Radical and Ionic Reaction Pathways in the Thermal Decomposition of Diacyl Peroxides[1]

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Abstract: Thermolysis of peroxides **5a,b** and **11a,b** has demonstrated that the cyclobutyl and cyclopropylmethyl groups are very sensitive structural probes of post-transition-state events in diacyl peroxide decomposition. Analysis of product mixtures indicates that ester formation (**6, 12,** and **14**) results in large part from ion-pair, not radical-pair, collapse. Even **5c,** which decomposed principally by free-radical pathways, gave a large proportion of ester (**6**) by the ion-pair pathway. Further, **5a,b** underwent the "Leffler carboxy inversion" reaction to give carbonic anhydride (**7**) in which the migrating R group suffered some carbon skeleton rearrangement. Evidence is presented to support the proposal that rearrangement of the alkyl group results from a process that occurs after the migration of R from C to O. CIDNP studies indicated that the alkyl radicals produced from **5a, 11a,** and **11b** had in large majority the structures of the starting R groups. Signal enhancement due to the CIDNP phenomenon was seen in only one product having a rearranged R group. A mechanistic scheme consistent with previous work is proposed to account for the observed results.

Introduction

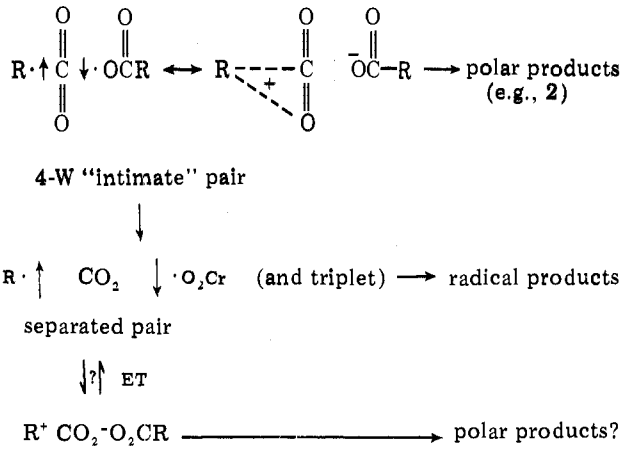
On the chemical borderline between polar and radical reactions one intriguing problem deals with the origin of ionic and radical products in the thermolysis of certain diacyl peroxides (see structure **1** as an example). By way of background[1-7] there is general agreement that the "Leffler carboxy inversion" product, carbonic anhydride **2** (in which R_2CH has migrated to oxygen with almost complete retention of configuration[2,3] and with little or no scrambling of pertinent oxygen[3b,6,20]), is formed by an ionic process in which R_2CH migration is concerted. There is also general agreement that R_2CHX, formed by abstraction of X from solvent or solute S-X, and recombination–disproportionation products, e.g., R_2CHCHR_2, R_2CH_2, and $RCH{=}R'$, are formed by radical processes. However, evidence exists indicating that ester **3** can be formed by an indirect, polar process[2,3,4] involving thermal decomposition of the intermediate carbonic anhydride (**2**) as well as by a direct process usually viewed as involving cage-recombination of acyloxy-alkyl radical pairs.[2,5,6,20] Walling[7] provided kinetic evidence that both polar and radical products arise from a common rate-determining transition state and, hence from a common initial intermediate, **4-W**. Walling[7] hypothesized that **4-W** partitioned as shown in Scheme I. Recently Lawler and co-workers[5b] reported CIDNP evidence for electron transfer from neopentyl to *m*-chlorobenzoyloxy radical thereby providing evidence for the electron-transfer process shown in Scheme I. In this report we present data indicating that (1) formation of carbonic anhydride (**2**) involves, in part, a nonconcerted route; (2) ion pair collapse is a major pathway to formation of ester (**3**); (3) electron transfer between separated radical pairs and ion pairs is not a major pathway; (4) the major ion-radical "differentiation" process, indeed, occurs early on the reaction coordinate.

$(R_2CHCO_2)_2$ **1** $\quad R_2CHCO_2CO_2CHR_2$ **2** $\quad R_2CHCO_2CHR_2$ **3**

Results and Discussion

Unsymmetrical Peroxides. Product Identification. The major products of thermal decomposition of each of the unsymmetrical diacyl peroxides **5a,b** were the esters **6a-c**, the carbonic anhydrides **7a-c**, and *m*-chlorobenzoic acid. The decomposition of peroxide **5c** followed a course different from **5a,b** and will be discussed separately below. Esters **6** were made by alternate synthesis and their identities as thermolysis reaction products were confirmed by VPC and NMR identification.

Scheme I



Carbonic anhydrides, **7**, were also synthesized and samples of 95-99% purity were characterized by titration and by IR and NMR spectroscopy. The identities of **7** as thermolysis reaction products were confirmed by treating reaction mixtures with dibutylamine or diethylamine, a process which converts the carbonic anhydrides **7a-c** to their respective urethanes **8a-c** or **9a-c** rapidly and in good yield. Reaction products were compared by VPC with alternately prepared samples of **8** and **9**. When acetonitrile was the solvent for decomposition of **5a,b**, carboximides **10a-c** were also formed as thermolysis products. This fact was established by alternate synthesis of **10a-c** using VPC for comparison of samples from the two sources. Experimental details are in the Experimental Section.

Unsymmetrical Peroxides. Quantitative Analysis. Thermolyses of peroxides **5a-c** were conducted in CCl_4, $CHCl_3$, and acetonitrile at concentrations of 0.04 and 0.4 M. The latter concentration was studied so as to mimic concentrations used in CIDNP experiments (described below). Reaction temperatures of 40, 50, or 60 °C were selected so as to provide a convenient reaction rate. The starting peroxides were 95-99.5% pure as determined by iodometric titration. Quantitative analyses of ester products **6** and carboximides **10** were performed by VPC using internal standards. Excellent resolution of isomeric mixtures of **6** was achieved using diethylene glycol succinate (DEGS) as the liquid phase. Quantitative analysis for carbonic anhydrides **7** was performed by adapting the method of Johnson and Funk,[8] which involved destroying the anhydride with excess morpholine and back-titrating the base. When reaction aliquots were treated with dibutylamine, VPC

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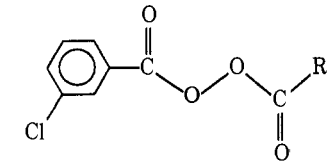
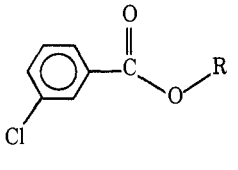
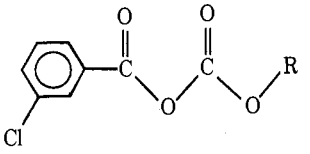


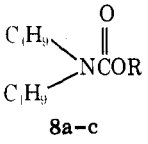
5a, R = cyclobutyl
b, R = cyclopropylmethyl
c, R = 3-butenyl



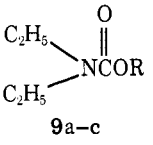
6a–c



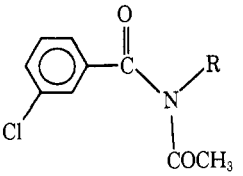
7a–c



8a–c



9a–c



10a–c

separation of the isomeric urethanes (**8**) allowed an estimate of the isomeric composition of **7**. Control experiments with independently prepared **7a,b** showed that the structure of R had little effect on the ratio of attack by the amine on the alkoxycarbonyl or aroylcarbonyl groups. Thus, **7a** gave 17% of *N,N*-dibutyl-*m*-chlorobenzamide and 83% of **8a**, while **7b** gave 14% of the benzamide and 86% of **8b**. (No correction is made in the following tables for this slight differential reactivity between **7a** and **7b**.) *m*-Chlorobenzoic acid was identified by melting point and quantitatively analyzed by titration with standard base.

Unsymmetrical Peroxides. Product Studies. Product distributions for the thermal decompositions of peroxides **5a,b** are shown in Tables I–IV. The following points are pertinent. (1) In examining Table I it is evident that ester **6** is formed with extensive rearrangement of group R. Since the cyclobutyl radical can be expected to be structurally stable at these temperatures,[9] the formation of **6a–c** is indicative of the intervention of an ionic pathway in ester formation. (2) The R group of carbonic anhydride **7** also shows rearrangement indicating that a nonconcerted mechanistic component intervenes in this "Leffler carboxy inversion" reaction. (3) The extent of rearrangement in R in ester **6** differs markedly from that in **7**. This indicated that the carbonic anhydride **7** was not a precursor of **6**. This fact was confirmed by studies on the stability of **7** (described below) and showed that ester **6** was a primary product, probably one of ion-pair collapse. (4) An increase in solvent polarity increased the yield of ester **6** at the expense of **7** indicating that the transition state leading to ester is more polar than that leading to carbonic anhydride. In fact in acetonitrile solvent the R cation was trapped by solvent[7] and the total yield of ion-pair products, **6** plus **10**, reached 73%. Scheme II rationalizes the formation of **10**. (5) By comparing Tables I and II it can be seen that a tenfold increase in concentration in starting **5a** has a small effect on product distribution, at least in the more polar solvents. This indicated that little, if any, induced decomposition accompanied unimolecular decomposition of **5a** at the higher concentration required for CIDNP studies (described below). Also, the concentration change in $CHCl_3$ had little or no effect on the (approximate) half-life of **5a**. (6) In comparing Tables I and III it can be seen that lowering the reaction temperature 10 °C had little effect on the

Scheme II

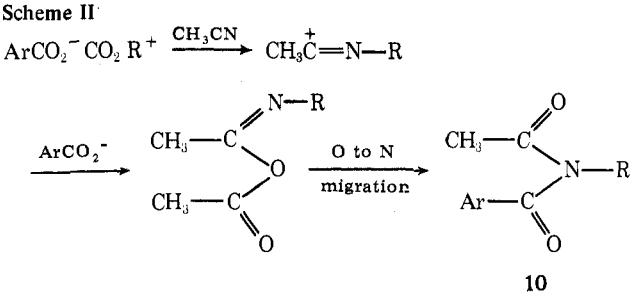


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Table I. Products of Thermolysis of 0.04 M **5a** at 60 °C in Three Solvents

	CCl_4 (5 h)		$CHCl_3$ (5 h)		CH_3CN (2 h)	
product	yield, %	ratio[a]	yield, %	ratio[a]	yield, %	ratio[a]
6 (total)	21		53		24	
6a		18		15		30
6b		74		73		58
6c		8		12		12
7 (total)	75		33		10	
7a[b]		83		83		>96[c]
7b		17		14		<4
7c		<1		2		
acid[d]	6		6		9	
10 (total)					49	
10a						33
10b						61
10c						6

[a] Isomeric composition. [b] Ratios are those of isomeric urethanes **8** except where noted. [c] Ratios of **9a** and **9b**; **9c** was not detected. [d] *m*-Chlorobenzoic acid.

Table II. Products of Thermolysis of 0.4 M **5a** at 60 °C in Three Solvents

	CCl_4 (5 h)		$CHCl_3$ (5 h)		CH_3CN (2 h)	
product	yield, %	ratio[a]	yield, %	ratio[a]	yield, %	ratio[a]
6 (total)	30		53		33	
6a		20		19		27
6b		76		72		60
6c		4		9		13
7 (total)	50		29		10	
7a[b]		79		85		>95
7b		21		15		<5
7c		<1		1		
acid[d]	3		<1		1	
10 (total)					31	
10a						33
10b						60
10c						7

[a,b,d] See footnotes of Table I.

Table III. Products of Thermolysis of 0.04 M **5a** at 50 °C in Two Solvents

	CCl_4 (24 h)		$CHCl_3$ (24 h)	
product	yield, %	ratio[a]	yield, %	ratio[a]
6 (total)	21		55	
6a		17		16
6b		78		71
6c		5		13
7 (total)	64		38	
7a[b]		88		81
7b		12		18
7c		<1		1
acid[d]	7		8	

[a,b,d] See footnotes of Table I.

Table IV. Products of Thermolysis of 0.04 M **5b** at 40 °C in Two Solvents

product	$CHCl_3$ (4 h) yield, %	$CHCl_3$ (4 h) ratio[a]	CH_3CN (4 h) yield, %	CH_3CN (4 h) ratio[a]
6 (total)	58		30	
6a		13		30
6b		67		57
6c		20		13
7 (total)	21		15	
7a[b]		7		4[c]
7b		90		93
7c		3		3
acid[d]	10		11	
10 (total)			46	
10a				22
10b				72
10c				6

[a,b,d] See footnotes of Table I. [c] Ratios of 9a-c.

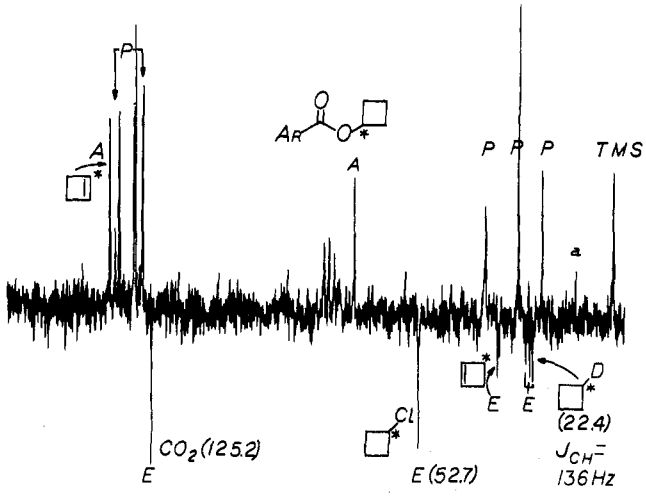
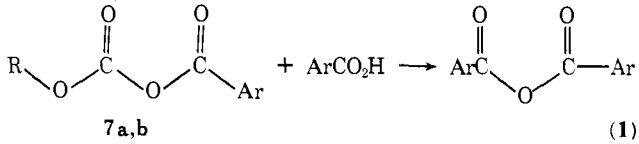


Figure 1. ^{13}C spectrum of **5a** in $CDCl_3$ at 75 °C. Signals (δ_{Me_4Si}) due to starting **5a** are labeled P (in the aromatic C region all those between the P "brackets" are due to **5a**). Signals labeled A or E are enhanced: cyclobutene olefinic C, A at 136.8; alkoxy C of **6a**, A at 69.8; cyclobutene aliphatic C, E at 31.2. The signal labeled a, at 10.1, is probably an enhanced absorption; we assign it to the methine carbon of ester **6b**. The remaining signals are identified with chemical shifts in the spectrum.

product distribution, giving further indication that esters **6** were not a result of thermal decomposition of **7**. (7) In examining Table IV it is apparent that the reactivity of **5b** is similar to that of **5a**. The fact that **6a, 7a,** and **10a** are produced as decomposition products of **5b** is direct evidence that the cyclopropylmethyl cation, not the cyclopropylmethyl radical, is a major intermediate in the reaction. The cyclopropylmethyl radical has been prepared and rearranges rapidly and exclusively to the 3-butenyl radical.[10]

Unsymmetrical Peroxides. Product Stability Studies. With the finding that carbonic anhydride (**7**) was formed with some rearrangement of the migrated alkyl group we undertook studies of **7** to determine if a given preformed **7** (e.g., **7a** from **5a**) was an intermediate in the formation of rearranged **7** and if it was an intermediate in the formation of ester **6**. We thought the former possibility unlikely since all previously observed rearrangements (^{18}O scrambling) of carbonic anhydrides involved acyl-oxygen cleavages[11] while a conversion of **7a** to **7b** would require an alkyl-oxygen cleavage. Alkyl-oxygen cleavages occur with certain carbonic anhydrides[12] but such cleavages accompany decomposition, not rearrangement. The following experiments demonstrated that **7a-c** are primary products, stable under most reaction conditions, and, where unstable, lead to products other than ester **6** and rearranged **7**. (1) Since dibutylamine reacted with **7a** to give **8a, 7b** to give **8b**, etc., the rearranged urethanes (observed on VPC) did not arise from this derivatization reaction. (2) Heating 0.27 M samples of **7a-c** in $CHCl_3$ with added *m*-chlorobenzoic acid at 60 °C for 5 h produced no change in the titer for **7**, no change in the NMR spectra of the reaction and, by VPC, of the resulting urethanes (**8a,b** only), no rearrangement in **7a,b,** and less than 1% of esters **6a** and **6b**, respectively. (3) Pure **7a** added to a reacting system of **5a** in $CHCl_3$ could be totally accounted for as unchanged **7a** by titration and by VPC of the resulting urethane mixture (**8**). (4) When **7a** and **7b** were heated for 2 h at 60 °C in CH_3CN with 1 molar equiv of *m*-chlorobenzoic acid, reaction 1 occurred under certain condi-

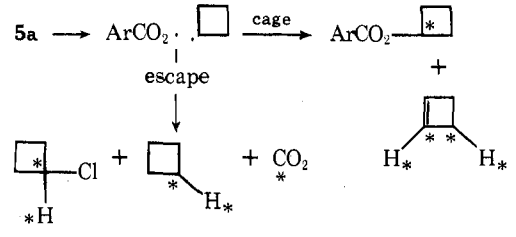


7a,b (1)

tions. This was evidenced by titration results which accounted for 98-100% of *total* anhydride in all reactions, and by accompanying VPC results (after dibutylamine treatment) which showed reduced yields of **8a,b** and exalted yields of *N,N*-dibutyl-*m*-chlorobenzamide. Under conditions mimicking both 0.04 and 0.4 M reaction conditions these stability studies can be summarized as follows: (a) under 0.04 M conditions **7a** was stable; (b) under 0.4 M conditions 22% of **7a** remained and a 70% yield of $(ArCO)_2O$ was produced; (c) under 0.04 M conditions 75% of **7b** remained and a 25% yield of $(ArCO)_2O$ was produced. In all reactions none of ester **6** was produced and no rearrangement of unreacted **7** was observed. We conclude from the above that carbonic anhydrides **7a-c** and esters **6a-c** are primary reaction products.

Unsymmetrical Peroxides. CIDNP Results. Thermolysis of **5a** in the presence of the radical scavengers iodine and galvanoxyl produced little change in product distribution. Yet free radicals were produced when 0.4 M **5a** was heated at 70 °C in $CDCl_3$ as evidenced by the CIDNP effects observed in both ^1H and ^{13}C spectra of reacting solutions. Representative ^{13}C and ^1H spectra are recorded in Figures 1 and 2 with assignments summarized in the captions. The assignments of enhanced ^1H and ^{13}C signals agree with published NMR chemical shifts (cyclobutane, cyclobutene) or chemical shifts of authentic samples (CO_2, **6a, 6b,** cyclobutyl chloride). Cyclobutyl chloride (low yield) and **6a** have also been identified in VPC traces. It is evident from Figures 1 and 2, which are representative of a number of experiments, that cyclobutyl is the only alkyl radical produced in quantity from **5a**. Only in ^{13}C spectra of reacting **5a** did we observe a weak CIDNP signal (δ 10.1, A) attributable to a polarized, rearranged product: the methine C of **6b**. Application of the Kaptein[13] and Closs[14] rules to the mechanism of Scheme III with a cyclobutyl-*m*-chlorobenzoyloxy polarizing pair gives a prediction for signal phasing consistent with the observed results. From integration of NMR spectra of crude product mixtures it appears that **5a**

Scheme III[a]



[a] Starred atoms showed A or E.

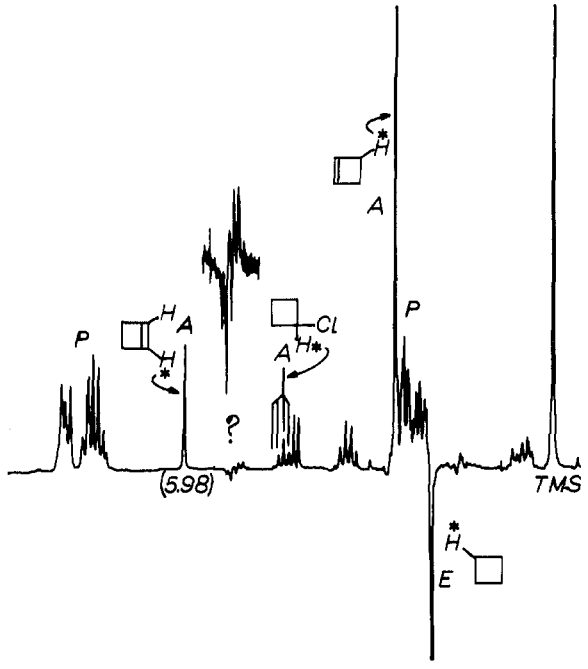


Figure 2. ^{1}H spectrum of **5a** in $CDCl_3$ at 75 °C; signals (δ_{Me_4Si}) due to starting **5a** are labeled P; those labeled A or E are enhanced; those unlabeled grew without enhancement; vinyl H of cyclobutene, A[5] at 5.98; H-1 of cyclobutyl chloride, weak A at 4.42; aliphatic H of cyclobutene, strong A at 2.56; cyclobutane H, strong E at 1.95. The signal labeled with a question mark (at 5.2) is not a multiplet effect. We tentatively assign the emission signal to the H bound to the alkoxy carbon of ester **6a.** This signal overlaps with the analogous signal in carbonic anhydride **7a** which is responsible for the absorption portion of the signal. The weak signals seen just upfield from the cyclobutane E and near the methinyl H of multiplet ester **6b** (1.26) are not enhanced.

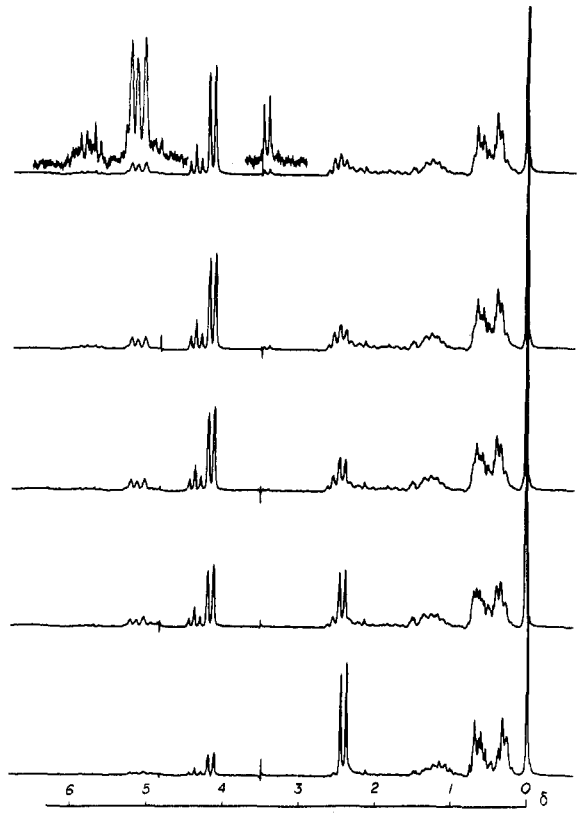
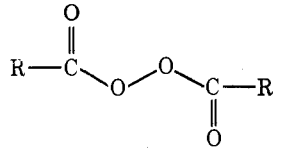


Figure 3. Partial ^{1}H NMR spectrum of **5b** in $CDCl_3$ at 70 °C. In the bottom trace thermolysis has just started; the top trace is of a completed reaction. The doublet at 2.3 is due to the CH_2CO group of **5b.** The signals at 4.15 ($-CH_2O$ of **6b**), 4.35 ($-CH_2O$ of **6c**), and 5.20 (-HCO of **6a**) grow normally. These signals overlap the analogous signals due to **7b**, **7c**, and **7a.**

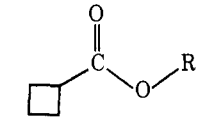
in $CDCl_3$ reacts by a free-radical pathway to the extent of 5-10%.

In the case of **5b**, in a number of attempts under conditions successful for **5a**, *no* CIDNP effects were observed in ^{1}H and ^{13}C NMR spectra of reacting solutions (see Figure 3). We conclude that **5b** reacts exclusively by an ionic pathway in $CDCl_3$.

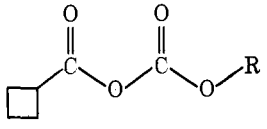
Symmetrical Peroxides. Product Studies. The thermal decomposition of bis(cyclobutanecarbonyl) peroxide (**11a**) was investigated briefly by Kaptein,[13] Hart,[15] and Reutov.[16] Bis(cyclopropylacetyl) peroxide (**11b**) was investigated by Hart and Cipriani[17] and most recently by Oae, Fujimori, and co-workers.[6] The thermolysis of **11a** has been discussed[13,15,16] exclusively in terms of a free-radical process, but two authors[15,16] did note the formation of ester as a significant product. Hart[17] discussed the thermolysis of **11b** noting the high yield of ester and unusually reactive nature of this primary peroxide. Oae[6] and co-workers were successful in trapping the carbonic anhydride (**15b**) and ester (**14b**) from **11b** but did not detect rearrangement. In all of the above cases ester formation was attributed to collapse of an acyloxy-alkyl radical pair. In retrospect, formation of a high yield of ester by this route conflicts with the picture presented by Kochi's[9a] results wherein direct photolysis of **11a,b** gave ester in less than 5% yield.



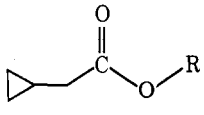
11a, R = cyclobutyl
b, R = cyclopropylmethyl
c, R = 3-butenyl



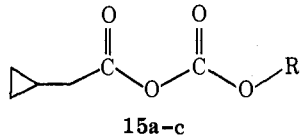
12a-c



13a-c



14a-c



15a-c

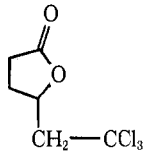


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Table V. Products of Thermolysis of 0.04 M **11a** and **11b** in $CHCl_3$

11a at 60 °C (3 h)			**11b** at 40 °C (2 h)		
product	yield, %	ratio	product	yield, %	ratio
12 (total)	13		**14** (total)	32	
12a		29	**14a**		19
12b		68	**14b**		71
12c		<3	**14c**		10
13 (total)	23	*a*	**15** (total)	38	*a*
acid	12		acid	10	

[a] Ratio not determined; see text.

We have begun a reinvestigation of the thermolysis of **11a,b.** The results of our initial product studies are summarized in Table V. With both peroxides thermolysis yielded polar

Table VI. Products of Thermolysis of 0.04 M **5c** at 60 °C (43 h) in Two Solvents

	$CHCl_3$		CH_3CN	
product	yield, %	ratio	yield, %	ratio
6 (total)	1		5	
6a		15		31
6b		70		38
6c		15		41
7 (total)[a]	9	*b*	19	*b*
acid	5		11	
other	*c*		*d*	

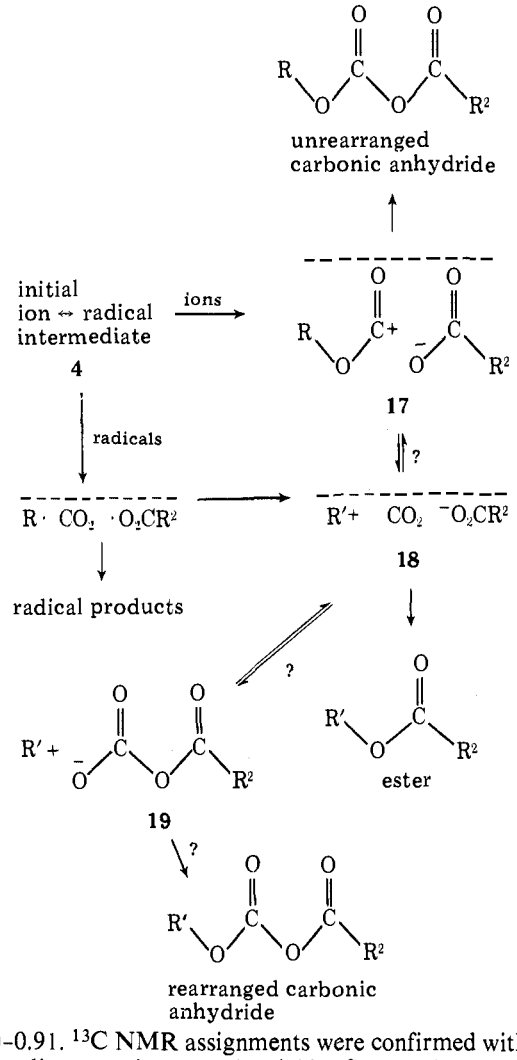
[a] Yield of total anhydride, **7** plus diaroyl. [b] Yield of **8** from dibutylamine treatment too low to determine isomeric ratios; *N,N*-dibutyl-*m*-chlorobenzamide identified by VPC. [c] Other products: lactone **16** (70%) and chlorobenzene (70%). [d] Carboximides **10** (2%); ratios of **10a:10b:10c** were 19:60:21.

products in significant quantity. Esters **12** and **14** were formed with extensive rearrangement in R. Dibutylamine reacts with **13** and **15** almost exclusively at the alkanoyl carbonyl group producing the corresponding *N,N*-dibutylcarboxamide in high yield, thus giving the urethanes (**10**) in low yield. VPC traces of the dibutylamine-treated reaction show small peaks at the retention times of **10a-c**, indicating that **13** and **15** are rearranged, but this conclsuion must be considered tentative. In addition to the products listed in Table V **11a** produced significant amounts of cyclobutyl chloride and cyclobutane as identified by ^1H and ^{13}C NMR. We suspect, on this basis, that **11b** gave cyclopropylmethyl chloride and 4-chloro-1-butene as well. NMR evidence for this is discussed below.

Symmetrical Peroxides. CIDNP Studies. ^1H CIDNP effects attending the thermolysis of **11a,b** in hexachloroacetone have been reported by Kaptein.[13] Our ^1H and ^{13}C results in $CDCl_3$, leading to substantially the same conclusions as Kaptein's, are elaborated briefly here. With **11a**, strong multiplet effects (A/E at H_α, δ 4.4) attend the formation of cyclobutyl chloride. A net effect attends the formation of cyclobutane (A, ^1H at δ 1.95). From ^1H decoupled ^{13}C spectra one can attribute the net polarizations to cyclobutyl-halomethyl polarizing radical pairs (enhanced signals due to C_2Cl_6, $CDCl_5$, $CHCl_3$, and cyclobutane? are evident). In both ^1H and ^{13}C spectra of reacting solutions of **11a** the signals due to the ^{13}C's of cyclobutyl chloride, $^{13}CO_2$ (δ 125.2), and the ^{13}C-O (δ 68.7, 69.0) and ^1HC-O (δ 4.98, 3.90) atoms of esters **12a,b** grew normally. The story of **11b** is similar: multiplet effects which gave evidence of the cyclopropylmethyl to 3-butenyl rearrangement[10,13] dominated the rather complex ^1H CIDNP effects. Again, the key ^1H doublet at δ 4.01 (CH_2O of **14b**), the ^{13}C signal at δ 69.0 (CH_2O of **14b**), and the signals for $^{13}CO_2$ and rearranged esters grew normally during the course of the reaction. All of the CIDNP evidence of experiments in this series of peroxides indicates that decarboxylation of acyloxy radicals is too rapid to permit singlet-triplet mixing in acyloxy-alkyl radical pairs.

Thermolysis of *m*-Chlorobenzoyl 4-Pentenoyl Peroxide (5c). The thermolysis of the more thermally stable **5c** took a course different from its isomeric counterparts. The product distributions in two solvents are shown in Table VI. The major product from reaction in chloroform solvent was the crystalline lactone **16**, apparently a product of decomposition induced by reaction of trichloromethyl on **5c**.[18] The structure assignment of **16** rests on its elemental analysis, the observation of a strong IR absorption at 1785 cm^{-1} (γ-lactone), and interpretation of its ^1H and ^{13}C NMR spectra. ^1H NMR decoupling experiments confirmed the CCl_3-CH_2-CHO-CH_2- structural sequences. Thus, irradiation at δ 4.36 (-CH-O) caused the collapse of the CCl_3-CH_2- signals to an AB quartet (δ 2.79, 2.40, J_{gem} = 15 Hz) and simplified the signals spanning δ 1.70-0.91. ^{13}C NMR assignments were confirmed with gated decoupling experiments. The yields of esters **6** are low and in the range expected for a radical pair collapse pathway. However, the formation of the isomeric mixture of **6** points to ion-pair collapse as the route of formation, and confirmation of this is found in the formation of the ion pair capture products (**10a-c**) in acetonitrile. CIDNP studies of the thermolysis of **5c** required a temperature of 120 °C, which in turn required use of a higher boiling solvent, hexachloroacetone. Under these conditions *m*-chlorobenzoyloxy-4-butenyl polarizing radical pairs are formed as deduced by the following key evidence. Intense net effects were seen in ^1H spectra: E at 4.35, t (CH_2O of **6c**); A at 3.5, t, and E at 2.5, q ($ClCH_2CH_2$- of 4-chloro-1-butene). Confirming data were found in ^{13}C spectra: A at 63.9 and 164.2 (CH_2OCO of **6c**); E at 124.9 (CO_2). Examination of the NMR spectra of product mixtures in hexachloroacetone indicated that a small amount of carbon skeleton rearrangement had occurred.

Scheme IV



Discussion

Origin of the Carbon-Skeleton Rearrangements. We propose Scheme IV as a point of departure for discussion of the carbon-skeleton rearrangements. In Scheme IV we start with a single initial intermediate as proposed by Walling[7] and envision its irreversible partitioning down radical and ionic pathways. We propose that in the first ion pair, **17**, an R group has migrated, structurally intact, from C to O. Collapse of **17** would give carbonic anhydride without a rearranged R group. Cationic decarboxylation of **17** would yield **18**, in which rearrangement of R to R′ would occur. Ion pair **18** is the precursor of ester and acetonitrile capture products. We consider two

pathways for the origin of rearrangement in the carbonic anhydrides. Cationic recapture of CO_2 would reconvert **18** to **17**, which upon collapse would give rearranged carbonic anhydride. Alternately, anionic capture of CO_2 would convert **18** to **19**, the collapse of which would, likewise, give rearranged carbonic anhydride.

The following points amplify Scheme IV.

(1) If electron transfer in "separated" radical pairs were a major route to ion pair **18** one should expect to see, as did Lawler and co-workers,[5b] CIDNP effects attending the formation of rearranged products, in this case, ester **6b** from peroxide **5a**. Further, these effects should be as strong as those attending reactions of the radical pair precursor since electron transfer should not "attenuate" the CIDNP effect in this case. We do observe, in ^{13}C spectra of reacting **5a**, a weak effect (A) attributable to the polarized methine carbon of **6b**. However, this net effect is decidedly weaker than that observed in the formation of **6a** from **5a** (see Figures 1 and 2), and cyclobutyl radical is the major radical produced from **5a**. Further, ion pairs are produced from the decomposition of **5b** in reactions that produce no CIDNP-detectable radicals. Thus, we conclude that such electron transfer as observed by Lawler[5b] is not required for ion-pair production and that, when it occurs, it is a minor pathway.

(2) Regarding the proposal of ion pair **17** (perhaps solvent separated), the occurrence of partial ion pairing in the carboxy inversion process is supported by the ^{18}O scrambling studies of Denny[19] and Oae and Fujimori.[11,20]

(3) Cationic decarboxylation of **17** might be expected to be exothermic. Using 92 kcal as the ΔH_f of CH_3OCO^+,[21a] a model for the cation of **17**, an exothermicity ranging between 4 and 27 kcal can be estimated for gas-phase decarboxylation leading to a simple secondary[21c] or tertiary carbonium ion. An analogy for the proposed cationic decarboxylation can be found in the results of Beak and co-workers,[21d] who investigated the silver ion assisted decomposition of alkyl chloroformate esters as a route to carbocations. Further, conversion of **17** to **18** should be facilitated in more polar solvents thereby leading to higher yields of ester (and solvent-capture products) at the expense of carbonic anhydride. This is observed. One might, based on the relative solvolytic reactivity of the cyclobutyl and homoallyl systems, predict that the conversion of **17a** to **18** should be more rapid than the conversion of **17c** to **18**. This should give a high ratio of **6**/**7** starting from **5a** and a low ratio of **6**/**7** starting from **5c**. In comparing the data of Tables I and VI ($CHCl_3$ and CH_3CN solvents), the prediction seems to be borne out. (At present, the only temperature at which we have data to compare is 60 °C.)

(4) All of our control experiments with carbonic anhydrides **7a** and **7b** show that under reaction conditions preformed **7** is not a source of rearranged R groups in **6** or **7**.

(5) In an initial attempt to lengthen the lifetime of "loose" ion pair **18**[22] we examined the thermolysis of peroxide **5a** in solvents of increasing viscosity. If successful, a longer lived **18** should give ester **6** with a higher proportion of **6c**,[23] and, if **18** "returns" to **17** or goes to **19**, then an increase in the proportion of **7b** and **7c** in the carbonic anhydride (**7**) should be observed. The results are summarized in Table VII. As can be seen, an increase in solvent viscosity does result in a greater proportion of **6c** in the isomeric ester mixture. Paralleling this change is a small but definite increase in extent of rearrangement in the carbonic anhydride **7**. These results are consistent with the proposal of CO_2 recapture as the source of rearrangement in **7**. Olah and co-workers[25] have observed the methylation of CO_2 by methyl fluoroantimonate in SO_2ClF at low temperature. Also, the reaction of alkoxides with CO_2 yields alkyl carbonate anions.[12a] Thus the Scheme IV counterparts of cationic and anionic capture of CO_2, perhaps not the best analogies, are, nonetheless, known reactions.

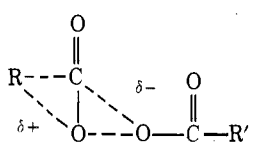
Table VII. Products of Thermolysis of 0.04 M **5a** at 80 °C (7 h) in Solvents of Increasing Viscosity

	cyclohexane		decalin		Nujol	
products	yield, %	ratio	yield, %	ratio	yield, %	ratio
6	20		26		25	
6a		32		25		21
6b		60		62		64
6c		8		13		15
7	36		42		42	
7a		91		87		85
7b		8		11		12
7c		1		2		3
acid	31		29		29	

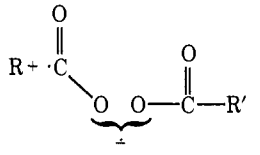
(6) In the thermolysis of C=^{18}O labeled peroxide **11b**, investigated by Oae, Fujimori, and Kozuka,[6] the oxygen label was found to be scrambled, to the extent of 20%, into the alcohol oxygen of carbonic anhydride **15b**. Since no scrambling of label was detected in unreacted peroxide (**11b**)[6] and since scrambling of ^{18}O labels in carbonic anhydrides occurs by acyl-oxygen cleavage,[6] some alkyl-oxygen cleavage must accompany the formation of carbonic anhydride **15b**. The results of these authors are readily interpreted in terms of Scheme IV.

The Ion–Radical "Differentiation" Process. Since acyloxy radicals (C_α—C=O still intact) are likely precursors for the alkyl radicals produced in the thermolyses of **5a**, **11a**, and **11b**, and C to O migration (C_α—C=O broken) is implicated in ion production, the major ion-radical differentiation process must precede carbon skeleton rearrangement on the reaction coordinate. Some idea regarding the timing of this differentiation is obtained from the CIDNP effects attending the decompositions of **11a,b**. With **11a**, for example, ester **12** was formed without net polarization; likewise, CO_2 was formed without net polarization. Both results indicate that the second decarboxylation step occurs very rapidly[26] and that any cyclobutyl-cyclobutanecarbonyloxy radical pair has a lifetime too short for singlet-triplet mixing, less than 10^{-10} s. By this time, then, ion-radical sorting apparently has occurred. This places the event in the lifetime of the Noyes "primary pair"[27] which for our purposes is the same as intermediate **4**.[7]

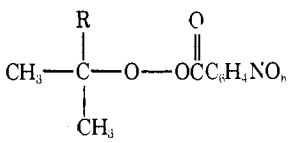
Limitations on the Structure of 4. Several authors have proposed structures for the initial intermediate **4**. Walling's[7] is shown in Scheme I. Oae and Fujimori's is shown as **4-O**,[6,20] and Leffler's as structure **4-L**.[4] It would seem certain that in



4-O



4-L



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4 C to O migration cannot be complete (i.e., **4** is not an "intimate" version of ion pair **17**) for two reasons. (1) Carboxylates do not react with carbonium ions by one-electron transfer. For example, the ratio of k_{ET} to k_{NUC} has an upper limit below 10^{-3} in the reaction of triphenylmethyl cation with carboxylate.[28] (2) If one-electron transfer did occur, the resulting alkoxycarbonyl radical should be too stable to suffer decarbox-

ylation before spin polarization could occur. For example, *tert*-butoxycarbonyl radical (observable by ESR) decarboxylates with $k_1 = 10^{5.2}$ s^{-1} at 27 °C.[29] Whether intermediate **4** is bridged or not is undetermined. The ability of the cyclopropylmethyl group (as an example) to stabilize positive charge is well-known and its enhancement of the formation and ionic partitioning of an intermediate such as **4-L** can be envisioned. The order of reactivity for the series of diacyl peroxides **11**,[6,20] R = cyclobutyl < c-$C_3H_5CH_2$ < isopropyl < cyclohexyl, does not parallel that for solvolysis of the corresponding tosylates, isopropyl ~ cyclohexyl < cyclobutyl < c-$C_3H_5CH_2$. However, such a parallel should appropriately be expected only if **11** underwent a concerted two-bond rupture directly to ion pair **18** (Scheme IV).

The effectiveness of a neighboring cyclopropylmethyl functionality (cyclopropylmethyl α, β, or γ to a reaction site) to participate in cation formation is always overshadowed by the participation (in or after the rate-determining transition state) of the cyclopropane ring electrons at the electron-deficient site.[30] Thus, C–O *bridging* by cyclopropylmethyl would not be expected to enhance the rate of reaction of **11b** over that of other primary diacyl peroxides.[15,17] Hedaya and Winstein[31] have demonstrated that the nature of R in peresters **21** greatly influenced the rate of heterolytic cleavage of the peroxide link. The reactivity order for R, which ranged over five powers of ten, was CH_3 < primary < secondary < benzyl < *p*-methoxybenzyl < 4-camphyl < phenyl < *tert*-butyl. Winstein in fact proposed a transition state with R *bridging* C and O to account for the observed reactivity order, for the similarity with pinacol rearrangement migratory aptitudes, and for the quantitative migration of R from C to O. The reactivity order for a series of symmetrical diacyl peroxides **11**[1b,11] with a similar array of R groups can be drawn up. The relative *k*'s at 70 °C in CCl_4 range over six powers of ten, significant C to O migration is observed upon reaction, but the reactivity order for R (of **11**) differs significantly from that of Winstein's: 1-apocamphyl < secondary < benzyl ≪ *tert*-butyl.

In summary of this section we would argue that, in intermediate **4**, C to O migration has not taken place and that, at present, Leffler's unbridged structure (**4-L**) best accounts, as a transition state model, for the response that R groups make to electron deficiency developing in the C_1–C_2 bond of diacyl peroxides as the bond is weakened in the transition state.[7,20]

Summary

The results reported herein amplify the understanding of the mechanism of diacyl peroxide thermolysis. The specific points amplified were summarized at the end of the introduction. The cyclobutyl and cyclopropylmethyl groups have been shown to be very sensitive structural probes of post-transition-state events in these thermolyses. As such they present an approach complementary to previously used kinetic[7] and (elegant) ^{18}O scrambling studies.[3,6,11,20]

Walling's single transition state hypothesis[7] has been generally accepted, but not really tested, since its proposal. The use of the cyclobutyl and cyclopropylmethyl moieties enhances the precision with which ionic and radical products can be discerned. This may permit more sensitive tests (e.g., temperature effects) of radical vs. ion production in these thermolyses.

Experimental Section

General. IR spectra were recorded on a Perkin-Elmer 337 or 283 spectrometer. NMR spectra were recorded on a Perkin-Elmer R-12, Varian A-60, or Bruker WH-90 DS spectrometer. Chemical shifts are reported as δ_{Me_4Si} for ^1H and ^{13}C NMR spectra. Elemental analyses were done by Midwest Microlabs, Inc., Indianapolis, Ind. VPC analyses were performed on a Hewlett-Packard 5750 research chromatograph with flame ionization detector.

The following columns were used for VPC analyses: A, 15% EGA on Chromosorb W (AW and DMCS), 15 ft × 0.125 in. aluminum tubing; B, 15% DEGS on Chromosorb W (AW and DMCS), 9 ft × 0.125 in. stainless steel tubing; C, 10% SE-30 on Chromosorb W-HP, 6 ft × 0.125 in. stainless steel tubing; D, 20% FFAP on Chromosorb W (AW and DMCS), 3 ft × 0.125 in. stainless steel tubing.

m-Choroperoxybenzoic acid, cyclobutanol, cyclopropylmethanol, 3-buten-1-ol, cyclobutanamine hydrochloride, and cyclopropylmethanamine hydrochloride were obtained from Aldrich Chemical Co. Cyclobutanecarboxylic acid was obtained from Ash Stevens Inc. and 4-pentenoic acid from P and B Research Chemicals. Cyclopropylacetic acid was synthesized from ethyl vinylacetate and diiodomethane by the Simmons–Smith procedure described by Kochi and Bacha.[32] 3-Butenamine was prepared by the method of Robert and Mazur.[33]

^{13}C CIDNP Experiments. All CIDNP spectra were recorded on a Bruker WH 90DS FT NMR spectrometer equipped with a Nicolet 1180 computer. Solutions of the peroxide, 0.4–0.5 M in $CDCl_3$, were sealed in 10-mm NMR tubes and placed in the probe preheated to 75 °C. After 30 s was allowed for thermal equilibration, 250 scans were accumulated in 8K memory using a pulse width of 3.5 μs (35° flip). The acquisition time was 0.82 s and spectral width 5000 Hz. Even though three to four spectra were recorded continuously on the same sample, only the first 250 scans showed polarization. To ensure correct phasing a few drops of benzene were used in the reaction of the symmetrical peroxides **10a,b**. Hexachloroacetone solvent with external Me_2SO-d_6 for a lock signal was used in the case of **5c**. The temperature of the probe in this case was 120 °C, and in the case of **5b** was 60 °C. Me_4Si was the internal standard in all the experiments.

^1H CIDNP Experiments. Essentially the same procedure as above was used for recording ^1H CIDNP spectra: 5-mm NMR tubes, 25 scans, 3-μs pulse width, 4.1-s acquisition time, 1000-Hz spectral width.

Syntheses of the Peroxides. All the unsymmetrical peroxides (**5**) were prepared by the following general procedure. A suspension of 4.06 g of 85% *m*-chloroperbenzoic acid in 100 mL of hexanes was cooled to −79 °C. To this was added 2.37 g of the corresponding acid chloride followed by dropwise addition of 1.6 g of pyridine. After stirring for 3 h at −79 °C, the mixture was warmed to 0 °C and extracted with cold dilute HCl, 5% sodium carbonate, and water. The organic layer was dried over anhydrous sodium sulfate and the volume was reduced to about 25 mL in vacuo. Peroxides **5a,b** separated as white crystals on cooling the solution to −20 °C. They were filtered at 0 °C. Last traces of solvent were removed in vacuo. Peroxide **5a** was a solid at room temperature and **5b** a liquid. Peroxide **5c** was a liquid at as low as −15 °C, but could be recrystallized at −78 °C from pentane. The peroxides could be stored pure at −18 °C for several days without decomposition. All the peroxides prepared in this way were shown to be 95–100% pure by iodometric titration. **5a**: IR (CCl_4) 1805, 1770 and 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8–7.27 (m, aromatic), 3.34 (quintet, J = 8.8 Hz, CH), 2.53–2.25 (m, 2 CH_2), 2.2–1.99 (m, CH_2); ^{13}C NMR ($CDCl_3$) δ 170.8, 162.13 (C=O), 135.27, 134.31, 133.66, 130.24, 129.82 and 125.98 (aromatic), 34.29 (CH), 25.65 (2 CH_2), 19.12 (CH_2). **5b**: ^1H NMR ($CDCl_3$) δ 8.00–7.43 (m, aromatic), 2.44 (d, J = 6.84 Hz, CH_2), 1.16 (m, CH), 0.758–0.2 (m, 2 CH_2); ^{13}C NMR ($CDCl_3$) δ 135.28, 134.37, 132.53, 130.27, 129.78 and 127.9 (aromatic), 35.39 (CH_2), 6.85 (CH), 4.8 (2 CH_2). **5c**: IR (smear) 1808, 1775, and 1225 cm^{-1}; ^1H NMR (CCl_3COCCl_3) δ 7.93–7.35 (m, aromatic), 6.07–5.46 (m, =CH) 5.12 (m, =CH_2), 2.55 (m, 2 CH_2); ^{13}C NMR (CCl_3COCCl_3) 167.06 and 160.69 (C=O), 135.02 (=CH), 134.64, 133.67, 132.53, 129.73, 129.30, and 128.71 (aromatic), 116.35 (=CH_2), 28.80, 28.21 (2 CH_2).

Cyclobutanecarbonyl peroxide (**11a**) was prepared by the procedure of Kochi and Bemis[34] and cyclopropylacetyl peroxide (**11b**) by the procedure of Hart and Cipriani.[16] **11a**: ^1H NMR ($CDCl_3$) δ 3.301 (quintet, CH), 2.671–2.00 (m, 3 CH_2); ^{13}C NMR ($CDCl_3$) δ 170.15 (C=O), 34.41 (CH), 25.57 (2 CH_2), 19.04 (CH_2). **11b**: ^1H NMR ($CDCl_3$) δ 2.36 (d, J = 7 Hz, CH_2), 1.33–0.89 (CH), 0.74–0.17 (m, 2 CH_2); ^{13}C NMR ($CDCl_3$) δ 168.46 (C=O), 35.33 (CH_2), 6.74 (CH), 4.69 (2 CH_2).

Syntheses of Cyclobutyl-, Cyclopropylmethyl-, and 3-Butenyl-*m*-chlorobenzoyl Carbonates, 7. The three isomeric carbonates **7a–c** were prepared in 50–60% yield by reaction of *m*-chlorobenzoic acid with the corresponding alkyl chloroformate in the presence of triethylamine.[35] The alkyl chloroformates used in the preparations were made

by the reaction of the corresponding alcohol with a 12.5% solution of phosgene in benzene. The carbonates prepared in this way were shown to be 95–100% pure by titration.[8] **7a**: IR (smear) 1803 and 1747 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.2 (m, aromatic), 5.11 (quintet, OCH), 2.6–2.0 (m, $(CH_2)_3$). **7b**: IR (smear) 1805 and 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.2 (m, aromatic), 4.18 (d, J = 7.0 Hz, OCH_2), 1.28 (m, CH), 0.7–0.3 (m, CH_2CH_2). **7c**: IR (smear) 1810 and 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.2 (m, aromatic), 5.8 (m, CH), 5.27 and 5.02 (2 m, $=CH_2$), 4.37 (t, J = 6.7 Hz, OCH_2), 2.52 (q, J = 7 Hz, CCH_2).

Syntheses of Cyclobutyl Cyclopropylmethyl, and 3-Butenyl *m*-Chlorobenzoates, 6. The esters **6a–c** were prepared by reacting equimolar quantities of the corresponding alcohol and *m*-chlorobenzoyl chloride in the presence of a slight excess of pyridine. They were purified by vacuum distillation. **6a**: IR (smear) 1725, 1290, 1258, 1204, and 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.98–7.22 (m, aromatic), 5.20 (quintet, J = 7.31 Hz, OCH), 2.62–2.00 (m, 2 CH_2), 1.88–1.50 (m, CH_2); ^{13}C NMR ($CDCl_3$) δ 164.68 (C=O), 136.41, 134.6, 132.84, 129.66, and 127.77 (aromatic), 69.8 (OCH), 30.48 (2 CH_2), 13.71 (CH_2). **6b**: IR (smear) 1725, 1290, 1258, 1128, and 1085 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.01–7.4 (m, aromatic), 4.15 (d, J = 7.0 Hz, OCH_2), 1.26 (m, CH), 0.71–0.27 (m, 2 CH_2); ^{13}C NMR ($CDCl_3$) δ 165.44 (C=O), 136.16, 134.58, 132.8, 129.676, and 127.79 (aromatic), 70.07 (OCH_2), 9.93 (CH), 3.34 (2 CH_2). **6c**: IR (smear) 1725, 1290, 1260, 1130, 1090, and 1077 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.00–7.21 (m, aromatic), 6.09–5.64 (m, =CH), 5.64–5.03 (m, $=CH_2$), 4.35 (t, J = 6.7 Hz, OCH_2), 2.5 (q, J = 7 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ 165.28 (C=O), 136.26, 134.64, 132.32, 129.73, and 127.79 (aromatic), 133.88 (=CH), 117.54 ($=CH_2$), 64.41 (OCH_2), 33.17 (CH_2). Anal. ($C_{11}H_{11}ClO_2$) C, H, Cl.

Syntheses of the Aliphatic Esters, 12 and 14. The esters **12a–c** and **14a–c** were prepared by the reaction of the corresponding acid chloride and alcohol in presence of pyridine. They were purified by distillation in vacuo and characterized by NMR spectroscopy. Compounds **12** have been prepared previously.[36] **12a**: ^1H NMR ($CDCl_3$) δ 4.98 (m, OCH), 3.06 (m, CH), 2.51–1.41 (m, CH_2's); ^{13}C NMR ($CDCl_3$) δ 68.69 (OCH), 38.24 (CH), 30.45 (2 CH_2, alcohol), 25.29 (2 CH_2, acid), 18.46 (CH_2, alcohol), 13.61 (CH_2, acid). **12b**: ^1H NMR ($CDCl_3$) δ 3.9 (d, J = 7 Hz, OCH_2), 2.75 (m, CH, acid), 2.46–1.74 (3 CH_2, acid), 1.12 (m, CH, alcohol), 0.66–0.18 (m, 2 CH_2, alcohol); ^{13}C NMR ($CDCl_3$) δ 173.14 (CO), 68.99 (OCH_2), 38.36 (CH, acid), 25.41 (2 CH_2, acid) 18.52 (CH_2, acid), 9.95 (CH, alcohol), 3.18 (2 CH_2, alcohol). **12c**: ^1H NMR ($CDCl_3$) δ 6.02–5.58 (m, +CH), 5.1 (m, $=CH_2$), 4.12 (t, OCH_2), 3.1 (m, CH), 2.5–1.72 (m, 4 CH_2); ^{13}C NMR ($CDCl_3$) δ 134.20 (=CH–), 117.11 ($=CH_2$), 63.29 (OCH_2), 38.30 (CH), 33.26 (CH_2, alcohol), 25.35 (2 CH_2, acid), 18.52 (CH_2, acid). **14a**: ^1H NMR ($CDCl_3$) δ 4.95 (m, OCH), 2.20 (d, CH_2), 2.5–1.4 (m, CH_2, alcohol), 1.30–0.8 (m, CH, acid), 0.65–0.06 (m, CH_2, acid); ^{13}C NMR ($CDCl_3$) δ 173.2 (C=O), 67.75 (-OCH), 39.59 (CH_2CO), 30.59 (2 CH_2, alcohol), 7.0 (CH), 4.41 (2 CH_2). **14b**: ^1H NMR ($CDCl_3$) δ 3.87 (d, OCH_2), 2.18 (d, CH_2), 1.34–0.83 (m, 2 CH), 0.66–0.07 (4 CH_2); ^{13}C NMR ($CDCl_3$) δ 173.32 (C=O), 68.99 (OCH_2), 39.49 (CH_2), 9.93 (CH, alcohol), 7.01 (CH, acid), 4.37 (2 CH_2, alcohol), 3.18 (2 CH_2, acid). **14c**: ^1H NMR ($CDCl_3$) δ 6.02–5.58 (m, =CH), 5.11 (m, $=CH_2$), 4.15 (t, OCH_2), 2.39 (q, CH_2), 2.21 (d, CH_2CO), 1.25–0.81 (m, CH), 0.65–0.06 (m, 2 CH_2); ^{13}C NMR ($CDCl_3$) δ 173.15 (C=O), 134.21 (=CH), 117.16 ($=CH_2$), 63.44 (OCH_2), 39.49 (CH_2, acid), 33.22 (CH_2, alcohol), 7.01 (CH), 4.42 (2 CH_2).

Syntheses of *N,N*-Di-*n*-butylcyclobutyl-, Cyclopropylmethyl-, and 3-Butenylurethanes, 8. Compounds **8a–c** were prepared by reacting the corresponding alkyl chloroformate with an excess (1:3) of *N,N*-di-*n*-butylamine. Similarly prepared were the diethylurethanes **9a–c**. Anal. **8a** ($C_{13}H_{25}NO_2$), C, H, N.

Syntheses of *N,N*-Di-*n*-butyl-*m*-chlorobenzamide and Cyclobutanecarboxamide. These amides were prepared by treating the corresponding acid chloride with excess di-*n*-butylamine.

Syntheses of *N*-Acetyl-*N*-*m*-chlorobenzoylcyclobutyl-, Cyclopropylmethyl-, and 3-Butenylamines, 10. Compounds **10a–c** were prepared by the following general procedure. The amine hydrochloride (2.16 g) was dissolved in 50 mL of 2 N NaOH and 50 mL of benzene was added. The mixture was cooled to 5 °C and *m*-chlorobenzoyl chloride (3.5 g) was added dropwise to the vigorously stirred mixture. After stirring for 1 h, the benzene layer was washed, dried, and concentrated in vacuo. The resulting crude product was recrystallized from hexane. To 1.5 g of the *m*-chlorobenzamide prepared as above were added 20 mL of cyclohexane and 1.5 g of phosphorus pentachloride. The mixture was refluxed for 3 h and the solvent was then removed in vacuo. The resulting yellow oil was added dropwise to a suspension of 1.5 g of anhydrous sodium acetate in 30 mL of dimethylformamide. After the mixture was stirred for 16 h, ether was added and the mixture was washed several times with water. The ether layer was dried and concentrated. The residue was chromatographed on silica gel to remove unreacted amide. The product was further purified by vacuum distillation, overall yields about 30%. **10a**: IR (smear) 1685, 1665, 1295, and 1235 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.7–7.33 (m, aromatic), 4.52 (quintet, J = 8.3 Hz, NCH), 2.16 (s, CH_3), 2.35–2.07 (m, 2 CH_2), 1.84–1.57 (m, CH_2); ^{13}C NMR ($CDCl_3$) δ 173.15 and 171.53 (C=O), 137.77, 135.23, 133.13, 131.22, 129.14, and 127.14 (aromatic), 52.65 (NCH), 30.1 (2 CH_2), 25.46 (CH_3), 15.54 (CH_2). **9b**: IR (smear) 1695, 1665, 1365, 1350, 1330, and 1235 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.64–7.42 (m, aromatic), 3.67, (d, J = 7.3 Hz, NCH_2), 2.19 (s, CH_3) 1.1 (m, CH), 0.55–0.22 (m, 2 CH_2); ^{13}C NMR ($CDCl_3$) δ 173.33 and 173.09 (C=O), 137.79, 135.09, 132.40, 130.24, 128.56, and 126.58 (aromatic), 50.71 (NCH_2), 26.07 (CH_3), 10.97 (CH), 3.90 (2 CH_2). **9c**: IR (smear) 1685, 1665, 1365, 1350, and 1215 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6–7.34 (m, aromatic), 5.6–5.2 (m, =CH), 5.04 (m, $=CH_2$), 3.85 (t, J = 6.8 Hz, NCH_2), 2.36 (q, J = 6.8 Hz, CH_2), 2.16 (s, CH_3); ^{13}C NMR ($CDCl_3$) δ 172.81 (C=O), 135.24, 134.72, 132.19, 130.18, 128.62, and 126.47 (aromatic), 134.72 (=CH), 117.63 ($=CH_2$), 45.69 (NCH_2), 33.60 (CH_2), 26.19 (CH_3). Anal. ($C_{13}H_{14}ClNO_2$), C, H, N, Cl.

Thermal Decomposition of the Peroxides. The solvents used for the decomposition were purified before use by standard procedures. The general method employed for the decomposition and subsequent analysis of the products is as follows. A solution of 1.02 g of a peroxide (**5a–c**, 0.004 mol) in 100.0 mL (or 10.0 mL) of the solvent was heated in a constant-temperature bath for a sufficient time to complete more than 98% of the reaction (see Tables I–VII for times). The product mixture was then extracted several times with 30-mL portions of 5% aqueous bicarbonate to remove *m*-chlorobenzoic acid. The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was dissolved and made up to 10.0 mL with carbon tetrachloride. The bicarbonate extracts were combined and acidified with HCl. The acidified solution was extracted several times with ether. The combined ether extracts were washed with distilled water and ether was distilled in vacuo. The residue was dissolved in aqueous methanol and titrated with standard NaOH to determine the yield of acid. The CCl_4 solution was analyzed for other products as follows.

To 1.0 mL of the product solution *n*-propyl *m*-chlorobenzoate was added as an internal standard, followed by the addition of a slight excess of *N,N*-di-*n*-butylamine. After 15 min of reaction, the excess amine was neutralized with dilute HCl and the organic layer was analyzed by VPC on either column A or B for the rearranged esters **6a–c** (column B gave better separation of isomers than column A).

The total amount of carbonate in the product mixture was determined by a procedure originally used by Johnson and Funk[8] for anhydrides. To a 2-mL portion of the CCl_4 solution was added an excess of 0.05 M morpholine in methanol. After 15 min, the excess morpholine was titrated with standard methanolic HCl using a mixed indicator prepared by dissolving 0.55 g of methyl orange and 0.04 g of methylene blue in 50 mL of methanol. The end point was a color change from green to amber. A blank titration was done and the total yield of carbonate was calculated from the difference between blank and sample. The percentage composition of rearranged carbonates was determined by measuring the area of peaks due to the rearranged urethanes **8a–c** (or **9a–c**) in the same chromatogram used to calculate the yield of esters **6**. The yields of **9a–c** in the acetonitrile decompositions were determined on column C using *N,N*-di-*n*-butylcyclobutanecarboxamide as an internal standard.

The viscosity experiments were carried out by heating **5a** in cyclohexane, decalin, and mineral oil at 80 °C for 7 h. The product solution in the case of cyclohexane solvent was worked up and analyzed as described above. In the case of decalin, after extraction with bicarbonate, the reaction mixture was analyzed without removal of solvent. In the case of mineral oil, 10.0 mL of the reaction mixture, after bicarbonate extraction, was treated with di-*n*-butylamine and the internal standard was added. After neutralization of the excess amine, an aliquot was extracted with an equal volume of methanol and the methanol layer was analyzed for esters and urethanes. The

total yield of acid in these three solvents was determined by a combination of titration and VPC methods. The yield of free acid was determined by bicarbonate extraction and subsequent titration. The amount of *N,N*-di-*n*-butyl-*m*-chlorobenzamide was determined by VPC on column C using *N,N*-di-*n*-butylcyclobutanecarboxamide as internal standard. The *m*-chlorobenzamide arose from two sources: from reaction of dibutylamine at the benzoyl carbonyl of **7** (0.15 of total), and from reaction with *m*-chlorobenzoic anhydride. The latter anhydride arose from the slow (acid consuming) reaction of **7** with *m*-chlorobenzoic acid. Thus the yield of *N,N*-dibutyl-*m*-chlorobenzamide reflected the yield of *m*-chlorobenzoic acid from the thermolysis. The yield of acid was calculated as follows: total anhydride = yield of **7**; acid = free acid + (yield of *m*-chlorobenzamide − 0.15 of undecomposed **7**).

The yields of lactone **16** and chlorobenzene from the decomposition of **5c** were determined on column D using ethyl trichloroacetate as the internal standard. The response factor for the lactone **16** was calculated using a pure sample isolated from the product mixture. **16**: IR 1785, 1180, 1145, and 1050 cm^{-1}; ^1H NMR (C_6D_6) δ 4.36 (m, CH), 2.79 and 2.40 (2 q, J_{gem} = 15, J_{vic} = 6.3 and 4.4 Hz, CH_2CCl_3), 1.90 (m, α CH_2), 1.70–0.918 (m, β CH_2); ^{13}C NMR (C_6D_6) δ 174.99 (C=O), 96.56 (CCl_3), 76.17 (OCH), 59.50 (CH_2CCl_3), 28.59 (αC), 27.94 (βC). Anal. ($C_6H_7O_2Cl_3$), C, H, Cl, O.

The analyses of products in the decomposition of **11a,b** followed the same pattern as in the case of the unsymmetrical peroxides (**5**) except that *n*-butyl cyclobutanecarboxylate was used as the internal standard. Column B was used for the analysis of rearranged esters and urethanes.

Stability of the Carbonates 7. A. Acetonitrile. In a typical experiment 0.1160 g of **7a** was dissolved in 100 mL of CH_3CN. To a 10-mL portion of the solution excess morpholine was added. After 15 min of reaction, the excess was titrated with HCl. Another 10-mL portion was heated at 60 °C for 2 h and then treated with morpholine. From another 10 mL, the solvent was removed in vacuo and the volume was made up to 1.0 mL with CCl_4. The CCl_4 solution was treated with a slight excess of di-*n*-butylamine. After 15 min the excess amine was neutralized and the organic layer was analyzed by VPC for **8a** and *N,N*-di-*n*-butyl-*m*-chlorobenzamide on column C. To the remaining 70 mL, 0.05 g of *m*-chlorobenzoic acid was added and all the above three experiments were repeated. A 10-mL portion after addition of acid was heated for 2 h at 60 °C and then analyzed by VPC as before. A bicarbonate extraction was done to remove any unreacted acid before the CH_3CN solution was concentrated for VPC analysis. Since CH_3CN is soluble in water, an equal volume of chloroform was added every time an extraction was done on any CH_3CN solution.

B. Chloroform. A 0.4 M solution and a 0.04 M solution of **5a** in $CHCl_3$ were heated under nitrogen at 60 °C for 2 h. To each reaction mixture 0.001 mol of **7a** was added and heating was continued for 3 h. Titration of the product showed that the amount of **7** present corresponded to that usually obtained in a decomposition plus the amount of **7a** added during the heating period. There was no indication that **7a** decomposed during the reaction.

A solution of 0.004 mol of **7a** and 0.001 mol of *m*-chlorobenzoic acid in 15 mL of $CHCl_3$ and a like solution prepared with 0.004 mol of **7b** were heated under nitrogen for 5 h at 60 °C. Analysis of the product by the methods described previously showed no decrease in the titer for **7a,b**, 1% or less conversion of **7a** to **6a** or **7b** to **6b**, and, from VPC analysis of the resulting urethanes (**8**), no rearrangement in **7a** or **7b**.

Acknowledgments. The authors thank the following sources for partial support of this work: the donors of the Petroleum Research Fund, administered by the American Chemical Society, funds from an institutional grant from the American Cancer Society, and funds from the College of Arts and Sciences of the University of Louisville. The ^{13}C NMR spectrometer used in this work was purchased with the help of Grant CHE 76-05683 from the National Science Foundation.

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