	10
A ^c	Lead	131	-1.5 to -2.0	36	54	1.5	0.94	10	3
A ^c	Lead	84	-1.0 to -1.6	44	46	1.0	0.11	10	2.5
A	Mercury	65.2	<i>ca.</i> -1.8	42	58	1.4	0.79		3
A	Platinum	62	<i>ca.</i> -1.4	30	68	2.3	1.99	2	1
C	Mercury	65.2	<i>ca.</i> -2.2	42	54	1.3	0.61	4	48
C	Vitreous carbon	58	<i>ca.</i> -1.8	40	60	1.5	0.99		
C	Graphite	50		38	62	1.1	0.16		0.5
C	Magnesium-mercury	65.2	<i>ca.</i> 2.4	39	58	1.5	1.01	3	40
D	Magnesium-mercury	65.2	<i>ca.</i> 2.2	32	67	2.1	1.80	1	6

^a Electrolytes: A, ketone 0.3M-sodium acetate 2.4M-acetic acid 2.0M, in methanol; B, ketone 0.2M-tetra-n-butylammonium acetate 0.63M, in methanol; C, ketone 0.06M-lithium chloride 0.1M-acetic acid 0.05M, in ethanol; D, ketone 0.06M-tetra-n-butylammonium acetate 0.1M-acetic acid 0.05M, in ethanol. ^b Calculated for $K = \% \text{eq-OH}/\% \text{ax-OH}$. ^c Undivided cell.

TABLE 3

Effect of solvents and supporting electrolytes on the stereochemistry of cathodic reduction of 4-t-butylcyclohexanone^a

Solvent	Dielectric constant (25°)	Electrolyte cation	% <i>ax</i> -OH	% <i>eq</i> -OH	<i>eq</i> -OH/ <i>ax</i> -OH	$-\Delta G_{20}/$ kJ mol ⁻¹ ^b	% RH	% Total current efficiency ^c
DMF	38.7	Bu ⁿ ₄ N ⁺	15	77	5.1	3.98	8	37
DMF		Li ⁺	23	70	3.0	2.71	7	47
MeOH	32.6	Bu ⁿ ₄ N ⁺	28	71	2.5	2.27	1	5
MeOH		Li ⁺	28	69	2.5	2.20	3	43
EtOH	24.3	Bu ⁿ ₄ N ⁺	31	62	2.0	1.69	7	7
EtOH		Li ⁺	42	54	1.3	0.61	4	48
Bu ⁿ O(CH ₂) ₂ OH		Li ⁺	31	69	2.2	1.95	<0.5	55
Bu ⁿ OH	17.1	Li ⁺	18	80	4.4	3.63	2	44

^a Electrolyses in a divided H cell at *ca.* 20°; mercury cathode, 2F mol⁻¹, constant current density (62.5 mA cm⁻²), substrate 0.01M, electrolyte 0.1M, acetic acid 0.05M. ^b Calculated from $K = \% \text{eq-OH}/\% \text{ax-OH}$. ^c Calculated on the basis of ketone consumed for a 2e reduction.

The ratio of stereoisomeric alcohols is unaffected by changes in proton donor and the use of quinol was found to lead to efficient reduction.

TABLE 4

Effect of added hydrogen donor on the cathodic reduction of 4-t-butylcyclohexanone^a

Donor	% <i>ax</i> -OH	% Total current efficiency ^b
Solvent (EtOH)	30	80
Acetic acid 0.96M	42	30
Acetic acid 0.05M	44	48
Quinol 0.01M	42	83

^a Substrate 0.01M, electrolyte LiCl (0.1M) in anhydrous EtOH, mercury pool cathode, constant current density (62.5 mA cm⁻²). ^b Calculated on the basis of ketone consumed for a 2 F mol⁻¹ reduction.

A more extensive examination of the effect of cation was pursued for reduction in ethanol using quinol as proton donor. The results, given in Table 5, show clearly that the highest stereoselectivity (low negative or positive values of

reductions may be carried out on a several gram scale in conventional cells.

Reduction at amalgamated cathode. The effect of cation on the stereochemistry of the reduction at mercury might arise from (a) a bulk solution effect, (b) the prior formation by metal deposition of an amalgam with subsequent chemical reduction, and (c) prior formation of an amalgamated cathode at which electron transfer takes place. Possibility (b) was eliminated by allowing 4-t-butylcyclohexanone to be stirred together with a Mg-Hg amalgam (1% Mg w/w) in a solution corresponding to electrolysis conditions. After several hours at room temperature no detectable reduction had occurred. Possibility (c) was also eliminated by cathodically reducing 4-t-butylcyclohexanone (0.01M) at a similar amalgam in ethanol-quinol (0.01M) in the presence of either LiCl (0.1M) or Bu₄Ni (0.1M). In each case the current efficiency for alcohol formation and the ratios of the stereoisomers were identical with the corresponding result at a clean mercury cathode (*cf.* Table 2).

Cathodic Reduction of Dihydroisophorone (2), trans-Decalin-2-one (3), and trans-4a-Methyldecalin-2-one (4).—

Having established conditions which give highly stereoselective reduction of the model compound (1) it was desirable to see if similar reduction of larger ketones could be achieved. Accordingly the stereochemistry of the products of cathodic reduction of the ketones (2)—(4) was examined and the results are summarised in Table 6.

For a given substrate the trends evident for 4-*t*-butylcyclohexanone are found for the larger ketones, *i.e.* greater stereoselectivity increases with the cation used in the order $Zn^{2+} > Mg^{2+} > Li^+ > Bu_4N^+$. However, the degree of stereoselectivity thus obtained is considerably less than for 4-*t*-butylcyclohexanone.

DISCUSSION

The results contained in Tables 2—6 show that it is changes in the electrolyte cation which cause the most

These observations are reminiscent of the effects of cations on reduction potentials of quinones¹² and aromatic hydrocarbons.¹³ The cyclic voltammetric behaviour in acetonitrile of trifluoroacetophenone and the reactions of the corresponding radical anion are also strongly cation dependent.¹⁴ Similarly the stereochemistry of the pinacols formed cathodically from acetophenone is influenced by the cation of the supporting electrolyte.¹⁵

Such results have been explained consistently in terms of the ion-pairing of key intermediates. Incorporation of this idea into the accepted mechanism for cathodic ketone reduction is represented for compound (1) in the Scheme. The assumption of rapid transfer of the second electron is based on the absence of pinacols in the

TABLE 5

Effect of electrolyte cations on the stereochemistry of cathodic reduction in ethanol of 4-*t*-butylcyclohexanone^a

Electrolyte cation	Charge/ion radius ^e	% <i>ax</i> -OH	% <i>eq</i> -OH	<i>eq</i> -OH/ <i>ax</i> -OH	$-\Delta G_{20}/$ kJ mol ⁻¹	% RH	% Total current efficiency ^e
Bu ₄ N ⁺	0.2 ^f	33	65	1.97	1.63	2	7.1
Li ⁺	1.7	42	54	1.29	0.63	4	48
Mg ²⁺ ^b	3.0	≥98	≤2	0.02	> -9.5	<i>d</i>	84
Zn ²⁺ ^b	2.7	≥98	≤2	0.02	> -9.5	<i>d</i>	44

^a Electrolysis carried out in a divided H cell at *ca.* 20°; mercury cathode, current density 62.5 mA cm⁻², solvent dry ethanol, substrate 0.01M, electrolyte 0.1M, acetic acid 0.5M. ^b Acetic acid replaced by 0.01M quinol. ^c Calculated on the basis of ketone consumed for a 2e reduction. ^d Trace amounts of hydrocarbon detected. ^e Crystal ion radii for 12 co-ordinated metal ions, L. Pauling, 'The Nature of the Chemical Bond,' Oxford University Press, Oxford, 1960, 3rd edn., p. 469. ^f Ion radius estimated from models, R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 1965, 2nd edn., p. 125.

TABLE 6

Effect of electrolyte cation on the product distribution for the cathodic reduction of ketones (2)—(4)^{a,f}

Ketone	cation	% <i>ax</i> -OH	% <i>eq</i> -OH	<i>eq</i> -OH/ <i>ax</i> -OH	$-\Delta G_{20}/$ kJ mol ⁻¹ ^g	% Total current efficiency ^e
(2)	Li ⁺ ^b	20	80	4	3.39	42
	Mg ²⁺ ^b	54	46	0.85	-0.39	5
	Zn ²⁺ ^b	78	22	0.28	-3.09	<i>ca.</i> 2
(3)	Bu ₄ N ⁺ ^c	23	77	3.35	2.90	8
	Li ⁺ ^c	42	58	1.38	0.79	47
	Zn ²⁺ ^d	58	42	0.72	0.79	<i>ca.</i> 2
(4)	Bu ₄ N ⁺ ^e	29	71	2.45	2.18	10
	Li ⁺ ^c	44	56	1.27	0.58	52

^a Divided cell, mercury cathode, constant current density (62.5 mA cm⁻²). Substrates 0.01M in dry ethanol. ^b 0.1M-LiCl, MgCl₂, Zn(ClO₄)₂. ^c 0.3M-Bu₄N⁺LiCl. ^d Saturated (*ca.* 0.27M) solution of Zn(ClO₄)₂. ^e Calculated on the basis of ketone consumed for a 2 F mol⁻¹ reduction. ^f Additional volatile compound detected, in some experiments up to 2% total product, assumed to be hydrocarbon. ^g Calculated for $K = \% eq\text{-OH}/\% ax\text{-OH}$.

pronounced effect on the ratio of axial:equatorial alcohols. That this is a bulk solution effect, and not a consequence of the formation of amalgamated cathodes, is shown by the identical dependence of the axial:equatorial ratio on cation for reduction at both a clean and an amalgamated cathode. The equilibrium ratio of axial:equatorial alcohol is, for 4-*t*-butylcyclohexanone, *ca.* 1:9 and placing cations in an order of effectiveness for disturbing the ratio in favour of axial product gives the sequence $Zn^{2+} > Mg^{2+} > Li^+ > Bu_4N^+$. In addition the effect is more pronounced in ethanol than in DMF which, because of its high donor power, is particularly effective at solvating cations.

¹² T. Fujinaga, K. Izutsu, and T. Nomura, *J. Electroanal. Chem. Interfacial Electrochem.*, 1971, **29**, 203.

¹³ L. A. Avaca and A. Bewick, *J. Electroanal. Chem. Interfacial Electrochem.*, 1973, **41**, 405.

products. Presumably at the very negative potentials employed the stationary concentration of radicals of the type R₂ĊOH is very low.

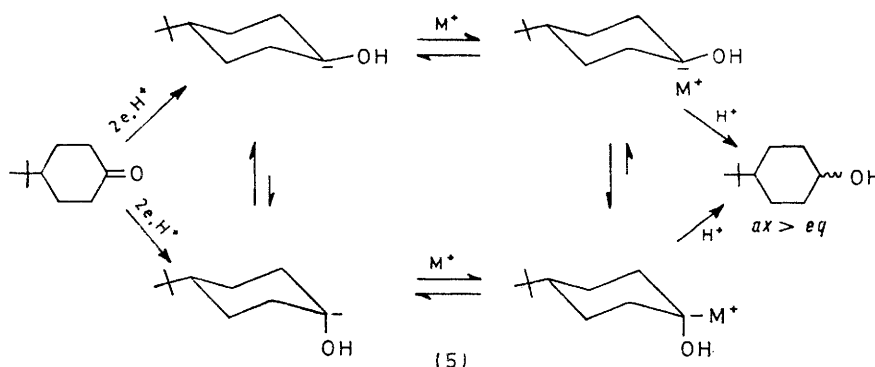
A good working hypothesis for the control of stereochemistry by added cation follows consideration of the Scheme. For cathodic reduction the stereochemistry determining step is the final protonation of carbanions of the type R₂ĊOH [*e.g.* (5)]. Tight ion pairing (for which the order of effectiveness of cation is $Zn^{2+} \sim Mg^{2+} > Li^+ > R_4N^+$), would displace the conformational equilibrium of the carbanions in favour of that ion-paired conformer with an axial OH. The inversion of carbanions is relatively slow and therefore rapid protonation

¹⁴ C. P. Andrieux and J. M. Saveant, *Bull. Soc. chim. France*, 1973, 2090.

¹⁵ A. Bewick and H. P. Cleghorn, *J.C.S. Perkin II*, 1973, 1410.

of the intermediates¹⁶ would lead to products in which the isomer ratio reflected the position of the conformational equilibrium between the epimeric carbanions. These are 'non-Curtin-Hammett' circumstances which have good precedent in the interception, by protonation, of nitrogen inversion.¹⁷

A detailed description of the types of ion-paired intermediates (contact or solvent separated) cannot be attempted; the nature of other anions present (Cl^- , ClO_4^- , AcO^-), and the unknown degrees of solvation of all ions, must further complicate the predictive usefulness of the hypothesis. It is relevant, however, that a detailed study, using e.s.r. spectroscopy, of the solvation of ion-paired fluorenone ketyl radical-anions allows an



SCHEME $\text{M}^+ = \text{Li}^+, \text{MgCl}^+, \text{or } \text{ZnClO}_4^+$

estimate of the relative concentrations of contact and solvent separated ion pairs.¹⁸ One conclusion is that at least for Li^+ in alcohol solvent there is a significant concentration of tight, contact, ion pairs.

The lower stereoselectivity found for reduction of the more highly substituted ketones (Table 6) is consistent with, for a given cation, the ion-pairing interaction being weaker with larger carbanions.

EXPERIMENTAL

Organic Substrates.—4-t-Butylcyclohexanone (1) (Koch-Light, practical grade) was recrystallised from ethanol prior to use in electrochemical experiments.

3,3,5-Trimethylcyclohexanone (2) was prepared from the corresponding alcohol (Courtorch Chemicals Ltd.) by Jones oxidation¹⁹ and purified by careful distillation under reduced pressure.

trans-Decalin-2-one (3).— $\Delta^{1,8\alpha}$ -Octalin-2-one was prepared from cyclohexanone and methyl vinyl ketone essentially by an established method²⁰ although initial condensation was *via* the pyrrolidine enamine derivative. $\Delta^{1,8\alpha}$ -Octalin-2-one was converted into *trans*-decalin-2-one by a lithium-liquid ammonia reduction.²¹

trans-4a-Methyldecalin-2-one (4). The unsaturated ketone was similarly prepared by an established method²⁰ which was subsequently reduced as for (3).

¹⁶ D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, p. 155.

¹⁷ M. J. T. Robinson, 'Conformational Analysis,' ed. G. Chiurdoglu, Butterworths, London, 1971, p. 637.

¹⁸ K. Nakamura, B. F. Wong, and N. Hirota, *J. Amer. Chem. Soc.*, 1973, **95**, 6919.

Supporting Electrolytes.—Sodium acetate, magnesium chloride, lithium chloride, and tetra-n-butylammonium iodide were from commercial sources and required no further purification. Magnesium and zinc perchlorate were prepared by addition of an equivalent of metal carbonate to a solution of perchloric acid. The perchlorates were recrystallised from aqueous methanol and dried at 80° in air immediately before use.

Solvents.—Absolute ethanol was dried over magnesium. Dimethylformamide was redistilled and stored over molecular sieve (4A) prior to use. Spectroscopic grade dimethylformamide (B.D.H.) was used for cyclic voltammetric experiments. 2-Butoxyethanol was redistilled prior to use and stored over molecular sieve.

Electrochemical Experiments.—Preparative scale electrolyses were carried out either in undivided cells or, more

usually, in conventional H cells with sintered glass separators. The separation of anolyte and catholyte was found to be necessary in order to obtain reproducible results. Cathodes used were lead or vitreous carbon plates, graphite rods, or a mercury pool. A Chemical Electronics Ltd. TR2A potentiostat was used for potentiostatic electrolyses. Reference potentials were measured against s.c.e. or a silver wire immersed in the electrolyte. Current was monitored using a Chemical Electronics Ltd. electronic integrator. Amperostatic electrolyses were carried out using a Coutant Electronics Ltd. power supply or with a TR2A potentiostat modified to supply a constant current. Cyclic voltammetric and polarisation curves were recorded using a RB1 waveform generator in conjunction with a TR2A potentiostat and a Hewlett-Packard 7035B X-Y recorder. The micro-electrodes were either vitreous carbon (0.08 cm²) or a hanging mercury drop.

Analysis and Characterisation of Products.—In a typical experiment the catholyte was diluted with an equal volume of water and shaken with benzene. The combined organic layer from several extractions was washed with a brine solution, dried (MgSO_4), and the benzene removed under reduced pressure. The residue was analysed by g.l.c. (Perkin-Elmer F11; polypropylene glycol; Chromosorb P 60—80 mesh) and ¹H n.m.r. spectroscopy. Quantitative measurements obtained from integrations of g.l.c. peak areas were corrected by response factors obtained in the usual way by reference to internal standards.

¹⁹ K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 1946, 39.

²⁰ J. A. Marshall and W. I. Fanta, *J. Org. Chem.*, 1964, **29**, 2501.

²¹ R. L. Augustine, *J. Org. Chem.*, 1958, **23**, 1853.

4-t-Butylcyclohexanols. The axial and equatorial alcohols were identified by a comparison of their g.l.c. retention times with commercially available authentic samples. The composition of the mixture of epimeric alcohols was also determined from the ^1H n.m.r. spectra, δ (60 MHz; CCl_4) 3.33br (*1ax*-H, m) and 3.82sh (*1eq*-H, m). Isomer ratios obtained from the relative areas of these signals were in accord with those obtained by g.l.c.

4-t-Butylcyclohexane. The hydrocarbon was identified by g.l.c. peak enhancement with an authentic sample.

3,3,5-Trimethylcyclohexanols. The composition of mixtures of the epimeric alcohols were obtained from g.l.c. analysis (retention times, *eq*-OH > *ax*-OH), by g.l.c. peak enhancement using authentic samples of alcohols with a known axial : equatorial ratio, and by ^1H n.m.r., δ (60 MHz; CDCl_3) 3.43br (*1ax*-H, m) and 4.0sh (*1eq*-H, m).

1,1,3-Trimethylcyclohexane. This was identified by g.l.c. peak enhancement. Standard Clemmensen reduction of 3,3,5-trimethylcyclohexanone gave the required hydrocarbon, b.p. 76° at 50 mmHg, δ (CDCl_3) 0.8 (9 H, s) and 0.9—2.1 (10 H, m).

trans-Decalin-2-ol and trans-4a-methyldecalin-2-ol. The epimeric alcohols were identified by g.l.c. comparison, on two columns, with authentic samples prepared by reduction of the corresponding ketones with sodium borohydride (15% polypropylene glycol on Chromosorb P 60—80 mesh and 15% Carbowax 1 500 on Chromosorb W).

Inadequate separation precluded quantitative measurement of the equatorial and axial alcohols by g.l.c. so the isomer composition was obtained by integration of the n.m.r. signals of the methine protons at C(1): δ (100 MHz; CDCl_3) *trans*-decalin-2-ol 3.28br (*1ax*-H, m) and 3.75sh (*1eq*-H, m); *trans*-4a-methyldecalin-2-ol 3.28br (*1ax*-H, m) and 3.77sh (*1eq*-H, m).

Test for pinacol formation. The absence, according to g.l.c., of pinacol among the products of cathodic reduction of

4-*t*-butylcyclohexanone was confirmed by subsequent g.l.c. analysis of the products with added pinacol, *i.e.* 1,1'-*di*-hydroxy-4,4'-*di*-*t*-butylbicyclohexyl. This was prepared by heating, under reflux for 3 h, a benzene (10 ml) solution of 4-*t*-butylcyclohexanone (5.0 g) over magnesium turnings (1.0 g) and mercury(II) chloride (1.0 g). Water (20 ml) was added and the mixture heated for 30 min. The mixture was filtered after a further addition of water (50 ml) and the residue was washed with benzene (100 ml). The combined filtrate and washings were dried (MgSO_4), filtered, and evaporated. The residue was distilled (110° at 0.1 mmHg) and recrystallisation from light petroleum (b.p. 60 — 80°) gave the product, m.p. 210 — 220° , ν_{max} (Nujol) $3\ 450\ \text{cm}^{-1}$, δ (CDCl_3 -[$^2\text{H}_6$]DMSO) 0.83 (18 H, s), 1.00—2.17 (18 H, m), and 2.48—3.05 (2 H, m) (Found: M^+ , 310.288. $\text{C}_{20}\text{H}_{38}\text{O}_2$ requires M , 310.287).

For the products of electrochemical reduction of 3,3,5-trimethylcyclohexanone, decalin-2-one, and 4a-methyldecalin-2-one, g.l.c. analysis on a polar column gave no indication of products with retention times in excess of those for the monoalcohols. Distillation of the product mixture left no significant residue.

Attempted Reduction of 4-t-Butylcyclohexanone at a Magnesium-Mercury Amalgam.—An amalgam was prepared by completely dissolving clean magnesium turnings (0.3 g) in mercury (30 g) and this formed the electrode pool of a standard H cell. A solution of 4-*t*-butylcyclohexanone (0.42 g) in dry ethanol (12 ml) and acetic acid (1.0 ml) was stirred above the amalgam for 16 h. The solution was worked up in the usual way to yield 0.41 g of recovered organic material which, according to g.l.c. analysis, was entirely starting material.

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