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Electroorganic Reactions. Part 45. The Highly Stereoselective Electrochemical Hydrodimerisation of Methyl 4-tert-Butylcyclohex-1-enecarboxylate.

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Abstract:
Methyl 4-tert-butylcyclohex-1-enecarboxylate undergoes 1 F reduction at a mercury cathode in DMF solution to give as the major single product a hydrodimer in which the cyclohexyl rings are joined axially and the methoxycarbonyl groups are also axial. The structure is confirmed by X-ray crystallography. Kinetic experiments, combined with force field calculations, indicate radical-anion/radical-anion coupling which is under stereoelectronic control and which dictates diaxial coupling of the cyclohexyl rings. Protonation of the resulting dimeric dianion is under thermodynamic control.

Methyl 4-tert-butylcyclohex-1-enecarboxylate (**1a**) was chosen as a compound to be used in exploration[1] of the stereoselectivity of cathodic hydrogenation [to methyl *cis* and *trans* 4-tert-butylcyclohexanecarboxylate (**2**)]. As an activated alkene it is also expected to undergo electrohydrodimerisation (EHD) and the conformationally biased cyclohexyl system should allow unambiguous structure determination of the products and thereby throw light on stereoselectivity, if any, and possibly give clues to mechanism.

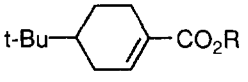
There is much current interest in stereoselective EHD reactions following recent demonstrations of highly stereoselective cyclohydrodimerisations of cinnamates (**3**) to all-*trans* cyclopentanones (**4**) which may also be prepared[2,3] with good diastereoselectivity when R is a chiral auxiliary (e.g. a d.e. of >95% is obtained[3] for R = S-(-)-borneol).

The cathodic hydrogenation[1] of (**1a**) revealed that the stereochemical course of the reaction was much influenced by reaction conditions and that the results had to be interpreted with caution because of interference from epimerisation in the basic conditions of electrolysis and from differential hydrolysis of the *cis* and *trans* products. Nevertheless, it was shown that the reaction was under kinetic control (*cis*-rich product) under conditions where epimerisation and hydrolysis were minimised, i.e. low conversion to the cyclohexane at ambient temperature. Key results from the earlier work are summarised in Table 1. For comparison it should be noted that the ratio of isomers of (**2**) expected for thermodynamic control, from calculation and epimerisation experiments[1], is *cis*:*trans* = 13:87. Coulometry showed[1] that protic conditions were necessary for 2 F reduction (hydrogenation); in the absence of proton donor smooth 1 F reduction was observed. This is consistent with EHD and consequently we now report on the products of such reduction. Three cyclohex-1-enecarboxylic acid esters (**1a** - **1c**) have been used in this investigation.

Table 1. Cathodic hydrogenation[a] of methyl 4-tert-butylcyclohex-1-enecarboxylate (**1a**) [Ref. 1]

Solvent	Proton source	Charge (F mol^{-1})	Cyclohexane (**2**,%)	*cis* : *trans* [b]
THF	H_2O[c]	2.2	24	79:21
THF	MeOH[c,d]	13.1	14	69:31
DMF	Hydroquinone[e]	4.0	95	62:38

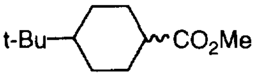
a. Divided cell, Hg cathode, constant current (4.2 mA cm^{-2}), substrate 0.01-0.03 mol dm^{-3}; b. determined by g.l.c.; c. ca. 4 mol dm^{-3}; d. Pt cathode, therefore competing hydrogen evolution; e. 0.05 mol dm^{-3}.



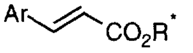
(**1**) a R = Me

b R = $PhCH_2$

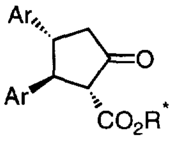
c R = 4-t-Bu.C_6H_4-



(**2**) *Cis* and *trans* isomers



(**3**)



(**4**)

Results and Discussion: *Electrochemical Behaviour.* - The results of cyclic voltammetric and coulometric experiments are given in Table 2. At low scan rates the cyclic voltammograms show chemically irreversible reduction peaks and the peak potentials (E_{pc}) measured at 0.3 V s^{-1}, were used to establish the working potential for the coulometric and preparative experiments. The coulometric results suggest that the behaviour of the benzyl ester (**1b**) differs significantly from that of the others. The potentials for the reversible reductions (E^o) were determined for the two substrates undergoing 1 F reduction on the coulometric time-scale (**1a** and **1c**) by increasing the scan rate to a value where the reduction process was chemically reversible. The E^o values allow a proper comparison of the ease of reduction to radical-anions and the methyl ester (**1a**) is significantly more difficult to reduce than the 4-t-butylphenyl ester (**1c**). Also for the cinnamates an aryloxy substituent significantly changes E^o (Table 2) but not surprisingly the electronic effect of changing from the methyl to the 4-t-butylphenyl ester is larger in the cyclohexene system than the electronic effect of changing from methyl to phenyl in the cinnamate system, where the presence of a common phenyl group in conjugation with the double bond facilitates the reduction of the cinnamates considerably compared to the reduction of the cyclohex-1-enecarboxylates.

Controlled Potential Preparative Electrolysis. - The preparative-scale experiments were carried out at or close to the irreversible reduction peak potentials (E_{pc}, given in Table 2) in DMF-Et_4NBr (0.1M) electrolyte using a divided cell at a mercury pool cathode and a graphite counter electrode. Electrolysis was continued until the background current level was reached and the charge consumption in F mol^{-1} noted; the work-up procedure involved first quenching the electrolyte in water.

For the three cyclohex-1-enecarboxylic acid esters three types of behaviour were found. Compound (**1a**) underwent a surprisingly stereoselective hydrodimerisation (this is the most significant result), (**1b**) gave 2 F reductive cleavage of the benzyl group. Preparative reduction of (**1c**) was problematical, probably because of concomitant hydrolysis under the basic conditions of electrolysis. It gave significant 2 F hydrogenation of the double bond despite the coulometric result recorded in Table 2 and the reaction-order determined in the kinetic experiments (Table 3 below).

Table 2. Cyclic voltammetry and coulometry[a]

Ester	-E° (V *vs.* SCE)[b]	-E$_{pc}$ (V *vs.* Ag/AgBr)[c]	n (F mol^{-1})
Methyl (**1a**)	2.533	2.28	1
Benzyl (**1b**)	-	1.98	2
4-t-Butylphenyl (**1c**)	2.307	1.88	1
Methyl cinnamate (**3**, R*=Me)[4]	1.778	-	1
Phenyl cinnamate(**3**, R*=Ph)[4]	1.631	-	1

a. DMF-Et$_4$NBr (0.1M); b. Hg/Pt-electrode (d=0.6mm), 100 V s^{-1}, C° (**1a**) = 7 mM, C° (**1c**) = 2 mM; c Hg bead-electrode, 0.3 Vs^{-1}, C° (**1a-1c**) *ca.* 3mM

Reduction of methyl 4-tert-butylcyclohex-1-enecarboxylate (**1a**). - In three separate experiments the charge consumption ranged from 1.08 - 1.16 F mol^{-1} and a crude product was obtained in yields of 63%, 82% and 96% based on the weights of substrate (**1a**) and the product mixture. Separation of the product mixture by column chromatography turned out to be problematical because of difficulty in monitoring the eluent, which contained no chromophores. However a single compound (**5**) crystallised from a methanol solution of the crude product and this was purified. Subtraction of its ^{1}H nmr spectrum from that of the crude product suggested the presence of one other significant product together with traces of unreacted starting material and unknown impurities. The ratio of (**5**) to the unknown product or products was 59:41and in absolute terms (**5**) was obtained in 36% and the unknown(s) in 30% yield. The data on the impure second product(s) are not adequate for structural assignment.

High resolution mass spectrometry indicated that (**5**) is a hydrodimer (M$^+$, m/z=394.308; calculated for $C_{24}H_{42}O_4$ = 394.308) and ^{13}C nmr spectroscopy suggested a reasonably symmetrical structure with little chemical shift difference for the corresponding carbon nucleii in two cyclohexyl units. Furthermore the sharpness of the singlets observed in the ^{1}H nmr spectrum for the ester methyl group and the ring t-butyl groups is consistent with a symmetrical hydrodimer; the lowest field, 2H, signal was observed at δ 2.59 (at both 80 and 250 MHz) and is probably due to equivalent and equatorial methine protons (with CO$_2$Me axial).

The signal is only slightly broadened which indicates coupling to adjacent protons of less than 4 Hz. However, although relatively simple, the spectrum could not be completely assigned. The structural problem was solved by X-ray crystallography which gave for (**5**) the structure in Figure 1.

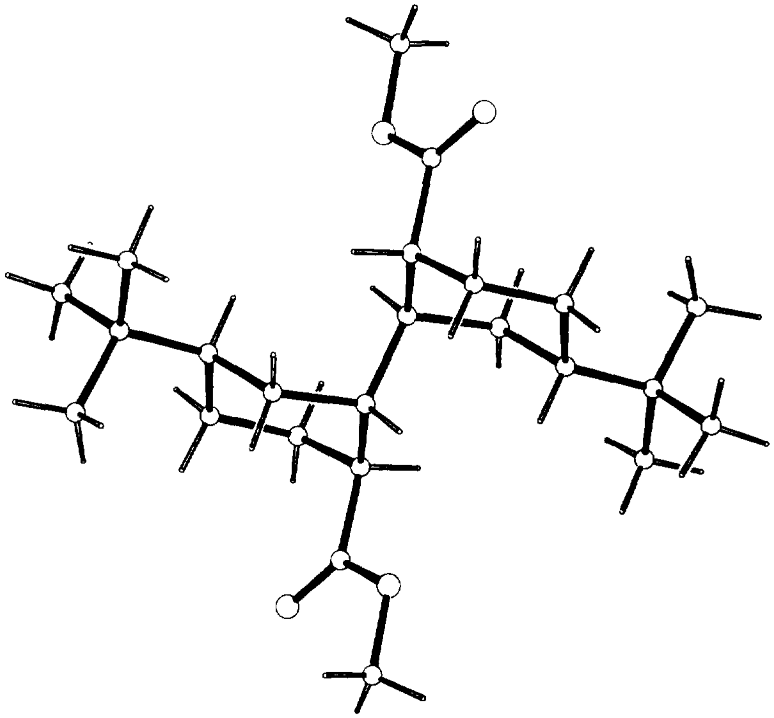
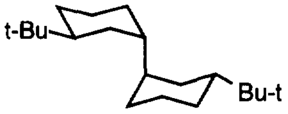


Figure 1 X-Ray Crystallographic Structure of Product (5)

The fact that compound (**5**) is the largest single product is remarkable. The difference in strain energy between bicyclohexyls linked diequatorially *vis à vis* diaxially has been estimated by comparing structures (**6**) and (**7**) using a force-field programme (see Experimental). This indicates that structure (**6**), with the rings linked di-equatorially, is more stable than (**7**), with diaxial linking, by 1.6 kcal mol^{-1}; the same programme calculates the conformational free energy difference between an equatorial and axial isopropyl substituent on a cyclohexane ring to be 1.7 kcal mol^{-1} in favour of the equatorial conformer. Thermodynamic control would therefore demand that the di-equatorial coupling of cyclohexyl rings would be favoured *cf.* diaxial by *ca.* 15:1. The mechanistic consequences of the observed diaxial coupling are discussed further (below) in the light of kinetic experiments and further calculation.

Reduction of benzyl 4-tert-butylcyclohex-1-enecarboxylate (**1b**). - In this case electrolysis under the same conditions used for (**1a**) resulted in consumption of 1.86 F and the only product isolated from electrolysis was 4-t-butylcyclohex-1-enecarboxylic acid. in 83% isolated yield. Controlled potential coulometry, which involves extrapolation to complete electrolysis, gave a value of 2 F (Table 2); a 2 F reaction going to 83% completion corresponds to an expected value of 1.66 F. This is sufficiently close to the observed value of 1.86, given likely losses of material on work-up, to reconcile the preparative and coulometric results.

(6)



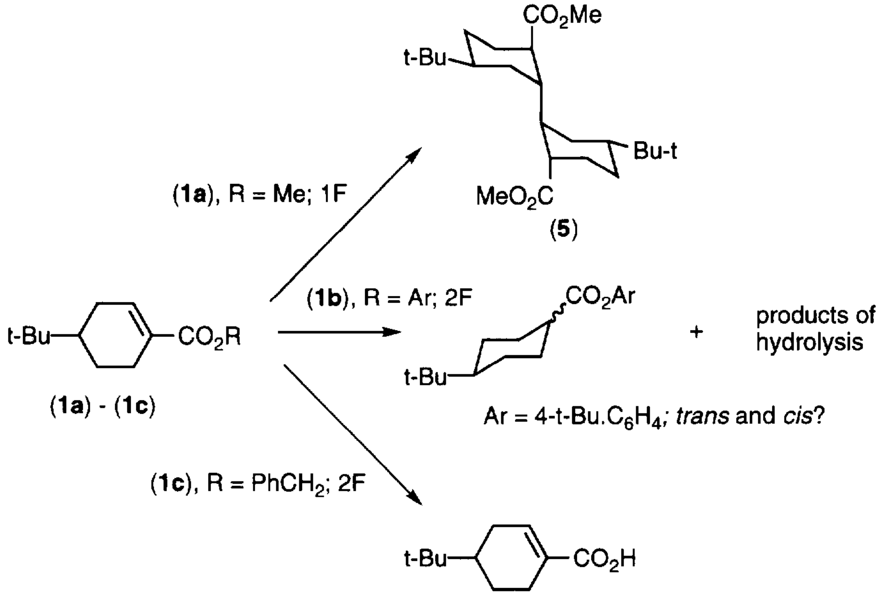
(7)

Reduction of (4-t-butylphenyl)-4-tert-butylcyclohex-1-enecarboxylate (**1c**). - The coulometric experiment gave clean 1 F electrolysis (Table 2), consistent with hydrodimerisation, whereas the preparative electrolysis proceeded to 1.3 F and gave the parent cyclohexane as the predominant (2 F) product (57 %, probably a mixture of *cis* and *trans* isomers) together with smaller amounts of 4-t-butylphenol and 4-t-butyl-cyclohex-1-enecarboxylic acid. By similar calculation a 2 F product in 57 % corresponds to consumption of 1.14 F mol^{-1}. However, the material balance is poor and it is known[4] from preparative electroreduction of aryl cinnamates that the aryl esters may hydrolyse under electrolysis conditions. Consequently, some EHD products could have been formed but lost in work-up.

The different predominant reactions of the cyclohex-1-enecarboxylates (**1a**) - (**1c**) upon cathodic reduction are summarised in Scheme 1.

Kinetics. - The mechanism of electrohydrodimerisation reactions has been re-examined and at least for reduction of cinnamic acid esters in largely aprotic media it is clear from kinetic and other experiments[4] that the rate-determining step is dimerisation of the radical-anions (radical-ion/radical-ion coupling) and not nucleophilic addition of the radical-anion to the starting material (radical-ion/substrate coupling). In this context kinetic data have been determined for the key ester (**1a**) and, for comparison, for the aryl ester (**1c**). Similar data for methyl cinnamate and for phenyl cinnamate are available[4].

For the two esters (**1a**) and (**1c**) the combined reaction order[5] in substrate and radical-anion was determined by derivative cyclic voltammetry (DCV)[5] by determining the scan-rate ($v_{0.6}$) necessary to achieve a certain degree of conversion, $R_I' = 0.6$, as a function of substrate concentration, where R_I' is the ratio between the derivative peak currents in the reverse and forward voltammetric scan[5]. For (**1a**) the reaction order $\{1 + d \log[v_{0.6}/\mathrm{Vs}^{-1}]/d \log[C^o(\mathbf{1a})]\}$ was equal to 1.94 whereas for (**1c**) the value was somewhat lower, 1.7, and the reaction order plot showed some curvature, Figure 2. A reaction order equal to 2 is in agreement with a dimerisation reaction but it does not make the distinction between radical-ion/radical-ion and radical-ion/substrate coupling with the coupling step being rate determining[6]. The distinction may be made by application of linear sweep voltammetry (LSV) if the reaction is sufficiently fast to be under purely kinetic control. At high concentrations (7 mM) and scan rates in the range 0.1 - 1.0 Vs^{-1} the follow-up reactions of the radical-anions derived from (**1a**) and (**1c**) are close to being under purely kinetic control but a combination of adsorption problems and relatively slow heterogeneous electron transfer complicates the measurements. However, the most sensitive parameter in the distinction between radical-ion/radical-ion and radical-ion/substrate coupling, the value of the half-peak width ($E_{p/2}$-E_p), determined at the two sweep rates 0.1 and 1.0 Vs^{-1} show (Table 3) that the dimerisation is of the radical-ion/radical-ion type with rate determining coupling. The theoretical value of $E_{p/2}$-E_p under purely kinetic conditions is 38.8 mV for radical-ion/radical-ion dimerisation with rate determining coupling whereas the value is 58.3 mV for the radical-ion/substrate coupling with rate determining coupling[6], and influence from heterogeneous kinetics or deviations from purely kinetic conditions will tend to widen and not narrow the peak. Based on the radical-ion/radical-ion mechanism with rate determining coupling the second order rate constants for the coupling step may be determined for the two substrates from the $v_{0.6}$ values and the corresponding theoretical data (see the Experimental section). The rate constants are given in Table 3.



Scheme 1

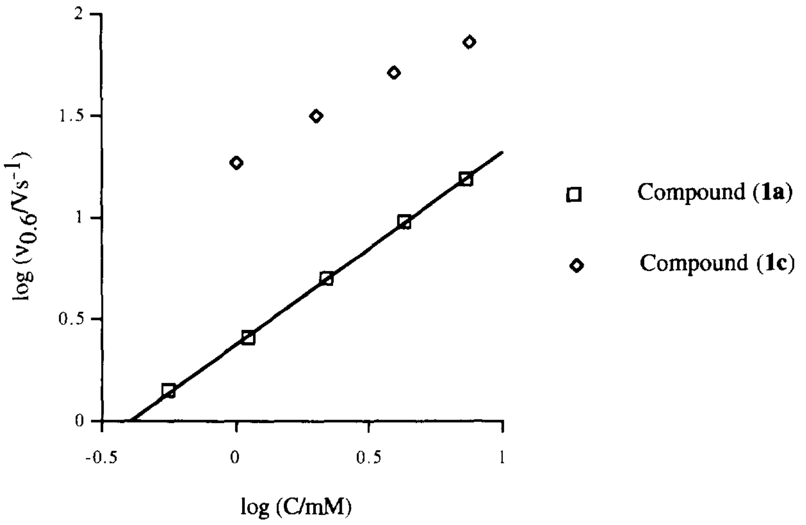
Table 3. Peak widths and second order rate constants[a]

Ester	$E_{p/2}-E_p$/mV,[b]	$E_{p/2}-E_p$/mV,[b]	$k/M^{-1}s^{-1}$ [c]
	$v = 1\ Vs^{-1}$	$v = 0.1\ Vs^{-1}$	
Methyl (**1a**)	45.0	43.6	$(9.7 \pm 0.4) \times 10^3$
4-t-butylphenyl (**1c**)	46.7	41.7	$(7.4 \pm 0.8) \times 10^4$

a. DMF (0.1 M Et_4NBr), Hg/Pt-electrode, $E^o-E_{SW} = 0.2$ V, t = 27° C. b. C^o(**1a**) = 7 mM, C^o(**1c**) = 8 mM. c. Second order rate constant calculated from the $v_{0.6}$-values (see text) and theoretical data for the radical-anion/radical-anion dimerisatin mechanism with rate determining coupling. C^o(**1a**) = 0.5, 1, 2, 4 and 7 mM. C^o(**1c**) = 1 and 2 mM

The logarithm of the rate constants for radical-anion/radical-anion coupling in the cinnamate series are linearly related[4] to the E^0 values; the more easily reduced substrates are the more reactive. Similar relations have been found for other radical-ion/radical-ion coupling reactions[7] and this trend is displayed also for the two cyclohex-1-enecarboxylates (**1a**) and (**1c**) (Tables 2 and 3).

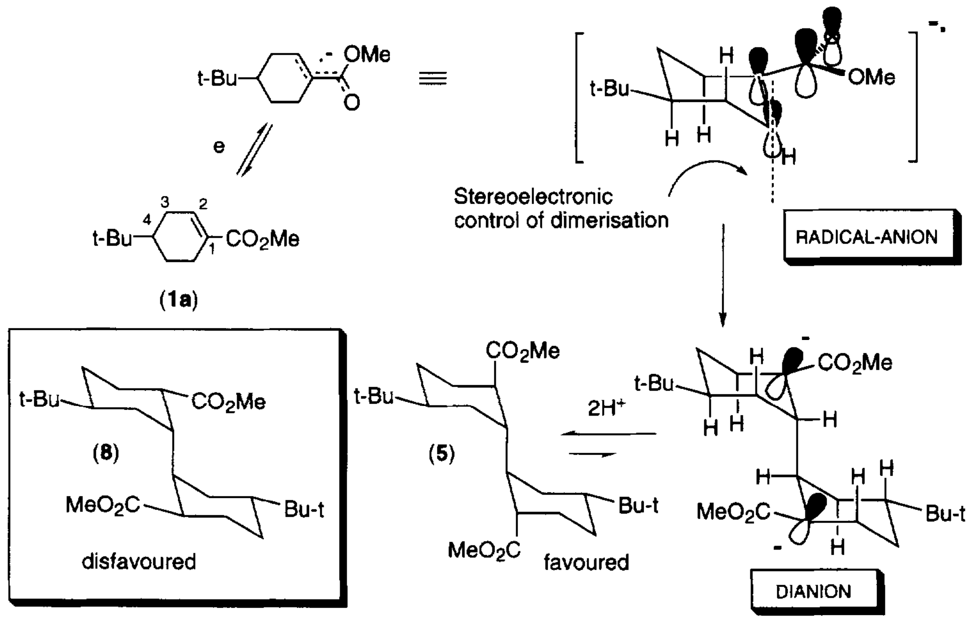
Figure 2. Reaction order plots



Force Field Calculations. - Stereoelectronic control dictates that the π-radical-anions involved will combine orthogonally and therefore the axial coupling of the cyclohexyl rings is to be expected. The dimeric dianion so formed is converted into the product (**5**) by protonation. Force-field calculations (see Experimental Section) on structure (**5**) and the isomer with two equatorial methoxycarbonyl groups (**8**) indicate that (**5**) is the more stable by *ca.* 3.5 kcal mol^{-1}. Because isomers with equatorial substituents are usually the more stable in substituted cyclohexane systems the origin of this reversal in stabilities needs comment.

The axially-linked bicyclohexyl system turns out to be very resistant to rotation about the axial C-C bond, e.g. C(2)-C(2') in structure (**5**). According to the programme used the barrier to such rotation is > 4000 kcal mol^{-1} and the conformation of (**5**) as written, and as determined for the solid state by X-ray crystallography, is in a deep energy well. Consequently it was assumed that all relevant conformations will have the bicyclohexyl skeleton fixed as in (**5**). The effects of minimising the conformational energies of the CO_2Me groups in equatorial *vs.* axial positions were then examined and comparison of the minimum energy conformers so obtained gave the overall figure of 3.5 kcal mol^{-1} referred to above. The biggest difference, on calculated total energies of 39.65 kcal mol^{-1}, for (**5**) and 43.13 kcal mol^{-1}, for (**8**) are in the contributions from bending strain (8.64 and 12.51 respectively). The origin of the extra strain in (**8**) appears to be reflected in the high barrier to rotation calculated for the equatorial *vs.* axial CO_2Me groups. Figures for rotation from the minimum energy conformations of the equatorial and axial CO_2Me groups, i.e. around the C(1)-CO bonds, are 1700 kcal mol^{-1} and 35.2 kcal mol^{-1} respectively.

Conclusions. - The results obtained for (**1a**) on preparative, coulometric and voltammetric time-scales all support the conclusion that the radical-anions generated from methyl 4-tert-butylcyclohex-1-enecarboxylate (**1a**) combine orthogonally in the slow step of the 1F EHD reaction leading, under kinetic control, to the relatively strained axial C-C coupling. Subsequent protonation is thermodynamically controlled and leads to the major product (**5**) in which the methoxycarbonyl groups are also axial. This is illustrated in Scheme 2.



Scheme 2

The cleavage of the benzyl group in the reduction of (**1b**) is relatively easy to explain. There is good literature precedent[8] for such cleavage of benzyl esters of carboxylic acids and the reaction has been put to synthetic use in the deprotection[9] of benzyl-protected amino acids. The driving force for the reaction, which causes cleavage of the initially formed radical-anion to be faster than dimerisation (or protonation), is stabilisation of both fragments (the benzyl radical and the carboxylate anion). The cleavage reaction consumes 2 F because the benzyl radical is further reduced to the corresponding carbanion which protonates to give toluene. In our case toluene would have been lost during work-up and no attempt was made to isolate it.

For reduction of (**1c**) there is conflict between on the one hand the kinetic results obtained on a voltammetric time-scale and the clean 1 F reduction determined by controlled potential coulometry, and on the other hand the observation on a preparative time-scale of competing 2 F hydrogenation and hydrolysis. Although both the coulometric and preparative experiments are steady state techniques there are significant differences in conditions. The coulometry is carried out at on small amounts of material and in a cell with a high electrode surface area to volume ratio. Complete electrolysis during coulometry takes a much shorter time than it does in the larger scale experiments. Also, the quality of the solvent differs; the coulometric experiments were run with DMF purified and dried as for cyclic voltammetry whereas preparative experiments were run using reagent grade DMF .

Experimental: *Starting materials.*- 4-t-Butylcyclohex-1-enecarboxylic acid was prepared by Birch reduction of 4-t-butylbenzoic acid as reported[10]. Esterification was achieved by standard methods. Treatment with methanol in the presence of hydrochloric acid gave *methyl 4-t-butylcyclohex-1-enecarboxylate* (**1a**) in 97% yield; bp 72-74° C/0.2 mm., ν_{max}/cm^{-1} 1715 (C=O), 1655 (C=C); δ_H, 0.9 (9H, s, t-Bu), 1.0-2.7 (7H, ring hydrogens), 3.7 (3H, s, CO_2CH_3), 7.0 (1H, m, C=CH). *Benzyl 4-t-butylcyclohex-1-enecarboxylate* (**1b**) was obtained by conversion into the acid chloride with thionyl chloride followed by treatment with benzyl alcohol. The ester was purified by distillation under reduced pressure. Yield 68%, bp 178-182° C/1.6 mm, ν_{max}/cm^{-1} 1714 (C=O), 1653 (C=C); δ_H, 0.9 (9H, s, t-Bu), 1.0-2.7 (7H, ring hydrogens), 5.15 (2H, s, Ar**CH**$_2$), 7.03 (1H, m, C=**CH**), 7.35 (5H, s, C_6H_5); m/z 272.178 (M^+ 16.0%, $C_{18}H_{24}O_2$ requires 272.177), 165.1 (24%), 91.1 (100%). For *4-t-butylphenyl 4-t-butylcyclohex-1-enecarboxylate* (**1c**) a mixture of the phenol and acid were treated with $POCl_3$ and after aqueous work-up the crude ester was recrystallised from ethanol. Yield 76%, mp 115-117° C, ν_{max}/cm^{-1} 1721 (C=O), 1649 (C=C); δ_H, 0.89 (9H, s, t-Bu), 1.35 (10H, s, 1ring hydrogen plus t-Bu), 1.65-2.85 (6H, br, ring hydrogens), 7.0 (2H, d, 3-H and 5-H of ArH), 7.2 (1H, m, C=**CH**), 7.4 (2H, d, 2-H and 6-H of Ar**H**); m/z 314.223 (M^+ 12.8%, $C_{21}H_{30}O_2$ requires 314.224), 165.1 (100%).

Electrochemical experiments.- For preparative electrolysis the methods, equipment and cell have been described[1]. The procedure is typified by the reduction of methyl 4-t-butylcyclohex-1-enecarboxylate (**1a**). The ester (**1a**, 0.8g, 0.004 mol), in DMF-Et_4NBr (0.1M), was reduced at a mercury pool cathode in a two-compartment cell with a microporous polypropylene separator (Celgard 2500, Hoechst-Celanese). The cathode potential was -2.18 V (*vs.* Ag/AgBr) and reaction continued until 1.08 F mol^{-1} had passed. The catholyte was quenched in ice-water (300g), neutralised, and the crude organic product extracted into ether. Subsequent drying and evaporation gave a mixture of products (0.77g, *ca.* 96%). The *hydrodimer* (**5**) crystallised from a methanol solution of the crude product (yield 36%); mp 186-187° C; δ_H, 0.8 (18H, s, 2xt-Bu), 1.16 (6H,br), 1.6 (6H, br), 2.03 (1H, br), 2.08 (1H, br), 2.44 (2H, s), 2.59 (2H, br), 3.7 (6H, s, 2xCO_2**CH**$_3$); δ_C, 23.0, 24.0, 25.5 (3xCH_2, C-4, C-5, C-8), 27.3 (C-1), 32.35 (C-3), 33.4, 40.1, 40.8 (3xCH, C-2, C-6, C-7), 51.7 (C-10), 176.3 (C-9); m/z 394.308 (M^+ 41.7%, $C_{24}H_{42}O_4$ requires 394.308), 362.3 (33%), 277.2 (56%), 165.1 (13%), 57.1 (100%); Found: C, 72.85%, H, 10.61% ($C_{24}H_{42}O_4$ requires 73.10% and 10.66%).

Electrodes, cells and instrumentation. - For the kinetic measurements the electrodes, cells and instrumentation, together with procedures for measurement and data handling for derivative cyclic voltammetry and linear sweep voltammetry, were as described[11, 12] previously.

Determination of E^o values. - For (**1a**) and (**1c**) these were determined as the midpoint between the potential of the reduction peak and the potential of the corresponding oxidation peak. Anthracene was used as an external reference, i.e. the E^o-value for anthracene was determined against the reference electrode used for the esters and converted into the value *vs.* SCE using E^o = -1.92 V (*vs* SCE) for anthracene[13]. The values given in Table 2 are averages of at least 3 sets of measurements, and the relative precision of the values is *ca.* ±3 mV.

Kinetic measurements. - The values of $\nu_{0.6}$ determined at the different concentrations of (**1a**) and (**1c**) were used to determine the combined reaction order in substrate and radical-anion as described in the main text and demonstrated in Figure 2. For each concentration the $v_{0.6}$ value used for determination of the reaction order was converted into a second-order rate constant using theoretical data (obtained by digital simulation, as described in ref. 4) for the radical-anion/radical-anion dimerisation mechanism with rate-determining coupling (see text). The average of the rate constants, k, obtained for **(1a)** is given in Table 3. The reaction-order plot for **(1c)** was curved (Figure 2) and consequently the rate constant for **(1c)** was calculated from data for the two lowest concentrations of substrate; this data was judged to represent the "cleanest second-order" reaction.

Force-field Calculations.- The programme used was PCMODEL V 5.0 (Serena Software, Bloomington, Indiana, USA).

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