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Mechanism for Diacyl Peroxide Decomposition

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The presence of ion-pair intermediates in diacyl peroxide decomposition has been established. Various substituted (4-X-phenyl)phenylacetyl Y-benzoyl peroxides and three corresponding 4-X-benzhydryl-4-nitrobenzoic carbonic anhydrides (X = CH_3, H, Cl) were prepared. All compounds decomposed in 90% acetone–water (v/v), giving the ionic products ester, alcohol, and acid. The fraction of ester (R) was similar to that found in the solvolysis of substituted benzhydryl-*N*-nitrosoamides, indicating a similar spectrum of ion-pair intermediates. The yield of ester product could be increased markedly by the addition of common ion. The mixed carbonic carboxylic anhydrides were not products of peroxide decomposition in either nucleophilic or nonnucleophilic solvents and showed a lower decomposition rate than the peroxide. Lastly, both the peroxide and the mixed carbonic carboxylic anhydride decomposed in chloroform with net retention. Neither CIDNP nor any radical abstraction product was detected.

Introduction

The decomposition of symmetric primary alkyl and aroyl diacyl peroxides generally proceeds through homolytic cleavage of the peroxide linkage and affords typical radical products. The mechanism for the decomposition of symmetric secondary and tertiary alkyl and also unsymmetric diacyl peroxides is considerably more complex. Since the first isolation of a "carboxy inversion product" by Leffler[3] in 1950, there have been many papers implicating ionic intermediates in diacyl peroxide decompositions.[4–8]

A comprehensive review of diacyl peroxide decomposition was given by Walling.[4a] On the basis of kinetic and product studies, Walling suggested that both ionic and radical pathways branch from a common "spin-diradical ion-pair" intermediate (I) (Scheme I). Criticism, by Leffler,[5] has resulted in minor modifications of Walling's intermediate.

Evidence that ion-pair intermediates arise via charge transfer between radical pairs from a diacyl peroxide has been provided by Lawler.[6] This mechanism was based on the observed CIDNP in the decomposition of *tert*-butylacetyl *m*-chlorobenzoyl peroxide, which was interpreted as arising from polarized, rearranged products of ion-pair intermediates.

Recently, a more detailed mechanism for diacyl peroxide decomposition has been proposed by Taylor[7] to explain carbon skeleton rearrangements observed in both carboxy inversion product and ester. Taylor's study supports our initial observation[9] of ion-pair intermediates in diacyl peroxide decomposition.

This paper provides definitive evidence for the presence of ion-pair intermediates in diacyl peroxide decomposition. A common intermediate from which branching of ionic and radical pathways takes place may be unnecessary and is in fact contrary to some of our results. A simpler mechanism in which both ionic and radical pathways branch directly from the diacyl peroxide is consistent with all of the facts.

Scheme I

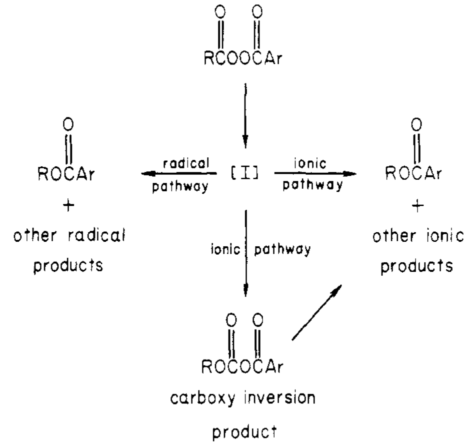

Table I. Nonsolvolytic Peroxide Decomposition

$$\underset{\mathbf{1}}{\text{X-PhY-PhCHCO}_2\text{O}_2\text{CPh-Z}} \longrightarrow \underset{\mathbf{5}}{\text{X-PhYPhCHO}_2\text{CPh-Z}}$$

X	Y	Z	% ester (recryst yield)
4-CH_3O	H	4-NO_2	90 [b,d]
4-CH_3O	H	H	80 [b,d]
4-CH_3	H	4-NO_2	83 [90] [a]
H	H	4-NO_2	90 [90] [a]
H	H	3-Cl	87 [98] [a], 81,[b] 90 [c]
4-Cl	H	4-NO_2	95 [b,d]
4-Cl	H	3-Cl	75 [90] [a]
4-NO_2	H	3-Cl	90 [b,e]
4-NO_2	H	4-NO_2	80 [95] [a]
4-NO_2	4-NO_2	4-NO_2	30 [a,e]

[a] Prepared by DCC coupling of the acid and peracid; yield in brackets is that of dicyclohexylurea. [b] Prepared from acid chloride, peracid, and amine. [c] Prepared from the acid chloride and salt of the peracid. [d] Yield by gas chromatography. [e] Yield by infrared spectroscopy.

The substituted diphenylacetyl benzoyl peroxides **1a–f**, (Scheme II) and the corresponding carbonic carboxylic anhydrides **2a–c** were chosen to be studied for two reasons: (1) It was thought that the extraordinary stability of the benzhydryl cation and benzoate anion would afford an exclusively ionic peroxide decomposition. (2) The energy surface of benzhydryl–benzoate ion-pair reactions is well defined and it was thought that this peroxide decomposition would afford intermediates that could be explained

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[1] This work was taken from the Ph.D. Dissertation of R. J. Linhardt, The Johns Hopkins University, 1979, available from University Microfilms, Ann Arbor, MI.

[2] To whom correspondence should be addressed.

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[8] K. Fujimori and S. Oae, *Tetrahedron*, **29**, 65 (1973).

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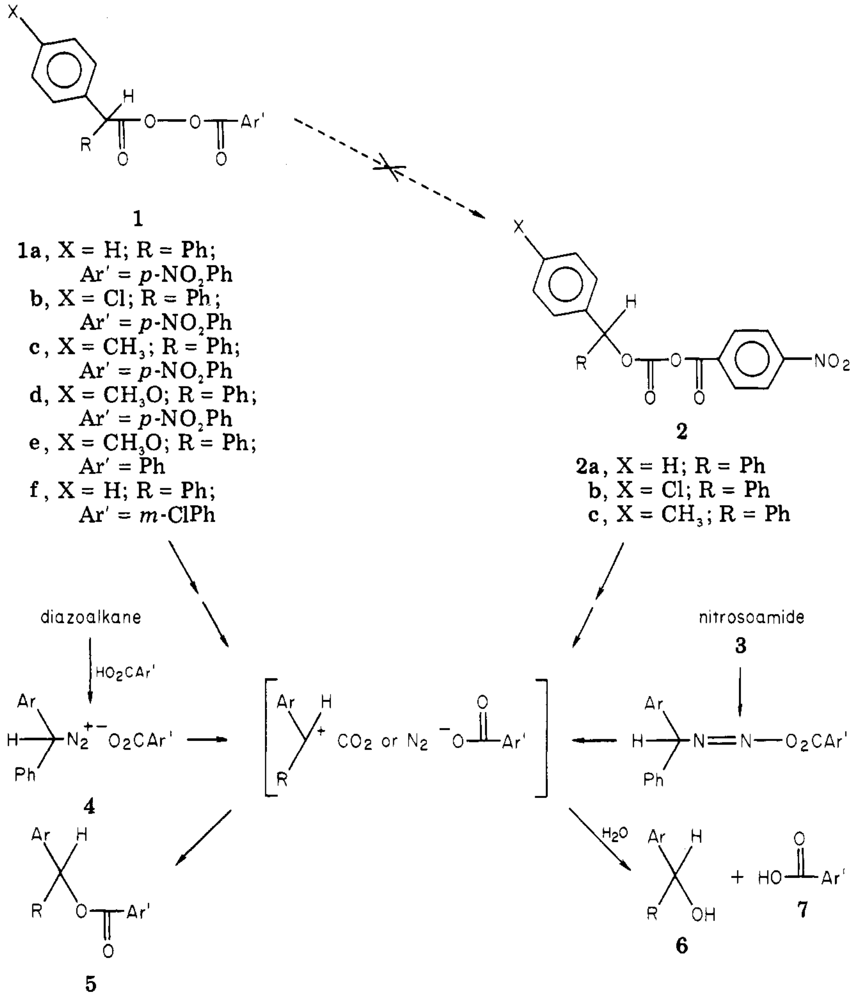
Scheme II. Solvolysis



1a, X = H; R = Ph; Ar' = p-NO$_2$Ph
b, X = Cl; R = Ph; Ar' = p-NO$_2$Ph
c, X = CH$_3$; R = Ph; Ar' = p-NO$_2$Ph
d, X = CH$_3$O; R = Ph; Ar' = p-NO$_2$Ph
e, X = CH$_3$O; R = Ph; Ar' = Ph
f, X = H; R = Ph; Ar' = m-ClPh

2a, X = H; R = Ph
b, X = Cl; R = Ph
c, X = CH$_3$; R = Ph

in terms of this energy surface.

Results and Discussion

Preparation and Decomposition in Nonnucleophilic Solvents. Diacyl Peroxides. Peroxides (**1a–f**), prepared by established procedures, were characterized by low-temperature NMR and IR spectra and decomposed below −20 °C.

All attempts to prepare and isolate peroxides **1a–f** resulted in isolation of the benzhydryl benzoate ester in high yield (Table I). No other decomposition products were detected by IR, NMR, or gas chromatography when these peroxides were decomposed in halogenated solvents, ether solvents, or in toluene. Therefore, if radicals are involved, they do not escape from the solvent cage.[10] Green's[11] earlier work had shown the related 4-bromobenzoyl phenylacetyl peroxide gave only 2% scavengable radicals during decomposition in benzene. Vilkas[12] found no scavengable radicals in 4-nitrobenzoyl (phenylethyl)acetyl peroxide decomposition. Since the level of scavengable radicals is so low in Green's case, none are expected in our cases.

The stereochemistry of peroxide decomposition in methylene chloride showed 13% net retention, indicating the involvement of a benzhydryl radical or cation.

Phenylacetyl 4-nitrobenzoyl peroxide **1g** decomposed in benzene to give benzyl-4-nitrobenzoic carbonic anhydride **2d**, benzyl 4-nitrobenzoate, and diphenylmethane.

The rates of decomposition of **1a–f** were not measured as they decomposed rapidly at temperatures below −20 °C. However, phenylacetyl 4-nitrobenzoyl peroxide, **1g**, decomposed at $t_{1/2}$ = ca. 2.6 min by NMR in deuterochloroform at 25 °C.

Mixed Carbonic Carboxylic Anhydrides. The mixed carbonic carboxylic anhydrides **2a–c** were isolable and, except for **2c**, were easily characterized. **2c** was pure by its spectral data but gave an unsatisfactory analysis, which suggested contamination by ester.

The inversion compounds **2a–c** decomposed on melting and in chloroform-d and nitromethane-d_3, affording quantitative yields of ester. The optically active inversion compound **2c** decomposed to ester with at least 29% retention in chloroform.

The first-order kinetics of these decompositions showed rate enhancements with increasing solvent polarity (Table II). The $\sigma+$ Hammett treatment gave ρ values of −3.83 in chloroform-d and −4.36 in nitromethane-d_3. The $\sigma+$ Hammett ρ value obtained by Goering and Hopf[13] for 4-substituted benzhydryl 4-nitrobenzoates in 90% aqueous acetone was ρ = −3.9. These values, coupled with 29% net retention in ester, strongly suggest the intermediacy of a

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Table II. Rates of Carbonic Carboxylic Anhydride Decomposition

$\text{4-X-PhPhCHOCOO}_2\text{CPh-4-NO}_2 \longrightarrow$
2

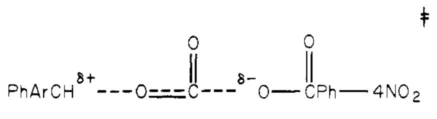
$\text{4-X-PhPhCHO}_2\text{CPh-4-NO}_2$
5

		half-life, min[a,b]		
solvent[e]	dielec const, ϵ^5	2b (X = Cl)	2a (X = H)	2c (X = CH_3)
$CDCl_3$	4.7	1470, 2180[c]	955, 923[c]	41.2[c]
$(CD_3)_2CO$	20.7	869	[7.4, 100]	24.8
CD_3NO_2	35.9	89.6	48.7	4.8
$(CD_3)_2SO$	46.7	[2.3]	[1.3]	<0.5

[a] Rates of carbonic anhydride disappearance determined by NMR at 0.1 M and $T = 36.0$ °C. [b] Curve fit by linear regression typically with a variance r between 0.90 and 0.99. [c] Rates by UV at 25.8 °C (5×10^{-5} M in $CHCl_3$). [d] Rates listed in brackets are of decompositions affording 4-nitrobenzoic anhydride and benzhydryl alcohol as products. [e] Hammett treatment (σ^+) for $CHCl_3$, $\rho = -3.83$ for CD_3NO_2, $\rho = -4.36$. [f] Rates were Reproducible within 10%.

benzhydryl–benzoate ion pair. No evidence of radical involvement in carbonic carboxylic anhydride decomposition has ever been reported.[14]

The activation parameters for this decomposition in chloroform-*d* are as follows: (**2a**) $\Delta H^{\ddagger}_{36} = 13.5$ kcal/mol, $\Delta S^{\ddagger}_{36} = -37.5$ cal/(deg mol); (**2b**) $\Delta H^{\ddagger}_{36} = 13.2$ kcal/mol, $\Delta S^{\ddagger}_{36} = -39.2$ cal/(deg mol); (T = 0 and 36 °C); they are similar to those reported by Tarbell[14] for carbonic carboxylic anhydride (**2d**). As suggested by Tarbell, these very negative $\Delta S^{\ddagger}$ values require a highly ordered transition state and suggest a simultaneous cleavage of two bonds (A) leading to ion-pair intermediates.



$$\mathrm{PhArCH}^{\delta+}\text{---}\mathrm{O}\text{===}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{---}{}^{\delta-}\mathrm{O}\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ph}\text{—}4\mathrm{NO}_2 \quad \ddagger$$

(A)

The decomposition of **2a** in acetone-d_6 and dimethyl-d_6 sulfoxide as well as **2b** in dimethyl-d_6 sulfoxide affords the benzhydryl alcohol and 4-nitrobenzoic anhydride instead of the ester. These products are consistent with a nucleophilic attack at the carbonic carboxylic anhydride's carbonyl. This mechanism is related to the ionic chain mechanism of carbonic anhydride decomposition described by Tarbell.[14] However, the reaction is not a chain as alcohol results[15] in place of the symmetric dialkyl carbonate. The rate of decomposition of **2a** showed a 10-fold rate decrease with a freshly opened bottle of acetone-d_6 in place of one opened a week before. This is suggestive of Tarbell's observation of the importance of trace impurities.

In summary, the decompositions in nonnucleophilic solvents of both diacyl peroxides and mixed carbonic carboxylic anhydrides indicate the importance of an ionic pathway that leads to ion-pair intermediates.

Decomposition of Peroxides and Mixed Carbonic Carboxylic Anhydrides in Nucleophilic Solvents. So that capturable ionic intermediates in hydroxylic solvents could be tested for, both the diacyl peroxides and the mixed carbonic carboxylic anhydrides were decomposed in aqueous acetone.

Diacyl Peroxides. Diacyl peroxides **1a–f** solvolyzed in aqueous acetone to give only three products: ester, alcohol, and acid (Scheme II). The alcohol **6**, obtained as a major product, provides the first definitive evidence for the presence of an ion-pair intermediate in peroxide decomposition. Alcohol as a major product can only arise from ion-pair intermediates.

Benzhydryl ion pairs are intermediates in the solvolysis of benzhydryl esters,[13] halides,[16] thiocyanates,[16] diphenylmethanediazonium benzoates,[16] and benzhydrylnitrosobenzamides.[17] All of these compounds solvolyze in aqueous acetone to give benzhydryl alcohols and in alcoholic solvents to give benzhydryl ethers.

The benzhydrylnitrosobenzamides **3** and diphenylmethanediazonium benzoates **4** are of particular interest because they give gas-separated benzhydryl–benzoate ion pairs similar to those produced in the diacyl peroxide and carbonic carboxylic anhydride decomposition (Scheme II).

The solvolysis of peroxides **1a–f** in 90% aqueous acetone gave a mixture of alcohol **6**, acid **7**, and ester **5** (Scheme II). The fraction of substrate leading to ester is the "R value", where R = [ester]/([ester] + [alcohol]). The R values obtained in these peroxide decompositions (Table III) are sensitive to substituent effects, temperature effects, and salt effects. This system can be best treated by using the Winstein[18] solvolysis mechanism.

The solvolytic decomposition of various diacyl peroxides in 90% aqueous acetone (Table III) shows decreasing R values when substitutents are used to stabilize the benzhydryl cation: p-Cl, R = 0.46; p-H, R = 0.40; p-CH_3, R = 0.38. The R value for **1d** (p-CH_3O, R = 0.54) does not reflect this trend as it is thermally unstable even at −78 °C, affording some ester prior to solvolysis.

The R values were found to increase for **1f** with decreasing temperature. Finally, and most important, the ester yield was doubled when **1d** or **1e** was solvolyzed in the presence of a 5-fold excess of common ion. This result is consistent with the common ion effects observed in both (4-methoxyphenyl)lphenylmethanediazonium benzoate (**4**) (R = 0.62–0.95)[16] and N-(4-methoxybenzhydryl)-N-nitrosobenzamide (**3**) decomposition (R = 0.45–0.89).[20] This not only provides unambiguous evidence for a dissociated carbonium ion intermediate but also for ion-pair return to ester.

Solvolysis of peroxide **1g** in methanol-d_4 gave benzyl methyl ether (40%) and approximately equal amounts of benzyl 4-nitrobenzoate and carbonic carboxylic anhydride **2d** (60%). No evidence of benzyl methyl carbonate was seen (by NMR). Carbonic carboxylic anhydride **2d** failed to give benzyl methyl ether in methanol-d_4 under the reaction conditions.

So that the behavior of radicals under nucleophilic conditions could be determined, diphenylacetyl *tert*-butyl perester was decomposed in 90% aqueous acetone. In addition to benzhydryl *tert*-butyl ether (51% by NMR), the decomposition of this perester afforded small quantities of benzhydrol (3.8%) and benzophenone (1.4%). This perester was studied in detail by Bartlett[19] and undergoes a purely radical decomposition. The small amount

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[14] D. S. Tarbell, *Acc. Chem. Res.*, **2**, 269 (1969), and references contained within.

[15] Alcohol product requires the presence of 0.1% trace water.

[16] A. F. Diaz and S. Winstein, *J. Am. Chem. Soc.*, **88**, 1318 (1966).

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[18] S. Winstein, B. Appel, R. Baker, and A. Diaz, *Spec. Publ.—Chem. Soc.* **No. 19**, 109–130 (1965).

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[20] K. J. Abbey, Ph.D. Thesis, The Johns Hopkins University, Baltimore, MD, 1975.

Table III. Solvolytic Decomposition of Diacyl Peroxides[a,b]

$$\underset{\mathbf{1}}{\text{ArPhCHCO}_2\text{O}_2\text{CAr}'} \xrightarrow{\text{H}_2\text{O}} \underset{\mathbf{6}}{\text{ArPhCHOH}} + \underset{\mathbf{5}}{\text{ArPhCHO}_2\text{CAr}'} + \underset{\mathbf{7}}{\text{Ar}'\text{CO}_2\text{H}}$$

compd	Ar	Ar′	% yield[h]	*T*,[g] °C	no salt,[c,d] *R*	added sald,[c,d] *R*
1b	4-ClPh	4-NO_2Ph	95	15	0.46	*e*
1a	Ph	4-NO_2Ph	79	15	0.40	*e*
1c	4-CH_3Ph	4-NO_2Ph	96	15	0.38	*e*
1d	4-CH_3OPh	4-NO_2Ph	>90	15	0.54	$\xrightarrow{+\text{PNB}^f}$ 0.96
1e	4-CH_3OPh	Ph	83	15	0.64	$\xrightarrow{+\text{B}^f}$ 0.95
1f	Ph	3-ClPh	75	15	0.50	*e*
1f	Ph	3-ClPh	>75	0	0.56	*e*

[a] Compounds decomposed in 90% aqueous acetone v/v, 25 °C. [b] Amine hydrochloride present during peroxide decomposition. [c] R = [ester]/([ester] + [alcohol]). [d] Products analyzed by gas chromatography. [e] Not determined. [f] PNB and B = *tetra-n*-butylammonium 4-nitrobenzoate and benzoate, respectively. [g] Calculated final temperature after aqueous acetone is injected. [h] % Yield = 200([alcohol] + [ester])/([acid chloride] + [peracid]).

Table IV. Decomposition of Mixed Carbonic Carboxylic Anhydrides in 90% Aqueous Acetone

$$\underset{\mathbf{2}}{\text{ArPhCHOCOO}_2\text{CAr}'} \xrightarrow{\text{H}_2\text{O}} \underset{\mathbf{6}}{\text{ArPhCHOH}} + \underset{\mathbf{5}}{\text{ArPhCHO}_2\text{CAr}'} + \underset{\mathbf{7}}{\text{Ar}'\text{CO}_2\text{H}^e}$$

compd	Ar	ester + alcohol % yield	temp, °C	no salt, *R*	added salt, *R*
2b	4-ClPh	>90[a]	36	0.40[b]	*f*
2a	H	>90[a]	36	0.49[b]	*f*
2c	4-CH_3Ph	90[c]	36	0.65[c]	$\xrightarrow[+\text{PNB}^d]{}$ 0.024[c]

[a] Minimum yield by infrared. [b] By titration as determined from the t_∞ point of kinetic runs. [c] By gas chromatography. [d] PNB = *tetra-n*-butylammonium 4-nitrobenzoate. [e] Ar′ = 4-NO_2Ph. [f] Not determined.

of alcohol obtained from this perester apparently arose from the reaction of the benzhydryl radical with oxygen. The radical source of this alcohol is further substantiated by the formation of both benzophenone and large amounts of tetraphenylethane (20% by NMR). Neither benzophenone nor tetraphenylethane were found in diacyl peroxide or carbonic anhydride decompositions.

Mixed Carbonic Carboxylic Anhydrides. The *R* values obtained in the aqueous acetone solvolysis of carbonic carboxylic anhydrides **2a–c** (Table IV) show effects of substituents that are the opposite of those observed in peroxide decomposition and expected on the basis of carbonium stability. More surprising is the effect of common ion on compound **2c**. The 4-methylbenzhydrol is obtained to the near exclusion of ester product when common ion is added (R = 0.024). Instead of acting to suppress the formation of solvolysis product, the 4-nitrobenzoate anion acts as a nucleophile as discussed above. This decomposition provides an alternate pathway to alcohol and hence decreased *R* values. **2a** and **2b** give less stable carbonium ions, and the nucleophilic pathway becomes relatively more important. The rates of solvolysis (Table V) of the carbonic anhydrides in aqueous acetone determined by NMR (at 0.1 M) is over twice that of the titrimetric rate (at 0.04 M). This rate enhancement at increased concentration indicates that the bimolecular nucleophilic mechanism is operating.

So that the ion-pair component of mixed carbonic carboxylic anhydride decomposition could be determined, **2a** and **2c** were solvolyzed in alcohol solvents (Table VI). The product of the ion-pair pathway is a benzhydryl ether, whereas the nucleophilic pathway gives only benzhydryl alcohol. **2a** afforded a substantial fraction of alcohol (42% in ethanolysis and 24% in methanolysis), but the ion-pair pathway was found to be the major mode of decomposition. **2c** gives no alcohol, and thus its decomposition pathway presumably occurs entirely through ion-pair intermediates by alkyl–oxygen fission.

Table V. Rates of Solvolysis of Mixed Carbonic Carboxylic Anhydrides ArPhCHOCOO$_2$CAr′[e]

	half-life at 36 °C, min		
	2b, Ar = 4-ClPh	**2a**, Ar = H	**2c**, Ar = 4-CH_3Ph
acetone-d_6/D_2O[a,d]	54.7	21.5	18.0
acetone/H_2O[c,d]	134	118	150[b]

[a] Rate by NMR at 0.1 M. [b] At 0 °C. [c] Rate by titration at 0.04 M. [d] 90% aqueous acetone v/v, at 25 °C. [e] Ar′ = 4-NO_2Ph.

Table VI. Solvolysis of Carbonic Anhydrides in Alcohol[e]

$$\underset{\mathbf{2}}{\text{ArPhCHOCOO}_2\text{CAr}'} \xrightarrow{\text{ROH}} \underset{\mathbf{8}}{\text{ArPhCHOR}} + \underset{\mathbf{5}}{\text{ArPhCHO}_2\text{CAr}'} + \text{CO}_2 + \underset{\mathbf{7}}{\text{Ar}'\text{CO}_2\text{H}} + \underset{\mathbf{6}}{\text{ArPhCHOH}} + \underset{\mathbf{9}}{\text{Ar}'\text{CO}_2\text{OCAr}'}$$

compd	Ar	solvent	% yield[a,b]	% ion pair[a,c]	R[a,d]
2a	Ph	methanol	100	80	0.21
		ethanol	100	67	0.32
2c	4-CH_3Ph	methanol	100	100	0.19

[a] Determined by NMR. [b] % Yield = 100(([ether] + [alcohol] + [ester])/[carbonic anhydride]). [c] % Ion pair = 100(([ester] + [ether])/([ether] + [alcohol] + [ester])). [d] R = [ester]/([ester] + [ether]). [e] Ar′ = 4-NO_2Ph, T = 25 °C.

The *R* values obtained from the alcoholysis of these compounds show an unexpectedly large fraction of solvolysis product. The R value ($R = 0.32$) for **2a** in ethanol (Table VI) is substantially lower than that for *N*-benzhydryl-*N*-nitrosobenzamide (**3**) ($R = 0.42$) in the same solvent.[17] The benzhydrylbenzamide has been found to produce both intimate and solvent-separated ion pairs directly upon decomposition.[20] The lower R value in the mixed carbonic carboxylic anhydride suggests the direct production of a large fraction of solvent-separated ion pairs upon decomposition.

Stereochemistry of Diacyl Peroxide and Carbonic Carboxylic Anhydride Decomposition. The 4-methylbenzhydrol was resolved as the hemiphthalate with $d(+)$-α-methylbenzylamine and hydrolyzed by the method of Kenyon[22] to (−)-4-methylbenzhydrol of high optical purity. (Other workers[13b,23-25] have reported difficulty[26] in repeating Kenyon's resolution.)

The decomposition of peroxide **1c**, prepared from (+)-(4-methylphenyl)phenylacetic acid[21] in methylene chloride, gives (−)-4-methylbenzhydryl benzoate with 17% net retention (17% of the rotation of optically pure ester). Similarly, decomposition of **1c**, prepared from (+)-(4-methylphenyl)phenylacetyl chloride in 90% aqueous acetone, affords the ester with 15.9% net retention and (−)-4-methylbenzhydrol with 0.8 ± 0.2% net retention. The decomposition of (−)-**2c** in methylene chloride afforded the ester with 29% net retention.[45b]

The ester obtained from mixed carbonic carboxylic anhydride in methylene chloride and from diacyl peroxide in both methylene chloride and 90% aqueous acetone showed substantial loss of optical activity (15.9–29% net retention). This is consistent with the view that the ester is formed as a result of ion-pair return. A comparable amount of retention (13.4–25.6% net retention) is observed in ester formed from *N*-nitroso-4-chlorobenzamide decomposition in the same solvents.[17] The alcohol formed from diacyl peroxide decomposition in 90% aqueous acetone shows one-fifteenth the retention observed in the ester product. This parallels the results obtained when optically active *N*-nitroso-4-chlorobenzhydryl)naphthamide is decomposed in ethanol; the solvolysis product (benzhydryl ether) shows one-seventh the retention observed in the ester product.[17]

Radical Precursors to Ionic Intermediates. The presence of ion pairs as the immediate precursors of products does not preclude the intermediacy of radical pairs. A charge-transfer mechanism similar to that proposed by Lawler,[6] where ion pairs are derived from radical pairs, however, does not appear to be operating in our systems. We base this conclusion on the negative results of two experiments: (1) Failure to observe CIDNP in any product afforded in either solvolytic or nonsolvolytic peroxide decomposition; (2) The decomposition of benzoyl peroxide in the presence of diphenylmethane afforded small amounts of the anticipated benzhydryl benzoate (<3%) and benzhydrol (<2%). The ratio of benzhydrol to benzhydryl benzoate, however, was the same whether the decomposition was performed in pure acetone or in 90% aqueous acetone. This decomposition also gave 2% tetraphenylethane from recombination of benzhydryl radicals. At the concentrations used (0.04 M), induced decomposition is unimportant.[27] Thus, a large fraction of the ester is being formed from encounters by the diphenylmethyl and benzoyloxy radicals. If charge transfer were operating between these radicals, then the ion pair formed would partition between alcohol and ester products in aqueous acetone but only yield ester in dry acetone.

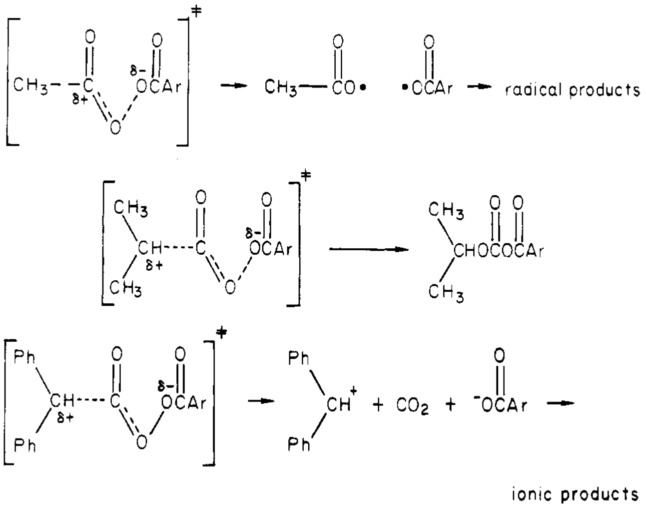

Figure 1. Proposed transition states for diacyl peroxide decompositions.

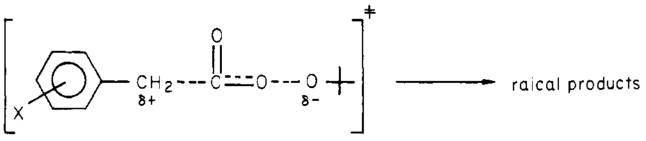

Figure 2. Transition state proposed for phenylacetyl *tert*-butyl perester decomposition.

Discussion

Mechanism for Diacyl Peroxide Decomposition. On the basis of this work, several general conclusions can be advanced: (1) Peroxides **1a–f** decompose through ion-pair intermediates with no evidence of any radical processes. (2) Carbonic carboxylic anhydrides **2a–c** decompose through ion-pair intermediates with the possibility of some concurrent decomposition that proceeds through nucleophilic attack at the carbonyl. (3) A mixture of solvent-separated and intimate ion pairs are obtained from both peroxide and mixed carbonic carboxylic anhydride decomposition.

The data presented in our recent communication[9] and that described herein are, for the most part, consistent with the mechanism proposed by Taylor, Govindan, and Kaelin[7] (Scheme III). It is, however, our contention that Walling's "intimate ion-paired spin-diradical intermediate"[4a] is unnecessary. All results appear equally consistent with the branching of the radical and ionic pathways directly from the diacyl peroxide (Scheme IV).

The three pathways can all be described with gradations of bond-breaking in similar transition states. The transition states proposed are described in Figure 1 for three diacyl peroxides, each with a structural bias toward one of the three modes of decomposition. These transition states are similar to that used by Bartlett[28] to explain rate

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(21) A. McKenzie and S. T. Widdows, *J. Chem. Soc.*, **107**, 709 (1915).

(22) A. G. Davies, J. Kenyon, B. J. Lyons, and T. A. Rohan, *J. Chem. Soc.*, 3474 (1954).

(23) R. G. Broidy, Ph.D. Thesis, The University of Wisconsin, Madison, WI 1963.

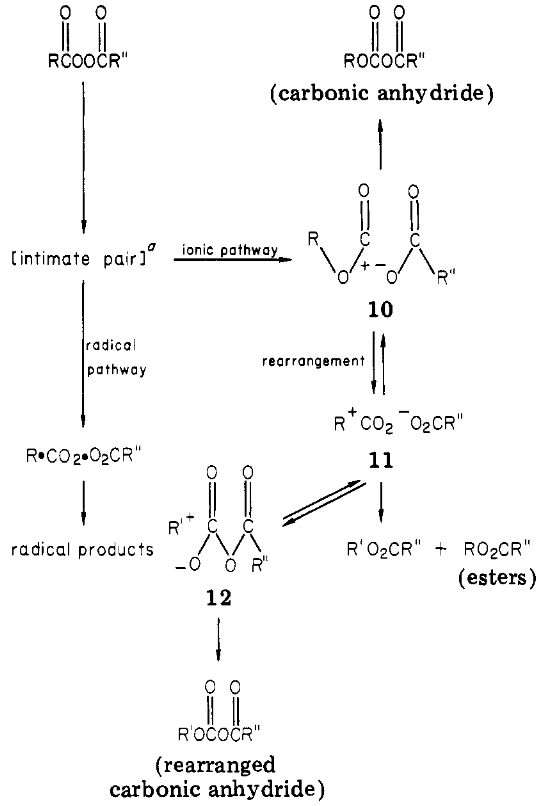
(24) J. P. Guetté, M. Perlat, J. Capillon, and D. Bouchert, *Tetrahedron Lett.*, **28**, 2412 (1974).

(25) J. Kice and G. C. Hanson, *J. Org. Chem.*, **38**, 1410 (1973).

(26) The hemiphthalate we prepare is of the same optical purity as that obtained by Goering and Hopf (ref 13), yet hydrolysis with ethanolic sodium hydroxide results in an alcohol of more than twice the optical purity reported by Goering and Hopf (ref 13). The reduction of the hemiphthalate with lithium aluminum hydride (refs. 13, 23–25) appears to racemize the resulting alcohol.

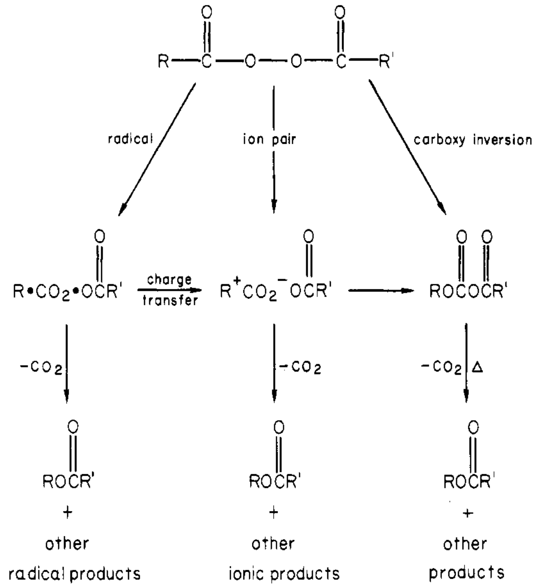
(27) D. F. DeTar and C. Weis, *J. Am. Chem. Soc.*, **79**, 3041 (1957).

Scheme III. Taylor's Mechanism for the Decomposition of Diacyl Peroxides



[a] Walling's intimate ion-pair intermediate.

Scheme IV. Proposed Mechanism for Diacyl Peroxide Decomposition



accelerations observed in the decomposition of phenylacetyl *tert*-butyl peresters in polar solvents, even though only radical products are obtained (Figure 2).

The branching of pathways directly from diacyl peroxide is consistent with both solvent and substituent effects on the rate of decomposition. Leffler presents the kinetic argument for direct branching from peroxide most succinctly: "However, there are some other instances of structural and solvent effects on the k_{radical} and $k_{\text{ion pair}}$ that are more difficult to rationalize. In the decomposition of isobutyryl peroxide, for example, polar solvents increase both k_{radical} and $k_{\text{ion pair}}$, so that it is necessary to assume that the transition state for the radical reaction is almost as polar as for the ion-pair reaction."[5]

The polar transition states proposed for ion-pair, radical, and carboxy inversion pathway are ideally suited to explain the rate effects described by Leffler.

The results of product studies performed by Taylor[7] are also consistent with the branching of pathways directly from diacyl peroxide. Taylor points out that his yield of ester increases at the expense of decreasing yields of carboxy inversion compound when polar solvents are used. The polarity of the proposed transition states (Figure 1) are clearly in accord with Taylor's observation.

The ^{18}O labeling experiments performed by Oae[29] on the symmetric cyclopropylacetyl peroxide, labeled in the carbonyl oxygens, affords ester with ^{18}O label in both oxygens. This randomization of ^{18}O is most easily visualized as occurring through the refixation of carbon dioxide by the cyclopropylmethyl cation. The ^{18}O experiments are therefore consistent with both ours and Taylor's mechanism.

Taylor's mechanism (Scheme III) branches the two ionic peroxide decomposition pathways (carboxy inversion and ester forming) at ion-pair intermediate **10**. Collapse of this intermediate gives a carboxy inversion product while decarboxylation gives a second ion pair **11**, which can collapse to form ester. The absence of carboxy inversion compounds as products in the decomposition of diphenylacetyl benzoyl peroxides strongly suggests that branching is taking place at the peroxide. Internal return (ion-pair collapse) of ion pair **10** should always occur to some extent, thus requiring the formation of a carboxy inversion product.

The decomposition of phenylacetyl 4-nitrobenzoyl peroxide in methanol affords benzyl methyl ether, benzyl 4-nitrobenzoic carbonic anhydride, and benzyl 4-nitrobenzoate. No benzyl methyl carbonate was detected. If carboxy inversion product is being formed by the collapse of ion pair **10** as Taylor proposes, some methanol capture producing benzyl methyl carbonate would be expected.

Although most experimental evidence described within is consistent with branching from Walling's intermediate, as proposed by Taylor, all of this experimental evidence is consistent with branching directly from diacyl peroxide.

Finally, the branching of pathways directly from diacyl peroxide is the simplest mechanism available that adequately explains all the experimental evidence. There is no reason, therefore, to suggest an intermediate for which there is little, if any, direct evidence.

Experimental Section

General Procedures. IR spectra were run on a Model 457 Perkin-Elmer spectrophotometer. NMR spectra were obtained on either a Varian T-60, a Varian A-60, or a JEOL Co. MH-100 spectrometer. Elemental analysis were performed by Galbraith Laboratories, Inc., Knoxville, TN. VPC analysis were performed on 5 ft × 0.25 in. columns using 1.5% OV-101 on Chromosorb G. Optical rotations were measured on a Perkin-Elmer Model 141 automatic polarimeter. Complete experimental details are contained in ref 1.

Diphenylacetic Acids. The following compounds were synthesized through adaptations of literature procedures and gave satisfactory analyses and the expected spectral properties: (4-methoxyphenyl)phenylacetic acid;[30,34] (4-methylphenyl)phenyl-

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(28) P. D. Bartlet and C. Rüchardt, *J. Am. Chem. Soc.*, **82**, 1756 (1960).

(29) S. Oae, K. Fujimori, S. Kozuka, and Y. Uchida, *J. Chem. Soc., Perkin Trans 2*, *II*, 1844 (1974).

(30) K. Sisido, H. Nozaki, M. Nozaki, and K. Okano, *J. Org. Chem.*, **19**, 1699 (1954).

acetic acid;[21] (4-chlorophenyl)phenylacetic acid;[31] bis(4-nitrophenyl)acetic acid.[32]

(+)-(4-Methylphenyl)phenylacetic acid was resolved by the method of McKenzie and Widdows;[21] mp 81.0–82.5 °C; $[\alpha]^{21.5}{}_D$ 14.5°, *c* 0.974, *l* = 1 acetone (lit.[21] mp 83–84°, $[\alpha]^{19.5}{}_D$ +14.6°, *c* 4.214, *l* = 2, acetone). Its spectral properties were identical with those of the racemic compound.

(4-Nitrophenyl)phenylacetic acid was prepared by the acid hydrolysis of (4-nitrophenyl)phenylacetonitrile[33] and recrystallized from carbon tetrachloride, affording colorless crystals (67%), mp 113–115 °C.

Diphenylacetyl Chlorides. (4-Chlorophenyl)phenylacetyl chloride,[31] (4-methylphenyl)phenylacetyl chloride,[31] and (4-methoxyphenyl)phenylacetyl chloride[34] were prepared from the corresponding acid with freshly distilled oxalyl chloride.[35] (4-Nitrophenyl)phenylacetyl chloride was prepared from the acid and phosphorous pentachloride in chloroform.

Optically Active (4-Methylphenyl)phenylacetyl Chloride. The optically active acid chloride prepared from (+)-(4-methylphenyl)phenylacetic acid (with $[\alpha]^{21}{}_{436}$ +26.74°, *c* 1.092, *l* = 1, acetone) showed $[\alpha]^{21}{}_{436}$ +11.90°, *c* 1.588, *l* = 1, chloroform.

Hydrolysis of 0.1 g of acid chloride gave 0.09 g of (+) (4-methylphenyl)phenylacetic acid with $[\alpha]^{22}{}_{436}$ +18.89°, *c* 1.05, *l* = 1, acetone. The optical purity of the acid chloride was at least 70%.

Peroxybenzoic Acids. Peroxybenzoic acid was prepared from dibenzoyl peroxide.[38] 4–-Nitroperoxybenzoic acid (85%) and 3-chloroperoxybenzoic acid (85%) were obtained from Aldrich. The 3-chloroperoxybenzoic acid was purified[37] to 97% (iodine titration).[36]

Sodium Salt of 3-Chloroperoxybenzoic Acid. The sodium salt of the peracid was prepared using the 97% peracid by an adaptation of the procedure of Akiba and Simamura[39] for the sodium salt of peroxybenzoic acid. The salt, mp 330–336 °C dec, was assayed for purity by suspending 0.1 g in 25 mL of methylene chloride, washing with 0.3 N sulfuric acid, drying over anhydrous magnesium sulfate, and concentrating in vacuo. The resulting colorless solid, mp 91–92 °C dec, gave an infrared spectrum identical with the technical grade (85%) peracid and could be titrated iodiometrically for a more precise assay. The sodium salt of the peracid was used immediately after preparation because it decomposed upon sitting.

Substituted Diphenylacetyl Benzoyl Peroxides. Nonsolvolytic Product Studies. Method I. The following procedure was typical, although several nonhhydroxylic solvents were used in place of methylene chloride and tri-*n*-butylamine instead of pyridine. Reaction temperatures of −78 °C rather than −42 °C gave essentially identical results.

Diphenylacetyl chloride, 0.523 g (2.27 mmol), and 3-chloroperoxybenzoic acid, 0.392 g (2.27 mmol), were reacted in 50 mL of methylene chloride at −42 °C with 0.180 g (2.27 mmol) of pyridine in 10 mL of methylene chloride for 5 h. Workup gave 0.660 g (90%) of benzhydryl 3-chlorobenzoate, mp 105–107 °C. Recrystallization from hexane afforded 0.587 g (81%) of analytically pure ester, mp 115.5–116.5 °C. The mixed melting point with authentic ester gave no depression. The spectral data were as follows: IR (CCl_4) 1731 (s) cm^{-1}; NMR ($CDCl_3$) δ 7.12 (s, 1 H, benzhydryl), 7.15–8.10 (m, 14 H, Ar).

Method II. To a stirred suspension of 1.00 g (5.14 mmol) of sodium 3-chloroperoxybenzoate in 10 mL of methylene chloride at 4 °C was added dropwise over 5 h 0.704 g (3.04 mmol) of diphenylacetyl chloride in 15 mL of methylene chloride. After 3 h at 4 °C, sodium chloride was removed by Celite filtration. The resulting solution was concentrated in vacuo, affording 0.93 g of colorless ester. Recrystallization resulted in 0.88 g (90%) of pure ester, mp 115–117 °C.

Method III. Diphenylacetic acid (1.34 g, 6.3 mmol), 3-chloroperoxybenzoic acid (85%) (1.09 g, 6.3 mmol), and dicyclohexylcarbodiimide (1.3 g, 6.3 mmol) in methylene chloride–ether (1:1), according to the procedure of Greene and Kazan,[40] afforded 1.6 g (79%) of ester, mp 105–110 °C. Recrystallization from hexane afforded 1.5 g (74%) of pure benzhydryl 3-chlorobenzoate, mp 115–117 °C. When 85% peracid was used, a small amount (ca. 10% by infrared spectroscopy) of the symmetric diaroyl peroxide was usually detected. The symmetric 3-chlorobenzoyl peroxide [mp 122 °C dec (lit.[41] mp 123 °C dec)] and 4-nitrobenzoyl peroxide [mp 155–156 °C dec (lit.[41] mp 155–165 °C dec)] were occasionally isolated from reaction mixtures.

Benzhydryl Benzoate Esters. The esters prepared by methods I, II, and III (Table I) were identical in all respects with esters prepared by the method of Goering and Blanchard.[42]

Optically Active (4-Methylphenyl)phenylacetyl 4-Nitrobenzoyl Peroxide and Its Nonsolvolytic Decomposition. Optically active (+)-(4-methylphenyl)phenylacetic acid ($[\alpha]^{21.5}{}_D$ +14.5°, *c* .974, *l* = 1, acetone) (0.401 g, 1.89 mmol), 4-nitroperoxybenzoic acid (0.345 g, 1.89 mmol), and dicyclohexylcarbodiimide (0.390 g, 1.89 mmol) in methylene chloride–ether (1:1, v/v) by the method of Greene and Kazan[40] afforded 0.535 g (83%) of (−)-4-methylbenzhydryl 4-nitrobenzoate as yellow crystals: mp 78.5–81.5 °C; $[\alpha]^{21}{}_{436}$ −3.93°, *c* 3.59, *l* = 1, chloroform. Crystallization from isooctane afforded 0.490 g of colorless crystals (14% retention): mp 84–86 °C, $[\alpha]^{21}{}_{436}$ −3.90°, *c* 3.13, *l* = 1, chloroform.

Low-Temperature NMR Spectroscopy of Peroxides. I. Diphenylacetyl 4-Nitrobenzoyl Peroxide. To an NMR tube cooled to −78 °C and containing 24.6 mg (0.10 mmol) of diphenylacetyl chloride and 18.3 mg (0.10 mmol) of 4-nitroperoxybenzoic acid, 0.5 mL of acetone-d_6 was added. The tube was shaken, and the NMR spectrum taken at −55 °C showed a superposition of the NMR spectra of the acid chloride and the peracid. To this mixture was added 18.5 mg (0.10 mmol) of tri-*n*-butylamine in 0.1 mL of acetone-d_6 via syringe at −78 °C. The NMR spectrum at −55 °C showed the following: ($(CD_3)_2CO$) δ 5.54 (s, 1 H, benzhydryl), 6.82–7.48 (m, 10 H Ar), 7.84–8.44 (m, 4 H, Ar).

This NMR spectrum persisted at −55 °C. The solution was then warmed to 20 °C; the resulting spectrum was identical with that of benzhydryl 4-nitrobenzoate. No benzhydryl signal corresponding to the mixed carbonic carboxylic anhydride was observed.

II. Diphenylacetyl 3-Chlorobenzoyl Peroxide. This peroxide was prepared in the same manner as the 4-nitro analogue: NMR ($(CD_3)_2CO$) δ 5.57 (s, 1 H, benzhydryl), 7.02–7.97 (m, 14 H, Ar).

Low-Temperature Infrared Spectroscopy of Diphenylacetyl 3-Chlorobenzoyl Peroxide. To a mixture of 1.088 g (4.7 mmol) of diphenylacetyl chloride and 0.814 g (4.7 mmol) of 3-chloroperoxybenzoic acid in 10 mL of methylene chloride at −78 °C was added dropwise 0.874 g (4.7 mmol) of tri-*n*-butylamine in 15 mL of methylene chloride with stirring. After 1 h, this solution was siphoned into a precooled (−78 °C) low-temperature infrared cell: IR (CH_2Cl_2) 1799 (m), 1768 (s) cm^{-1}.

On warming to 5 °C over a period of 10 min, the peroxide was completely converted to benzhydryl 3-chlorobenzoate (1723 (s) cm^{-1}). No infrared bands associated with the mixed carbonic carboxylic anhydrides were observed (vide infra).

Phenylacetyl 4-Nitrobenzoyl Peroxide. The peroxide was prepared by the reaction of 1.08 g (7.0 mmol) of freshly distilled phenylacetyl chloride [bp 60–62.5 °C (1–2 mm) (lit.[43] bp 102 °C (17 mm))] with 1.22 g (7.0 mmol) of 4-nitroperoxybenzoic acid, in the presence of 0.55 g (7.0 mmol) of pyridine, according to the

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[37] N. N. Schwartz and J. H. Blumberg, *J. Org. Chem.*, **29**, 1976 (1964).

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[39] K. Akiba and O. Simamura, *Tetrahedron*, **26**, 2519 (1970).

[40] F. D. Greene and J. Kazan, *J. Org. Chem.*, **28**, 2168 (1963).

[41] A. T. Blomquist and A. J. Buselli, *J. Am. Chem. Soc.*, **73**, 3883 (1951).

[42] H. L. Goering and J. P. Blanchard, *J. Am. Chem. Soc.*, **76**, 5405 (1954).

[43] L. C. Raiford and H. P. Lankelma, *J. Am. Chem. Soc.*, **47**, 119 (1925).

method of Lamb et al.[44] After the reaction mixture was washed and then dried over anhydrous magnesium sulfate, it was concentrated in $^1/_4$ of its original volume. The resulting mixture was suction filtered, affording 0.5 g of yellow crystals. **Caution**: These crystals spontaneously detonated. The peroxide could be preserved if, immediately after suction filtration, it was placed in 50 mL of petroleum ether at 0 °C. The peroxide could then be stored under petroleum ether at −20 °C for several days. Nuclear magnetic resonance and infrared spectra could be obtained by using a fast scan: IR (CCl_4) 1812 (w), 1781 (s), 1350 (m) cm^{-1}; NMR ($CDCl_3$) δ 3.87 (s, 2 H, CH_2), 7.35 (s, 5 H, Ar), 8.23 (s, 4 H, Ar).

Phenylacetyl 3-chlorobenzoyl peroxide was also found to **spontaneously detonate**: IR (CCl_4) 1810 (w), 1780 (s) cm^{-1}.

Diphenylacetyl *tert*-butyl perester was prepared by the literature procedure.[19]

Resolution of 4-Methylbenzhydrol. The racemic hemiphthalate (mp 123–124 °C)[22] (73 g, 211 mmol) was converted to diastereomeric salts in 1 L of refluxing ethyl acetate with 25.8 g (213 mmol) of *d*(+)-α-methylbenzylamine ($[\alpha]^{20}_{D}$ +36°, $l = 1$, neat). After 16 h at 20 °C, 67 g of crystals (mp 132–137 °C) were obtained.

Seven recrystallizations from ethyl acetate afforded 14.5 g (15%) of the optically active salt, mp 147–148 °C dec.

The optically active salt (1 g, 2.14 mmol) was suspended in 100 mL of ether with 50 mL of 10% hydrochloric acid (kept below 10 °C). The ether was dried over anhydrous magnesium sulfate and triturated with petroleum ether, affording 0.59 g (80%) colorless crystals: mp 114–116 °C; $[\alpha]^{23}_{D}$ −8.52°, c 0.904, $l = 1$, chloroform (lit.[22] mp 114–114.5 °C; $[\alpha]_{D}$ +18.5°, c 1.15, $l = 2$, benzene, and lit.[13] mp 114–119 °C, $[\alpha]^{24}_{D}$ −8.08°, c 0.62, $l = 4$, chloroform).

The optically active hemiphthalate was converted to the optically active alcohol by the method of Davies and Kenyon:[22] mp 61–63 °C; $[\alpha]_{D}$ −23.26°, $l = 1$, c .144, carbon disulfide; $[\alpha]^{25}_{436}$ −20.25°, $l = 1$, c 0.284, chloroform; $[\alpha]^{22}_{D}$ −9.66°, $l = 1$, c 0.100, benzene (lit.[22] mp 61–63 °C, $[\alpha]_{D}$ = +26.90°, $l = 2$, c 1.378, carbon disulfide; lit.[13] mp 57–68 °C, $[\alpha]^{24}_{435}$ −8.18°, $l = 4$, c 0.409, chloroform; and lit.[24] $[\alpha]^{22}_{D}$ −1.5°, c 5, benzene). The alcohol resolved by the method described in ref 13 was calculated to be 16% optically pure by NMR using chiral shift reagents.[24]

Benzhydryl-4-nitrobenzoic Carbonic Anhydride (2a). To a solution of 15 g (81.4 mmol) of benzhydrol in 100 mL of dry tetrahydrofuran was added 3.43 g (81.4 mmol) of sodium hydride (57% oil dispersion). After being stirred for 0.5 h at 50 °C under nitrogen, the clear solution of salt was cooled to −78 °C, and carbon dioxide (Matheson "bone dry" 99.8% minimum) was bubbled into the mixture for 30 min, resulting in a thick gel. The reaction vessel was flushed with dry nitrogen, and 50 mL of tetrahydrofuran was added. A solution of 14.8 g (80.0 mmol) of 4-nitrobenzoyl chloride in 50 mL of tetrahydrofuran was added dropwise over a period of 0.5 h at −78 °C with vigorous stirring. After an additional 0.25 h at −78 °C, the mixture was poured cold onto a mixture of 200 mL of water and 200 mL of ether.

The ether layer was dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo, affording a clear yellow oil. Trituration with petroleum ether afforded 17.8 g (58%) of white crystals, mp 74.5–75.5 °C dec.

Two crystallizations from hexane gave analytically pure, colorless needles (48%), mp 84.5–85.5 °C dec. Quantitative evolution of carbon dioxide was observed on heating to 110 °C: IR (CCl_4) 1820 (s), 1762 (m), 1353 (m) cm^{-1}. NMR ($CDCl_3$) δ 6.95 (s, 1 H, benzhydryl), 7.44 (s, 10 H, Ar), 8.32 (s, 4 H, Ar), UV ($CHCl_3$) λ_{max} 262 nm.

Anal. Calcd for $C_{21}H_{15}NO_6$: C, 66.84; H, 4.01; N, 3.71. Found: C, 66.71; H, 4.01; N, 3.52.

The same procedure used for **2a** afforded 4-chlorobenzhydryl-4-nitrobenzoic carbonic anhydride (2b) (48%) (mp 88–89 °C dec) and 4-methylbenzhydryl-4-nitrobenzoic carbonic anhydride (2c) (46%) (mp 66.5–67.5 °C dec).

Optically Active 4-Methylbenzhydryl-4-nitrobenzoic Carbonic Anhydride. Application of the above procedure with 250 mg (1.25 mmol) of optically active (−)-4-methylbenzhydrol ($[\alpha]^{25}_{D}$ −9.86°, c 0.284, $l = 1$, chloroform) in 10 mL of dry tetrahydrofuran gave the optically active carbonic carboxylic anhydride. The yellow solid product was dissolved in hot hexane, filtered, and stored at −20 °C. Two distinguishable crystal forms resulted. Physical separation afforded 10 mg of (−)-4-methylbenzhydrol as colorless needles (mp 64–65 °C) and 25 mg (5%) of (−)-4-methylbenzhydryl-4-nitrobenzoic carbonic anhydride (mp 59–61 °C dec, $[\alpha]^{25}_{D}$ −3.96°, c 0.480, $l = 1$, chloroform, and the same spectral properties as the racemic compound).

Stereochemistry of the Nonsolvolytic Decompositon of (−)-4-Methylbenzhydryl-4-nitrobenzoic Carbonic Anhydride (2c). (−)-4-Methylbenzhydryl-4-nitrobenzoic carbonic anhydride (4.8 mg, mp 59–61 °C dec, $[\alpha]^{25}_{436}$ −8.96°, c 0.480, $l = 1$, chloroform) was decomposed in 1 mL of chloroform for 12 h at 25 °C. The infrared spectrum was identical with that of 4-methylbenzhydryl-4-nitrobenzoate and showed a rotation of $[\alpha]^{25}_{436}$ −8.14° (c 0.430,[45a] $l = 1$, chloroform). This ester showed a minimum[45b] of 29% retention.[45c]

Kinetics of Nonsolvolytic Decomposition of Carbonic Carboxylic Anhydrides. The rate determination was conducted with a Varian T-60 nuclear magnetic resonance spectrometer at 36.0 ± 0.5 °C. From (1) the rate of disappearance of the benzhydryl proton signal of the mixed carbonic carboxylic anhydride and (2) the rate of appearance of the benzhydryl proton signal of the benzhydryl benzoate ester. The signal intensities were determined by electronic integration and planimetry and was reproducible to ±5%. Runs were followed for 2 half-lives.

2c was insufficiently soluble at 36 °C in deuterochloroform for NMR kinetics. The rates for **2a**, **2b**, and **2c** were determined by UV spectroscopy at a concentration of 5×10^{-5} M in chloroform by following the change in optical density of each mixed carbonic carboxylic anhydride. The kinetics were performed on a Varian Technitron Model 635 UV spectrophotometer at 25.8 ± 0.2 °C.

General Method for Obtaining the Rate of Decomposition by Titration. The decomposition of benzhydryl 4-nitrobenzoic carbonic anhydride in 90% aqueous acetone at 36 °C was followed by titration of 4-nitrobenzoic acid at −15 °C in anhydrous acetone after removal of the 90% acetone and carbon dioxide in vacuo.

General Method for Determining "*R* Values" in Mixed Carbonic Carboxylic Anhydride Solvolysis. The R values, [ester]/([ester] + [alcohol]), could be determined either titrimetrically (calculated from the t_∞ point) or gas chromatographically.

In the presence of added salt, titration failed to give reliable R values. Thus, an extractive workup (the same used for the study of salt effects in the diacyl peroxide decomposition) followed by gas chromatographic analysis was used.

General Method for the Preparation and Solvolysis of Substituted Diphenylacetyl Benzoyl Peroxides. To a mixture of 0.1846 g (0.80 mmol) of diphenylacetyl chloride and 0.1381 g (0.80 mmol) of 3-chloroperoxybenzoic acid, 3.00 mL (volume at 25 °C) of pure acetone was added dropwise with rapid cooling to −78 °C in a dry ice–acetone bath. To the stirred mixture was added dropwise 1.00 mL of a 0.80 M solution of tri-*n*-butylamine in pure acetone. The sides of the reaction vessel were washed with an additional 1.00 mL of pure acetone. After stirring for 1 h, the reaction mixture was allowed to warm to −50 °C, and 20.00 mL of 87.5% aqueous acetone (v/v at 25 °C) at 25 °C was injected in <1 s. *m*-Terphenyl (0.010 g, 0.040 mmol was added, and the mixture was dried over anhydrous potassium carbonate, filtered, and analyzed by gas chromatography.

Effect of Added Salt. The peroxide was prepared by the preceding method in pure acetone. A 5-fold excess of the desired salt (4.00 mmol) was dissolved in the 20 mL of 87.5% aqueous acetone at 25 °C. *m*-Terphenyl (0.010 g, 0.040 mmol) was added, and the mixture was added to 100 mL of benzene, washed with water, 5% hydrochloric acid, and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. The resulting oil was dissolved in 5 mL of pure acetone and

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[44] R. C. Lamb, L. L. Vestal, G. R. Cipau, and S. Debnath, *J. Org. Chem.*, **39**, 2096 (1974).

[45] (a) The loss of carbon dioxide was compensated for when the final concentration was calculated. (b) A net retention of 29% was a minimum value since no assay of optical purity of the carbonic carboxylic anhydride was made. (c) The rotation of the optically pure ester was calculated (ref 13, 23, and 24).

analyzed by gas chromatography.

Control Run I. A mixture of 0.1333 g (0.40 mmol) of benzhydryl 4-nitrobenzoate, 0.0737 g (0.40 mmol) of benzhydrol, and 0.1775 g (0.80 mmol) of tri-*n*-butylamine hydrochloride in 90 aqueous acetone at 25 °C was stirred for 1 h. It was then dried over excess anhydrous potassium carbonate and analyzed by gas chromatography. The result of the analysis was consistent with the known proportions of the mixture.

Control Run II. In an NMR tube containing 25 mg (0.0662 mmol) of benzhydryl-4-nitrobenzoic carbonic anhydride, 0.3 mL of acetone-d_6 was added. To this solution, 13.3 mg (0.0515 mmol) of tri-*n*-butylamine hydrochloride in 0.3 mL of acetone-d_6 was added dropwise by syringe. The NMR spectrum showed a simple superimposition of the spectrum of each compound. To this mixture, 67 μL of D_2O was added. The kinetics of the decomposition of the mixed carbonic carboxylic anhydride under these conditions and at 36 °C were determined: $t_{1/2}$ = ca. 100 min.

Control Run III. Following the general method for peroxide preparation and solvolysis, tandem runs of (4-methoxyphenyl)-phenylacetyl 4-nitrobenzoyl peroxide were prepared and solvolyzed (both without added salt). After the addition of *m*-terphenyl standard, one reaction mixture was dried with anhydrous potassium carbonate, filtered, and analyzed by gas chromatography. The other reaction mixture was treated by the extractive workup previously described for runs with added salt and analyzed by gas chromatography. Both runs analyzed identically within experimental error.

Product Analysis by Gas Chromatography. A standard mixture was prepared containing all of the known components in approximately the same concentrations as in the unknown mixture. Standard and unknown mixtures were injected back-to-back three times. A response factor (peak area/molar concentration) was calculated for each component in the standard, which provided the relative concentrations of each component in the unknown mixture. The absolute concentrations were calculated by using *m*-Terphenyl as a standard.

Analyses were run at a column temperature of 140–170 °C with a flow rate of 40 mL/min. After 10 min the column temperature was programmed linearly at 10 °C/min to 280 °C and held at this upper temperature. Approximate retention times of these compounds follow: diphenylmethanes, 1–3 min; benzhydryl alcohols, 3–6 min; benzophenones, 5–8 min; *m*-terphenyl (this compound was used as a standard), 15–20 min; tetraphenylethanes, 20–24 min; benzhydryl benzoates, 22–26 min.

Optically Active (4-Methylphenyl)phenylacetyl 4-Nitrobenzoyl Peroxide and Its Solvolytic Decomposition. Optically active (+)-(4-methylphenyl)phenylacetyl chloride ($[\alpha]^{22}{}_{436}$ +11.90°, *c* 1.588, *l* = 1, chloroform) was converted to peroxide, solvolyzed in 90% aqueous acetone according to the procedure used for the racemic compound, poured into 250 mL of ether, washed with 5% hydrochloric acid, water, 5% sodium bicarbonate, and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo.

The crude product mixture (75 mg, $[\alpha]^{22}{}_{436}$ −2.05°, *c* 4.305, *l* = 1, chloroform) had an NMR spectrum showing both 4-methylbenzhydrol (ca. 40%) and 4-methylbenzhydryl 4-nitrobenzoate (ca. 60%). The two components were separated on a 20 cm × 20 cm × 2 mm preparative silica gel plate.[46a] The plate was eluted with 10% ether–petroleum ether and then with 20% ether–petroleum ether. The plate showed two bands:[46b] alcohol (R_f 0.35) and ester (R_f 0.66). The components were identified by R_f and by infrared spectra. The ester, 27 mg, showed 15.9% net retention ($[\alpha]^{21}{}_{436}$ −3.11°, *c* 2.11, *l* = 1, chloroform). The alcohol, 5 mg, showed 0.8% ± 0.2% net retention ($[\alpha]^{21}{}_{546}$ −0.183°, *c* = 0.50, *l* = 1, carbon disulfide).

Decomposition of Phenylacetyl 4-Nitrobenzoyl Peroxide. Product Studies. A 1-mL aliquot of the peroxide–petroleum ether suspension at −20 °C, containing from 0.03 to 0.07 g of peroxide, was placed in a chilled (0 °C) 5-mL round-bottom flask. The solvent was removed rapidly (<1 min) under vacuum. To the resulting colorless solid, 10 mL of solvent at 25 °C was added rapidly by injection. The solution formed was allowed to sit at 25 °C for 2 h and then concentrated in vacuo.[47] The resulting solid (or oil) was weighed, and NMR and IR spectra were taken.

A large-scale decomposition was performed by using 0.16 g of phenylacetyl 4-nitrobenzoyl peroxide in 100 mL of benzene at 25 °C. After 2 h the reaction mixture was concentrated in vacuo, affording a colorless solid. This material was recrystallized from chloroform–hexane, resulting in the isolation of 0.07 g of benzyl-4-nitrobenzoic carbonic anhydride; mp 64–64.5 °C (lit.[14] mp 64.5–66.0 °C); IR ($CHCl_3$) 1815 (s), 1752 (m), 1353 (m) cm^{-1}; NMR ($CDCl_3$) δ 5.42 (s, 2 H, CH_2), 7.2–7.55 (m, 5 H, Ar), 8.38 (m, 4 H, Ar).

Kinetic Studies. The rate of decompositon of the phenylacetyl peroxide was measured by NMR in deuterochloroform at 25 °C, as described for the mixed carbonic carboxylic anhydrides.

Decomposition of Diphenylacetyl *tert*-Butyl Perester in 90% Aqueous Acetone. To 10 mL of 90% aqueous acetone in a 50-mL round-bottom flask, 109 mg (0.382 mmol) of freshly recrystallized perester (mp 59.5–61.5 °C dec) was added. The solution was blanketed with an atmosphere of nitrogen, and the flask was capped. The reaction mixture was warmed for 44 h at 36.0 °C, then diluted with 50 mL of ether, dried over anhydrous magnesium sulfate, and concentrated in vacuo. Drying afforded 100 mg of oil which gave an NMR spectrum with two major benzhydryl proton signals, one corresponding to benzhydryl methyl ether (51%) and the other to tetraphenylethane (20%).

The oil dissolved in 0.5 mL of chloroform was spotted on a 20 cm × 20 cm × 2 mm preparative silica gel (containing binding but no fluorescence indicator) plate. Elution with petroleum ether–ether (7:1 v/v at 25 °C) gave the following bands: (1) R_f 0–0.04; (2) R_f 0.12–0.18; (3) R_f 0.25–0.38; (4) R_f 0.38–0.49; (5) R_f 0.49–0.62. Components 2 and 3 were tentatively identified as benzhydrol and benzophenone since authentic samples ran to the same R_f when spotted on the side of the preparative plate. The five bands were each extracted into ether and concentrated in vacuo. Components 2–4 were identified by exact match of their IR with those of authentic samples. Component 5, and fluorescent[48] band, gave very few IR bands and was identified instead by an undepressed mixed melting point with authentic material. The components were identified as follows: (1) ester or polyester, 8.0 mg;[19] (2) benzhydrol, 2.1 mg (3.8%); (3) benzophenone, 0.8 mg (1.4%); (4) benzhydryl *tert*-butyl ether, 17.0 mg (22.3%); (5) tetraphenyl ethane, 9.0 mg (8.5%).

Decomposition of Benzoyl Peroxide in the Presence of Diphenylmethane in Acetone. A mixture of 67.3 mg (0.40 mmol) of diphenylmethane and 98.9 mg (0.40 mmol) of benzoyl peroxide in 10 mL of both 90% aqueous and dry acetone, in thick-walled glass tubes, was degassed (three freeze/thaw cycles) and sealed.

Decomposition and Workup. The sealed tubes were heated at 100 °C for 5 h, cooled on ice, broken open, poured onto 50 mL of chloroform, washed with saturated sodium bicarbonate, dried over anhydrous magnesium sulfate, and concentrated in vacuo, affording 60–100 mg of bicarbonate insoluble oils which were analyzed by gas chromatography.

Attempt to Observe CIDNP in Peroxide Decomposition. A mixture of 59.2 mg (0.240 mmol) of diphenylacetyl chloride and 43.9 mg (0.240 mmol) of 4-nitroperoxybenzoic acid was dissolved in 0.5 mL of acetone-d_6 and cooled to −78 °C. To this mixture 44.5 mg of tri-*n*-butylamine in 0.1 mL of acetone-d_6 was added dropwise by syringe. The mixture was allowed to react for 1 h at −78 °C and then 67.0 μL of D_2O was added. The mixture was placed in the probe of a Varian T-60 NMR spectrometer (at 36 °C) and scanned several times at a 50-s sweep time. No enhanced emission or absorption was observed. This decomposition resulted in the expected mixture of alcohol and ester.

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[46] (a) The optically active alcohol did not racemize on silica (ref 13). (b) There was a small amount of 4-nitrobenzoic acid (0.8 mg) at the origin, and some streaking was seen in the ester band.

[47] Solvolysis in methanol-d_4 (0.12 g of peroxide in 2 mL of methanol-d_4) gave the volatile benzyl methyl ether and was analyzed directly by NMR without concentration in vacuo.

[48] This is probably a small amount of tetraphenylethylene, which runs to the same R_f as tetraphenylethane.

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Registry No. **1a**, 81505-79-5; **1b**, 81505-80-8; **1c**, 81505-81-9; (–)-**1c**, 81505-82-0; **1d**, 81505-83-1; **1e**, 81505-84-2; **1f**, 71530-87-5; **1g**, 81505-85-3; **2a**, 71491-85-5; **2b**, 81505-86-4; **2c**, 81505-87-5; (–)-**2c**, 81505-88-6; **2d**, 13137-24-1; (4-chlorophenyl)phenylacetyl-3-chlorobenzoyl peroxide, 81505-89-7; (4-nitrophenyl)phenylacetyl-3-chlorobenzoyl peroxide, 81505-90-0; (4-nitrophenyl)phenylacetyl-4-nitrobenzoyl peroxide, 81505-91-1; bis(4-nitrophenyl)acetyl-4-nitrobenzoyl peroxide, 81505-92-2; diphenylacetyl *tert*-butyl perester, 13144-32-6; benzoyl peroxide, 94-36-0.

Supplementary Material Available: Complete procedures for the preparation and spectral data for (4-nitrophenyl)phenylacetic acid, (4-nitrophenyl)phenylacetyl chloride, 4-chlorobenzhydryl 4-nitrobenzoic carbonic anhydride, and 4-methylbenzhydryl 4-nitrobenzoic carbonic anhydride are available (4 pages). Ordering information is given on any current masthead page.

Synthesis of Fluorinated Acetylenes[1]

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New routes to fluorinated acetylenes were developed on the basis of additions of iodofluorocarbons to silylacetylenes. Free radical addition of α,ω-diiodoperfluoroalkanes to (trimethylsilyl)acetylene gave the iodotrimethylsilyl olefins $Me_3SiIC{=}CH(CF_2)_nCH{=}CISiMe_3$, which reacted with potassium *tert*-butoxide or DBU to give the (trimethylsilyl)acetylenes and, with an excess of the base, the free diacetylenes. Perfluoroalkyl iodides similarly gave (perfluoroalkyl)acetylenes. The addition of perfluoroheptyl iodide to phenylacetylene, followed by treatment with potassium *tert*-butoxide gave 1-phenylperfluorononyne. The peroxide-catalyzed reaction of perfluoroalkyl iodides and bis(trimethylsilyl)acetylene gave 1:1 adducts, $R_F(Me_2SiCH_2I)C{=}CHSiMe_3$, resulting from intramolecular hydrogen abstraction by the initially formed vinyl radical. However, the thermal reaction of perfluoroalkyl iodides and diiodides with bis(trimethylsilyl)acetylene in the presence of free iodine gave the (trimethylsilyl)acetylenes, which were desilylated with potassium fluoride. A route to diacetylenes was investigated on the basis of addition of perfluoroiodo compounds to ethylene, dehydroiodination, brominations, and eliminations.

Although perfluoroalkyl-substituted primary acetylenes have been known for three decades, (perfluoroalkylene)diacetylenes, $HC{\equiv}C(CF_2)_nC{\equiv}CH$, have not been reported. Haszeldine[2,3] originally prepared 3,3,3-trifluoropropyne by the addition of trifluoromethyl iodide to acetylene (70–80%) followed by dehydrohalogenation (75%). (Perfluoroethyl)acetylene was prepared similarly.[4] Henne and Nager[5] developed a high-yield multistep route to 3,3,3-trifluoropropyne that avoided the use of acetylene under pressure; bromination of 3,3,3-trifluoropropene was followed by dehydrohalogenation, another bromination, dehydrohalogenation, and dehalogenation (Scheme I). More recently,[6] this approach was used to prepare the perfluorobutyl, perfluorohexyl, and perfluorooctyl analogues.

Scheme I

$$CF_3CH{=}CH_2 \xrightarrow{Br_2} CF_3CHBrCH_2Br \xrightarrow{KOH} CF_3CHBr{=}CH_2 \xrightarrow{Br_2} CF_3CBr_2CH_2Br \xrightarrow{KOH} CF_3CBr{=}CHBr \xrightarrow{Zn} CF_3C{\equiv}CH$$

Scheme II[a]

$$I(CF_2)_nI + CH_2{=}CH_2 \longrightarrow ICH_2CH_2(CF_2)_nCH_2CH_2I \xrightarrow{KOH} CH_2{=}CH(CF_2)_nCH{=}CH_2 \xrightarrow{Br_2} BrCH_2CHBr(CF_2)_nCHBrCH_2Br$$

$$BrCH_2CHBr(CF_2)_4CHBrCH_2Br \xrightarrow{KOH} CH_2{=}CBr(CF_2)_4CBr{=}CH_2 \xrightarrow{Br_2} BrCH_2CBr_2(CF_2)_4CBr_2CH_2Br \xrightarrow{KOH} BrCH{=}CBr(CF_2)_4CBr{=}CHBr$$

[a] n = 4 or 6.

Using α,ω-diiodoperfluoroalkanes as starting materials, available from the telomerization of tetrafluoroethylene with iodine,[7] we approached the synthesis of α,ω-diacetylenes using Henne's sequence (Scheme II). Reactions of ethylene with 1,4-diiodoperfluorobutane and 1,6-diiodoperfluorohexane, followed by dehydrohalogenations, have been reported to give the corresponding α,ω-diolefins.[8] Bromine adducts of these olefins were obtained in 74–91% yields. The reaction of 3,3,4,4,5,5,6,6-octafluoro-1,2,7,8-tetrabromooctane with potassium hydroxide in methanol gave 2,7-dibromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene. Another bromination followed by reaction with methanolic potassium hydroxide gave a complex product mixture, the major component of which was isolated by GC and identified as the desired 1,2,7,8-tetrabromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene. Although moderately good yields were obtained for each step of the sequence, overall yields were poor. Therefore, this approach to diacetylenes was abandoned.

(Trimethylsilyl)acetylene Additions. The trimethylsilyl group is a convenient blocking group for the synthesis of acetylenes. The synthesis of arylacetylenes has recently been accomplished by using a paladium-catalyzed coupling of aromatic halides with (trimethylsilyl)acetylene, followed by desilylation of the resulting arylacetylene derivatives with nucleophiles.[9,10]

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