Alkyl radical generation using cyclohexa-1,4-diene-3-carboxylates and 2,5-dihydrofuran-2-carboxylates

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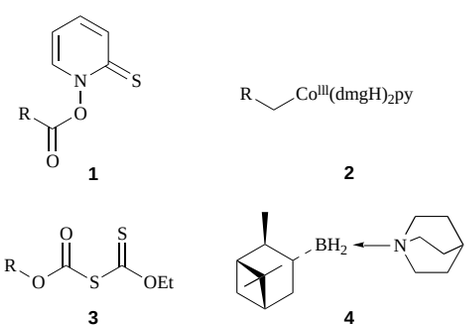
3-Methylcyclohexa-1,4-diene-3-carboxylic acid and 2-methyl-2,5-dihydrofuran-2-carboxylic acid were prepared by Birch reduction and alkylation of benzoic and furoic acid respectively and converted to alkyl esters. Cyclohexadienyl and 2,5-dihydrofuranyl radicals were generated by hydrogen abstraction and characterised by EPR spectroscopy. The esters decomposed thermally in the presence of a radical initiator to generate alkyl radicals which could be trapped with moderate efficiency by halogen donors or alkenes. Loss of methyl to afford an alkyl benzoate was an important side reaction at higher temperatures. From the thermal reaction of hex-5-enyl 3-methylcyclohexa-1,4-diene-3-carboxylate the rate constant for hydrogen abstraction from the ester by hexenyl radicals was determined to be 0.82×10^5 dm^3 mol^{-1} s^{-1} at 140 °C.

Introduction

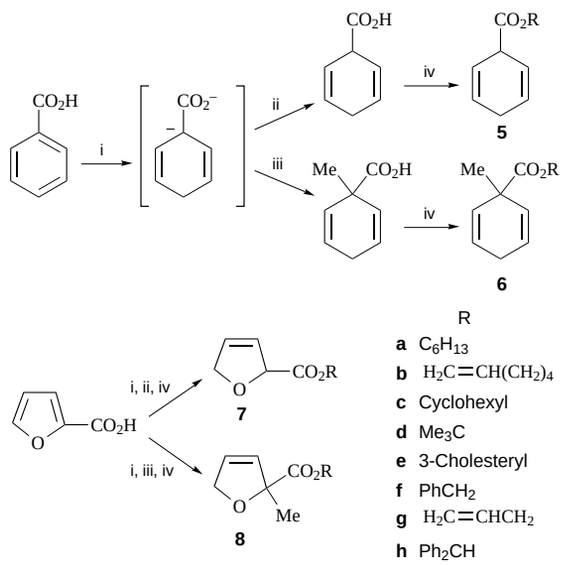
The steady increase over the last few years in the use of free radical methodology in organic synthetic procedures has emphasised the need for new types of free radical precursors which will selectively produce a specific radical at low temperatures. Organotin and organosilicon reagents continue to be popular, as do esters of thiohydroxamic acids (**1**) developed by Barton and co-workers.[1,2] Organocobalt complexes (**2**) react by



homolytic substitution at carbon followed by loss of a cobaloxime radical[3] and they are effective precursors for constructing three- and five-membered rings.[4] *S*-Alkoxycarbonyl dithiocarbonates (**3**) have recently been exploited, particularly for the formation of lactones.[5] Chiral amine-boranes, *e.g.* **4**, have been developed as polarity-reversal catalysts for enantioselective hydrogen abstraction reactions.[6] The ideal radical precursor should smoothly afford a single radical under mild experimental conditions, act as a hydrogen or halogen donor so it can be easily incorporated into chain sequences, and should not produce toxic or pungent-smelling by-products. Clearly, none of the available precursors fulfil all these criteria and hence the need for improved reagents. We have investigated the induced decomposition of esters of cyclohexa-1,4-diene-3-carboxylic acids (**5**, **6**) and esters of 2,5-dihydrofuran-2-carboxylic acids (**7**, **8**), examined the intermediate radicals by EPR spectroscopy and studied inter- and intra-molecular addition reactions of carbon-centred radicals generated therefrom. Part of this research was published as a preliminary communication.[7]

Results and discussion

Ester series were synthesised as outlined in Scheme 1. Various

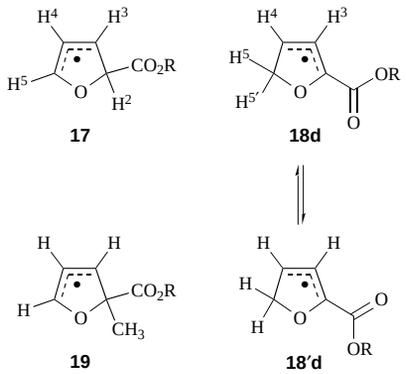


Scheme 1 i; Li/NH_3, ii; NH_4Cl, iii; MeI, iv; $COCl_2/Et_2O$ followed by ROH/py

experimental procedures for the partial reduction of aromatic carboxylic acids have been reported, employing different alkali metals, amines and different hydrogen donors.[8–10] We found, however, that best results were obtained by adding just sufficient lithium metal to a solution of benzoic or furoic acid in liquid ammonia to produce a permanent blue coloration.[11–13] Quenching with ammonium chloride gave good yields of 1,4-dihydrobenzoic acid, or 2,5-dihydrofuroic acid whereas addition of excess iodomethane afforded the 1-methyl-substituted acids in yields >90%. Conversion to the esters was straightforward, except for **6d** which was obtained by reaction of the corresponding acid chloride with lithium *tert*-butoxide.

Esters **5** to **8** contain allylic or bisallylic hydrogens which will be readily abstracted by initiator radicals to produce delocalised cyclohexadienyl radicals **10** or dihydrofuranyl radicals. Formation of the aromatic ring in **12** was expected to provide the driving force for fragmentation of **10** with initial production of an alkoxycarbonyl radical **11**, which would undergo β-scission to give an alkyl radical R$^\bullet$ together with CO_2. The alkyl radicals could take part in intra- or inter-molecular reactions (*e.g.* with substrate X) before continuing the chain by reacting with

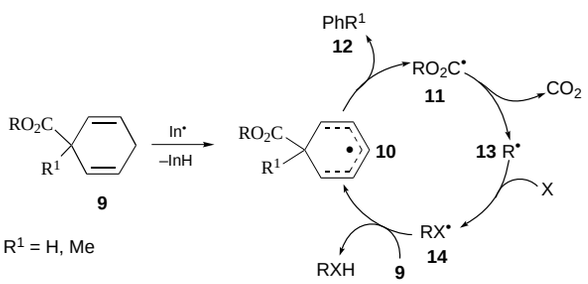
Table 1 EPR parameters for dihydrofuranyl radicals[a]



Radical	R	T/K	$a(H^2)$	$a(H^3)$	$a(H^4)$	$a(H^5)$	$a(H^{5'})$	a(other)
17c	*c*-C_6H_{11}	240	20.9	13.5	2.0	13.5	—	
18c	*c*-C_6H_{11}	240	—	2.2	10.0	32.1	32.1	
17d	Bu^t	220	34.8	13.5	2.1	13.5	—	
18d[b]	Bu^t	220	—	2.1	9.9	32.1	32.1	
18d[b]	Bu^t	220	—	2.1	9.8	31.4	31.4	
18d[c]	Bu^t	390	—	2.3	9.8	31.3	31.3	
17g	Allyl	240	34.7	13.6	2.0	13.6	—	
19c	*c*-C_6H_{11}	220	—	13.4	1.95	13.4	—	0.27(3 H)
19h	Benzyl	220	—	13.4	2.0	13.4	—	

[a] All *g*-factors = 2.003 ± 0.001, hfs/G (1 mT = 10 G) were checked by computer simulations. [b] Two conformers. [c] Average spectrum.

another molecule of ester **9** (Scheme 2). Thus, the products of the chain would be the adduct, RXH, and aromatic compound **12** or, for a suitably unsaturated R$^\bullet$, cyclisation could



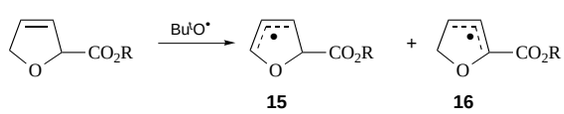
Scheme 2

be induced. A similar sequence was envisaged with chain propagation by dihydrofuranyl radicals which would fragment to afford 2-methylfuran and an alkyl radical. The aromatic by-products from these processes (toluene, 2-methylfuran) would be comparatively benign and could be easily removed because of their volatility.

In exploratory experiments, reactions of unmethylated esters **5d**, **5f**, **5g**, **7d** and **7f** with *N*-bromosuccinimide (NBS) and bromotrichloromethane were performed in an attempt to trap the released alkyl radicals as bromides, RBr. Product analysis showed that benzene or furan was formed, in agreement with the expected decarboxylation, but yields of Bu^tBr and $PhCH_2Br$ were low (≤12%). To probe the reaction in greater depth, the paramagnetic intermediates were examined by EPR spectroscopy.

EPR study of intermediates from esters 5–8

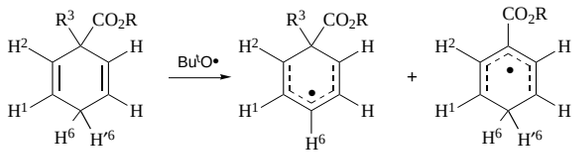
Solutions of individual esters and di-*tert*-butyl peroxide in *tert*-butylbenzene were photolysed with UV light in the microwave cavity of an EPR spectrometer at various temperatures. The unmethylated, dihydrofuranyl esters **7c**,**d** and **g** all showed the presence of the expected dihydrofuranyl radical **15** together with a second radical identified as **16**. The EPR parameters (Table 1) were similar to those previously reported[14,15] for dihydrofuranyl radicals generated by addition of various radicals



to furan. Spectra assigned to radicals of type **18** showed evidence of conformational plurality. Only for **18d** (R = Bu^t) were the signals sufficiently strong and well defined for definitive analysis. In that case, two conformers with slightly different hyperfine splittings (hfs) were distinghished at 220 K (Table 1); line broadening occurred in the range 300–390 K, above which a single average spectrum was observed. *syn*- and *anti*-Conformers about the ring-carbon to carbonyl–carbon bond have been detected by NMR spectroscopy for several furan carbaldehydes[16] and thiophene carbaldehydes.[17] Similarly, acyl radicals generated by abstraction of the formyl hydrogens from these aldehydes show two conformations in their EPR spectra.[18] It is probable therefore, that the pair of spectra obtained for **18d** represent *syn*- and *anti*-conformers, *i.e.* **18d** and **18′d**, although it was not possible to assign individual spectra to a particular conformer. A rough estimate of the barrier to interconversion of the two conformers, which were nearly equal in concentration, could be made from the coalescence temperature (*ca.* 350 K) and the low temerature difference in the hfs of H^5 [$k/s^{-1} = 6.2 \times 10^6(\Delta a)$],[19] *i.e.* k(350 K) *ca.* 4×10^6 s^{-1} which, when combined with a normal pre-exponential factor for bond rotation of 10^{13} s^{-1}, leads to an activation barrier of *ca.* 40 kJ mol^{-1}. This is close to barriers reported for bond rotation in aromatic carbaldehydes (46, 32 kJ mol^{-1})[20,21] and significantly more than the barriers for related acyl radicals (≤16 kJ mol^{-1}).[18] Not surprisingly, therefore, the barrier in radical **18** is closest to that of the model species (aldehydes) in which the atoms of the rotor have the same hybridization. It was evident that hydrogen abstraction took place unselectively at the two allylic sites.

EPR spectra obtained on hydrogen abstraction from the unmethylated ester **5d** showed that hydrogen abstraction also took place unselectively at the two bisallylic sites and both types of cyclohexadienyl radical were characterised (Table 2). In the 3-methyl series a single cyclohexadienyl radical, with parameters similar to those of related radicals reported in the literature,[22] was observed in each case (Table 2). As expected, the hfs

Table 2 EPR parameters of substituted cyclohexadienyl radicals[a]



20 **21** **22** (R^3 = H)

Radical	R	*T*/K	*a*(2 H^1)	*a*(2 H^2)	*a*(H^6)	*a*(H'^6)
22d	Bu^t	210	8.30	2.30	45.10	46.00
21d	Bu^t	210	2.70	9.20	13.70	
21a	Hexyl	220	2.70	9.20	13.20	
21b	*c*-C_6H_{11}	215	2.75	9.30	13.40	
21d	Bu^t	220	2.70	9.25	13.40	
21e	Cholesteryl	240	2.75	9.25	13.30	
21f	$PhCH_2$	220	2.70	9.20	13.25	
21g	Allyl	220	2.65	9.20	13.35	
21h	Ph_2CH	220	2.70	9.25	13.40	

[a] All *g*-factors 2.003 ± 0.001, hfs/G were checked by computer simulations.

Table 3 Product yields[a] from the reaction of cyclohexa-1,4-diene-3-carboxylates and 2,5-dihydrofuran-2-carboxylates with NBS[b]

Ester	R	Conversion of **6** or **8** (%)	PhMe or 2-MF[c]	RBr	$PhCO_2R$
6a[d]	C_6H_{13}	<50	7	3[d]	4
6c	C_6H_{11}	~75	20	20[e]	15
6d	Bu^t	~60	47	40	5
6f	$PhCH_2$	~80	nd	70 (63)[f]	10
8f	$PhCH_2$	~90	nd	63	nd[g]

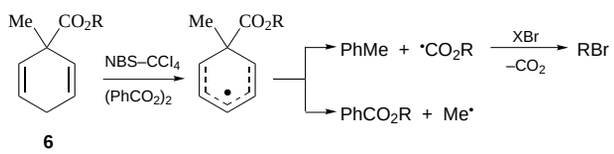
[a] mol% by GLC; nd = not determined. [b] Volatile hydrocarbon (RH) yields nd because of losses during reflux. [c] 2-Methylfuran. [d] *ca.* 10% dibromides observed. [e] *ca.* 7% dibromides observed. [f] Isolated yield. [g] $PhCO_2H$ and PhCHO also formed.

of the ring hydrogens showed little variation as the ester group changed. Spectra weakened significantly when the temperature of the cavity was raised, but were otherwise unchanged. For most of the esters, spectra were too weak for detection above *ca.* 350 K, but in no case was the spectrum of an alkyl radical $R^•$, from decarboxylative fragmentation of **21**, observed. Even strongly stabilised radicals (R = allyl, $PhCH_2$, Ph_2CH) were not detected, although the spectra of the parent cyclohexadienyl radicals appeared to weaken more quickly as the temperature was raised in these cases.

The EPR observations established that abstraction of hydrogen alpha to the carboxylate function (H^2 in **7** and H^3 in **5**) took place readily to give intermediate radicals which were incapable of fragmentation with loss of CO_2. This would drastically reduce the yield of the desired products and hence, in subsequent research, esters **6** (and **8**) with C(3) [and C(2)] blocked by a methyl group, were employed.

Reactions of 6 and 8 with halogen sources and with alkenes

Individual esters were refluxed in tetrachloromethane with NBS and a catalytic amount of lauroyl peroxide as initiator. It proved difficult to obtain complete consumption of the reactant under these conditions, particularly for esters of primary and secondary alcohols but, by adding a second equivalent of NBS, together with additional peroxide after *ca.* 10 h, and continuing the reflux, satisfactory conversions were achieved for secondary, tertiary and benzylic esters. Product analyses showed toluene (or 2-methylfuran) and alkyl bromide (RBr) but these were accompanied by small amounts of the corresponding aromatic ester ($PhCO_2R$) (Scheme 3). Product yields, which are given in Table 3, showed that the ester chain decompositions, as outlined in Scheme 2, were efficient for benzylic and tertiary esters, but poor for primary esters. The formation of the aromatic



6

Scheme 3

esters indicated that loss of a methyl radical from the intermediate cyclohexadienyl radical **10** competed to a minor extent with the main fragmentation *via* an alkoxycarbonyl radical. Experiments with cyclohexadienyl carboxylic acids containing branched 3-substituents (**9**, R = H, $R^1 = Pr^i$ or Bu^t) demonstrated that alkyl loss became the predominant process with these substituent types.[23]

The low product yields from primary and secondary esters were due partly to low reactant conversion and partly to polybromination. Under some reaction conditions alkoxycarbonyl radicals **11** can undergo a competing α-scission with formation of an alkoxyl radical and carbon monoxide,[24,25] eqn. (1).

$$R^• + CO_2 \longleftarrow RO_2C^• \longrightarrow RO^• + CO \qquad (1)$$

11

Careful search was made for alcohols derived from the alkoxyl radicals but none were detected. A number of unidentified products were present in the chromatograms obtained from reaction of the primary ester, **6a**, and therefore α-scission cannot be excluded in this case, but it is probably minor, under the present reaction conditions, for alkoxycarbonyl radicals derived from the other esters. To see if decarboxylation could be improved at higher temperatures, reaction of the cyclohexyl ester, **6c**, was carried out at 100 °C with bromoform as the halogen donor. Only low conversion was achieved, yields of toluene and bromocyclohexane were low and cyclohexyl benzoate was more important than in the NBS reaction (Table 4). Reactions were also carried out with *tert*-butyl hypochlorite and *N*-bromobis(trimethylsilyl)amine[26] (Table 4). With both reagents good conversion could be achieved, but yields of the alkyl halides were not significantly greater than in the NBS reactions, cyclohexyl benzoate was a major by-product and problems with polyhalogenation were also encountered.

The usefulness of esters **6** as radical sources for intermolecular additions was explored by means of thermally initiated reactions with acrylonitrile. The ester and alkene with di-*tert*-butyl peroxide in *tert*-butylbenzene solvent were degassed and sealed into a Pyrex tube which was heated at 140 °C for *ca.* 20 h. Product analyses (Table 5) revealed toluene, the expected

Table 4 Reactions of cyclohexyl 3-methylcyclohexa-1,4-diene-3-carboxylate (**6c**) with various halogen donors[a]

Halogen donor	Reaction conditions	Conversion (%)	PhMe	RX[b]	$PhCO_2R$[b]
$CHBr_3$	100 °C, Bu^tPh, AIBN, 60 h	*ca.* 50	20	10	25
Bu^tOCl	80 °C, CCl_4, *hv*, 5 h	*ca.* 50	20	12[c]	30
$(Me_3Si)_2NBr$	80 °C, CCl_4, AIBN, 2 h	*ca.* 75	10[d]	20[e]	25

[a] Yields in mol% by GLC. [b] R = cyclohexyl. [c] Polychlorocyclohexanes also formed. [d] Bromotoluene isomers formed. [e] Polybromocyclohexanes also formed.

Table 5 Product yields[a] from reaction of esters **6** with acrylonitrile (X) at 140 °C in Bu^tPh[b]

Ester	R	PhMe	RXH	RX_2H	RX_3H	RH	$PhCO_2R$
6a	C_6H_{13}	48	18	11	7	30	48
6c	*c*-C_6H_{11}	46	22	13	4	28	53
6d	Me_3C	49	40	17	4	31	41
6e	Ch[c]	42	—	—	—	—	—
6f	$PhCH_2$	57	26	—	—	*d*	51
6g	Allyl	24	3	3	—	*e*	20

[a] Yields in mol% by GLC. [b] Conversion of **6** was *ca.* 50% in each case. [c] Ch = cholesteryl; no Ch containing products detected. [d] RH = PhMe in this case. [e] Too volatile for accurate analysis; 5% of hexa-1,5-diene observed.

adducts (RXH) together with oligomers, the direct reduction products (RH) and aromatic esters ($PhCO_2R$). The sizeable amounts of RH formed showed that the alkyl radicals R$^\bullet$ abstracted hydrogen from ester **6** in competition with addition to acrylonitrile. The yields of adducts increased for branched alkyl radicals but, as might be expected, were lower for the delocalised benzyl and allyl radicals. The aromatic esters $PhCO_2R$ were formed in very significant yields showing that methyl radical loss from **10** competes more effectively with alkoxylcarbonyl loss at the higher temperature of the acrylonitrile experiments.

The ready formation of oligomers, and the fact that comparatively large quantities of initiators were needed to achieve complete conversion of the esters, seemed to imply that hydrogen abstraction from **6** was a relatively slow process. To assess this aspect of the mechanism, the hexenyl ester **6b** (0.91 mol dm^{-3}) was decomposed at 140 °C in *tert*-butylbenzene. The observed products, *i.e.* methylcyclopentane, hex-1-ene, cyclohexane, toluene and hex-5-enyl benzoate, were consistent with the mechanism of Scheme 2. The system was therefore used as a free radical clock to determine the rate constant of hydrogen abstraction from **6b** (k_H) by primary hexenyl radicals from the ratio of methylcyclopentane to hex-1-ene and the known concentration of **6b** {$k_H = k_c$[hex-1-ene]/[methylcyclopentane][**6b**]}. From an experiment in which the conversion of **6b** was limited to *ca*. 10% the measured ratio of hex-1-ene to methylcyclopentane was 0.010 hence, $k_H/k_c(140\ °C) = 1.3 \times 10^{-2}$ dm^3 mol^{-1}. Using the known rate constant for hex-5-enyl radical cyclisation (6.2×10^6 s^{-1} at 140 °C),[27–29] we obtain $k_H = 0.82 \times 10^5$ dm^3 mol^{-1} s^{-1} at 140 °C. Thus, k_H for **6b** lies between values reported for hydrogen abstraction from cyclohexa-1,4-diene by ethyl[30] and hex-5-enyl[31] radicals, *viz*. 0.58×10^5 (at 27 °C) and 2.3×10^5 (at 50 °C), respectively. In view of the differences in the temperatures at which the rates were measured, hydrogen abstraction from **6b** is a little slower than from cyclohexa-1,4-diene. However, most of the difference is probably statistical because **6b** has only half as many available hydrogens as cyclohexa-1,4-diene. Significantly, esters **6** transfer hydrogen to alkyl radicals *ca*. 150-fold slower than does tributyltin hydride at 140 °C.

In conclusion, hydrogen is readily abstracted from esters of type **6** (or **8**) to give cyclohexadienyl (**10**) (or dihydrofuranyl) radicals. For benzyl, tertiary alkyl and secondary alkyl substituents, radicals **10** mainly fragment to give alkyl radicals, although loss of methyl becomes increasingly important as the temperature is raised above *ca*. 80 °C, and accounts for *ca*. 50% of the decomposition by 140 °C. The released alkyl radicals can be trapped by halogen donors to give alkyl halides in moderate yields. The esters also take part in chain addition reactions with alkenes to afford moderate yields of adducts. Hydrogen transfer from **6** to carbon-centred radicals is much slower than from tributyltin hydride and therefore, in olefin alkylations, and cyclisations where direct reduction is a problem with tin reagents, the ester method will be a useful alternative.

Experimental

^{1}H NMR spectra were recorded at 200 or 300 MHz and ^{13}C NMR spectra at 75 MHz, in $CDCl_3$ solution with tetramethylsilane ($\delta_H = \delta_C = 0$) as reference. Coupling constants are expressed in Hz. Ether refers to diethyl ether. Light petroleum refers to the fraction boiling in the range 40–60 °C. Mass spectra were obtained with 70 eV electron impact ionisation on a Kratos M25RF spectrometer. GLC–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 GLC data, the detector response was calibrated with known amounts of authentic materials (or close analogues) and dodecane, or heptane was added as a standard. EPR spectra were obtained with a Bruker ER 200D spectrometer operating at 9.1 GHz with 100 kHz modulation. Samples of the substrate (*ca.* 40 mg) and di-*tert*-butyl peroxide (30 μl) in *tert*-butylbenzene (0.5 cm^3) (occasionally cyclopropane) were degassed by bubbling nitrogen for 20 min and photolysed in the resonant cavity by light from a 500 W super pressure mercury arc lamp. EPR spectra were simulated with a program due originally to Heinzer.[32]

Materials

Cyclohexa-1,4-diene-3-carboxylic acid[9] and 2,5-dihydrofuran-2-carboxylic acid[12] were made according to the literature procedures and converted to esters **5** and **7** by standard procedures *via* the acid chlorides. *tert*-Butylcyclohexa-1,4-diene-3-carboxylate **5d**; bp 200 °C/1 Torr (Kugelrohr); δ_H 1.47 (9 H, s), 2.69 (2 H, m), 3.62 (1 H, m), 5.7–6.0 (4 H, m); δ_C 25.9, 28.0, 42.7, 80.8, 122.7, 126.0, 171.9. Allyl cyclohexa-1,4-diene-3-carboxylate **5g**; δ_H 2.71 (2 H, m), 3.78 (1 H, m), 4.62 (2 H, br d, *J* 7), 5.26 (1 H, d, *J* 12), 5.36 (1 H, d, *J* 17), 5.7–6.0 (4 H, m). Cyclohexyl 2,5-dihydrofuran-2-carboxylate **7c** bp 130 °C/1 Torr, δ_H 1.1–2.0 (11 H, m), 4.7–5.0 (2 H, m), 5.2 (1 H, m), 5.8–6.1 (2 H, m); δ_C 23.9, 25.7, 27.3, 31.8, 31.9, 73.7, 77.0, 84.9, 125.3, 129.4, 171.0; *m/z* 196 ($M^{\bullet+}$, 2), 55 (100). *tert*-Butyl 2,5-dihydrofuran-2-carboxylate **7d** δ_H 1.48 (9 H, s), 4.7–4.9 (2 H, m), 5.4 (1 H, m), 5.8–6.1 (2 H, m); δ_C 28.1, 77.0, 84.9, 125.2, 128.9, 170.5 (quat. C not obs.). Allyl 2,5-dihydrofuran-2-carboxylate **7g** δ_H 4.66 (2 H, m), 4.7–5.0 (2 H, m), 5.2–5.4 (3 H, m), 5.91 (2 H, m), 6.10 (1 H, m); δ_C 65.6, 76.7, 84.4, 118.6, 124.7, 129.4, 131.7, 170.9.

3-Methylcyclohexa-1,4-diene-3-carboxylic acid

Benzoic acid (15 g, 123 mmol) was dissolved in liquid ammonia (900 cm^3) and lithium wire (2.2 g, 314 mmol) was added in small portions until a permanent deep-blue colour appeared. An excess of methyl iodide (25 cm^3, 400 mmol) was then added dropwise, leading to discharge of the colour and formation of a white solid. After evaporation of the ammonia, ice–water (100 cm^3) was added and the suspension was acidified with 50% H_2SO_4. The mixture was extracted with ether (4×100 cm^3), the combined ether layers were washed with saturated sodium thiosulfate solution (100 cm^3), water (100 cm^3) and dried ($MgSO_4$).

Distillation at 85 °C/0.4 Torr (Kugelrohr) gave the acid (17.1 g, 95%) as an oily white solid (mp 36 °C); δ_H 1.4 (3 H, s), 2.6 (2 H, m), 5.8 (4 H, m), 12.3 (1 H, br s); δ_C 26.6 (CH_3), 27.7 (CH_2), 44.1 (C), 125.4 (CH), 128.5 (CH), 182.6 (CO_2); *m/z* (%) 138 ($M^{\bullet+}$, 2), 123 (1), 93 (100), 91 (80), 77 (90), 65 (26), 51 (31), 45 (16), 39 (49), 27 (23).

Typical procedure for preparation of esters

Benzyl 3-methylcyclohexa-1,4-diene-3-carboxylate 6f. To a stirred solution of 3-methylcyclohexa-1,4-diene-3-carboxylic acid (4 g, 29 mmol) in dry ether (30 cm^3) was added dropwise a solution of oxalyl chloride (4.42 g, 35 mmol) in dry ether (25 cm^3). The solution was stirred at room temperature for 18 h and then refluxed for 2 h. The product was distilled at 62 °C/0.2 Torr (Kugelrohr) to yield the acid chloride (3.9 g, 86%). The acid chloride (1.2 g, 7 mmol) in dry ether (25 cm^3) was added dropwise to equimolar amounts of pyridine (0.56 g, 7 mmol) and benzyl alcohol (0.79 g, 7 mmol) in dry ether (25 cm^3). The solution was stirred at room temp. for 2 h, filtered, washed with HCl (50 cm^3 of 0.25 M), water (50 cm^3), dried ($MgSO_4$) and distilled to yield **6f** as a colourless liquid (1.5 g, 90%); bp 108 °C/0.1 Torr (Found: C, 78.97; H, 7.37. $C_{15}H_{16}O_2$ requires C, 78.92; H, 7.06%); δ_H 1.4 (3 H, s), 2.6 (2 H, br s), 5.1 (2 H, s), 5.8 (4 H, m), 7.3 (5 H, m); δ_C 26.4 (CH_2), 27.9 (CH_3), 44.5 (C), 66.9 (OCH_2), 125.1 (CH), 128.2 (CH), 128.5 (CH), 129.0 (CH), 129.1 (CH), 136.7 (C), 175.4 (CO); *m/z* (%) 93 (89), 91 (100), 77 (78), 65 (50), 51 (29), 41 (20), 39 (49); CI MS, found: MH^+ 229.1233, $C_{15}H_{17}O_2$ requires 229.1229.

Hexyl 3-methylcyclohexa-1,4-diene-3-carboxylate 6a. A procedure similar to the above gave **6a** (76%); bp 76 °C/0.1 Torr (Kugelrohr): δ_H 0.85 (3 H, t, *J* 7), 1.3 (9 H, m), 1.6 (2 H, m), 2.6 (2 H, br s), 4.05 (2 H, t), 5.8 (4 H, m); δ_C 14.4 (CH_3), 22.9 (CH_2), 25.9 (CH_2), 26.3 (CH_3), 27.7 (CH_2), 28.9 (CH_2), 31.7 (CH_2), 44.2 (C), 65.3 (CH_2), 124.5 (CH), 129.2 (CH), 175.5 (CO); *m/z* (%) 220 (2), 137 (16), 136 (40), 119 (50), 118 (79), 91 (70), 65 (44), 43 (100), 41 (65), 39 (40); CI MS, found: MH^+, 223.1701, $C_{14}H_{23}O_2$ requires 223.1698.

Hex-5-enyl 3-methylcyclohexa-1,4-diene-3-carboxylate 6b. A similar procedure afforded **6b** (60%); bp 82 °C/0.1 Torr (Kugelrohr); δ_H 1.33 (3 H, s), 1.45 (2 H, m), 1.65 (2 H, m), 2.07 (2 H, m), 2.65 (2 H, br s), 4.08, (2 H, t, *J* 7), 4.95 (1 H, d, *J* 10), 5.00 (1 H, ddt, J_{trans} 17, J_{gem} 1.6, $J_{allylic}$ 1.7), 5.78 (4 H, m), 5.80 (1 H, m); δ_C 25.2 (CH_2), 25.9 (CH_2), 27.4 (CH_3), 28.0, (CH_2), 33.24 (CH_2), 43.9 (C), 64.7 (OCH_2), 114.8 (CH_2), 124.3 (CH), 128.8 (CH), 138.312 (CH), 175.1 (CO); CI MS, found: MH^+, 221.1533, $C_{14}H_{21}O_2$ requires 221.1542.

Cyclohexyl 3-methylcyclohexa-1,4-diene-3-carboxylate 6c. A similar procedure yielded **6c** (61%); bp 98 °C/0.8 Torr (Kugelrohr); δ_H 1.32 (3 H, s), 1.42 (6 H, m), 1.74 (4 H, m), 2.63 (2 H, s), 4.76 (1 H, m), 5.78 (4 H, m); δ_C 23.4 (CH_2), 25.5 (CH_2), 26.0 (CH_2), 27.4 (CH_3), 31.1 (CH_2), 43.9 (C), 72.4 (OCH), 124.2 (CH), 129.0 (CH), 174.5 (CO); *m/z* (%) 138 (3), 93 (100), 92 (32), 91 (41), 83 (60), 77 (33), 55 (78), 41 (42), 39 (21); CI MS, found: MH^+ 221.1548, $C_{14}H_{21}O_2$ requires 221.1542.

Diphenylmethyl 3-methylcyclohexa-1,4-diene-3-carboxylate 6h. A similar procedure yielded **6h** as white needles (27%); mp 99–100 °C (from light petroleum); δ_H 1.4 (3 H, s), 2.7 (2 H, br s), 5.85 (4 H, m), 6.8 (1 H, s), 7.3 (10 H, m); δ_C 21.6 (CH_3), 22.7 (CH_2), 39.9 (CH), 120.3 (CH), 122.5 (CH), 123.4 (CH), 124.1 (CH), 136.2 (C), 169.0 (CO) (C_{phenyl} obscured by overlap); *m/z* (%) 167 (65), 165 (38), 152 (23), 139 (10), 115 (13), 89 (16), 83 (100), 82 (70), 76 (20), 70 (26), 63 (51), 51 (47), 50 (31), 39 (53).

Cholesteryl 3-methylcyclohexa-1,4-diene-3-carboxylate 6e. The procedure was similar except that THF was used as solvent and only 0.8 equiv. of cholesten-3β-ol was employed. Ester **6e** was purified by chromatography on neutral alumina the column being developed with cyclohexane–ethyl acetate (93:7); yield 55%; mp 147–151 °C (from light petroleum); δ_H 0.7 (3 H, s), 0.85 (6 H, s), 0.9 (3 H, s), 1.05 (3 H, s), 1.3 (3 H, s), 1.0–2.1 (28 H, br m), 2.65 (2 H, s), 4.6 (1 H, m), 5.35 (1 H, d), 5.8 (4 H, s); δ_C 11.86 (CH_3), 18.72 (CH_3), 19.37 (CH_3), 21.04 (CH_2), 22.57 (CH_3), 22.83 (CH_3), 23.84 (CH_2), 24.29 (CH_2), 25.94 (CH_2), 27.47 (CH_3), 27.61 (CH_2), 28.02 (CH), 28.24 (CH_2), 31.86 (CH_2), 31.92 (CH_2), 35.80 (CH), 36.18 (CH_2), 36.60 (C), 36.97 (CH_2), 37.94 (CH_2), 39.52 (CH_2), 39.73 (CH_2), 42.31 (C), 43.80 (C), 50.00 (CH), 56.13 (CH), 56.69 (CH), 74.19 (CH), 122.57 (CH_2), 124.22 (CH), 128.90 (CH), 139.69 (CH), 174.61 (CO).

***tert*-Butyl 3-methylcyclohexa-1,4-diene-3-carboxylate 6d.** To *tert*-butyl alcohol (1.41 g, 19 mmol) in dry THF (40 cm^3), under nitrogen, was slowly added butyllithium (15 cm^3 of a 1.6 M solution in hexane). After 30 min a solution of 3-methylcyclohexa-1,4-diene-3-carbonyl chloride (3.0 g, 19 mol) in THF (40 cm^3) was added dropwise. The mixture was refluxed for 1 h, cooled and water (100 cm^3) was added. The aqueous phase was extracted with ether (4 ×100 cm^3), the combined organic layers were dried ($MgSO_4$) and distilled to give **6d** as a colourless oil (79%); bp 82 °C/0.8 Torr (Kugelrohr); δ_H 1.25 (3 H, s), 1.4 (9 H, s), 2.6 (2 H, br s), 5.75 (4 H, m); δ_C 21.6 (CH_3), 23.1 (CH_2), 23.6 (CH_3), 40.1 (C), 76.1 (C), 119.7 (CH), 124.9 (CH), 170.0 (CO); *m/z* (%) 138 (1), 93 (63), 91 (28), 77 (26), 57 (100), 41 (33), 39 (15).

2-Methyl-2,5-dihydrofuran-2-carboxylic acid.[9] The acid was prepared from furoic acid by a procedure similar to that above for 3-methylcyclohexa-1,4-diene-3-carboxylic acid. The product decomposed on distillation and so was purified by chromatography on SiO_2 eluting with cyclohexane–ethyl acetate (90:10); δ_H 1.6 (3 H, s), 4.8 (2 H, m), 5.8–6.1 (2 H, m), 8.9 (1 H, brs).

Benzyl 2-methyl-2,5-dihydrofuran-2-carboxylate 8f. 2-Methyl-2,5-dihydrofuran-2-carboxylic acid (1.7 g, 13 mmol) in dry ether (15 cm^3) was added dropwise to a solution of thionyl chloride (4.5 cm^3) in dry ether (10 cm^3). The solution was stirred for 30 min, the excess thionyl chloride and the ether were removed on a rotary evaporator and then the crude acid chloride, in ether (15 cm^3), was added to benzyl alcohol (0.75 g, 7 mmol) and pyridine (0.45 g, 6 mmol) in ether (10 cm^3). The solution was stirred for 10 min, acidified with dil. HCl, and the aqueous layer was extracted with ether (2 × 25 cm^3). The combined ether layers were dried ($MgSO_4$) and distilled to give **8f** (bp 165 °C/1 Torr, Kugelrohr) which was further purified by chromatography on SiO_2 eluting with cyclohexane–ethyl acetate (95:5); yield 39%; δ_H 1.58, (3 H, s), 4.78 (2 H, m), 5.17 (2 H, s), 5.8–6.1 (2 H, m), 7.35 (5 H, m); δ_C 24.7, 67.1, 76.4, 90.7, 128.4, 128.7, 128.8, 128.9, 129.0, 129.2, 130.4, 136.4, 173.7; *m/z* (%) 218 ($M^{\bullet+}$, 1), 108 9), 91 (87), 84 (62), 83 (100), 65 (30), 55 (68), 43 (29), 39 (32).

Cyclohexyl 2-methyl-2,5-dihydrofuran-2-carboxylate 8c. A similar procedure to that for **8f** yielded **8c** (31%); bp 120 °C/1 Torr; δ_H 1.1–2.0 (11 H, m), 1.52 (3 H, s), 4.75 (2 H, m), 5.8–6.0 (2 H, m); δ_C 23.8, 24.0, 24.4, 25.7, 31.6, 31.8, 73.2, 76.1, 90.4, 128.5, 130.5, 172.8; *m/z* (%) 210 ($M^{\bullet+}$, 2), 115 (13), 99 (29), 98 (21), 84 (26), 83 (100), 82 (24), 55 (79), 43 (33), 41 (53).

Reaction of 6f with NBS

Benzyl 3-methylcyclohexa-1,4-diene-3-carboxylate (1.3 g, 5.6 mmol) was added dropwise, over 2 h, to a refluxing solution of NBS (1.0 g, 5.6 mmol) and lauroyl peroxide (0.02 g) in CCl_4. The suspension was refluxed for 4 h and then NBS (1.0 g) and lauroyl peroxide (0.02 g) were added. After refluxing for 5 h the mixture was filtered and distilled to afford benzyl bromide (0.61 g, 63%); bp 81 °C/15 Torr; the ^{1}H and ^{13}C NMR spectra were identical to those of the authentic material. GC–MS analysis prior to distillation disclosed the presence of toluene and benzyl benzoate (Table 3).

Reaction of 6a,c,d and 8f with NBS

For each ester the method was similar to that described for **6f**, except that initial reflux period was 10 h and the final mixtures were analysed by GLC and GC–MS; products and yields are in Table 3.

Reaction of 6c with bromoform

Ester **6c** (0.2 g, 0.91 mmol), bromoform (0.23 g, 0.91 mmol) and 2,2′-azo(2-methylpropionitrile) (AIBN) (0.01 g) were dissolved in *tert*-butylbenzene (1 cm^3), sealed in a glass tube and heated at 100 °C for 60 h. Analysis by GC–MS showed toluene, bromocyclohexane, unreacted ester and cyclohexyl benzoate; yields in Table 4.

Reaction of 6c with *tert*-butyl hypochlorite

To a refluxing solution of **6c** (0.8 g, 3.6 mmol) in CCl_4 (40 cm^3) was added dropwise, over 10 min, freshly prepared *tert*-butyl hypochlorite (0.55 g, 5 mmol) in CCl_4 (20 cm^3). The solution was refluxed for 5 h under illumination from a 100 W tungsten lamp. The solvent was evaporated and the products were characterised by GC–MS; toluene, chlorocyclohexane, cyclohexyl benzoate, polychlorocyclohexanes and an unidentified by-product were observed (see Table 4).

Reaction of 6c with *N*-bromobis(trimethylsilyl)amine

To ester **6c** (0.6 g, 2.7 mmol), norbornylene (0.05 g) and AIBN (0.05 g) in CCl_4 (40 cm^3) was added *N*-bromobis(trimethylsilyl)amine [26] (0.5 g, 3 mmol) in CCl_4 (20 cm^3). The solution was refluxed for 2 h and analysed by GC–MS which showed: toluene, bromocyclohexane, cyclohexyl benzoate, bromotoluene isomers and several polybromocyclohexanes (see Table 4).

Reaction of esters 6 with acrylonitrile: typical procedure for 6f

The benzyl ester (0.1 g, 0.44 mmol), acrylonitrile (0.05 cm^3), di-*tert*-butyl peroxide (0.05 cm^3) and heptane (0.01 cm^3) were dissolved in *tert*-butylbenzene (0.4 cm^3) in a Pyrex tube. The mixture was degassed on a vacuum line by a series of freeze–pump–thaw cycles, the tube was flame sealed and heated at 140 °C in a GLC oven for 20 h. Products were analysed by GLC and GC–MS and yields are given in Table 5.

Kinetics of the reaction of hexenyl ester 6b

The ester **6b** (0.1 g, 0.45 mmol), di-*tert*-butyl peroxide (0.015 cm^3), heptane (0.01 cm^3) were dissolved in *tert*-butylbenzene (0.4 cm^3) and degassed in a Pyrex tube. The tube was flame sealed and heated at 140 °C for 25 h. GLC analysis revealed hex-1-ene (0.10%), methylcyclopentane (9.95%) and cyclohexane (0.29%) together with unreacted **6b**.

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