Evidence for Electron Transfer, Radical and Ionic Pathways in the Decomposition of Diacyl Peroxide

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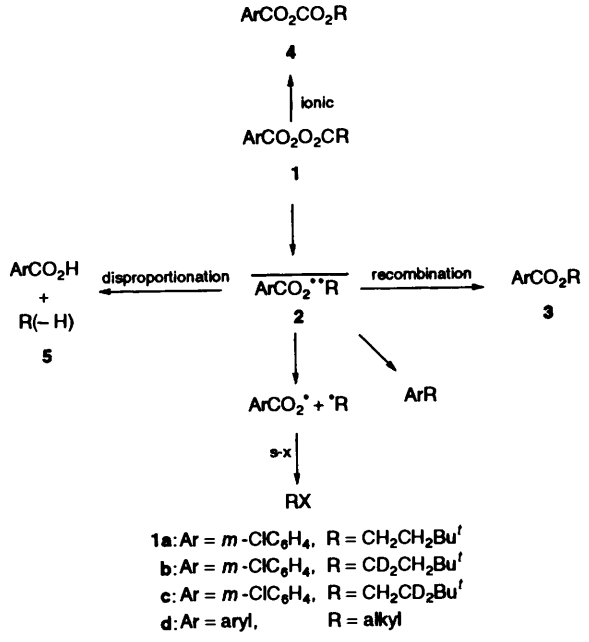
The thermal decomposition mechanism of 4,4-dimethylpentanoyl *m*-chlorobenzoyl peroxide and its α- and β-dideuteriated analogues is described. Product analyses and CIDNP studies suggest that all three pathways, electron transfer, radical and ionic, are operative in decomposition of these peroxides. Two pulsed-NMR techniques have been employed to eliminate distortions of CIDNP intensities arising from spin–lattice relaxation. These quantitative CIDNP studies have revealed an additional pure ionic pathway which competes with the radical pair electron transfer pathway to form rearranged reaction products.

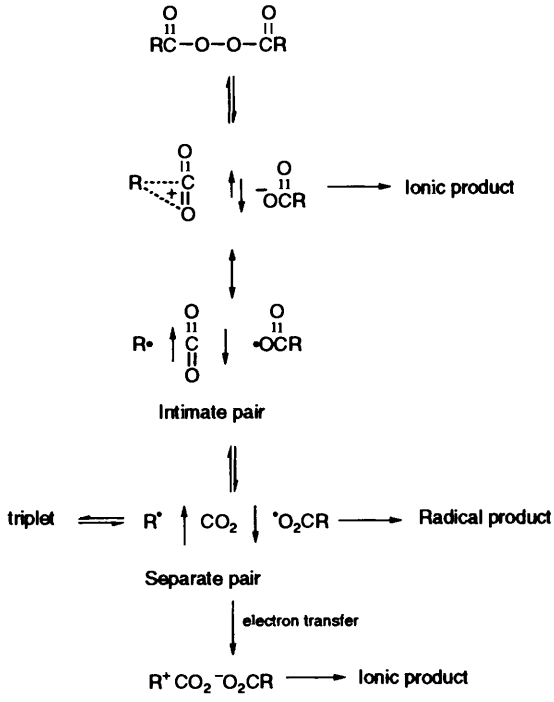
Acyl peroxides are one of the most frequently used sources of free radicals. The chemistry of thermolysis of the mixed diacyl peroxides of the general structure **1d** is, however, known to proceed by both free radical and ionic pathways, as shown in Scheme 1. Since the first isolation of a carboxy inversion



Scheme 1

product[2–9] **4d** by Leffler,[2a] evidence has accumulated that this product is formed by a concerted process in which an alkyl group migrates to electron deficient oxygen. Thus, nearly complete retention of configuration of the migrating group[2a,3,4,9b] and little or no ^{18}O scrambling between carbonyl and peroxide oxygens is found to occur.[3,5] The ionic character of the reaction is supported by large positive and negative ρ values for the variation of rate with substituents on the aryl and alkyl groups, respectively.[10] The other general reactions are radical scavenging by reaction with solvent to give RX, and formation of coupling and disproportionation products ArR, R(-H) **5d** and $ArCO_2R$ **3d** arising from radical recombination.

On the basis of kinetics and product studies, Walling[9a] proposed that both polar and radical products arise in a single rate determining step, as shown in Scheme 2, *via* a common transition state in which the radical or ionic nature of the reaction has not yet been established. On the other hand, Lawler and co-workers[6b] reported evidence for an electron



Scheme 2

transfer pathway, also shown in Scheme 2, which competes with radical coupling and disproportionation. This mechanism was based on the CIDNP observed from rearranged products in the decomposition of *tert*-butylacetyl *m*-chlorobenzoyl peroxide. Recently Leffler and Barbas[2c] have also suggested electron transfer within a neophylacyloxy radical pair to explain the formation of rearranged ester on the surface of silica. Taylor and co-workers,[7] however, found no need to invoke an electron transfer mechanism to explain their results for the thermal decomposition of cyclopropylacetyl cyclobutanecarbonyl and 4-pentenoyl *m*-chlorobenzoyl peroxides. They assert that: (i) formation of carboxy inversion product involves, in part, a nonconcerted route; (ii) ion pair collapse is a major pathway to formation of ester; (iii) electron transfer between separated radical pairs is not a major pathway; and (iv) the major ion–radical differentiation process occurs early on the reaction coordinate. Evidence for formation of ion pair intermediates from peroxides with R groups capable of forming especially stable cations has also been presented by Linhardt and co-workers.[8]

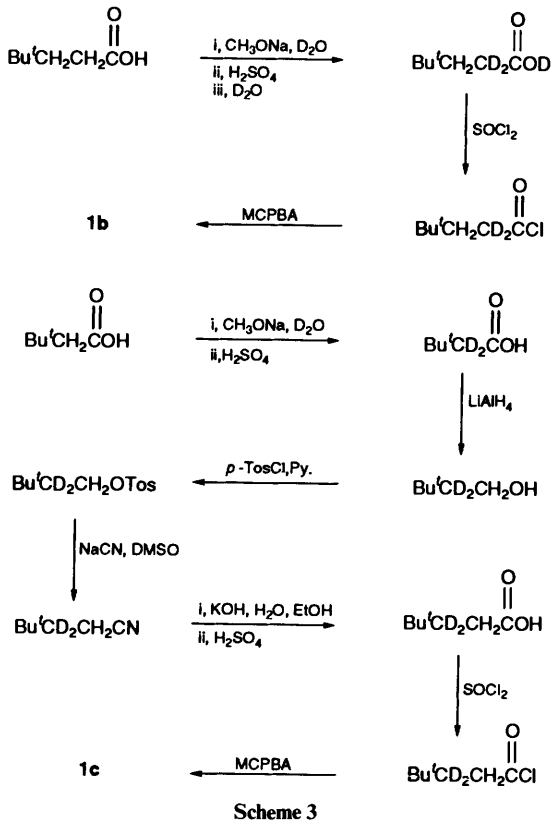
The fact that little or no CIDNP is observed during reactions

of the peroxides studied by Taylor and by Linhardt, *et al.*, was used as evidence against radical pair formation. The interpretation of these observations is complicated, however, because polarized signals are often difficult to detect in complex samples and the observation of CIDNP depends strongly on the relative rates of reaction and spin relaxation.[11] It is the purpose of this report to present further evidence, based both on CIDNP observations and product analysis, for electron transfer between radicals during decomposition of a mixed diacyl peroxide. The selection of 4,4-dimethylpentanoyl *m*-chlorobenzoyl peroxide, **1a** and its deuteriated analogues, **1b** and **1c**, for investigation was based on the observation that the 3,3-dimethyl-1-butyl carbocation, which could be produced in this case, would give a wider variety of rearranged products than in the previous study.[12] Of particular interest was the possibility of observing CIDNP from ethylene produced by fragmentation of the 2-*tert*-butylethyl cation.[12b]

Results and Discussion

Preparation, Decomposition and Product Identification.—Synthesis of the required deuteriated compounds was accomplished through the route outlined in Scheme 3.[11a,13-15] The percentage of deuterium was 98.7 ± 0.2% in **1b** and 97.3 ± 0.2% in **1c** determined by integration of ^{1}H NMR peaks due to the residual proton and comparison with the methylene protons at the unlabelled carbon. Peroxides **1a**, **1b** and **1c** were decomposed thermally in *o*-dichlorobenzene (ODCB), nitrobenzene (NB), and hexachloroacetone (HCA) at a concentration of 0.5 mol dm^{-3}. The reaction temperature of 125 °C for product analysis was selected so as to provide approximately the same conditions as employed to obtain CIDNP spectra. Temperatures 20–30 °C higher than this were used, however, for some CIDNP spectra to produce the maximum feasible rate of reaction so that more intense CIDNP signals would be detectable even from minor products. Individual decomposition products were identified by the ^{1}H and ^{13}C chemical shifts and spin–spin splittings of the signals in the NMR spectrum of the reaction mixture. Isobutylene, 2,2-dimethylbutane, carbon dioxide and ethylene were identified by literature chemical shift,[16] coupling constants and the expected splitting pattern of the deuteriated analogues. The assignments of other products were made by comparison with authentic samples and literature values[16] (see Experimental section).

Products.—Yields of all identified products from **1a–c** in three solvents, as estimated from 250 MHz ^{1}H NMR spectra of partially decomposed reaction mixtures, are listed in Tables 1–3. In order to minimize secondary reactions of the initially formed products samples were held at the reaction temperature for only *ca.* 120 s. During this period 80–90% of peroxide decomposed. With a heating time of 40 s the ^{1}H NMR intensities of the products were in the same ratio as those observed for the longer heating time, indicating that side reactions are unimportant. Lowering the initial peroxide concentration to 0.05 mol dm^{-3} or adding acid (0.1 mol dm^{-3} of *m*-chlorobenzoic acid to 0.25 mol dm^{-3} of **1a**) had a negligible effect on the product distribution or degree of decomposition. These results show that induced or acid catalysed decomposition of **1a–c** are negligible. Although several groups have shown in other cases[2b,3,4,17] that some ester, **3d**, arises from decomposition of the carboxy inversion product, **4d**, we have found that **4a–c** are stable under the reaction conditions (see Experimental section), indicating a negligible yield of esters **3a–c** from this pathway. Other examples of thermally stable carboxy inversion products have been reported by Oae,[4b] Taylor,[7] and Lamb.[10a] Among the possible esters **12**, **13** and **14** (Tables 1–3), which could be formed by rearrangement or fragmentation of the alkyl cation, only



Scheme 3

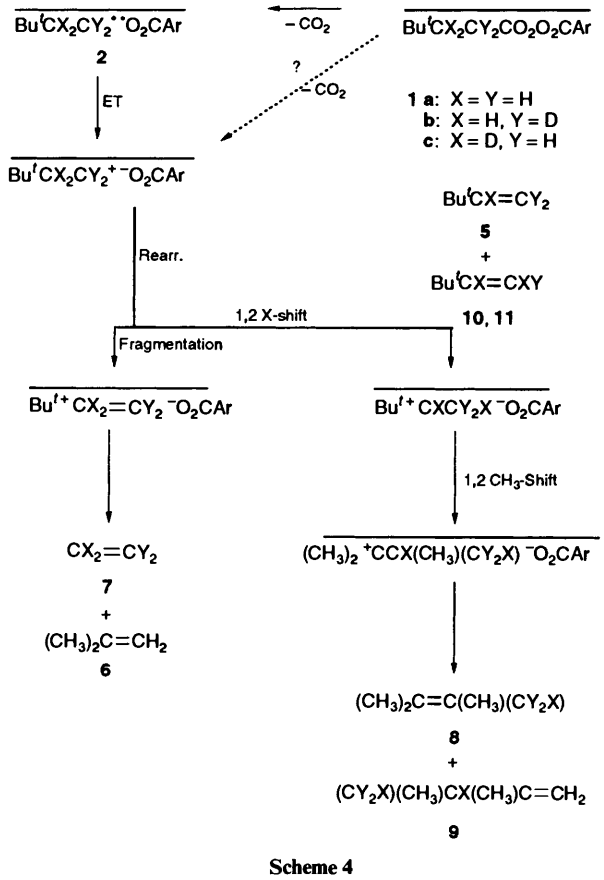
trace amounts of **14** were obtained (*ca.* 0.1%). This indicates that the unrearranged ester, **3**, is derived exclusively from the radical recombination pathway. Increasing the solvent polarity[18] had little effect on the yield of ester, increased the yield of carboxy inversion product and decreased the yield of scavengable radicals (comparison of ODCB and HCA). This result supports a decomposition mechanism consisting of parallel radical and ionic pathways, first suggested by Lamb and co-workers.[19] It is, however, also consistent with Walling's mechanism involving carboxy inversion product and radical pair formation from a common transition state,[9] but the lack of a solvent effect on ester formation differs from the observations of Walling and Sloan,[9b] and Taylor,[7] who found that the yield of ester increases with solvent polarity in instances where the alkyl group can form a cation more stable than the primary alkyl cation expected in the present case.

On the other hand, products **6**, **7**, **9**, **10**, **11**, in which the alkyl group has rearranged or fragmented, are formed during the reaction. Representative partial ^{1}H NMR spectra of the thermolysis mixtures showing these products are displayed in Fig. 1. All of these products can be explained by reactions shown in Scheme 4. Although radical rearrangements could give rise to some of these products, the occurrence of 1,2 shifts of the required type in simple alkyl radicals has not yet been shown unambiguously to occur in the liquid phase.[20] It is also found that the chloroalkane formed in substantial yield by radical scavenging in HCA is unrearranged, *i.e.* **16** and **17** are not formed. The appearance of a trace of *tert*-butyl chloride, **15**, suggests, however, that thermal fragmentation of the 3,3-dimethyl-1-butyl radical does occur to a small extent at 125 °C. In contrast, rapid rearrangement and fragmentation of the 3,3-dimethyl-1-butyl cation is supported by the observation of substantial yields of the corresponding alkenes and substitution products from deamination reactions of 3,3-dimethylbutylamine.[12] In the case of peroxide thermolysis, the carbocation could be formed either by electron transfer within the radical pair (see CIDNP discussion) or by direct heterolytic decar-

Table 1 Product yields from thermolysis[a] of peroxide **1a** in ODCB, NB and HCA

Product	Yield (%)[b] ODCB	NB	HCA
$(CH_3)_3CCH_2CH_2O_2CO_2AF$ (**4a**)	26.2 ± 3.3	23.0 ± 2.9	14.0 ± 1.5
$(CH_3)_3CCH_2CH_2O_2CAr$ (**3a**)	15.9 ± 1.9	14.2 ± 1.5	16.0 ± 2.2
$(CH_3)_3CO_2CAr$ (**12**)	—[c]	—[c]	—[c]
$(CH_3)_3CCH(CH_3)O_2CAr$ (**13a**)	—[c]	—[c]	—[c]
$(CH_3)_2CHC(CH_3)_2O_2CAr$ (**14a**)	*ca.* 0.1	*ca.* 0.1	*ca.* 0.1
$(CH_3)_3CCH{=}CH_2$ (**5a**)	10.2 ± 1.1	7.7 ± 0.6	6.4 ± 0.5
$CH_2{=}CH_2$ (**7a**)	1.8 ± 0.1	2.2 ± 0.1	0.71 ± 0.04
$(CH_3)_2C{=}CH_2$ (**6**)	2.5 ± 0.2	3.4 ± 0.3	*ca.* 0.4
$(CH_3)_2CH(CH_3)C{=}CH_2$ (**9a**)	3.8 ± 0.2	5.9 ± 0.4	1.4 ± 0.1
$(CH_3)_2C{=}C(CH_3)_2$ (**8a**)	—[c]	—[c]	—[c]
$(CH_3)_3CCH_2CH_2Ar$	1.1 ± 0.06	*ca.* 0.4	*ca.* 0.1
$(CH_3)_3CCH_2CH_3$	9.4 ± 0.9	—[d]	—[d]
$(CH_3)_3CCH_2CH_2OH$	—[d]	4.9 ± 0.2	*ca.* 0.4
$(CH_3)_3CCH_2CH_2Cl$	—[d]	—[d]	10.9 ± 0.9
$(CH_3)_3CCl$ (**15**)	—[d]	—[d]	*ca.* 0.1
$(CH_3)_3CCH(CH_3)Cl$ (**16a**)	—[d]	—[d]	—[c]
$(CH_3)_2CHC(CH_3)_2Cl$ (**17a**)	—[d]	—[d]	—[c]
Total identified products	71.0 ± 7	61.8 ± 6	50.5 ± 5

[a] 125 °C for 120 s. [b] The yields are based on initial peroxide = 100%. Average of three runs. The yields were calculated from 250 MHz ^{1}H NMR peaks. [c] Less than 0.02%. [d] This compound is not produced in this solvent.



Scheme 4

boxylation as indicated by the dotted, questioned pathway in Scheme 4. That the latter pathway may contribute to the cation-derived product is supported by a previous report[6a,11a] that an unexpectedly high yield of the less stable (Hoffman) rearranged alkene is formed when R = neopentyl. In analogous fashion, the peroxides **1a–c** form the 'Hoffman' product, **9**, as the only detectable alkene from the cation which would arise by consecutive 1,2 H- and CH_3-shifts and would produce two different alkenes (**8** and **9**). The stability of the carboxy inversion product under the reaction conditions also rules out that product as a source of the alkene.

Finally, the formation of a substantial yield of the unrearranged alcohol, 3,3-dimethylbutan-1-ol, during the thermolysis in nitrobenzene came as a surprise. Denny and Sherman[21] have attributed the formation of alkanols from mixed diacyl peroxides to hydrolysis of the carboxy inversion product, whereas Leffler and Barbas[2c] proposed that alcohols may be formed from diacyl peroxide decompositions on a silica gel surface by direct trapping of the corresponding cation by surface-bound water. In the present case, however, water was excluded from the medium as rigorously as possible. Although hydrolysis of carboxy inversion product by small amounts of residual water might account for the trace of alcohol formed in HCA, this could not account for the 10-fold increase in alcohol yield in NB. Furthermore, the ^{1}H CIDNP spectrum from **1a** and **1c** in NB exhibits an absorption signal at 3.9 ppm [Fig. 2(ii)] which could be due to the alcohol, suggesting that it may be formed in a novel radical scavenging reaction.

CIDNP Studies.—(*a*) *Qualitative enhancements.* Chemically induced dynamic nuclear polarization (CIDNP) provides a probe for the existence of radical pairs in chemical reactions.[22] Representative 60 MHz ^{1}H CIDNP observed during the thermolysis of peroxides **1a**, **1b** and **1c** in ODCB, NB and HCA are shown in Fig. 2. The 62.9 MHz ^{13}C CIDNP spectrum for **1a** is shown in Fig. 3. The peak assignments, presented in Tables 4 and 5 were made by comparison of the CIDNP signals with literature chemical shifts[16] (2,2-dimethylbutane, carbon dioxide and ethylene) or chemical shifts of authentic samples. The observation of CIDNP is consistent with the formation of the radical pair **2** (Scheme 1). If one assumes that *m*-chlorobenzoyloxy radical has a *g*-factor similar to that of benzoyloxy radical,[23c] it is possible to predict the sign (E or A) of the net CIDNP effect for the mechanism in Scheme 1 using the signs of hyperfine splitting constants of 3,3-dimethylbutyl radical[23] and Kaptein's rules.[24a] As expected for a radical pair with a large *g*-factor difference, virtually no distortion of multiplets due to multiplet effect CIDNP could be observed in the ^{1}H spectra, even when a small pulse angle was used for acquisition.[24b] Similar results have been obtained when the alkyl radical in the pair is propyl.[11d] These predictions of the signs of enhancements in Tables 4 and 5 agree with the observations in Figs. 2(*a*) and 3. Using HCA and NB as solvents gives qualitatively similar CIDNP spectra except for the appearance of different scavenging products. A principal scavenging product derived

Table 2 Product yields from thermolysis[a] of peroxide **1b** in ODCB, NB and HCA

Product	Yield (%)[b] ODCB	NB	HCA
$(CH_3)_3CCH_2CD_2O_2CO_2CAr$ (**4b**)	24.0 ± 3.1	25.2 ± 3.2	14.0 ± 1.5
$(CH_3)_3CCH_2CD_2O_2CAr$ (**3b**)	16.4 ± 1.8	13.4 ± 1.5	16.0 ± 2.1
(**12, 13b**)	—[c]	—[c]	—[c]
$(CH_3)(CD_2H)CHC(CH_3)_2D_2CAr$ (**14b**)	*ca.* 0.1	*ca.* 0.1	*ca.* 0.1
$(CH_3)_3CCH{=}CD_2$ (**5b**)	8.5 ± 0.8	5.3 ± 0.3	5.4 ± 0.3
(*Z*)-$(CH_3)_3CCH{=}CDH$ (**11b**)	0.77 ± 0.03	0.92 ± 0.05	0.70 ± 0.04
(*E*)-$(CH_3)_3CCH{=}CDH$ (**10b**)	0.83 ± 0.04	0.94 ± 0.05	0.73 ± 0.04
$CH_2{=}CD_2$ (**7b**)	1.3 ± 0.1	3.2 ± 0.2	0.65 ± 0.04
$(CH_3)_2C{=}CH_2$ (**6**)	1.5 ± 0.1	3.5 ± 0.2	*ca.* 0.4
$(CH_3)(CD_2H)CH(CH_3)C{=}CH_2$ (**9b**)	3.2 ± 0.1	4.3 ± 0.3	1.4 ± 0.1
$(CH_3)_2C{=}C(CH_3)(CD_2H)$ (**8b**)	—[c]	—[c]	—[c]
$(CH_3)_3CCH_2CD_2Ar$	1.6 ± 0.1	*ca. 0.4*	*ca.* 0.1
$(CH_3)_3CCH_2CD_2H$	8.6 ± 0.8	—[d]	—[d]
$(CH_3)_3CCH_2CD_2OH$	—[d]	4.1 ± 0.2	*ca.* 0.4
$(CH_3)_3CCH_2CD_2Cl$	—[d]	—[d]	10.6 ± 0.9
$(CH_3)_3CCl$ (**15**)	—[d]	—[d]	*ca.* 0.1
(**16b, 17b**)	—[d]	—[d]	—[c]
Total identified products	66.8 ± 7	61.4 ± 6	50.6 ± 5

[a,b,c,d] See footnotes of Table 1a.

Table 3 Product yields from thermolysis[a] of peroxide **1c** in ODCB, NB and HCA

Product	Yield (%)[b] ODCB	NB	HCA
$(CH_3)_3CCD_2CH_2O_2CO_2CAr$ (**4c**)	25.8 ± 3.3	23.6 ± 3.1	14.9 ± 1.6
$(CH_3)_3CCD_2CH_2O_2CAr$ (**3c**)	16.5 ± 2.0	13.8 ± 1.5	16.2 ± 2.2
(**12, 13c**)	—[c]	—[c]	—[c]
$(CH_3)(CH_2D)CDC(CH_3)_2O_2CAr$ (**14c**)	*ca.* 0.1	*ca.* 0.1	*ca.* 0.1
$(CH_3)_3CCD{=}CH_2$ (**5c**)	8.7 ± 0.8	6.2 ± 0.3	6.5 ± 0.3
(*E*)-$(CH_3)_3CCD{=}CDH$ (**10c**)	*ca.* 0.6	*ca.* 0.8	*ca.* 0.6
(*Z*)-$(CH_3)_3CCD{=}CDH$ (**11c**)	*ca.* 0.6	*ca.* 0.8	*ca.* 0.6
$CD_2{=}CH_2$ (**7c**)	1.6 ± 0.1	2.9 ± 0.2	0.63 ± 0.04
$(CH_3)_2C{=}CH_2$ (**6**)	1.8 ± 0.1	3.1 ± 0.1	*ca.* 0.4
$(CH_3)(CDH_2)CD(CH_3)C{=}CH_2$ (**9c**)	3.6 ± 0.2	4.8 ± 0.3	1.4 ± 0.1
$(CH_2)_2C{=}C(CH_2D)(CH_3)$ (**8c**)	—[c]	—[c]	—[c]
$(CH_3)CCD_2CH_2Ar$	1.4 ± 0.1	*ca* 0.4	*ca.* 0.1
$(CH_3)_3CCD_2CH_3$	8.5 ± 0.9	—[d]	—[d]
$(CH_3)_3CCD_2CH_2OH$	—[d]	3.8 ± 0.2	*ca.* 0.4
$(CH_3)_3CCD_2CH_2Cl$	—[d]	—[d]	9.1 ± 0.8
$(CH_3)_3CCl$ (**15**)	—[d]	—[d]	*ca.* 0.1
(**16c, 17c**)	—[d]	—[d]	—[c]
Total identified products	69.2 ± 7	60.3 ± 6	51.0 ± 5

[a,b,c,d] See footnotes of Table 1.

from 3,3-dimethylbutyl radical is 3,3-dimethylbutane in ODCB. This product is replaced by 3,3-dimethyl-1-chlorobutane when the solvent is HCA [Fig. 2 (ii)]. 3,3-Dimethylbutane, which might be expected by analogy with ODCB to be the scavenging product in NB, does not seem to be formed in that solvent. Instead, as mentioned above, a signal consistent with 3,3-dimethylbutan-1-ol is observed. The scavenging process in this case is far from obvious. In fact, the fate of radicals scavenged by solvent is poorly understood in both ODCB and NB.

In Scheme 1, carboxy inversion products are formed by a polar mechanism. Since this pathway does not involve radicals, these products are predicted to be unpolarized. Because the ^1H chemical shifts of the methylene groups of carboxy inversion and ester product are similar in ODCB, the signals are indistinguishable in Fig. 2(i). A useful solvent effect on these chemical shifts occurs when NB is used, however, making it possible, as in Fig. 2(ii), to show clearly that only the ester is polarized. The absence of CIDNP in the carboxy inversion product is also apparent in the ^{13}C CIDNP spectrum of **1a** (Fig. 3). The two methylene carbons (δ 67.67, 41.32) and two carbonyl carbons (δ 159.81, 148.78) of this product are not polarized.

The first clue from CIDNP that electron transfer is operating during decomposition of **1** is the appearance of absorption peaks 2X and 6X in Fig. 2(*b*) and emission peaks 2Y in Fig. 2(*c*). The CIDNP signal 2X,Y for ethylene is barely detectable in Fig. 2(*a*) as predicted since the protons responsible for both the E and A signals have the same chemical shift and therefore cancel. The signal from deuteriated ethylene, however, [2X in Fig. 2(*b*), 2Y in Fig. 2(*c*)] shows enhanced A and E, respectively, as expected. Furthermore, the polarized peak 6X in Fig. 2(*b*) indicates the occurrence of a 1,2-H shift and can only be explained by electron transfer followed by rearrangement, as in Scheme 4.

(*b*) *Relative CIDNP enhancement factors.* Schemes 1 and 4 indicate that ester **3**, alkene **5**, and all alkenes, **7**, **9**, **10** and **11** arising from fragmentation or rearrangement of the carbocation, are cage products originating in the same radical pair.[25] This mechanism therefore implies that the enhancements of the CIDNP signals should be the same in all products for nuclei

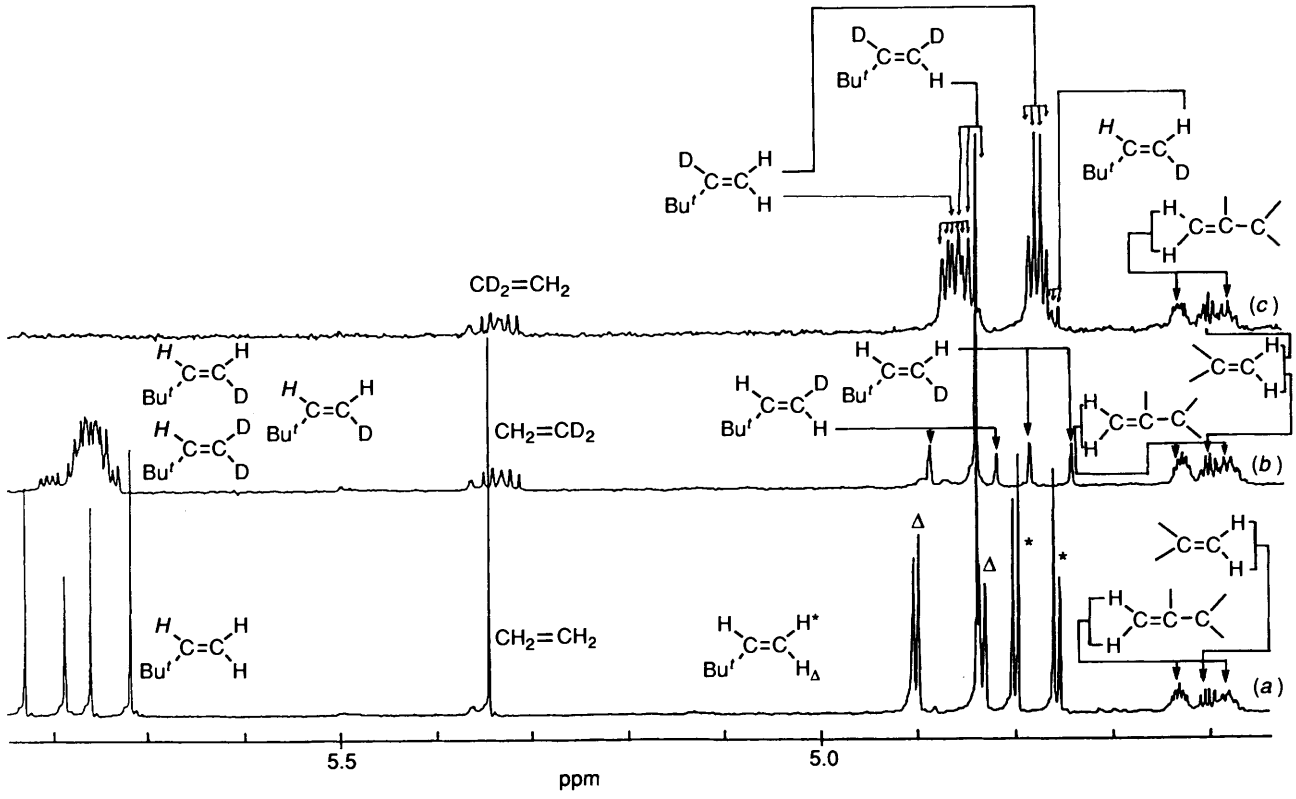


Fig. 1 Partial 250 MHz ^{1}H NMR spectrum of the product mixture obtained from the thermolysis of peroxide (*a*) **1a**, (*b*) **1b**, (*c*) **1c** in HCA. Each spectrum is a sum of 500 spectra collected with 20° pulse angle and repetition rate of one scan every 3.7 s. For illustrative purposes, resolution enhancement was carried out on the spectra using Lorentz–Gauss multiplication of the FID prior to Fourier transformation.

Table 4 Observed CIDNP in the ^{1}H NMR spectra of decomposing peroxides **1a**, **1b** and **1c** in ODCB, NB and HCA. **1a**: X=Y=H, **1b**: X=H; Y=D, **1c**: X = D; Y = H

						Polarization	
Peak No[a]	Product	μ	ε	g^b	A^b	predicted[c]	observed
1	$(CH_3)_3CCX{=}CY_2$	−	+	−	+	A	A
	$(CH_3)_3CCX{=}CY_2$	−	+	−	−	E	E
2	$CX_2{=}CY_2$	−	+	−	+, −	A	A
	$CX_2{=}CY_2$	−	+	−	+	A	A
	$CX_2{=}CY_2$	−	+	−	−	E	E
3	$(CH_3)_3CCX_2CY_2O_2CAr$	−	+	−	−	E	E
	$(CH_3)_3CCX_2CY_2O_2CAr$	−	+	−	+	A	A
4	$(CH_3)_3CCX_2CY_2Ar$					−[d]	E
	$(CH_3)_3CCX_2CY_2Ar$					−[d]	A
5	$(CY_2X)(CH_3)CX(CH_3)C{=}CH_2$	−	+	−	+	A	−[e]
6	$(CH_3)_3CCX{=}CXY$ (*cis*)	−	+	−	+	A	A
	$(CH_3)_3CCX{=}CXY$ (*trans*)	−	+	−	+	A	A
7	$(CH_3)_3CCX_2CY_2H$	−	−	−	+	E	E
	$(CH_3)_3CCX_2CY_2H$	−	−	−	−	A	A
8	$(CH_3)_3CCX_2CY_2Cl$	−	−	−	−	A	A
	$(CH_3)_3CCX_2CY_2Cl$	−	−	−	+	E	E

[a] Peak numbers refer to peaks identified in Fig. 2. [b] Hyperfine splitting and *g* factor for the radical involved are in ref. 23. Benzoyl radical was applied instead of *m*-chlorobenzoyloxy radical. [c] Predicted by using Kaptein's rules. [d] Kaptein's rules do not apply to this compound. [e] Not observed because of overlap of other peaks.

which occupied the same position in the radical. The relative enhancement factor of a net effect CIDNP signal (V_{rel}) can be determined from the experimentally observed intensity (I_{rel}) of the signal, which is free of relaxation distortion (see Experimental section), the yield (Y) of the product responsible for the signal, and the number (n) of nuclei giving rise to the signal [eqn (1)].[11a,b]

$$V_{rel} = I_{rel}/nY \quad (1)$$

The results of the calculation for peroxides **1a**, **1b** and **1c** are listed in Table 6. Unfortunately overlap with other peaks or insufficient intensity made determination of V_{rel} impossible for some important products, perhaps most notably **9a–c** which presumably arise from sequential H- and CH_3-shifts in the carbocation. It was nevertheless possible to determine V_{rel} in all three solvents for products **10** and **11** which arise from a shift of H (or D) from C-2 to C-1 in the alkyl group, and from the protons in ethylene [1,1-$^2H_2$], **7b** and **7c**, the product of cation

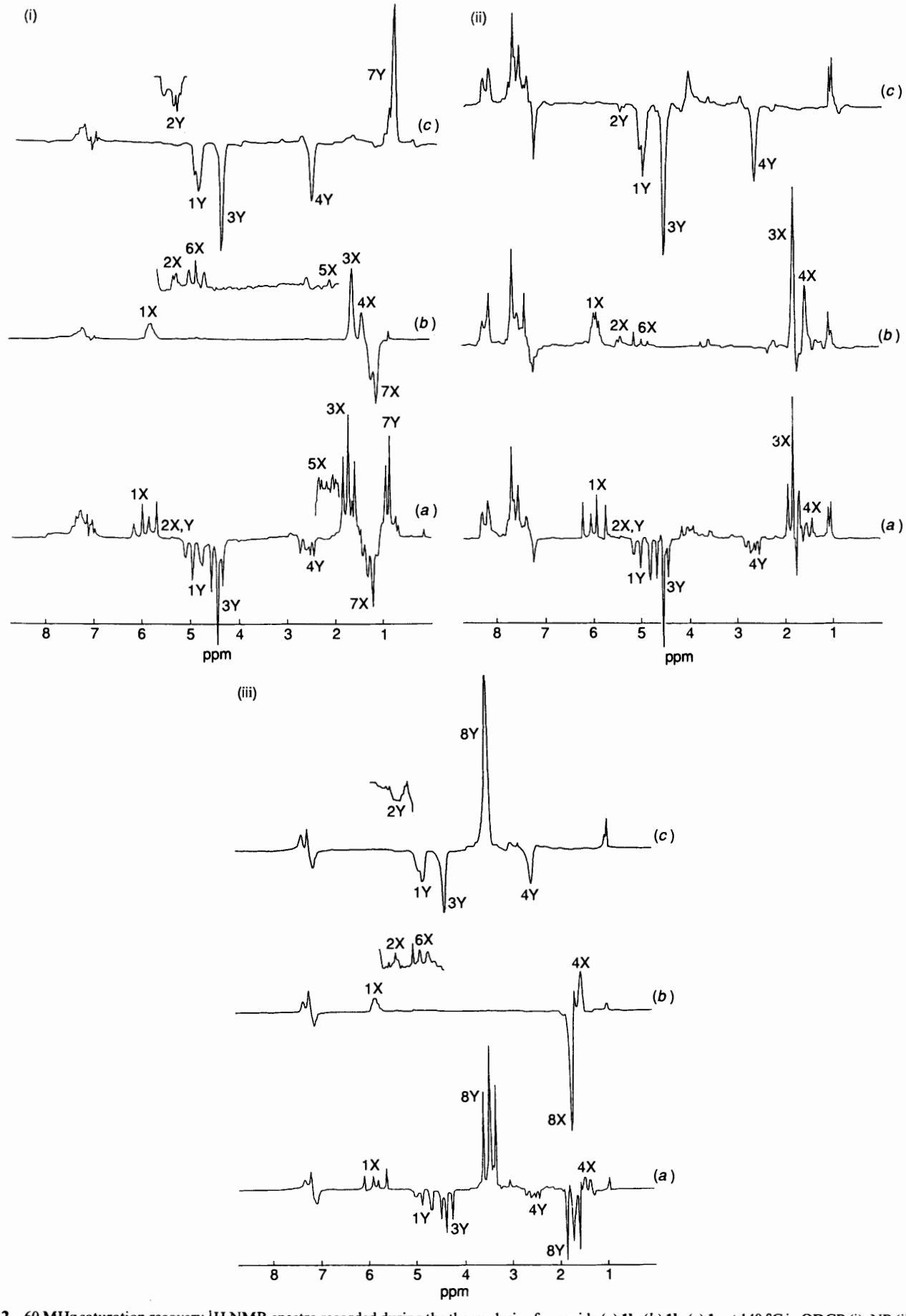


Fig. 2 60 MHz saturation recovery ^{1}H NMR spectra recorded during the thermolysis of peroxide (*a*) **1b**, (*b*) **1b**, (*c*) **1c** at 140 °C in ODCB (i), NB (ii) and HCA (iii). Each spectrum is one scan in a series recorded with 90° pulse angle, repetition rate of one scan every 7.2 s, and delay time (τ) of 5 s. The numbers refer to peak assignments in Table 4.

Table 5 Observed chemical shifts and CIDNP in the ^{13}C NMR spectrum of decomposing peroxide **1a** in ODCB

Peak No[a]	Product	Obs. chem. shift (δ)	μ	ε	g[c]	A[c]	Polarization predicted[c]	Polarization observed
1	$(CH_3)_3CCH_2CH_2O_2CAr$	165.02	−	+	+	−	A	A
2	$(CH_3)_2CH(CH_3)C{=}CH_2$	(151.04)[f]	−	+	−	+	A	—[d]
3	$(CH_3)_3CCH{=}CH_2$	150.09	−	+	−	−	E	E
4	$(CH_3)_3CCH_2CH_2Ar$(ipso)	145.95					—[e]	E
5	CO_2	125.2	−	−	+	−	E	E
6	$(CH_3)_3CCH{=}CH_2$	109.03	−	+	−	+	A	A
7	$(CH_3)_3CCH_2CH_2O_2CAr$	63.13	−	+	−	+	A	A
8	$(CH_3)_3CCH_2CH_2O_2CAr$	42.75	−	+	−	−	E	E
9	$(CH_3)_3CCH_2CH_3$	36.81	−	−	−	−	A	A
10	$(CH_3)_2CH(CH_3)C{=}CH_2$	(35.42)[f]	−	+	−	−	E	—[d]
11	$(CH_3)_3CCH{=}CH_2$	33.42	−	+	−	+	A	A
12	$(CH_3)_3CCH_2CH_2Ar$	31.33					—[e]	A
13	$(CH_3)_3CCH_2CH_2Ar$	30.65					—[e]	E
14	$(CH_3)_3CCH_2CH_3$	30.28	−	−	−	+	E	E
15	$(CH_3)_3CCH_2CH_2O_2CAr$	29.76	−	+	−	+	A	A
16	$(CH_3)_3CCH_2CH_2Ar$	29.76					—[e]	A
17	$(CH_3)_2CH(CH_3)C{=}CH_2$	(21.49)[f]	−	+	−	+	A	—[d]
18	$(CH_3)_3CCH_2CH_3$	8.63	−	−	−	+	E	E

[a] Peak numbers refer to peaks identified in Fig. 3. [b] Chemical shifts (δ) are relative to the ODCB peaks. [c] See footnotes of Table 4. [d] Too small to see. [e] Kaptein's rules do not apply to this compound.[25] [f] Authentic sample's chemical shift.

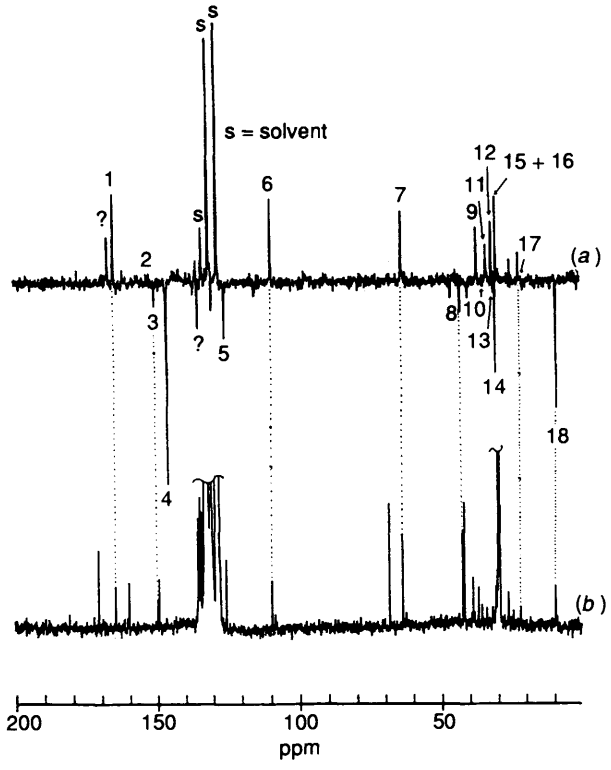


Fig. 3 (*a*) 62.9 MHz ^{13}C progressive saturation spectrum recorded during the thermolysis of peroxide **1a** in ODCB at 140 °C. The ^1H decoupled spectrum is one scan, the most intense in a series, and was collected with 90° pulse angle and a repetition rate of one scan every 5 s. The numbers refer to peaks identified in Table 5. (*b*) The spectrum of the decomposition mixture obtained from the thermolysis of peroxide **1a** in ODCB. The peroxide was decomposed for 120 s at 125 °C. The spectrum is an average of 6730 scans collected with 30° pulse and a repetition rate of one scan every 5 s.

fragmentation, as well as the esters **3a–c** and alkenes **5a–c**, arising from coupling and disproportionation, respectively, of the paired radicals. It is found that instead of being constant as expected, V_{rel} varies by about a factor of five for these products, the magnitude of enhancement decreasing in the order alkene (**5**) > ester (**3**) > ethylene (**7**). This effect is best shown in Fig. 4 which compares the observed ^1H CIDNP peaks for these products before and after reaction (left-hand side) with the relative intensities expected on the basis of the product yields (right-hand side). The same qualitative order of enhancements also shows up by comparing the ^{13}C CIDNP spectrum of **1a** with the corresponding spectrum of the products displayed in Fig. 3. In these spectra peak 6 due to alkene **5** is clearly more intense relative to the unpolarized spectrum than is the peak 7 from the ester **3**. Furthermore, an at most very weak ^{13}C CIDNP peak 2 appears for the double-rearrangement product **9** even though the methyl groups in this product show up clearly as peak 17 in the unpolarized spectrum. Similar results have been observed for other peroxides. For example, the CIDNP intensity of 2-methylbut-1-ene produced from the thermolysis of *tert*-butylacetyl *m*-chlorobenzoyl peroxide is *ca.* 5 times smaller than expected[11a] and that from but-1-ene produced from isovaleryl *m*-chlorobenzoyl peroxide is *ca.* 10 times too small.[26] Similarly, the intensities of ^1H CIDNP signals corresponding to rearranged products from 2-phenylpropionyl *m*-chlorobenzoyl peroxide are 5 times lower than expected.[27] It should also be pointed out that the range of V_{rel} for the corresponding set of products in Table 6 increases somewhat with solvent polarity.

Mechanism for Decomposition.—The simplest explanation for the range of V_{rel} displayed by products from these mixed peroxides is to invoke the presence of a purely ionic, and therefore non-CIDNP, route, capable of producing both rearranged and unrearranged products and making contributions to the yields of the products which increase in the order **5** < **3** < **7**,**9**. An obvious candidate is the route which also gives rise to the carboxy inversion product, **4**. The only elaboration of this mechanism required is explicit inclusion of the ion pair precursor to **4**. This intermediate appears in Scheme 5 as $\mathbf{4I}_1$. Its role as a precursor of **4** is supported by ^{18}O labelling studies of Denny[28] and Oae[4b] and by stereochemical studies which show that the R group in **4** migrates with retention.[3,4a] The carboxylium ion, $R{-}OC(=O)^+$, has also been shown by Beak and co-workers[29] to be an intermediate in the silver-assisted dechlorination of alkyl formates. As an intermediate in diacylperoxide decomposition it has been shown to undergo nucleophilic displacement of CO_2 either concertedly with net inversion[9b] or *via* formation of R^+ to give ion pair $\mathbf{4I}_2$ which is then trapped by a nucleophilic solvent such as acetonitrile.[7]

Table 6 Relative ^1H enhancements for the products obtained from the thermolysis of peroxides **1a**, **1b** and **1c**, in ODCB, NB and HCA

	Peroxide Product	V_{rel} ODCB	NB	HCA
1a[d]	$(CH_3)_3CCH_2CH_2O_2CAr$ (**3a**)	$(-1.0)^a \pm 0.14$	$(-1.0)^a \pm 0.13$	—[b]
	$(CH_3)_3CCH{=}CH_2$ (**5a**)	-1.03 ± 0.11	-1.31 ± 0.4	$(-1.0)^c \pm 0.1$
	$(CH_3)_3CCH{=}CH_2$ (**5a**)	1.31 ± 0.21	2.01 ± 0.28	$(1.14)^c \pm 0.14$
	$CH_2{=}CH_2$ (**7a**)	—[e]	—[e]	—[e]
	$(CH_3)_2CH(CH_3)C{=}CH_2$ (**9a**)	—[b]	—[b]	—[b]
1b[f]	$(CH_3)_3CCH_2CD_2O_2CAr$ (**3b**)	$(1.0)^a \pm 0.14$	$(1.0)^a \pm 0.15$	—[b]
	$(CH_3)_3CCH{=}CD_2$ (**5b**)	1.63 ± 0.17	2.15 ± 0.22	$(1.0)^c \pm 0.1$
	$(CH_3)_3CCH{=}CHD$ (**10b**, **11b**)	1.71 ± 0.27	2.19 ± 0.27	$(1.05)^c \pm 0.1$
	$CH_2{=}CD_2$ (**7b**)	0.46 ± 0.14	0.42 ± 0.13	$(0.52)^c \pm 0.05$
	$(CH_3)(CD_2H)(CH(CH_3)C{=}CH_2$ (**9b**)	—[b]	—[b]	—[b]
1c[h]	$(CH_3)_3CCD_2CH_2O_2CAr$ (**3c**)	$(-1.0)^a \pm 0.12$	$(-1.0)^a \pm 0.12$	—[b]
	$(CH_3)_3CCD{=}CH_2$ (**5c**)	-1.5 ± 0.15[g]	-1.68 ± 0.12[g]	$(-1.0)^{c,g} \pm 0.09$
	(CH)CCD=CHD (**10c**. **11c**)	—[b]	—[b]	—[b]
	$CD_2{=}CH_2$ (**7c**)	-0.69 ± 0.08	-0.4 ± 0.04	$(-0.52)^c \pm 0.06$
	$(CH_3)(CDH_2)CD(CH_3)C{=}CH_2$ (**9c**)	—[b]	—[b]	—[b]

[a] All CIDNP intensities are given relative to the intensity of ester peak except in HCA solvent. [b] Not determined because of overlap of CIDNP peak with other peaks. [c] CIDNP intensities are given relative to the intensity of **5**. [d] Average of two runs. [e] As described in text enhancement could not be calculated because of overlap of CIDNP peaks. [f] Average of three runs. [g] Uncorrected CIDNP peaks with overlap of **10c** and **11c**. [h] Average of two runs.

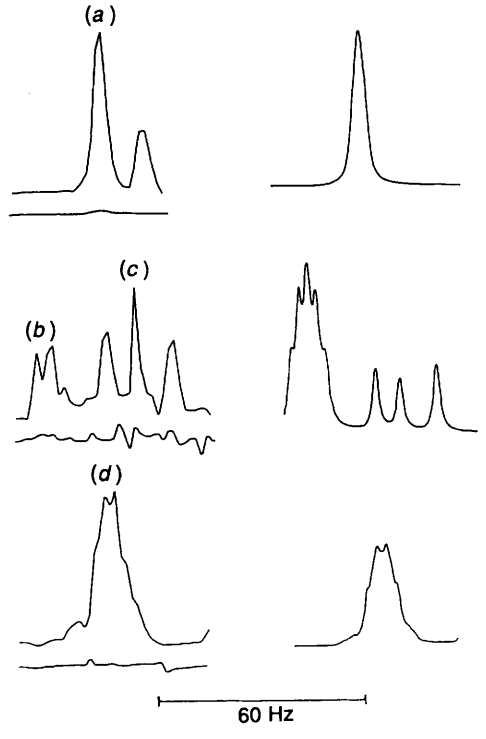


Fig. 4 Observed CIDNP spectra (left) and spectra predicted on basis of relative product yields (right). The observed spectrum is taken from Fig. 2 (i) (*b*). The spectrum obtained from the sample under identical spectrometer conditions after thermolysis is shown under the observed CIDNP spectrum. (*a*) Ester **3b**, (*b*) ethylene **7b**, (*c*) alkenes **10b**, **11b**, (*d*) alkene **5b**. In the simulated spectrum (*d*), the chemical shift of the vinyl proton (next to the *tert*-butyl group) of **10b** and **11b** was taken to be the same as that of **5b**. The peak to high field of **3b** in spectrum (*a*) arises from the coupling product between *m*-chlorophenyl and 3,3-dimethyl-1-butyl radicals and was not simulated.

Furthermore, the analogy between the chemistry of carboxylium and diazonium, $R{-}N_2^+$, should be a good one.[29] Saunders has shown,[12a] for example, that deamination of 3,3-dimethyl-1-butylamine gives products arising from sequential 1,2-H and 1,2-CH_3 shifts, analogous to **9**, but no detectable simple 1,2-H migration.

Applying this mechanism to the results at hand, we would say the following:

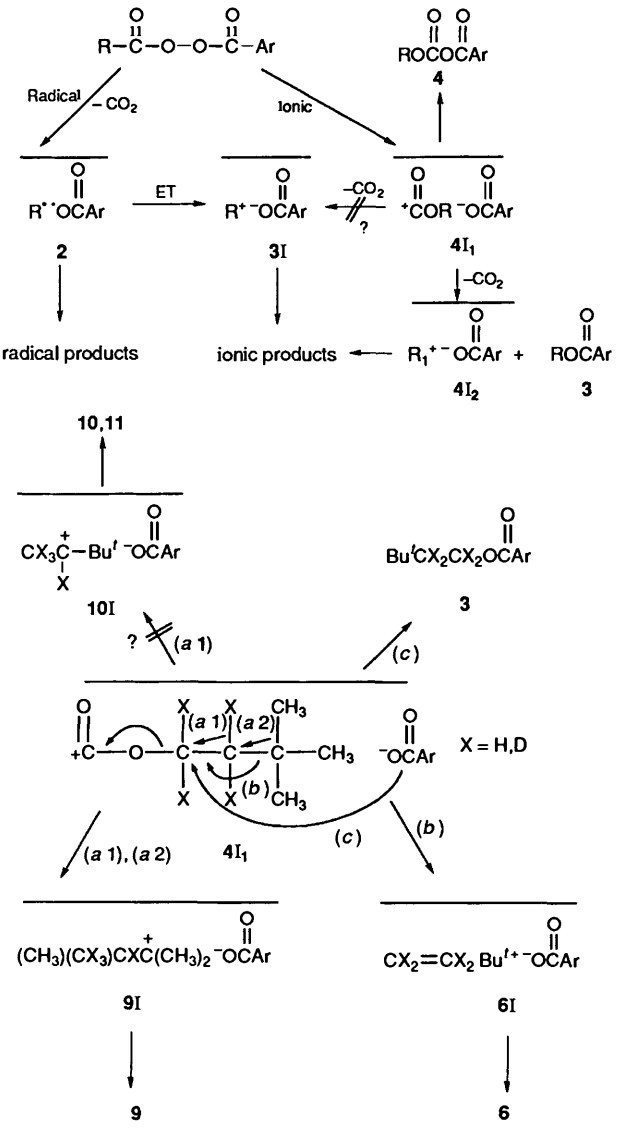
(i) The alkene **5**, which displays the largest CIDNP enhancement, is formed primarily by disproportionation of the radical pair. Nevertheless, the observation of low to moderate yields of the products **10** and **11** formed by 1,2-shifts indicates a cationic pathway as well. The failure to observe simple 1,2-shifts from the deamination reaction,[12a] however, suggests that the ion pair $\mathbf{4I}_1$ is not the precursor of these products. That leaves the ion pair **3I**, formed by electron transfer, as a more likely candidate. This implies that the ultimate source of **5** is the radical pair **2** and that there is no non-CIDNP contribution to this product.

(ii) The ester **3** also arises primarily from radical pair **2** by simple coupling of the alkyl and aroyloxy radicals.[30] The lower value of V_{rel} compared to **5**, however, suggests a contribution from ion pair $\mathbf{4I}_1$. This is supported by the formation of a trace of the doubly rearranged product **14**. The failure to detect ester **13**, either polarized or non-polarized, corresponding to a 1,2-H shift suggests that ion pair **3I** is unimportant in forming **3**.

(iii) Ethylene (**7**) exhibits the lowest value of V_{rel} which could be determined reliably. Although in principle a small amount could come directly from fragmentation of the alkyl radical in the pair **2**, it seems unlikely that the rate of this process would be fast enough to account for the observed CIDNP. The slowness of the fragmentation of the 3,3-dimethyl-1-butyl radical would seem to be confirmed by the observation of only trace amounts of *tert*-butyl chloride as a scavenging product in HCA. It is far more likely that ethylene arises from fragmentation of the alkyl cation. Since some CIDNP is observed, however, it must be concluded that at least a portion of the cation must arise from the radical pair *via* electron transfer. The fact that V_{rel} is lower than for **5** also implicates the non-radical-derived ion pair $\mathbf{4I}_1$. Therefore **3** should be considered to arise from both **3I** and $\mathbf{4I}_1$.

(iv) There is no evidence that product **9**, the result of sequential 1,2-H and 1,2-CH_3 shifts, exhibits CIDNP. The most economical origin of this product is the ion pairs $\mathbf{4I}_1$ and $\mathbf{4I}_2$. The analogy with the products of deamination support this interpretation.

(v) The effects of increasing solvent polarity, though qualitative, are revealing. The decrease of V_{rel} for both **3** and **7** on going from ODCB to the more polar NB is consistent with a greater role played by the purely ionic pathway *via* $\mathbf{4I}_1$. It is interesting that a corresponding increase in the yield of carboxy



Scheme 5

inversion product (**4**) does not seem to occur in this case, although the yield of this product does decrease markedly in the substantially less polar HCA (Tables 1–3). Furthermore, if one is to believe the insignificant change in V_{rel} for **5b** compared to the rearranged alkenes **10b** and **11b** upon changing the solvent, it would be concluded that the relative amount of electron transfer to form **3I** is insensitive to solvent polarity. Similar observations have been made for V_{rel} in products obtained from decomposition of *tert*-butylacetyl *m*-chlorobenzoyl peroxide.[11a] The explanation for the surprising difference in sensitivity to solvent polarity of formation of **3I** and **4I**$_1$ most likely lies in the very different means by which charge separation arises from the initially neutral precursors in the two cases.

Experimental

General—IR spectra were recorded on a Perkin-Elmer 257 spectrometer. NMR spectra were recorded on Varian A-60, EM-360A, Bruker WP-60, or WM-250 spectrometers. Chemical shifts are reported as δ(Me$_4$Si) for ^{1}H and ^{13}C NMR spectra. Relative areas of NMR peaks were determined by cutting out copies of the peaks and weighing them. All compounds were obtained from Aldrich Co. unless otherwise noted. ODCB, HCA and NB were vacuum distilled and stored in brown bottles at room temperature.

Syntheses of the Peroxides (**1a**, **1b**, **1c**).—All the mixed peroxides were prepared by the following general procedure.[11a,15] The reaction scale ranged from 5 to 20 mmol and yields were *ca.* 90% based on acid chloride. 5.5 mmol (1.2 g) of 80–90% *m*-chloroperbenzoic acid was suspended in 10 cm^3 pentane and cooled to −40 °C. To this was added 5 mmol of the corresponding acid chloride in 15 cm^3 of pentane followed by dropwise addition of 5 mmol (0.4 cm^3) of pyridine in 15 cm^3 of pentane. After stirring for 6 h at −40 °C, 25 cm^3 of diethyl ether was added. The reaction mixture was allowed to warm to room temperature for 5 min, filtered and then washed with 15 cm^3 portions of the following chilled solutions: 3 × 5% hydrochloric acid, water, 3 × 5% aqueous sodium hydrogen carbonate and water. The organic layer was dried briefly over anhydrous sodium sulfate at room temperature. The required amounts of this solution were mixed with ODCB, NB and HCA and the volatile components of the solvent mixture were removed by rotary evaporation. In order to remove residual amounts of water and ether, the solution was then pumped (1 mmHg, room temperature) for 1 h. The solution was then treated with solid anhydrous sodium carbonate to remove residual amounts of acidic impurities and was passed through a small column of anhydrous silica. The concentrations of small portions of the final peroxide solutions were determined by ^{1}H NMR spectroscopy using added methylene dichloride as an internal standard. All the peroxides prepared by this procedure were shown to be 95–98% pure by 250 MHz ^{1}H NMR spectroscopy. **1a**: ν_{max}(ODCB)/cm^{-1} 1860 and 1774; δ_H(HCA) 7.9–7.4 (m, aromatic), 2.444 (m, CH_2), 1.672 (m, CH_2) and 0.959 (s, 3 CH_3); δ_C(HCA) 168.18, 160.66 (C=O), 134.51, 133.58, 129.69, 129.16, 127.32 and 127.22 (aromatic), 37.97 (CH_2), 29.96 (C), 28.73 (3 CH_3) and 25.28 (CH_2–CO). **1b**: ν_{max}(ODCB)/ cm^{-1} 1805 and 1773; δ_H(HCA) 7.9–7.4 (m, aromatic), 1.663 (s, CH_2) and 0.960 (s, 3 CH_3); δ_C(HCA) 168.12, 160.64 (C=O), 134.52, 133.54, 129.66, 129.16, 127.29 and 127.21 (aromatic), 37.85 (CH_2), 29.94 (C), 28.73 (3 CH_3) and 24.80 (small quintet, CD_2CO). **1c**: ν_{max}(ODCB)/cm^{-1} 1807 and 1773; δ_H(HCA) 7.9–7.4 (m, aromatic), 2.429 (s, CH_2) and 0.975 (s, 3 CH_3); δ_C(HCA) 168.14, 160.64 (C=O), 134.51, 133.53, 129.66, 129.14, 127.26 and 127.20 (aromatic), 37.48 (small quintet, CD_2), 29.75 (C), 28.66 (3 CH_3) and 25.12 (CH_2–CO).

Syntheses of 4,4-*Dimethylpentanoyl*, 4,4-*Dimethyl*[2,2-$^2H_2$]-*pentanoyl and* 4,4-*Dimethyl*[3,3-$^2H_2$]*pentanoyl Chlorides*.—The acid chlorides were prepared[14f,g] by the reaction of the corresponding acid and thionyl chloride. An ether solution of 4,4-dimethyl[2,2-$^2H_2$]pentanoyl acid was treated with deuterium oxide three times to exchange the acidic proton before reacting with thionyl chloride. Products were purified by distillation (70–80%). Undeuteriated: b.p. 153–154 °C; ν_{max}(neat)/cm^{-1} 2960, 2870 and 1800; δ_H($CDCl_3$) 2.864 (m, CH_2), 1.614 (m, CH_2) and 0.924 (s, 3 CH_3). [2,2-$^2H_2$]: b.p. 156–157 °C; ν_{max}(neat)/cm^{-1} 2960, 2865, 2240, 2160 and 1800; δ_H($CDCl_3$) 1.627 (m, CH_2), 0.917 (s, 3 CH_3). [3,3-$^2H_2$]: b.p. 156–157 C; ν_{max}(neat)/cm^{-1} 2960, 2860, 2200, 2160, 2100 and 1800; δ_H($CDCl_3$) 2.851 (m, CH_2) and 0.915 (s, 3 CH_3).

Syntheses of 4,4-*Dimethylpentanoic and* 4,4-*Dimethyl*[3,-3-$^2H_2$]*pentanoic Acids*.—The acids were prepared[14e] by hydrolysis of the corresponding nitrile using potassium hydroxide in ethanol and water mixture which was refluxed vigorously for 2 days. They were purified by vacuum distillation (70–80%). Undeuteriated: b.p. 95–96 °C (8 mmHg); ν_{max}(neat)/cm^{-1} 1700; δ_H($CDCl_3$) 11.86 (s, OH), 2.356 (m, CH_2), 1.549 (m, CH_2) and 0.93 (s, 3 CH_3). [3,3-$^2H_2$]: b.p. 98–99 °C (8 mmHg); ν_{max}(neat)/cm^{-1} 2195, 2095 and 1710; δ_H($CDCl_3$) 11.6 (s, OH), 2.36 (m, CH_2) and 0.901 (s, 3 CH_3).

Synthesis of 4,4-*Dimethyl*[2,2-$^2H_2$]*pentanoic Acid*.—This acid was prepared from 4,4-dimethylpentanoic acid (9.8 g, 0.075 mol) and sodium methoxide (8.1 g) in 50 cm^3 of deuterium oxide by heating in a stainless steel high pressure reactor (inside radius: 3.5 cm, length: 11 cm). The method is essentially the same as that used by Saunders and Glaser.[13a] The undeuteriated acid was dissolved in 25 cm^3 of ether to which was added deuterium oxide (10 cm^3), and the mixture was shaken vigorously then separated (three times). The ether was removed *in vacuo*. Then the mixture of acid, sodium methoxide, and deuterium oxide in a reactor was heated in a heating mantle at 300 °C for 12 h (400 psi). After cooling, the mixture was acidified with 10% sulfuric acid (80 cm^3). The reaction mixture was extracted with 3 × 50 cm^3 portions of ether and the extract was washed with 3 × 30 cm^3 portions of water and dried with anhydrous magnesium sulfate. The ether layer was evaporated and crude acid was purified by vacuum distillation. The partially deuteriated acid was carried through the above sequence using 80 cm^3 of deuterium oxide to yield 7.1 g (71%) of deuteriated acid. B.p. 100 °C (8 mmHg); ν_{max}(neat)/cm^{-1} 2120, 2150 and 1710; δ_H($CDCl_3$) 11.2 (s, OH), 1.582 (m, CH_2) and 0.904 (s, 3 CH_3).

Syntheses of 4,4-*Dimethylpentano- and* 4,4-*Dimethyl*[3,3-$^2H_2$]*pentano-nitriles*. The nitriles were prepared[4d] by reacting the corresponding toluene-*p*-sulfonate with sodium cyanide in DMSO solution at 80–90 °C for 6 h. They were purified by distillation (60–70%). Undeuteriated: b.p. 168–169 °C; ν_{max}(neat)/cm^{-1} 2955, 2680 and 2240; δ_H($CDCl_3$) 2.31 (m, CH_2), 1.6 (m, CH_2) and 0.95 (s, 3 CH_3). [3,3-$^2H_2$]: b.p. 169–170 °C; ν_{max}(neat)/cm^3 2955, 2865, 2250, 2200, 2160 and 2095; δ_H($CDCl_3$) 2.33 (m, CH_2) and 0.93 (s, 3 CH_3).

Syntheses of 3,3-*Dimethylbutyl and* 3,3-*Dimethyl*[2,2-$^2H_2$]-*butyl Toluene*-p-*sulfonates*.—The corresponding alcohols were allowed to react with toluene-*p*-sulfonyl chloride in pyridine at room temperature for 16 h.[14b,c,d] After filtering the pyridine hydrochloride, the reaction mixture was diluted with hydrochloric acid and water and extracted with ether. The organic layer was washed with water and dried over anhydrous sodium sulfate. The ether was removed under reduced pressure and the oily ester was purified by vacuum distillation (82%). Undeuteriated: b.p. 136–137 °C (0.2 mmHg); ν_{max}(neat)/cm^{-1} 1360 and 1170; δ_H($CDCl_3$) 7.9–7.3 (aromatic), 4.13 (t, CH_2), 2.45 (s, CH_3), 1.58 (t, CH_2) and 0.89 (s, 3 CH_3). [2,2-$^2H_2$]: b.p. 137–138 °C (0.2 mmHg); δ_H($CDCl_3$) 7.9–7.3 (aromatic), 4.09 (m, CH_2), 2.45 (s, CH_3) and 0.89 (s, 3 CH_3).

Syntheses of 3,3-*Dimethylbutyl and* 3,3-*Dimethyl*[2,2-$^2H_2$] *Alcohols*.—The alcohols were prepared[14a] by reduction of the corresponding butyric acid with lithium aluminium hydride in ether. They were purified by fractional distillation (80%). Undeuteriated: b.p. 142–143 °C; δ_H($CDCl_3$) 3.71 (t, CH_2), 2.3 (s, OH), 1.51 (t, CH_2) and 0.95 (s, CH_3). [2,2-$^2H_2$]: b.p. 142–143 °C; δ_H($CDCl_3$) 3.68 (m, CH_2), 2.8 (s, OH) and 0.93 (s, 3 CH_3).

Synthesis of 3,3-*Dimethyl*[2,2-$^2H_2$]*butyric Acid*.—This acid was prepared from 3,3-dimethylbutyric acid (15.3 g, 0.17 mol) in the same manner as described above for the 4,4-dimethyl[2,2-$^2H_2$]pentanoic acid but the reactor was heated for 4 days and these procedures were carried out three times (33%). B.p. 189–191 °C; δ_H($CDCl_3$) 11.9 (s, OH) and 1.07 (s, 3 CH_3).

Synthesis of 3,3-*Dimethylbutylcarbonic* m-*Chlorobenzoic Anhydride* (**4a**).—A solution of 41.5 g (40.7 mmol) of 3,3-dimethylbutanol in 50 cm^3 of tetrahydrofuran was added to 1.63 g (40.7 mmol) of sodium hydride[8] (60% mineral oil dispersion, washed with pentane). After being stirred for 1 h at 60 °C in an oil bath under a nitrogen atmosphere, the reaction mixture was cooled to −78 °C. Carbon dioxide (99.9%, Matheson) was bubbled into the mixture for 3 h. 25 cm^3 of *m*-chlorobenzoyl chloride in 25 cm^3 of tetrahydrofuran was added dropwise with stirring to the reaction mixture. The temperature was not allowed to rise above −50 °C during the addition. After stirring for an additional 1 h below −50 °C and 1 h at room temperature, the reaction mixture was poured into a cold mixture of 100 cm^3 of ether and 200 cm^3 of water. The ether layer was washed successively with 2 mol dm^{-3} NaOH and water. The ether layer was then dried over anhydrous calcium chloride, filtered and concentrated *in vacuo*, affording a pale yellow oil. This product was a mixture of ester (**3a**) (40%) and carbonic anhydride (30%). ν_{max}(neat)/cm^{-1} 1810, 1750; δ_H($CDCl_3$) 8–7 (aromatic), 4.38 (t, CH_2), 1.7 (t, CH_2) and 0.99 (s, 3 CH_3); δ_C(HCA) 158.94, 147.86 (C=O), 67.08 (CH_2–OC=O), 41.04 (CH_2), 29.58 (C) and 29.26 (3 CH_3).

Syntheses of 3,3-*Dimethylbutyl* (**3a**), tert-*Butyl* (**12a**), 3,3-*Dimethyl*-2-*butyl* (**13a**) *and* 2,3-*Dimethyl*-2-*butyl* m-*Chlorobenzoate* (**14a**).—These esters were prepared from the corresponding alcohol and *m*-chlorobenzoic acid using an adaptation of the procedure of Brewster and Ciotti[31] or from the corresponding alcohol and *m*-chlorobenzoyl chloride by the procedure of Wheeler.[32] The products were purified by vacuum distillation. **3a**: 80%, b.p. 110 °C (0.1 mmHg); ν_{max}(neat)/cm^{-1} 3060, 2950, 2860, 1725 and 1130; δ_H($CDCl_3$) 8.1–7.4 (aromatic), 4.4 (t, CH_2), 1.73 (t, CH_2), 1.1 (s, 3 CH_3). **12a**: 33%, b.p. 115 °C (5 mmHg); ν_{max}(neat)/cm^{-1} 3060, 2970, 2920 and 1710; δ_H($CDCl_3$) 8–7.4 (aromatic) and 1.6 (s, 3 CH_3). **13a**: 57%, b.p. 110 °C (0.1 mmHg); ν_{max}(neat)/cm^{-1} 3060, 2960, 2900, 2860 and 1715; δ_H($CDCl_3$) 8–7.4 (aromatic), 4.9 (quartet, CH), 1.23 (d, CH_3) and 1.02 (s, 3 CH_3). **14a**: 25%, b.p. 110–112 °C (1.1 mmHg); ν_{max}(neat)/cm^{-1} 3060, 2960, 2930, 2870 and 1715; δ_H($CDCl_3$) 8–7.3 (aromatic), 2.35 (septet, CH), 1.55 (s, 2 CH_3) and 0.98 (d, 2 CH_3).

Synthesis of 3-(3,3-*Dimethylbutyl*) m-*chlorobenzene*.—This substituted benzene was prepared[33a] by reacting neopentyl toluene-*p*-sulfonate with *m*-chlorobenzylmagnesium chloride. Neopentyl toluene-*p*-sulfonate was prepared[14c] by the procedure of Tipson and *m*-chlorobenzylmagnesium chloride was prepared by the procedure of Gilman.[33b] The product was purified by vacuum distillation (8%, b.p. 121–122 °C, 2 mmHg). δ_H($CDCl_3$) 7.3–7 (aromatic), 2.56 (m, CH_2), 1.51 (m, CH_2) and 0.85 (s, 3 CH_3).

Synthesis of 3,3-*Dimethyl*-1-*butyl chloride*.—This chloride was prepared by allowing 3,3-dimethylbutanol to react with zinc chloride in concentrated hydrochloric acid.[34] The product was purified by fractional distillation (56%, b.p. 113–114 °C). ν_{max}(neat)/cm^{-1} 2960, 2860 and 720; δ_H($CDCl_3$) 3.53 (m, CH_2), 2.73 (m, CH_2) and 0.95 (s, 3 CH_3).

Synthesis of 2,2-*Dimethyl*-3-*butyl* (**16a**) *and* 2,3-*Dimethyl*-2-*butyl Chloride* (**17a**).—These chlorides were prepared by reacting 3,3-dimethylbutan-2-ol with zinc chloride in concentrated hydrochloric acid.[34] The products were purified by fractional distillation (60%, b.p. 109–110 °C). The product ratio was 1 (**16a**): 2 (**17a**) by NMR integration. **16a**: δ_H($CDCl_3$) 3.9 (quartet, CH), 1.45 (d, CH_3) and 1.01 (s, 3 CH_3). **17a**: δ_H($CDCl_3$) 1.89 (septet, CH), 1.54 (s, 2 CH_3) and 1.02 (d, 2 CH_3).

Analyses of Peroxide Decomposition Products.—Peroxide samples (0.5 mol in ODCB, NB and HCA) were decomposed in sealed glass tubes (3 mm for ^1H NMR, 5 mm for ^{13}C NMR) in an oil bath at 125 °C. The yield determination was achieved by the following procedure: (i) the ^1H NMR (250 MHz) spectrum

of the unreacted sample was obtained before decomposition to measure the areas of peroxide peaks relative to that of the solvent, or in the case of HCA, pentachloroacetone as an unreactive impurity; (ii) the sample was heated for the required period; (iii) the sample was cooled quickly and analysed at ambient temperature by ^{1}H NMR spectroscopy. The yield calculation was based on a comparison of product intensity (cut and weigh method) to the decrease in the initial peroxide intensity. For the ^{1}H NMR analysis, the 3 mm tube containing the decomposed peroxide was placed co-axially in a 5 mm NMR tube containing $CDCl_3$ used as a lock solvent. In order to determine whether saturation effects may be ignored for our pulse angle (20 °C) and repetition time (3.7 s), the same pulse angle and a longer pulse repetition rate of 13.7 s was applied to several samples. The change of relative peak intensities was in all cases less than 3%. For ^{13}C NMR analysis, a 5 mm NMR tube containing the decomposed peroxide was placed co-axially in a 10 mm NMR tube containing deuterium oxide used as the lock solvent. The spectra were collected using a 30° pulse angle with a repetition rate of one scan every 5 s and ^{1}H decoupled. Inasmuch as ^{13}C NMR spectra were not used for quantitative analysis, no effort was made to determine peak areas accurately.

Thermal Stability of Carboxy Inversion Product.—The thermal stability of **4** was investigated using 250 ^{1}H NMR spectroscopy by reheating the decomposed peroxide **1c** in HCA. When the decomposed peroxide **1c** was reheated for 120 s, the relative ^{1}H NMR peak intensities of ester and carboxy inversion products were the same as the first one approximately (*ca.* 2%). After reheating for 30 min, about one fifth of the peak intensity of the carboxy inversion product was decreased and replaced by one due to 3,3-dimethylbutanol. This slow rate of decomposition indicates that an insignificant amount of the ester would have been derived from the carboxy inversion product under our reaction conditions.

CIDNP Experiment.—The ^{1}H CIDNP spectra were recorded on a Bruker WP 60 and ^{13}C CIDNP were recorded on a Bruker WM 250 at 62.9 MHz. Both spectrometers were equipped with Bruker VT 1000 temperature controllers. The samples for ^{1}H CIDNP were prepared in the same manner as those for the product analysis, except that [$^2H_6$]DMSO was used for the external lock solvent. The samples for ^{13}C CIDNP were placed in a 10 mm NMR tube and recorded without field-frequency lock using ^{1}H broad band decoupling. All samples were inserted into a preheated NMR probe. The equilibrium temperature of the probe was determined by recording the ^{1}H spectrum of ethylene glycol. When the ^{13}C probe was used, the ^{1}H spectrum of ethylene glycol was recorded using the ^{1}H decoupler coil. Steady state spectra were recorded to determine ^{1}H chemical shifts and the sign of the CIDNP for individual peaks and saturation recovery (P_{sat}–τ–P_{obs}) for ^{1}H and progressive saturation (90–τ)n for ^{13}C spectra were taken to determine relative CIDNP intensities. The cutting and weighing method was used to determine the CIDNP intensity relative to the ester. The ^{1}H decoupling coils were used to generate the saturation pulse when the Bruker WP 60 NMR spectrometer was used for the saturation recovery experiment and the pulse sequence was timed by the gated decoupler. The necessary instrumental modifications have been described elsewhere.[11a,b] In order to obtain spectra which are free of relaxation distortions,[11b] 5 s of delay time (τ) was used for the saturation recovery method. This appears to be short enough under our reaction conditions to prevent relaxation but long enough to permit buildup of the CIDNP signal. When 2.5 τ was used, the spectrum was half as intense as the one for 5 s delay time and the change of relative peak intensities was less than 4%. A microprogram was used to achieve presaturation for the progressive saturation experiment. Collection was begun 30–40 s after the sample was placed in the preheated NMR probe. A series of free induction decays was collected while the decomposition proceeded to determine the time profile for appearance and disappearance of polarization in individual products. If the decomposition was not proceeding at a favourable rate, the temperature was changed on subsequent samples to obtain optimal CIDNP intensities.

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