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The autoxidation of aliphatic esters. Part 1. The reactions of *tert*-butoxyl and cumyloxyl radicals with neopentyl esters

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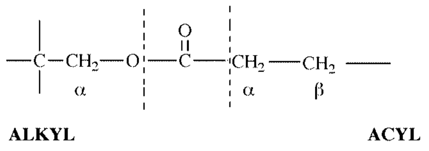
Six neopentyl esters have been selected, as models for pentaerythrityl esters used as lubricants, to study the selectivity of hydrogen abstraction by alkoxyl radicals. Kinetic and product data for the reactions of two oxygenated radicals, *tert*-butoxyl and cumyloxyl, with the six neopentyl esters between 408 and 438 K have been determined. They show that attack by the radicals occurs at the α- and subsequent positions on the acyl moiety as well as at the alkyl group. The selectivity of the reactions is discussed in terms of bond dissociation, steric and polar effects.

Introduction

The demands placed on lubricants have continuously increased with time, and the development of lubricant base fluids which are stable to thermo-oxidative degradation unlike conventional materials such as hydrocarbons is of crucial importance.

One class of compounds, the polyol esters, for example those derived from pentaerythritol, hold great promise as they have good oxidation properties, possess good viscometric properties over a wide temperature range and mix well with additives. They are already widely used as lubricants in a wide range of processes, in industry as well as in aviation and automotive engines. However, their further development still requires a thorough understanding of the mechanisms of their autoxidation.

Unfortunately the autoxidation of even relatively simple esters is not clearly understood.[1] There is not even general agreement about the position of the initial attack. For example, Jensen *et al.*[2] found that hydrogen abstraction reactions on pentaerythrityl tetraheptanoate occur on the acyl groups, particularly at β and subsequent positions, while others[3,4] have reported that attack on ester lubricants is more predominant on the alkyl groups (Scheme 1).

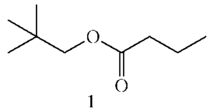


Scheme 1

Further, the lack of rate data for the reactions of peroxyl and alkoxyl radicals derived from esters is also hindering the development of chemical models to describe these oxidation systems.

In this paper we report on rate data for the reactions of *tert*-butoxyl and cumyloxyl radicals with esters: these can be considered as models for key propagation reactions in the autoxidation of esters. The few rate data that are available are limited to the reaction of *tert*-butoxyl with methyl alkanoates[5–8] and other alkyl acetates[5,8,9] and, like so much of the reported literature, these studies do not appear to be self-consistent in terms of which C–H bonds are preferentially attacked by the alkoxyl radical and whether these are on the alkyl or the acyl groups.

The sources of alkoxyl radicals in this study were the thermal decomposition of di-*tert*-butyl peroxide and dicumyl peroxide, and six neopentyl esters were chosen as substrates in order to allow for a systematic variation of structure. These were the neopentyl esters of butanoic (**1**), 2,2-dimethylpropanoic (**2**), 3,3-dimethylbutanoic (**3**), 2,2-dimethylbutanoic (**4**), 2-methylbutanoic (**5**), and 2-methylpropanoic (**6**) acids. Further, to test the mechanism, the reaction of *tert*-butoxyl radicals with [1,1-$^2H_2$]neopentyl butanoate (**1′**) was also studied. The neopentyl group was selected as the alkyl moiety to model the alkyl core of the pentaerythrityl esters. Furthermore, since these esters do not have β-alkyl C–H bonds they are not prone to pyrolytic elimination at elevated temperatures.



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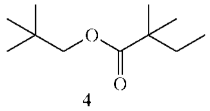

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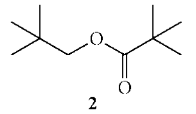

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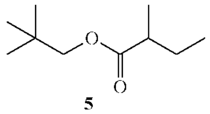

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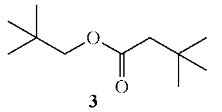

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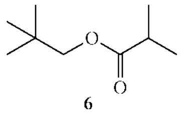

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Results

Decomposition of di-*tert*-butyl peroxide and dicumyl peroxide

The first-order decomposition rate constants of di-*tert*-butyl peroxide in esters **1**–**4** were obtained at four temperatures, between 408 and 438 K, by determining the concentration of peroxide throughout the reaction. These experiments were extended to esters **1′** at 438 K and **5** and **6** at 418 and 438 K. At least four experiments were carried out at each temperature (Table 1).

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The decomposition rate of the peroxide does not appear to be affected significantly in the different neopentyl esters, although both the Arrhenius parameters are generally lower than those reported in earlier experiments in other solvents.[10,11]

The two main liquid phase products obtained from di-*tert*-butyl peroxide are *tert*-butyl alcohol and acetone; over 90% of the peroxide consumed was recovered as these two products (Table 2). Their relative yields depend on the structure of the ester and the temperature (Table 3).

The decomposition of dicumyl peroxide in the neopentyl esters was studied at three temperatures, 298 K (by photolysis) and 418 and 438 K (by thermolysis). The main liquid phase products were 2-phenylpropan-2-ol and acetophenone, the ratio of yields being dependent on the structure of the ester and the temperature (Table 4). For these reactions, unlike those of di-*tert*-butyl peroxide, it was not possible to monitor the consumption of the peroxide by GC analysis and consequently the conversion of peroxide into alcohol and ketone could not be measured. However, from the data at the higher temperature (438 K) the product yields suggest that in most experiments all the peroxide was consumed in 1 hour.

Discussion

Di-*tert*-butyl peroxide decomposes to yield *tert*-butoxyl radicals [reaction (1a)], which in turn may fragment by β-scission

$$R'(CH_3)_2CO{-}OC(CH_3)_2R' \longrightarrow 2R'(CH_3)_2CO^{\bullet} \qquad (1)$$

[reaction (2a)] or react with the substrate, RH [reaction (3a)]. Similarly, the products from dicumyl peroxide include the corresponding ketone [reaction (2b)] and alcohol [reaction (3b)].

$$R'(CH_3)_2CO^{\bullet} \longrightarrow R'CO{-}CH_3 + CH_3^{\bullet} \qquad (2)$$

$$R'(CH_3)_2CO^{\bullet} + RH \longrightarrow R'(CH_3)_2COH + R^{\bullet} \qquad (3)$$

$$\text{a, } R' = CH_3; \qquad \text{b, } R' = C_6H_5$$

Table 1 Decomposition rate constants of di-*tert*-butyl peroxide in neopentyl esters

	$k_1/10^{-4}\ s^{-1}$			
Ester	408 K	418 K	429 K	438 K
1	1.00 ± 0.14	1.92 ± 0.08	5.02 ± 0.7	11.8 ± 1.5
1′	—	—	—	11.0 ± 0.1
2	0.92 ± 0.02	1.67 ± 0.09	4.42 ± 0.59	11.2 ± 0.4
3	0.87 ± 0.31	2.37 ± 0.20	5.56 ± 0.35	15.2 ± 0.9
4	1.08 ± 0.26	1.64 ± 0.04	4.42 ± 0.47	11.5 ± 1.8
5	—	2.17 ± 0.12	—	9.86 ± 0.2
6	—	1.67 ± 0.15	—	9.93 ± 1.6

Other reactions of the ester radicals, $R^{\bullet}$, include disproportionation [reaction (4)] and combination leading to dimers [reaction (5)].

$$R^{\bullet} + R^{\bullet} \longrightarrow RH + R(-H) \qquad (4)$$

$$R^{\bullet} + R^{\bullet} \longrightarrow R{-}R \qquad (5)$$

Termination reactions involving alkoxyl radicals will also occur, albeit to a much less significant extent.

One approach to determining the position of initial attack by the alkoxyl radicals on the esters is to identify the products from the esters and measure their yields. This, however, assumes that only the alkoxyl radicals and not the methyl radicals, from fragmentations (2a) and (2b), abstract hydrogen atoms from the esters. It also assumes that the site of the initial ester radical is fixed and once formed cannot move by either an intra- or intermolecular rearrangement.[9,12,13] We have investigated these aspects of the reactions and the results will be reported in a subsequent paper.

A second approach to monitoring the selectivity of hydrogen abstraction by the alkoxyl radicals is to use EPR spectroscopy.[9,14] These studies have identified some of the radicals formed and have allowed values to be obtained for the rate constants for hydrogen atom abstraction from a selection of esters by *tert*-butoxyl radicals, the latter being generated by photolysis of di-*tert*-butyl peroxide.

From the results of the present study, it is possible to obtain the ratio of rate constants k_{3a}/k_{2a} for each ester (Table 5) from the relative yields of acetone and *tert*-butyl alcohol (Table 3) by assuming that the relative yields of the products are directly proportional to the relative rates of reactions (2) and (3). Likewise, from the relative yields of acetophenone and 2-phenylpropan-2-ol, values of k_{3b}/k_{2b} can be determined for the six neopentyl esters studied (Table 6).

Comparison of the sets of data for the two radicals reveals, as expected, that, for a given temperature, the k_{3b}/k_{2b} ratios are

Table 3 Relative yields of *tert*-butyl alcohol to those of acetone from the decomposition of di-*tert*-butyl peroxide (DTBPO) in the neopentyl esters

	Relative yields			
Ester	408 K	418 K	429 K	438 K
1	1.04 ± 0.02	1.08 ± 0.03	0.95 ± 0.07	0.64 ± 0.03
1′	—	—	—	0.55 ± 0.02
2	0.89 ± 0.02	0.72 ± 0.04	0.56 ± 0.02	0.49 ± 0.02
3	1.35 ± 0.02	0.80 ± 0.02	0.70 ± 0.03	0.52 ± 0.03
4	1.21 ± 0.02	0.93 ± 0.06	0.78 ± 0.08	0.74 ± 0.10
5	—	1.13 ± 0.09	—	0.85 ± 0.10
6	—	1.19 ± 0.10	—	0.80 ± 0.05

Table 2 Yields of *tert*-butyl alcohol and acetone from the decomposition of di-*tert*-butyl peroxide (DTBPO) in neopentyl esters at 418 K

Ester	Time/h	DTBPO/ 10^{-4} mol[a]	DTBPO/ 10^{-4} mol[b]	*tert*-Butyl alcohol/ 10^{-4} mol	Acetone/ 10^{-4} mol	Product accountability[c]
1	1	4.3	1.8	2.6	2.4	1.00
1	3	4.4	0.6	4.0	3.6	1.00
2	1	4.6	2.1	2.1	2.7	0.96
2	3	4.2	0.5	3.3	4.1	1.00
3	1	6.7	3.2	3.3	3.8	1.01
3	3	4.6	0.3	4.0	4.7	1.01
4	1	5.3	2.4	2.8	2.8	0.97
4	3	5.2	0.5	4.2	4.4	0.91
5	1	5.0	2.3	2.9	2.5	1.00
5	3	4.9	0.6	4.1	3.7	0.91
6	1	3.9	2.2	1.8	1.4	0.94
6	3	3.4	0.5	3.2	2.8	1.03

[a] Initial value. [b] Value measured by GC analysis at the end of the reaction. [c] Total conc. of acetone and *tert*-butyl alcohol/conc. of DTBPO reacted.

Table 4 Yields of 2-phenylpropan-2-ol and acetophenone from the decomposition of dicumyl peroxide (DCPO) in neopentyl esters

Ester	T/K	Time of reaction/h	DCPO/ 10^{-4} mol[a]	2-Phenylpropan-2-ol/10^{-4} mol	Acetophenone/ 10^{-4} mol	Alcohol/ ketone
1	298	2	5.4	0.58	0.10	5.8
1	298	4	5.4	0.91	0.18	5.1
1	418	1	5.4	1.8	8.2	0.22
1	438	1	5.3	1.6	9.0	0.18
2	298	2	5.4	0.45	0.13	3.5
2	298	4	5.4	0.71	0.22	3.2
2	418	1	5.2	1.1	6.6	0.17
2	438	1	5.3	0.80	6.9	0.12
3	298	2	5.4	0.52	0.12	4.3
3	298	4	5.4	0.80	0.21	3.8
3	418	1	5.4	1.1	6.7	0.16
3	438	1	5.4	1.3	9.5	0.14
4	298	2	5.4	0.74	0.15	4.9
4	298	4	5.4	0.81	0.16	5.1
4	418	1	5.4	1.4	6.0	0.23
4	438	1	5.2	1.4	7.6	0.18
5	298	2	5.4	0.57	0.08	8.9
5	298	4	5.4	0.81	0.16	5.1
5	418	1	4.8	1.5	6.1	0.25
5	438	1	5.1	1.5	8.0	0.19
6	298	2	5.4	0.70	0.10	7.0
6	298	4	5.4	0.85	0.14	6.1
6	418	1	5.4	1.8	8.2	0.22
6	438	1	5.1	1.6	9.2	0.17

[a] Initial concentration of peroxide.

Table 5 The rate constants for *tert*-butoxyl radical hydrogen abstraction relative to fragmentation in neopentyl esters

Ester[a]	$(k_{3a}/k_{2a})/10^{-1}$ dm^3 mol^{-1}			
	408 K	418 K	429 K	438 K
1	2.59 ± 0.30	2.01 ± 0.09	1.75 ± 0.15	1.18 ± 0.05
1′	—	—	—	1.02 ± 0.02
2	1.64 ± 0.20	1.36 ± 0.35	1.03 ± 0.02	0.91 ± 0.01
3	2.47 ± 0.11	1.50 ± 0.13	1.30 ± 0.05	0.96 ± 0.02
4	2.23 ± 0.30	1.72 ± 0.13	1.43 ± 0.14	1.37 ± 0.11
5	—	2.12 ± 0.19	—	1.58 ± 0.08
6	—	2.22 ± 0.11	—	1.46 ± 0.03

[a] Concentration, 5.40 mol dm^{-3}.

Table 6 The rate constants for cumyloxyl radical hydrogen abstraction relative to fragmentation in neopentyl esters

Ester[a]	$(k_{3b}/k_{2b})/10^{-2}$ dm^{-3} mol^{-1}		
	298 K[b]	418 K[c]	438 K[c]
1	97.1 ± 10.4	4.03 ± 0.08	3.30 ± 0.15
2	60.6 ± 5.7	3.03 ± 0.17	2.28 ± 0.07
3	75.2 ± 7.7	3.13 ± 0.08	2.57 ± 0.02
4	84.7 ± 12.2	3.42 ± 0.07	2.76 ± 0.06
5	137 ± 21	4.55 ± 0.17	3.47 ± 0.08
6	111 ± 15	3.95 ± 0.17	3.05 ± 0.08

[a] Concentration, 5.40 mol dm^{-3}. [b] Cumyloxyl radicals generated by photolysis of dicumyl peroxide. [c] Cumyloxyl radicals generated by thermolysis of dicumyl peroxide.

significantly smaller than the corresponding values for k_{3a}/k_{2a}, reflecting the faster rate of fragmentation of the cumyloxyl radical. Furthermore, the ratios of k_{3a}/k_{2a} to k_{3b}/k_{2b} for all of the esters at a given temperature are sensibly constant. This suggests, assuming that the fragmentation rate constants, k_{2a} and k_{2b}, at a given temperature are independent of the structure of the ester, the rate constants k_{3a} and k_{3b} are similar and that the rate of hydrogen abstraction is effectively independent of the structure of the alkoxyl radical.

The assumption that the fragmentation rate constants for each alkoxyl radical do not vary significantly in the substrates studied, makes it possible to use the ratio k_{3a}/k_{2a} for the different ester substrates to compare their k_{3a} values. The same argument for k_{3b}/k_{2b} allows a comparison of values of k_{3b} for the esters.

The rate constants for hydrogen atom abstraction, k_{3a} and k_{3b}, are a summation of the values for reactions at the individual positions on the ester molecule. Thus, k_3 is given by eqn. (6), where $k_{\alpha\text{-alk}}$ is the rate constant for hydrogen abstraction from the α-alkyl position, $k_{\alpha\text{-acyl}}$, $k_{\beta\text{-acyl}}$ and $k_{\gamma\text{-acyl}}$ are the corresponding values for attack on the acyl group and $k_{\text{prim-alk}}$ and $k_{\text{prim-acyl}}$ are the rate constants for reaction of the primary C–H bonds on the alkyl and acyl groups, respectively and *a–f* refer to the number of hydrogens of each type. The data from the reactions of the structurally related esters can be used to provide information about the ease of hydrogen atom abstraction from the different sites on the neopentyl esters.

$$k_3 = ak_{\text{prim-alk}} + bk_{\alpha\text{-alk}} + ck_{\alpha\text{-acyl}} + dk_{\beta\text{-acyl}} + ek_{\gamma\text{-acyl}} + fk_{\text{prim-acyl}} \quad (6)$$

Two pieces of evidence point immediately to the importance of attack by the two alkoxyl radicals on the α-alkyl groups of the esters. The first comes from comparing the relative rates of hydrogen abstraction by *tert*-butoxyl radicals on neopentyl butanoate (**1**) and on [1,1-^{2}H$_2$]neopentyl butanoate (**1′**) which is 1.15 at 438 K (Table 5). As will be shown later, this is a significant isotope effect which indicates that α-alkyl hydrogen abstraction, $k_{\alpha\text{-alk}}$, makes a significant contribution to the overall rate constant k_{3a}.

Secondly, comparison of the k_3/k_2 values (Tables 5 and 6) for the reactions of neopentyl 2,2-dimethylpropanoate (**2**), which contains only primary and α-alkyl secondary hydrogens with those of the other esters which also contain α- and β-acyl hydrogens also strongly suggests that the α-alkyl hydrogens are susceptible to attack.

Comparison of these results for neopentyl 2,2-dimethylpropanoate (**2**) and 3,3-dimethylbutanoate (**3**) shows that the additional α-acyl CH$_2$ group in **3** does not make a large difference to the ratios k_3/k_2, *i.e.* to the overall rate constant k_3. This suggests that the alkoxyl radicals attack the α-alkyl in

Table 7 Relative rates of reaction of neopentyl esters with *tert*-butoxyl and cumyloxyl radicals

	Number of C–H bonds							Relative rates [Ester (**1**) = 100]							
	Alkyl		Acyl					*tert*-Butoxyl				Cumyloxyl			Rel rates (est)[a]
Ester	Prim	Sec α	Prim	Sec α	Sec β	Tert β	Temp	408 K	418 K	429 K	438 K	298 K	418 K	438 K	
1	9	2	3	2	2	—		100	100	100	100	100	100	100	100
2	9	2	9	—	—	—		63	67	59	77	62	75	69	61
3	9	2	9	2	—	—		95	75	74	81	77	78	78	76
4	9	2	9	—	2	—		86	86	82	116	87	85	84	91
5	9	2	6	1	2	1		—	105	—	134	141	113	105	132
6	9	2	6	1	—	1		—	110	—	124	114	98	92	103

[a] Estimated assuming the relative rates of reaction of alkoxyl radicals with C–H bonds in neopentyl esters are prim-alkyl, 1; prim-acyl, 1; sec-α-alkyl, 24; sec-α-acyl, 8; sec-β-acyl, 16; tert-α-acyl 40.

preference to α-acyl CH$_2$. Furthermore, comparison of the data for 3,3-dimethylbutanoate (**3**) and 2,2-dimethylbutanoate (**4**) shows that the β-acyl CH$_2$ is more reactive than the corresponding α-acyl hydrogens.

A series of separate experiments on the autoxidation of esters **1**–**4**, in which there was detailed analysis of the products, shows that very little attack occurs on the primary hydrogen atoms compared to the others.[15]

Finally, comparison of the data for the 2,2-dimethylbutanoate (**4**) and 2-methylbutanoate (**5**) esters shows that an α-acyl tertiary CH, as might be expected, is highly susceptible to attack by the alkoxyl radicals.

The relative ease of forming tertiary, secondary and primary radicals is understandable in terms of bond dissociation energies. The most interesting result is the relative rates of attack on the different secondary positions. The qualitative conclusions above suggest that the order of reactivity of the secondary C–H bonds in esters, to reaction with these alkoxyl radicals, is α-alkyl > β-acyl > α-acyl. This order would be predicted on polar grounds, since alkoxyl radicals are electrophilic and they might be expected to react preferentially at the more electron-rich α-alkyl C–H rather than the electron-deficient α-acyl positions[16] with the β-acyl positions having intermediate reactivity.

In Table 7, rate data are recorded, standardised to ester **1** having a reactivity of 100, together with the number and types of C–H bonds in each ester. It is now possible to gauge in more detail, from these relative *overall* rates of reaction of alkoxyl radicals with neopentyl esters, the relative susceptibility to attack by the radicals of each C–H bond in the esters.

Given the arguments above, estimates of the rates of reaction of the esters relative to that of **1** were calculated by assuming the relative reactivities of the different types of C–H bond towards the alkoxyl radicals. A good fit of the measured and estimated rates was obtained assuming the following reactivities; primary = 1; secondary α-alkyl = 24; secondary α-acyl = 8; secondary β-acyl = 16; tertiary α-acyl = 40.

Based on the reactivities above of the different C–H bonds towards alkoxyl radicals, it is possible to calculate the primary kinetic isotope effect, $k_{\alpha\text{-alk}}(\mathrm{H})/k_{\alpha\text{-alk}}(\mathrm{D})$, from the relative overall reactivities of **1** and **1′**, $k_{3a}(\mathrm{H})/k_{3a}(\mathrm{D})$, using eqn. (6). Thus assuming that $k_{\text{prim-alk}}$, $k_{\alpha\text{-acyl}}$, $k_{\beta\text{-acyl}}$ and $k_{\text{prim-acyl}}$ are unaffected by isotopic substitution, the isotope effect is calculated to be 1.7. Bearing in mind the reaction temperature (438 K), this value compares well with the reported primary kinetic isotope effects, at 313 K, for hydrogen atom abstraction from methylbenzene and [^{2}H$_3$]methylbenzene by *tert*-butoxyl and cumyloxyl of 2.4 and 2.6, respectively.[17,18]

A further observation from this work is that there do not appear to be significant changes in the relative reactivities of the C–H bonds in esters to attack by the alkoxyl radicals as the temperature is raised. This differs from the reported changes in the main point of attack of *tert*-butoxyl radicals on ethyl acetate, which switches from the α-alkyl to the α-acyl position on increasing the temperature from 300[9] to 413 K.[5]

The higher reactivity of the α-alkyl than the α-acyl hydrogen towards the alkoxyl radicals observed in the present study is in contrast with the more reactive α-acyl C–H bonds in simple unhindered esters from an EPR study reported by Bennett *et al.*[9] They argued that their results are accounted for better by considering the bond dissociation energies rather than the polar model described above. However, in a more recent study,[14] when using hindered esters such as neopentyl 3,3-dimethylbutanoate (**3**) and neopentyl 2,2-dimethylbutanoate (**4**), a more significant attack at the α-alkyl and β-acyl positions was noticed, compared with results obtained earlier for simpler esters.

While the study by Bennett *et al.* and ours both show clearly that no single site in esters is of paramount importance when considering the point of attack by alkoxyl radicals, there are nevertheless differences in detail. We attribute this, at least in part, to differences in experimental conditions used and in the structures of the esters studied. Work is currently underway to resolve these issues.

Experimental

(i) Preparation of the neopentyl esters

The ester substrates were synthesized by heating the carboxylic acid (1.2 mol) with neopentyl alcohol (1.0 mol) in toluene (250 cm^3) in the presence of concentrated sulfuric acid (0.8 cm^3) while stirring under nitrogen in a Dean–Stark apparatus. At the end of the reaction, the toluene solution containing the ester was washed with 10% (w/v) aqueous sodium carbonate solution, dried and the toluene removed under vacuum. The esters, which were purified by flash column chromatography (silica gel, 230–440 mesh) followed by distillation, had purities of >99.5% by GC analysis.

Neopentyl butanoate (1). Yield 66.3%; bp 164–165 °C (lit.[19] 165–166 °C); ^{1}H NMR (CDCl$_3$) δ 0.94 (9H, s), 0.96 (3H, t, J = 7.4 Hz), 1.67 (2H, m, J = 7.4 Hz), 2.31 (2H, t, J = 7.4 Hz), 3.77 (2H, s); ^{13}C NMR (CDCl$_3$) δ 13.98, 18.77, 26.91, 31.53, 36.58, 73.81, 174.11; MS(EI) *m*/*z* (relative intensity) 103 (20), 71 (100), 57 (43), 43 (56), 41 (21); MS(CI) *m*/*z* 176 (MNH$_4^+$), 159 (MH$^+$).

Neopentyl 2,2-dimethylpropanoate (2). Yield 33.7%; bp 162–164 °C (lit.[20] 162–164 °C); ^{1}H NMR (CDCl$_3$) δ 0.95 (9H, s), 1.22 (9H, s), 3.75 (2H, s); ^{13}C NMR (CDCl$_3$) δ 26.65, 27.46, 31.71, 39.16, 73.79, 178.64; MS(EI) *m*/*z* (relative intensity) 85 (31), 71 (29), 57 (100), 43 (30), 41 (25); MS(CI) *m*/*z* 190 (MNH$_4^+$), 173 (MH$^+$).

Neopentyl 3,3-dimethylbutanoate (3). Yield 42.5%; bp 184–186 °C; ^{1}H NMR (CDCl$_3$) δ 0.95 (9H, s), 1.04 (9H, s), 2.22 (2H, s), 3.75 (2H, s); ^{13}C NMR (CDCl$_3$) δ 26.48, 29.82, 30.99, 48.11, 73.54, 172.39; MS(EI) *m*/*z* (relative intensity) 99 (88), 71 (100), 57 (90), 43 (42), 41 (29); MS(CI) *m*/*z* 204 (MNH$_4^+$), 187 (MH$^+$).

Neopentyl 2,2-dimethylbutanoate (4). Yield 37.2%; bp 182–184 °C; ^{1}H NMR (CDCl$_3$) δ 0.85 (3H, t, $J = 7.5$ Hz), 0.95 (9H, s), 1.18 (6H, s), 1.59 (2H, q, $J = 7.5$ Hz), 3.74 (2H, s); ^{13}C NMR (CDCl$_3$) δ 9.21, 24.66, 26.42, 31.33, 33.35, 42.81, 73.58, 177.87; MS(EI) *m*/*z* (relative intensity) 99 (20), 71 (100), 70 (18), 43 (52), 41 (16); MS(CI) *m*/*z* 204 (MNH$_4^+$), 187 (MH$^+$).

Neopentyl 2-methylbutanoate (5). Yield 44.7%; bp 172–174 °C; ^{1}H NMR (CDCl$_3$) δ 0.92 (3H, t, $J = 7.4$ Hz), 0.95 (9H, s), 1.16 (3H, d, $J = 7.0$ Hz), 1.49 (1H, dm, $J = 13.7$ Hz), 1.70 (1H, dm, $J = 13.7$ Hz), 2.40 (1H, m, $J = 7.0$ Hz), 3.76 (1H, d, $J = 10.6$ Hz), 3.78 (1H, d, $J = 10.6$ Hz); ^{13}C NMR (CDCl$_3$) δ 11.61, 16.65, 26.42, 26.76, 31.31, 41.26, 73.43, 176.72; MS(EI) *m*/*z* (relative intensity) 85 (69), 71 (28), 57 (100), 43 (33), 41 (26); MS(CI) *m*/*z* 190 (MNH$_4^+$), 173 (MH$^+$).

Neopentyl 2-methylpropanoate (6). Yield 35.2%; bp 152–154 °C; ^{1}H NMR (CDCl$_3$) δ 0.99 (9H, s), 1.21 (6H, d, $J = 7.5$ Hz), 2.61 (1H, m, $J = 7.5$ Hz), 3.79 (2H, s); ^{13}C NMR (CDCl$_3$) δ 18.98, 26.38, 31.35, 34.13, 73.41, 177.02; MS(EI) *m*/*z* (relative intensity) 103 (18), 71 (88), 57 (41), 43 (100); MS(CI) *m*/*z* 176 (MNH$_4^+$), 159 (MH$^+$).

[1,1-^{2}H$_2$]Neopentyl butanoate (1′). [1,1-^{2}H$_2$]Neopentyl butanoate was synthesized from [1,1-^{2}H$_2$]neopentyl alcohol and butanoic acid. [1,1-^{2}H$_2$]Neopentyl alcohol was obtained by the reduction of methyl 2,2-dimethylpropanoate (Aldrich) using lithium aluminium deuteride (96% atom D).

The ester was purified by flash column chromatography followed by distillation. Its purity was over 99.3% by GC analysis.

[1,1-^{2}H$_2$]Neopentyl alcohol. Yield 62.3%; MS(EI) *m*/*z* (relative intensity) 75 (45), 57 (100), 56 (66), 41 (89), 39 (36).

[1,1-^{2}H$_2$]Neopentyl butanoate. Yield 58.4%; bp 164–165 °C; ^{1}H NMR (CDCl$_3$) δ 0.94 (9H, s), 0.96 (3H, t, $J = 7.32$ Hz), 1.67 (2H, m, $J = 7.39$ Hz), 2.31 (2H, t, $J = 7.41$ Hz); MS(EI) *m*/*z* (relative intensity) 105 (15), 73 (16), 71 (100), 57 (53), 43 (53), 41 (24); deuterium content ~96% (by MS).

(ii) Other reactants and products

Di-*tert*-butyl peroxide (Aldrich) was over 99% pure and cumyl peroxide (Aldrich) was over 98% pure and neither was purified further. Argon, helium and nitrogen (British Oxygen) were used without further purification.

(iii) Apparatus

Thermolysis experiments. A stainless steel autoclave (inside volume 4.87 cm^3), with a teflon seal and a magnet stirrer was constructed with a high pressure valve attached to the autoclave through 1.6 mm od stainless steel tubing.

For the reaction, the autoclave containing 1.0 cm^3 of an ester containing 2×10^{-2} mol dm^{-3} of di-*tert*-butyl peroxide or dicumyl peroxide was connected to a pressure line. The reactor was purged with argon for 30 min while stirring the substrate. After closing the high pressure valve, the autoclave was disconnected from the line and placed in an aluminium block. The block was heated (Jencons heating band 230 V, 320 W), the heating being controlled by a thermocouple which was inserted into the block and connected to a control unit (Electroserve). The temperature of the reactor was also monitored by a second thermocouple inserted into the wall of the reactor and connected to a thermometer (Fluke 51 K/J).

After the reaction, the autoclave was removed from the heating block and cooled to ambient temperature with a fan. Analysis was by GC and the identity of the products confirmed by GC-MS.

Photolysis experiments. The photolysis cell was constructed from a cylindrical piece of stainless steel of internal diameter 10 mm and length 20 mm, with optical Pyrex windows at each end. The windows were held in place with screw-on stainless steel caps with PTFE O-rings to form a seal between the window and the cap. A PTFE-coated magnetic follower was used inside the cell to enable the solution to be stirred. To allow for filling the vessel and analysis, there were three 2 mm bore stainless steel side arms, one sealed by a viton septum held in place by a screw-on septum cap. The other two arms were connected *via* glass-to-metal joints, to greaseless "rotaflo" taps.

The cell was heated by placing it in a thermostatted aluminium jacket with a Jencons heating band (230 V, 320 W). The temperature was controlled by a thermocouple which was inserted into the aluminium jacket, connected to an Electroserve unit.

The optical bench was equipped with a high intensity xenon arc lamp (300 W) fitted with a liquid light guide (Laser Lines Ltd).

Solutions (5 cm^3) of 0.5 mol dm^{-3} peroxide in neopentyl esters were placed in the cell and deoxygenated using nitrogen, *via* a needle through the septum.

(iv) Analysis

GC analyses were carried out on a Pye Unicam gas chromatograph (PU4500), fitted with a temperature programming facility and a flame ionisation detector (FID). Data collection was carried out with a Trio Trivector integrator. A Carbowax 20 M capillary column (Alltech), 30 m length, 0.25 mm id, 0.25 µm film thickness, was used. The flow rate (helium) was 1 cm^3 min^{-1} and the temperatures used were injector, 220 °C; detector, 250 °C; column, 50 °C for 5 minutes and thence to 180 °C at 8 °C min^{-1}. Peaks were identified by comparison of retention times of commercial or synthesized authentic samples and by gas chromatography–EI mass spectra obtained using a mass spectrometer (VG Autospec S Series A027) linked to a gas chromatograph (Hewlett Packard 5890 Series 2). The spectra were analysed using a VAX 3100 Workstation.

^{1}H and ^{13}C NMR spectra were obtained using JEOL 270 and Bruker MSL 300 spectrometers. Tetramethylsilane was used as the internal standard.

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