Homolytic dissociation of 1-substituted cyclohexa-2,5-diene-1-carboxylic acids: an EPR spectroscopic study of chain propagation †

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Hydrogen abstraction from 1-substituted cyclohexa-2,5-diene-1-carboxylic acids containing linear, branched and cyclic alkyl substituents, as well as allyl, propargyl (prop-2-ynyl), cyanomethyl and benzyl substituents, has been studied by EPR spectroscopy. For each carboxylic acid, EPR spectra of the corresponding cyclohexadienyl radicals were observed at lower temperatures, followed by spectra due to ejected carbon-centred radicals at higher temperatures. Rate constants, for release of the carbon-centred radicals from the cyclohexadienyl radicals, were determined from radical concentration measurements for the above range of substituents. The rate of cyclohexadienyl radical dissociation increased with branching in the 1-alkyl substituent and with electron delocalisation in the ejected carbon-centred radical; 3,5- and 2,6-dimethyl-substitution of the cyclohexadienyl ring led to reductions in the dissociation rate constants. Rate data for abstraction of bisallylic hydrogens from the cyclohexadienyl acids were also obtained for ethyl, *n*-propyl and isopropyl radicals. These results indicated a sharp drop in the rate of hydrogen abstraction as the degree of branching in the attacking radical increased. Small decreases in the hydrogen abstraction rate constants were observed for cyclohexadienes containing CO_2R substituents.

Introduction

1-Substituted cyclohexa-2,5-diene-1-carboxylic acids **1** are a new "pro-aromatic" class of potentially 'clean' reagents for free radical generation. Hydrogen abstraction takes place selectively from the bisallylic sites of **1** to generate delocalised cyclohexadienyl radicals **2** that dissociate by C–C bond scission at moderate temperatures to produce benzoic acid and an alkyl radical. The released alkyl radical may cyclise, if it is suitably unsaturated, or react with an added alkene (Z), and hence be transformed to a new C-centred radical RZ$^{\bullet}$ that can abstract hydrogen from more **1**. This constitutes a chain process that has potential synthetic applications.[1,2] The advantages of these carboxylic acids over organotin reagents, apart from the safety aspect, are that benzoic acid, which can easily be removed by an alkaline extraction, is a comparatively benign co-product, and that the H-transfer step is slower. Respectable yields of alkylated olefins were obtained for secondary, tertiary and delocalised alkyl radicals;[2] however, end product analyses showed that competition from an alternative β-scission of radical **2** to afford the hydroxyformyl radical **3** (formate radical) and an alkylbenzene (RPh) was significant for primary substituents R.

Kinetic information on the hydrogen transfer (k_H) and dissociation (k_d) steps would be very desirable as a tool for effective synthetic planning. A preliminary communication outlined the EPR spectroscopic method we developed for determining the rate constants for the chain propagation steps.[3] We now report our study of the effect of differing substituents R, and of alkyl substituents in the ring, on the kinetics of the dissociation and on the hydrogen transfer steps.

† Electronic supplementary information (ESI) available: measured radical concentrations and the corresponding rate constants at each temperature for each cyclohexadienyl acid. Computed heats of formation and selected geometric parameters are also available for each cyclohexadienyl radical and the species they dissociate to. For direct electronic access see http://www.rsc.org/suppdata/p2/b1/b104859g/

Results and discussion

Birch reduction–alkylation of benzoic acid affords 1-alkylcyclohexa-2,5-dienecarboxylic acids of type **1** in moderate to good yields.[4–9] The 1-alkyl acids **1a**–**l** were obtained in various yields by means of a modification of the procedure due originally to Birch.[4] The method was most efficient for primary and secondary alkyl substituents and particularly with benzyl chloride, allyl and propargyl bromides. Alkylations with cyanomethyl iodide, bromide and chloride were all examined in the synthesis of the cyanomethyl acid **1k**; yields, however, were moderate in all cases. Attempts to prepare an alkoxycarbonylmethyl acid by similar methodology using esters of haloacetic acids were not successful. Alkylation following Birch reduction in liquid ammonia was much more difficult with sterically hindered organohalides and, as described previously,[2] the pure *tert*-butyl acid **1h** could only be obtained in low yield. 1-Isopropyl- and 1-isobutyl-3,5-dimethylcyclohexa-2,5-diene-1-carboxylic acids **5a**,**b** were prepared in a similar way starting with 3,5-dimethylbenzoic acid. The 1-*n*-propyl-2,6-dimethylcyclohexa-2,5-diene-1-carboxylic acid **6** was made from the corresponding substituted benzoic acid. 1-Benzyl-2,3,4,5,6-pentadeuteriocyclohexa-2,5-diene-1-carboxylic acid **8** was obtained by use of pentadeuteriobenzoic acid.

Kinetic EPR spectroscopic study of the dissociation of 1-substituted cyclohexadienyl radicals (2)

Photolyses of solutions of **1** (R = *n*-alkyl) and di-*tert*-butyl peroxide (DTBP) in *tert*-butylbenzene solvent, without any additives, gave rise to *t*-BuOH, benzoic acid and RH as the main products, accompanied by minor amounts of alkylbenzenes RPh from the undesired fragmentation. The mechanism and propagation steps under these conditions were as shown in Scheme 1, except that no alkene (Z) was present, and chain termination was by bimolecular reactions of **2** and R$^{\bullet}$ ($2k_t$). Using the steady state approximation eqn. (1) may be derived,

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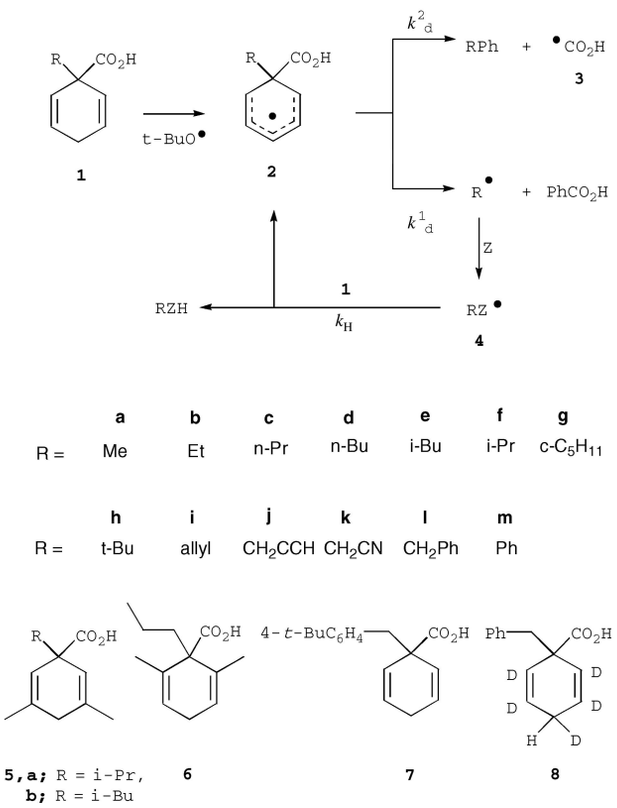
Table 1 9GHz EPR parameters for 1-substituted cyclohexadienyl-1-carboxylic acid radicals **2** in solution [a]

Structure No.	R	T/K	g-factor [b]	a(H^4)	a($H^{2,6}$)	a($H^{3,5}$)	a(H^{other})
2a	Me	220 [c]	—	13.2	9.2	2.7	—
2b	Et	295 [d]	2.0026	13.1	9.1	2.7	0.30(2H)
2c	*n*-Pr	270 [d]	—	13.2	9.1	2.7	0.32(4H)
2d	*n*-Bu	245 [d]	—	13.2	9.1	2.6	—
2f	*i*-Pr	220 [c]	2.0027	13.3	9.2	2.8	—
2g	*c*-C_5H_{11}	215 [c]	—	13.7	9.2	2.8	—
2h	*t*-Bu	145 [e]	2.0027	13.3	9.2	2.9	—
2i	Allyl	160 [e]	2.0026	13.2	9.2	2.7	—
2j	CH_2CCH	170 [f]	2.0026	13.3	9.2	2.7	1.3(1H)
2k	CH_2CN	245 [g]	—	13.3	9.2	2.7	—
2l	CH_2Ph	150 [f]	—	13.1	9.1	2.6	1.3(1H)
2m	Ph	220 [c]	—	13.4	9.3	2.7	—
5a(-H)$^\bullet$	*i*-Pr	240 [c]	2.0027	13.4	8.8	—	2.5(6H)
5b(-H)$^\bullet$	*i*-Bu	290 [d]	—	13.1	8.7	—	2.4(6H)
6(-H)$^\bullet$	*n*-Pr	340 [d]	—	12.8	—	2.6	8.7(6H)

[a] Hfs in G (10 G = 1.0 mT). [b] Non-quoted g-factors = 2.003 ± 0.001. [c] Solvent PhBu-*t*. [d] Solvent neat DTBP. [e] Solvent cyclopropane + *ca.* 20% *t*-BuPh. [f] Solvent cyclopropane. [g] Solvent *t*-BuPh + trace MeOH.



Scheme 1

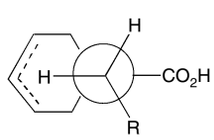
provided that the alternative β-scission to the hydroxyformyl radical (**3**) [k^2_d] is negligible. For low concentrations of acids **1**, or when k_H is small, eqn. (1) simplifies to the usual expression [eqn. (2)].[10]

$$k^1_d/2k_t + k_H/2k_t\{[\mathbf{1}][R^\bullet]/[\mathbf{2}]\} = [R^\bullet]^2/[\mathbf{2}] + [R^\bullet] \quad (1)$$

$$k^1_d/2k_t = [R^\bullet]^2/[\mathbf{2}] + [R^\bullet] \quad (2)$$

When solutions of individual acids **1a**–**m**, **5**–**8** and DTBP in an appropriate solvent were photolysed in the resonant cavity of an EPR spectrometer the corresponding cyclohexadienyl radicals **2** were generated by hydrogen abstraction by *tert*-butoxyl radicals and observed over specific temperature ranges. The hyperfine splittings (hfs) and g-factors for each radical are recorded in Table 1.

These hfs were similar to those of other cyclohexadienyl radicals[11] and were not very sensitive to the nature of the 1-substituent. In a few cases small, long-range hfs from hydrogen atoms of the 1-substituents were resolved and, interestingly, in the case of the low temperature spectra of the propargyl- **2j** and benzyl-substituted radicals **2l**, only one of the two available methylene hydrogens coupled with the unpaired electron. At these low temperatures the radicals adopted a preferred conformation about the ring–CH_2 bond (**9**) in which only one H-atom was favourably placed for interaction with the SOMO. At higher temperatures the rate of internal rotation about this bond became fast on the EPR timescale and the lines broadened. Although the spectral lines were sharper at still higher temperatures, the average hfs of the now equivalent methylene hydrogens were too small to resolve.



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For each carboxylic acid, EPR spectra were recorded over an appropriate range of temperatures to test for alkyl radical production. For acids **1a** and **1m** only the corresponding cyclohexadienyl radical **2** could be observed up to 360 K and, as expected, neither $CH_3^\bullet$ nor $Ph^\bullet$ radical production was observed. For all the other acids, however, the spectrum due to radical **2** weakened in some temperature range and was gradually replaced by that of the corresponding alkyl radical $R^\bullet$. On lowering the temperature, the inverse process was observed, and the spectrum of **2** was restored. The EPR spectral parameters of the released alkyl and substituted-alkyl radicals were all essentially identical to those given in the literature. These observations indicated that the chain propagation rate constants might be determined from EPR spectral measurements of the steady state radical concentrations by use of eqns. (1) or (2).

The importance of the alternative, undesired β-scission (k^2_d) producing the hydroxyformyl radical **3**, was appraised from the relative yields of alkylbenzene and benzoic acid determined by GC and NMR. The measured [$PhCO_2H$]/[RPh] ratios, from photolyses in DTBP at 300 K, were found to be *ca.* 20 and *ca.* 13 for **1b** and **1c** respectively, and no alkylbenzenes could be detected during photolyses of **1f**–**m**. It follows that diversion of cyclohexadienyl radicals **2** down this reaction channel can safely be neglected.

The concentrations of **2** and $R^\bullet$ were determined by the EPR method[12] from photolyses of known concentrations of **1b**,**c** and **1f** with DTBP, either neat or in *tert*-butylbenzene, directly in the EPR resonant cavity. From measurements of [$R^\bullet$] and [**2**] at two (or more) different acid concentrations [**1**] $k^1_d/2k_t$ and $k_H/2k_t$

Table 2 Kinetic data for release of C-centred radicals (k^1_d, E^1_d) from cyclohexadienyl radicals **2**

Acid	Delocalised radical	Released radical	$k^1_d/10^3$ s^{-1} (300 K)	log A_d/s^{-1}	$^aE^1_d$/kcal mol^{-1}	$^bE^1_d$/kcal mol^{-1}
1a	**2a**	Me$^\bullet$	≤0.001	—	—	≥18
1b	**2b**	Et$^\bullet$	0.040	16.9	21.3	15.0
1c	**2c**	*n*-Pr$^\bullet$	0.022	13.00	16.01	16.00
1f	**2f**	*i*-Pr$^\bullet$	0.96	9.97	10.14	13.75
1g	**2g**	*c*-$C_5H_{11}^\bullet$	1.34	11.24	11.21	13.55
1h	**2h**	*t*-Bu$^\bullet$	1070	12.19	8.85	9.57
1i	**2i**	Allyl	4450	12.71	8.45	8.72
1j	**2j**	$HCCCH_2^\bullet$	22.6	11.22	10.14	11.87
1k	**2k**	$NCCH_2^\bullet$	1.54	10.05	9.92	13.47
8	**2l**^{c}	$PhCH_2^\bullet$	1290	9.88	6.90	9.46
5a	**5a(-H)**$^\bullet$	*i*-Pr$^\bullet$	0.28	12.30	13.61	14.48
5b	**5b(-H)**$^\bullet$	$Me_2CHCH_2^\bullet$	0.53	14.5	16.2	14.11

^{a} 1 cal = 4.18 J. ^{b} Activation energies derived assuming all log (A_d/s^{-1}) values = 13.0 s^{-1}. ^{c} Pentadeuteriated isotopomer.

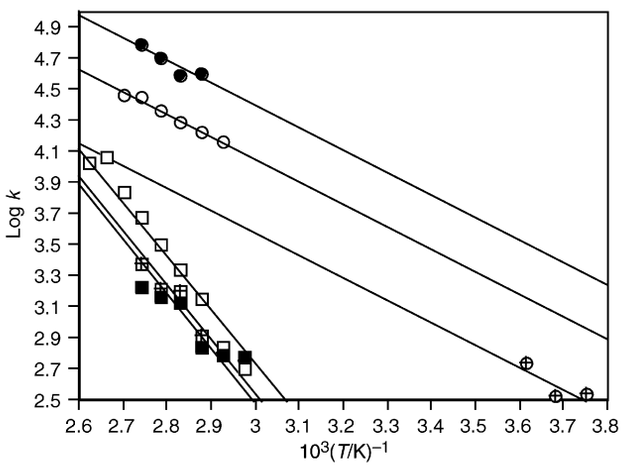

Fig. 1 Arrhenius plots of dissociation k^1_d and H-abstraction k_H rate constants from reactions of ethyl (**1b**), *n*-propyl (**1c**) and isopropyl (**1f**) acids. Filled circles; k_H for *n*-propyl radical abstracting from **1c**. Open circles; k_H for ethyl radical abstracting from **1b**. Crossed circles; k_H for isopropyl radical abstracting from **1f**. Open squares; raw k_d data for 4 mg acid sample. Crossed squares; raw k_d data for 0.3 mg acid sample. Filled squares; k_d corrected according to eqn. (1).

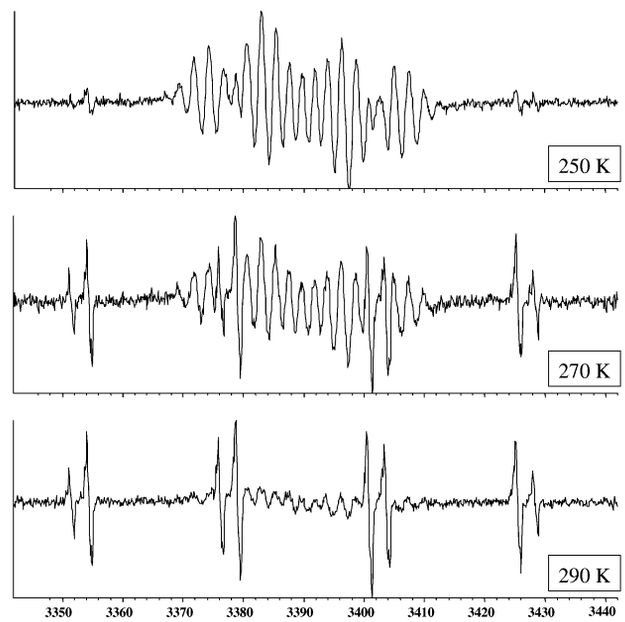

Fig. 2 9 GHz EPR spectra of radicals obtained on H-abstraction from 3,5-dimethyl-1-isopropylcyclohexa-2,5-dienecarboxylic acid (**5a**) in *tert*-butylbenzene solution. The upper spectrum at 250 K shows mainly the 3,5-dimethylcyclohexadienyl radical and the lower spectrum at 290 K shows mainly the ejected isopropyl radical (central region).

were obtained. Satisfactory solutions were obtained in this way for the two primary radicals Et$^\bullet$ and *n*-Pr$^\bullet$ (Table 2). Fig. 1 shows Arrhenius plots of the rate constants obtained for the *n*-propyl-substituted acid **1c**. The open squares and crossed squares show the raw data for two concentrations of **1c** plotted according to eqn. (2) and the filled squares show the corrected k^1_d data after use of eqn. (1) (see below).

For the other acids **1g**–**l** containing tertiary or stabilised radicals the [R$^\bullet$]/[**2**] ratios were effectively independent of the initial acid concentration, to within the limits of the experimental measurements. The rate constants for H-abstraction by *t*-Bu$^\bullet$, allyl, propargyl, cyanomethyl and benzyl radicals from **1** were therefore too small for measurement by this technique. However, the simplified eqn. (2) could then be used, in conjunction with the radical concentrations, to measure the dissociation rate constants k^1_d. For the acids **1g**–**j** and **5a**,**b**, radical generation was smooth and the absolute radical concentrations were readily obtained by double integration of suitable peaks from the two radicals. Fig. 2 shows an example of the quality of the data obtained from the carboxylic acid **5a**.

The rate constants obtained by use of eqn. (1), or eqn. (2) in conjunction with the well established $2k_t$ value of Fischer and co-workers,[13] corrected for changes in solvent viscosity as described previously,[14] are given in Table 2 for 300 K.

The cyanomethyl carboxylic acid **1k** was poorly soluble in *tert*-butylbenzene and therefore traces (10 μl) of methanol were added to improve spectral quality. In the case of the 1-benzyl carboxylic acid **1l** the spectrum of the released benzyl radical was complex and overlapped too extensively with the spectrum of the cyclohexadienyl radical **2l** for concentration measurements to be carried out successfully. To try and overcome this problem 1-(4-*tert*-butylbenzyl)cyclohexa-2,5-diene-1-carboxylic acid (**7**) was prepared. It was anticipated that the simpler hyperfine splitting pattern of the 4-*tert*-butylbenzyl radical would enable concentration measurements to be made. However, it was found that this acid was too poorly soluble in EPR compatible solvents for satisfactory spectra to be obtained. Instead, therefore, 1-benzyl-2,3,4,5,6-pentadeuteriocyclohexa-2,5-diene-1-carboxylic acid (**8**) was prepared and used. In this case the spectrum of the released benzyl radical was clear but that of the deuteriated cyclohexadienyl radical consisted of a single broad peak with no resolved fine structure. This spectrum overlapped with the normal, broad, central background signal present in control solutions, which had to be subtracted from the composite spectrum at each temperature. This correction procedure degraded the data to some extent and hence the kinetic data for release of benzyl are less accurate. A combined Arrhenius plot of the k^1_d values from all the acids spans a 200 K temperature range and nearly 5 orders of magnitude in k_d (Fig. 3) and demonstrates the good calibre of the data (see Supplementary Data for a complete list of rate constants at each temperature studied).† The measured

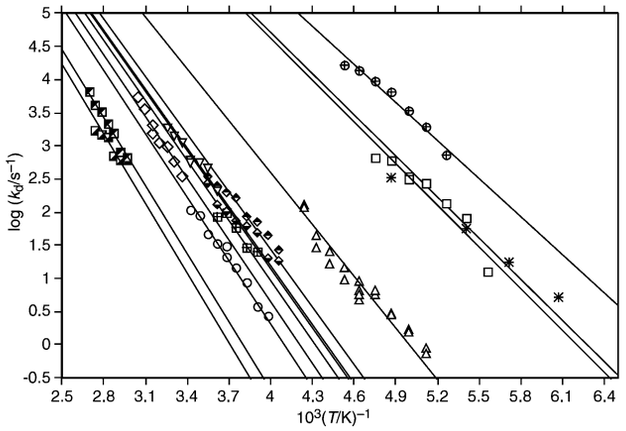

Fig. 3 Arrhenius plots of dissociation rate constants k^1_d for the range of 1-substituted (1-carboxylato)cyclohexadienyl radicals. Lines have been constrained to intersect the *y*-axis at log *A* = 13.0. Crossed circles; allyl-substituted radical **2i**. Open squares; *tert*-butyl-substituted radical **2h**. Stars; benzyl-substituted radical from acid **8**. Triangles apex-up; propargyl-substituted radical **2j**. Diamonds top and bottom filled; cyanomethyl-substituted radical **2k**. Triangles apex-down; cyclopentyl-substituted radical **2g**. Crossed squares; isopropyl-substituted radical **2f**. Open diamonds; isobutyl radical from acid **5b**. Open circles; isopropyl radical from acid **5a**. Squares filled left; ethyl-substituted radical **2b**. Squares filled right; *n*-propyl-substituted radical **2c**.

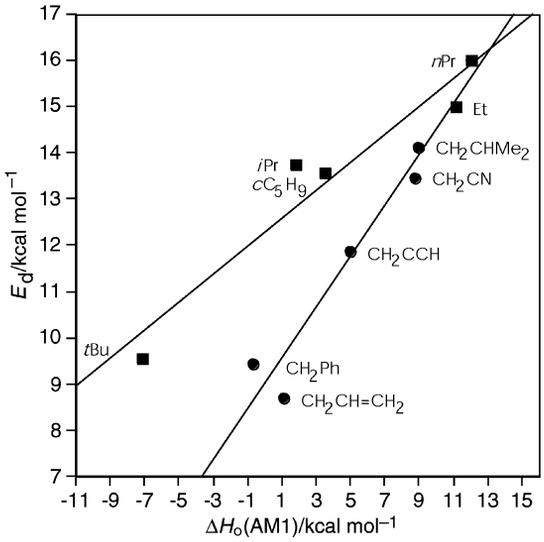

Fig. 4 Plot of the experimental activation energies for the cyclohexadienyl dissociations $^bE_d^1$ against the dissociation enthalpies computed using the AM1 method.

Arrhenius pre-exponential factors covered a considerable range (Table 2). The temperature ranges of individual experiments were quite short (40 ± 10 K) and hence accurate *A*-factors could not be obtained with this technique because of the long extrapolations involved. Deviations from the 'normal' value for unimolecular processes [log (A/s^{-1}) = 13] were not gross, hence it is probable that the true *A*-factors are close to this for all the dissociations. The final column of Table 2 shows the activation energies that correspond to assumed log (A/s^{-1}) factors of 13.

The experimental k^1_d values confirmed that the ease of fragmentation of the cyclohexadienyl radicals **2** increased dramatically with the degree of branching of the released alkyl radical. In fact, release of *t*-Bu$^\bullet$ was nearly 5 orders of magnitude faster than primary alkyl radical production at 300 K. Similarly, comparison of the data for dissociation of **2** to allyl or benzyl radicals, with that for dissociation to primary radicals, indicated that electron delocalisation in the released radical also led to sharply increased dissociation rates. Both the thermodynamic stabilisation of the released alkyl radical and steric strain in the initial cyclohexadienyl radical appeared to be important in controlling the fragmentation rates. 3,5-Dimethyl substitution in the cyclohexadienyl ring caused a reduction in k_d of about a factor of 3 for dissociation to *i*-Pr$^\bullet$. The effect of 2,6-dimethyl substitution was also investigated by means of the *n*-propyl-2,6-dimethyl acid **6**. For the unsubstituted acid (**1c**) dissociation of radical **2c** took place, under EPR conditions, in the temperature range 340–375 K. Surprisingly, however, for **6** only the 2,6-dimethylcyclohexadienyl radical could be observed over this whole temperature range, *i.e.* dissociation required higher temperatures, outside the accessible range. It follows that k_d for this acid radical is significantly smaller. In the case of 2,6-dimethyl substitution some steric assistance to dissociation might have been expected. However, the experimental result shows that this must have been minor and was outweighed by the additional stabilisation of the cyclohexadienyl radical due to methyl substitution. This latter effect would be expected to increase the activation energy of the dissociation step, as observed.

To probe the controlling influences underlying these dissociations, the structures and energies of a range of substituted cyclohexadienyl radicals **2**, and the products of both their fragmentation modes, were computed using the AM1 and PM3 semi-empirical SCF MO methods.[15,16] All structures were fully optimised with respect to all geometric variables. The RHF and UHF options were used for closed shell stable molecules and open shell radicals respectively (heats of formation of individual species, together with selected structural parameters, are given in the Supplementary Data).† The overall dissociation enthalpies are listed in Table 3. The rings of radicals **2** were all computed (AM1) to be planar with ∠C2–C1–C6 in the range 112.7 ± 0.7°, *r*(C1–C(O)OH) in the range 1.522 ± 0.002 Å and ∠R–C1–C(O)OH in the range 108 ± 1.5°, *i.e.* structures were insensitive to the nature of the substituent R. The exception to this was the R–C1 distance, which was longest at 1.565 for R = *t*-Bu, dropping to 1.556 for R = *i*-Pr, to 1.544 for R = Et and to 1.535 Å for R = Me. For all other substituents (R) this distance was computed to be 1.546 ± 0.002 Å. The PM3 computations showed a similar trend. The lengthening of this bond with increasing size of the attached substituent gave a clear signal that frontal strain in the radicals was important.

The AM1 computed reaction enthalpies ΔH_o (Table 3) for dissociation to R$^\bullet$ and $PhCO_2H$ reduced from 33.4 kcal mol^{-1} endothermic for R = Me, with increasing branching of the substituent, to 7.2 kcal mol^{-1} exothermic for R = *t*-Bu. The computed ΔH_o values for the alternative dissociation to $^\bullet CO_2H$ and RPh were all endothermic and, apart from the larger value for the R = Me case, were comparatively insensitive to the nature of R. In agreement with experiment, the AM1 computed ΔH_o values showed that, on thermodynamic grounds, dissociation of **2** to R$^\bullet$ and $PhCO_2H$ should be favoured for all substituents (except Me). The results of the PM3 computations corresponded less well with experiment, *i.e.* they implied that dissociation to $^\bullet CO_2H$ and PhR should be favoured for R = primary alkyl, as well as Me, contrary to observation.

A plot of the AM1 computed ΔH_o values, against the experimental activation energies ($^bE_d^1$), is shown in Fig. 4. The data divide into two groups with points for primary and delocalised radicals, all of type $RCH_2^\bullet$ falling on one line, and points for branched radicals on another line. Steric effects are expected to be small for all the radicals initially attached to the cyclohexadienyl ring by CH_2 groups and hence the lower line expresses the reduction in activation energy associated with increasing resonance stabilisation of the ejected radical. For this group of radicals, unit reduction in computed dissociation enthalpy corresponded to about 0.3 unit reduction in activation energy. It is noteworthy that the largest deviation from this straight line is for the benzyl case (radical **2l**) for which the measured activation energy had the largest error limits (see above).

Table 3 Computed dissociation enthalpies (ΔH_o) for substituted cyclohexadienyl radicals **2**[a]

Cyclohexadienyl	R	ΔH_o (AM1)→ R$^\bullet$ + $PhCO_2H$	ΔH_o (AM1)→ $^\bullet CO_2H$ + PhR	ΔH_o (PM3)→ R$^\bullet$ + $PhCO_2H$	ΔH_o (PM3)→ $^\bullet CO_2H$ + PhR
2a	Me	33.4	29.0	19.0	7.6
2b	Et	11.1	15.8	9.2	7.6
2c	*n*-Pr	12.0	15.8	9.1	7.7
2e	*i*-Bu	9.0	14.4	8.9	4.3
2f	*i*-Pr	1.8	14.6	0.4	5.5
2g	*c*-C_5H_9	3.5	15.5	−0.1	5.2
2h	*t*-Bu	−7.2	13.7	−8.9	4.3
2i	Allyl	1.1	17.1	0.4	7.0
2j	CH_2CCH	4.9	15.1	5.6	7.2
2k	CH_2CN	8.8	14.5	7.8	6.5
2l	CH_2Ph	−0.6	22.8	−1.7	10.4
2	Pentadienyl	−4.5	17.3	−4.9	7.1

[a] ΔH_o values in kcal mol^{-1}.

Table 4 Kinetic data for H-abstraction from 3-^{1}R,3-^{2}R-substituted cyclohexa-2,5-dienes by radicals R$^\bullet$ in solution

R$^\bullet$	^{1}R	^{2}R	$k_H/10^5$ s^{-1} (T/K)	log (A_H/s^{-1})	E_H/kcal mol^{-1}	Ref. No.
Me$^\bullet$	H	H	1.3 (300)	9.1	5.5	17
Et$^\bullet$	H	H	0.58 (300)	—	—	17
Et$^\bullet$	HO_2C	Et	0.14 (340)	8.4	6.6	tw[c]
n-Pr$^\bullet$	HO_2C	*n*-Pr	0.4 (340)	8.7	6.6	tw[c]
Hex-5-enyl	H	H	2.3 (323)	—	—	18
Hex-5-enyl	Me	O_2CR[a]	0.8 (413)	—	—	21
Hex-5-enyl	HO_2C	R[a]	0.2 (421)	—	—	1
$C_6H_{11}$$^\bullet$[b]	H	H	5 (323)	—	—	18
i-Pr$^\bullet$	HO_2C	*i*-Pr	0.003 (272)	7.9	6.6	tw[c]
t-Bu$^\bullet$	H	H	0.094 (300)	—	—	17
Cyclopropyl	H	H	79 (298)	—	—	20
$CCl_3$$^\bullet$	H	H	0.3 (300)	—	—	17
t-BuO$^\bullet$	H	H	540 (295)	—	—	19

[a] R = hex-5-enyl. [b] 2,2-Dimethylbut-3-en-1-yl. [c] tw = this work.

Increased branching in R will cause increased frontier strain in the initial cyclohexadienyl radical **2**. In addition, however, α-methyl substitution in R will also contribute to stabilisation of the released radicals due to hyperconjugation. The upper line expresses a combination of the two effects and shows that unit reduction in computed dissociation enthalpy corresponds to *ca.* 0.2 unit reduction in activation energy. These straight lines define Evans–Polanyi relationships ($E = a\Delta H_o + C$) having a values of 0.57 (lower line) and 0.32 (upper line) (Fig. 4). Many types of radical reactions obey such relationships. The observed a value, midway between 0 and 1 for the $RCH_2^\bullet$ radicals, is indicative of a transition state roughly halfway between reactants and products. The lower a value for branched radical expulsion implies an earlier, more reactant-like, transition state. This is entirely consistent with the longer R–C1 bonds computed for these radicals and with the participation of frontier strain. The AM1 computed ΔH_o value for the dissociation of the 1-(penta-2,4-dienyl)cyclohexa-2,5-diene-1-carboxylic acid radical was −4.5 kcal mol^{-1} (Table 3), hence, by use of the above empirical Evans–Polanyi relationship, a very low activation energy of 6.4 kcal mol^{-1} is predicted. The large extent of resonance stabilisation present in the ejected pentadienyl radical leads to the prediction of very rapid dissociation [k_d/s^{-1} (calc.) = 2×10^8 at 300 K].

Hydrogen abstraction from substituted cyclohexa-2,5-dienes

The concentrations of the initial radicals **2b** and **2c** and the ejected *n*-alkyl radicals were significantly affected by major changes in the initial concentrations of **1b** and **1c** (see above and Fig. 1) and hence k_H values could be determined for H-abstraction by Et$^\bullet$ and *n*-Pr$^\bullet$ radicals. Reference to eqn. (1) indicates that plots of {[R$^\bullet$]^2/[**2**] + [R$^\bullet$]} against {[**1**][R$^\bullet$]/[**2**]} should be linear having $k_H/2k_t$ as gradient and $k^1_d/2k_t$ as intercept. Experiments with the ethyl acid (**1b**) showed that a 10-fold variation in the concentration of the acid (0.2 to 0.02 mol dm^{-3}) caused about a 3-fold variation in {[**1b**][Et$^\bullet$]/[**2b**]}. Plots of {[Et$^\bullet$]^2/[**2b**] + [Et$^\bullet$]} against {[**1b**][Et$^\bullet$]/[**2b**]} for four different acid concentrations, in the above range, were naturally rather scattered, but satisfactory gradients and intercepts were obtained at a series of temperatures (see Supplementary Data, † and Fig. 1 for an Arrhenius plot of k_H) and the kinetic parameters derived in this way are given in Tables 2 and 4. For the *n*-propyl acid **1c**, measurements were made for two acid concentrations and the resulting Arrhenius plot for k_H is also shown in Fig. 1. For dissociation of radical **2f** to the *i*-Pr$^\bullet$ radical the effect of changing the concentration of **1f** was small because of the smaller rate of H-abstraction. From experiments with **1f** concentrations of 0.013 and 0.13 mol dm^{-3}, meaningful results could only be obtained for three temperatures in the middle of the dissociation range (Fig. 1) and the error limits on these kinetic parameters are consequently high. No effect on the radical concentrations was observed for different initial concentrations of acid **1e**, indicating that, as expected, k_H is even lower for the *tert*-butyl radical.

Rate constants (k_H) were derived from eqn. (1), in conjunction with the $2k_t$ values of Fischer and co-workers,[13] and are compared in Table 4 with literature data for a range of radicals abstracting from cyclohexa-1,4-diene[17–20] and various derivatives.[1,21] The estimated log(A_H) values were normal for bimolecular reactions of this type but, as indicated above, the Arrhenius parameters were not very reliable because of the limited temperature ranges, and therefore the rate constants are of most significance. In comparing the different k_H values it should be noted that cyclohexa-1,4-diene has 4 bisallylic hydrogens in comparison with the 2 bisallylic hydrogens of the 1,1-disubstituted analogues and hence, for comparison purposes, the k_H values for the former should be reduced by a statistical

factor of 2. In accord with expectation, the *t*-BuO$^{\bullet}$ radical abstracts most rapidly, followed by the σ-type cyclopropyl radical. The C-centred alkyl radicals show a large reduction in k_H along the series Me$^{\bullet}$ > Et$^{\bullet}$ ~ *n*-Pr$^{\bullet}$ > *i*-Pr$^{\bullet}$ > *t*-Bu$^{\bullet}$. This is readily explicable because the enthalpies of the hydrogen abstraction reactions also reduce in parallel. No major effect on k_H due to 1,1-disubstitution would be expected because the substituents are comparatively remote from the site of H-abstraction and attached to the ring at sp^3 hybridised C-atoms. However, the k_H values for the substituted acids **1** are somewhat smaller, even after taking account of the statistical factor. Compare, for example, the two k_H values for Et$^{\bullet}$ or the k_H values for *i*-Pr$^{\bullet}$ and *t*-Bu$^{\bullet}$ (Table 4). This is probably not an artifact of the different experimental techniques because the product analysis "clock" method, for the primary hex-5-enyl radical abstracting from 1-alkyl-1-CO_2R-substituted cyclohexadienyl rings,[1,21] showed a similar reduction in k_H compared to unsubstituted analogues. We conclude, therefore, that this type of substitution leads to a small reduction in the rate of H-abstraction by C-centred radicals.

Conclusions

The rate of hydrogen donation by **1** to branched radicals is comparatively slow and hence radicals RZ$^{\bullet}$ formed from, for example, addition to 1,1-disubstituted alkenes, will not be able to sustain chain reactions effectively. However, transformations of R$^{\bullet}$ which produce primary radicals [or O-centred, or vinyl], for example 5-*exo*-cyclisations, should be well suited to this methodology. The most useful cyclohexadienyl acids will contain branched R (high k^1_d) which are transformed to primary radicals, vinyl radicals or O-centred radicals on cyclisation (larger k_H). In no case will premature reduction of R$^{\bullet}$ to RH be a problem because the k_H values are nearly 2 orders of magnitude less than for H-donation by organotin hydrides.[10]

Experimental

^{1}H NMR spectra were recorded at 200 or 300 MHz and ^{13}C NMR spectra at 75 MHz, in $CDCl_3$ solutions with tetramethylsilane ($\delta_H = \delta_C = 0$) as reference. Coupling constants are expressed in Hz. EI mass spectra were obtained with 70 eV ionisation and CI spectra were obtained with isobutane as target gas on a VG Autospec spectrometer. GC-MS analyses were run on a Finnigan Incos 50 quadrupole instrument coupled to a Hewlett Packard HP 5890 chromatograph fitted with a 25 m HP 17 capillary column (50% phenyl methyl silicone). For the calculation of yields from GC data, the detector response was calibrated with known amounts of authentic materials (or close analogues). EPR spectra were obtained with a Bruker EMX 10/12 spectrometer operating at 9.5 GHz with 100 kHz modulation. Samples of the substrate (0.3 to 40 mg) and di-*tert*-butyl peroxide (0.01 to 0.5 cm^3), or *tert*-butylbenzene (up to 0.5 cm^3), in 4 mm od quartz tubes, were de-aerated by bubbling nitrogen for 20 min, and photolysed in the resonant cavity by light from a 500 W super pressure mercury arc lamp. For reactions performed in cyclopropane, the solution was degassed on a vacuum line using the freeze–pump–thaw technique, and the tube was flame sealed. In all cases where spectra were obtained, hfs were assigned with the aid of computer simulations using the Bruker Simfonia software package. For kinetic measurements, carboxylic acid samples were used in 'single shot' experiments, *i.e.* new samples were prepared for each temperature and each acid concentration, to minimise sample depletion effects. Signals were double integrated using the Bruker WinEPR software and radical concentrations were calculated by reference to a known concentration of DPPH, as described previously.[14]

Ether refers to diethyl ether. THF and ether were distilled under nitrogen from sodium benzophenone ketyl prior to use. Where dry DCM was used, it was distilled over CaH_2. Petroleum ether (PE) refers to the fraction boiling between 40 and 60 °C. Other organic compounds were used as received. Column chromatography was performed using BDH silica gel (40– 63 μm).

1-Methylcyclohexa-2,5-diene-1-carboxylic acid **1a**[22] and 1-cyclopentylcyclohexa-2,5-diene-1-carboxylic acid **1g**[2] were prepared as described in the literature. 1-Isopropylcyclohexa-2,5-diene-1-carboxylic acid **1f** was available from previous work.[1]

General procedure for preparation of 1-alkylcyclohexa-2,5-diene-1-carboxylic acids

Ammonia (300 cm^3) was added to benzoic acid (5 g, 41 mmol) with careful stirring. To this, Li (0.8 g, 0.115 mol) was added portionwise until a permanent blue colour persisted, followed by dropwise addition of the alkyl halide (0.117 mol). The reaction mixture was left for 1 h whilst the NH_3 evaporated and ice was added to the remaining solid followed by dilute H_2SO_4. The product was extracted with ether (3 × 150 cm^3) and the combined ethereal extracts were dried ($MgSO_4$) and the solvent was evaporated leaving a solid which was recrystallised in light petroleum, or purified by flash chromatography.

1-Ethylcyclohexa-2,5-diene-1-carboxylic acid (1b)[7,23]

Prepared using ethyl iodide (20.8 g, 0.133 mol). Purification by distillation on a Kugelröhr apparatus gave the title compound as a colourless oil (4.32 g, 69%); δ_H 0.85 (3H, t, CH_3), 1.74 (2H, q, CH_2), 2.65 (2H, s, bisallylic-H), 5.67–5.98 (4H, m, C=CH), 8.80 (1H, br s, CO_2H); δ_C 10.2 (CH_3), 25.8 (CH_2), 27.4 (CH_2), 46.4 (C), 125.8–126.9 (4 × CH), 180.7 (CO).

1-*n*-Propylcyclohexa-2,5-diene-1-carboxylic acid (1c)[23]

Prepared from 1-iodopropane (20.9 g, 0.123 mol) in dry ether (5 cm^3). The product was purified by Kugelröhr distillation to yield the title compound (4.47 g, 66%) as a white powder; mp 47 °C (lit.[23] 46–48.5 °C); δ_H 0.89 (3H, t), 1.28 (2H, m), 1.67 (2H, m), 2.65 (2H, s), 5.69–5.98 (4H, m), 11.10 (1H, br s); δ_C 14.1 (CH_3), 17.4 (CH_2), 26.0 (CH_2), 41.7 (CH_2), 47.7 (C), 125.8, 126.7 (4 × CH), 181.6 (C=O).

1-*n*-Butylcyclohexa-2,5-diene-1-carboxylic acid (1d)

Prepared using 1-iodobutane (22.04 g, 0.122 mol). The product was successfully purified by chromatography [SiO_2, light petroleum–EtOAc (4 : 1)] to give the carboxylic acid **1d** (1.74 g, 24%) as oily, colourless crystals; mp 59 °C; δ_H 0.94 (3H, t, *J* 6, CH_3), 1.26 (4H, m, 2 × CH_2), 1.75 (2H, t, *J* 4, CH_2C), 2.68 (2H, s, allylic-H), 5.75–5.98 (4H, m, olefinic-H); δ_C 14.0 (CH_3), 19.6–26.4 (CH_2), 26.1 (CH_2), 39.3 (C), 126.0–126.8 (4 × CH), 180.5 (C=O).

1-*tert*-Butylcyclohexa-2,5-diene-1-carboxylic acid (1h)[2]

Prepared using *tert*-butyl iodide (30.01 g, 0.164 mol). The product was chromatographed [SiO_2, light petroleum–EtOAc (4 : 1)] to give **1h** (3.2 g, 22%) as colourless needles; mp 100–102 °C (lit.[2] 101 °C); δ_H 1.00 (9H, s, $C(CH_3)_3$), 2.57–2.63 (2H, s, allylic-H), 5.88–6.10 (4H, m, olefinic-H); δ_C 26.0 (3 × CH_3), 26.2 (CH_2), 38.6 (C), 52.9 (C), 125.5, 126.2 (CH), 180.4 (C=O).

1-Allylcyclohexa-2,5-diene-1-carboxylic acid (1i)[26]

Prepared from allyl bromide (14.9 g, 0.123 mol) in dry ether (5 cm^3). The product was purified by Kugelröhr distillation to yield the title compound (4.28 g, 64%) as a colourless oil; δ_H 2.46 (2H, d), 2.65 (2H, s), 5.09 (2H, d), 5.66 (1H, m), 5.69–5.98 (4H, m), 11.19 (1H, br s); δ_C 26.0 (CH_2), 44.0 (CH_2), 47.5 (C), 118.3 (CH_2), 126.1, 126.3 (4 × CH), 132.7 (CH), 180.8 (C=O).

1-(Prop-2-ynyl)cyclohexa-2,5-diene-1-carboxylic acid (1j)

Prepared using propargyl bromide (26.45 g, 0.124 mol). The

product was distilled under reduced pressure to yield the title compound as a white solid; mp 74 °C; δ_H 2.0–2.04 (1H, s, acetylenic-H), 2.57–2.63 (2H, s, allylic-H), 2.69–2.72 (2H, s, CH_2CCH), 5.81–6.02 (4H, m, olefinic-H); δ_C 26.3 (CH_2), 30.0 (CH_2), 47.3 (C, ring), 70.9 (CH), 79.7 (C, chain), 125.5, 127.2, 128.5, 129.2 (CH), 178.9 (C=O) (Found: MH^+ 163.0766, $C_{10}H_{11}O_2$ requires *MH* 163.0759).

1-(Cyanomethyl)cyclohexa-2,5-diene-1-carboxylic acid (1k)

Prepared from iodoacetonitrile (10.2 g, 0.061 mol) in dry ether (20 cm^3). The product was purified with activated charcoal and recrystallised from pentane to yield the title compound (2.93 g, 58%) as white plates; mp 110 °C; δ_H 2.76 (2H, s), 2.81 (2H, s), 5.72–6.17 (4H, m); δ_C 26.1 (CH_2), 28.3 (CH_2), 45.8 (C), 116.5 (CN), 123.4, 129.4 (CH), 177.3 (C=O); *m*/*z* (%) 163 (M^+, 6), 123 (100), 122 (29), 117 (35), 115 (47), 105 (27), 91 (35), 79 (66), 77 (55), 51 (19) (Found: M^+ 163.0638, $C_9H_9O_2N$ requires *M* 163.0633). This compound was also prepared from bromo- and chloro-acetonitrile, in similar yields.

1-Benzylcyclohexa-2,5-diene-1-carboxylic acid (1l)[24,25]

Prepared from benzoic acid (8 g, 82 mmol) and benzyl chloride (29.2 g, 0.233 mol). The product was purified by recrystallisation from pentane to yield **1l** (7.24 g, 41%) as white needles; mp 76–77 °C (lit.[24] 76–77 °C); δ_H 2.27–2.63 (2H, m, allylic-H), 3.03 (2H, s, benzylic-H), 5.80–5.90 (4H, m, olefinic-H), 7.11–7.29 (5H, m, Ar-H); δ_C 25.0 (allylic-C), 46.1 (CH_2), 48.8 (C), 126.5, 126.7, 127.9, 130.7, 136.1 (CH), 179.7 (C=O).

1-Isopropyl-3,5-dimethylcyclohexa-2,5-diene-1-carboxylic acid (5a)

Prepared from 3,5-dimethylbenzoic acid (5.0 g, 33 mmol) and 2-iodopropane (18.38 g, 0.10 mol). The product was purified by recrystallisation from pentane, yielding **5a** (4.59 g, 71%) as white needles; mp 94–95 °C; δ_H 0.79–0.82 (6H, d, *J* 6, 2 × CH_3), 1.78 (6H, s, 2 × ring CH_3), 2.0–2.23 (1H, septet, *J* 6, $CHMe_2$), 2.48 (2H, s, allylic-H), 5.45 (2H, s, olefinic-H); δ_C 17.3 (CH_3), 22.9 (ring CH_3), 36.1 ($CHMe_2$), 36.3 (allylic-C), 54.2 (C), 119.4 (CH), 134.2 (C), 181.6 (C=O) (Found: MH^+ 195.1389, $C_{12}H_{19}O_2$ requires *MH* 195.1385).

1-Isobutyl-3,5-dimethylcyclohexa-2,5-diene-1-carboxylic acid (5b)

Prepared with 1-bromo-2-methylpropane to give a white solid which was purified by recrystallisation from pentane to yield **5b** (4.20 g, 61%) as white plates; mp 71 °C; δ_H 0.75–0.89 (6H, d, *J* 6, 2 × CH_3), 1.5–1.63 (2H, d, *J* 6, CH_2), 1.8 (6H, s, ring CH_3), 2.2 (1H, m, $CHMe_2$), 2.48 (2H, s, allylic-H), 5.45 (2H, s, olefinic-H); δ_C 17.3 (2 × CH_3), 22.9 (ring CH_3), 36.1 ($CHMe_2$), 36.3 (allylic-C), 45.2 (CH_2), 54.2 (C), 119.4 (CH), 134.2 (C), 181.6 (C=O) (Found: MH^+ 209.1549, $C_{13}H_{21}O_2$ requires *MH* 209.1542).

1-*n*-Propyl-2,6-dimethylcyclohexa-2,5-diene-1-carboxylic acid (6)

Prepared from 1-iodopropane (17.0 g, 0.1 mol) and 2,6-dimethylbenzoic acid (5 g, 33 mmol). The product was successfully purified by recrystallisation from pentane, to yield the title compound as white plates (3.42 g, 53%); mp 96–97 °C; δ_H 0.91 (3H, t, *J* 6, CH_3), 0.97–1.13 (2H, m, CH_2), 1.70 (6H, s, 2 × CH_3), 1.79–1.88 (2H, m, CH_2), 2.72 (2H, s, allylic-H), 5.72 (2H, s, =CH); δ_C 14.3 (CH_3), 16.6 (CH_2), 19.3 (2 × CH_3), 27.1 (CH_2), 32.5 (CH_2), 55.2 (C), 123.5 (CH), 130.3 (C), 179.9 (C=O) (Found: MH^+ 195.1382, $C_{12}H_{19}O_2$ requires *MH* 195.1385).

1-(4-*tert*-Butylbenzyl)cyclohexa-2,5-diene-1-carboxylic acid (7)

Prepared from 4-*tert*-butylbenzyl bromide (24.9 g, 0.123 mol) in dry ether (5 cm^3). The product was purified by recrystallisation from pentane to yield the title compound (3.65 g, 33%); mp 271 °C; δ_H 1.25 (9H, s, *tert*-butyl-H), 2.14–2.40 (2H, m, allylic-H), 2.88 (2H, s, benzylic-H), 5.46–5.83 (4H, m, olefinic-H), 6.90–7.12 (4H, m, aromatic-H).

1-Benzyl-2,3,4,5,6-pentadeuteriocyclohexa-2,5-diene-1-carboxylic acid (8)

Prepared from perdeuteriobenzoic acid (5 g, 39 mmol) and benzyl chloride (15.62 g, 0.123 mol) in dry ether (5 cm^3). The product was purified by recrystallisation from pentane to yield the title compound (4.81 g, 56%) as a white solid; mp 76–77 °C; δ_H 2.32, 2.51 (2H, 2 × s, allylic-H), 3.06 (2H, br s, CH_2), 6.8–7.8 (5H, m, Ar-H), 10.34 (1H, br s, CO_2H) (Found: MH^+ 220.1390, $C_{14}H_{10}D_5O_2$ requires *MH* 220.1386).

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