The product was purified by chromatography on Kiesel gel G (Merck) to give a clear oil or a solid in 55–61% yields.

7a: mp 40.0–41.0°; ir (CCl₄ solution) 1760 (vs), 1375 (s), 1350 (s), 1050 (s), 1032 cm⁻¹ (s); ¹H NMR δ 1.39 (s, 9 H) and 1.2–1.9 (complex m, 10 H).

7b: colorless liquid; ir (film) 1770 (vs), 1365 (s), 1328 (s), 1200 (s), 1150 (vs), 1080 (vs), 1030 cm⁻¹ (s); ¹H NMR δ 1.39 (s, 9 H) and 1.2–2.0 (complex m, 10 H).

8a: mp 46.5–47.5°; ir (CCl₄ solution) 1755 (vs), 1370 (s), 1215 (vs), 1190 (s), 1155 (vs), 1052 (m), 1030 cm⁻¹ (m); ¹H NMR δ 1.36 (s, 9 H) and 1.3–2.0 (complex m, 10 H).

8b: colorless liquid; ir (film) 1775 (vs), 1365 (s), 1295 (s), 1176 (s), 1145 (vs), 1080 (s), 1025 cm⁻¹ (m); ¹H NMR δ 1.36 (s, 9 H) and 1.3–2.0 (complex m, 10 H).

Thermal Decomposition of *tert*-Butyl Peroxy Esters (7 and 8). A solution of 0.5–1.0 mmol of the peroxy ester in a tenfold molar quantity of toluene, cumene, or bromotrichloromethane was placed in a pressure-resistant Pyrex ampoule. It was degassed with pure nitrogen and was heated at 110° for 24 hr. After the reaction was over, the reaction mixture was cooled to 0°, and the ampoule was very carefully opened. The isomer distribution in the product was determined by GLC prior to any treatments and is shown in Table II.²²

The free acids were isolated by conventional extraction methods. The comparison of the spectral properties and melting points of the isolated acids with those of authentic samples showed the geometry of the starting peroxy esters being retained.

References and Notes

(1) Presented at the International Symposium on Fluorine Chemistry, Santa Cruz, Calif., July 1973, No. 0-45.

(2) G. A. Carlson and G. C. Pimental, *J. Chem. Phys.*, **44**, 4053 (1966); D. E. Milligan, M. E. Jacox, and J. J. Comeford, *ibid.*, **44**, 4058 (1966).

(3) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965).

(4) C. Lifshitz and W. A. Chupka, *J. Chem. Phys.*, **47**, 3439 (1967).

(5) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).

(6) G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34**, 523 (1956); G. Herzberg, *Annu. Rev. Phys. Chem.*, **9**, 357 (1958); G. Herzberg, *Proc. Chem. Soc., London*, 116 (1959).

(7) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(8) (a) L. A. Singer and N. P. Kong, *Tetrahedron Lett.*, 2089 (1966); 643 (1967); *J. Am. Chem. Soc.*, **88**, 5213 (1966); **89**, 5251 (1967); (b) L. A. Singer and J. Chen, *Tetrahedron Lett.*, 4849 (1969); (c) M. S. Liu, S. Soloway, D. K. Wedegaertner, and J. A. Kampmeier, *J. Am. Chem. Soc.*, **93**, 3809 (1971); (d) J. A. Kampmeier and R. M. Fantazier, *ibid.*, **88**, 1959 (1966); (e) R. M. Fantazier and J. A. Kampmeier, *ibid.*, **88**, 5219 (1966).

(9) (a) T. Ando, F. Namigata, H. Yamanaka, and W. Funasaka, *J. Am. Chem. Soc.*, **89**, 5719 (1967); (b) T. Ando, H. Yamanaka, F. Namigata, and W. Funasaka, *J. Org. Chem.*, **35**, 33 (1970); (c) L. J. Altman and R. C. Baldwin, *Tetrahedron Lett.*, 2531 (1971); (d) L. J. Altman and J. C. Vederas, *Chem. Commun.*, 895 (1969); (e) L. A. Singer and J. Chen, *Tetrahedron Lett.*, 939 (1971); (f) J. Hatem and B. Waegell, *ibid.*, 2019 (1973).

(10) K. L. Williamson, Y.-F. Li Hsu, F. H. Hall, S. Swager, and M. S. Coulter, *J. Am. Chem. Soc.*, **90**, 6717 (1968).

(11) R. A. Moss and R. Gerstl, *Tetrahedron*, **23**, 2549 (1967).

(12) G. Köbrich and W. Goyert, *Tetrahedron*, **24**, 4327 (1968).

(13) H. Musso, *Chem. Ber.*, **101**, 3710 (1968), and references cited therein.

(14) In the NMR spectra of the methyl esters of 2 and 3, the peak of the methoxy group of the exo ester appeared at a field ca. 0.05 ppm higher than the one of the corresponding endo ester (methyl ester of 2a, 3.73; of 2b, 3.77; of 3a, 3.57; of 3b, 3.61). The peak of the ethoxy group of the monoethyl esters of norcarane-7,7-dicarboxylic acid showed a similar tendency (exo ethyl ester, 1.27 and 4.15; endo ethyl ester, 1.29 and 4.20). This tendency may possibly be a good aid to the determination of the stereochemistry of these type of compounds, which otherwise is often very troublesome.

(15) L. A. Singer in "Organic Peroxides", Vol. I, D. Swern, Ed., Wiley, New York, N.Y., 1970, p 265.

(16) P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *J. Am. Chem. Soc.*, **87**, 2590 (1965).

(17) A. D. Walsh, *Discuss. Faraday Soc.*, **2**, 21 (1947); L. Pauling, *J. Chem. Phys.*, **51**, 2767 (1969).

(18) K. Mislow, "Introduction to Stereochemistry", W. A. Benjamin, New York, N.Y., 1965, p 19; K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

(19) R. C. Bingham and M. J. S. Dewar, *J. Am. Chem. Soc.*, **95**, 7180, 7182 (1973).

(20) J. Hine and S. J. Ehrenson, *J. Am. Chem. Soc.*, **80**, 842 (1958).

(21) Bromochlorocarbene was generated by the treatment of dibromochloromethane with potassium *tert*-butoxide at −20 to −10°.

(22) It was confirmed, by separate experiments, that the isomer ratios given in Tables I and II showed no appreciable change, and no ring-opening products were detected by GLC, after the reaction mixture was kept under the reaction conditions for an additional 4 and 10 hr, respectively.

Substituent Effects on the Thermal Decomposition of *I,I*-Dibenzoyldioxyiodobenzenes in Chloroform. An Observed Linear Free Energy Relationship[1]

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The preparation and characterization of 14 symmetrically substituted *I,I*-dibenzoyldioxyiodobenzenes, ArI(OOCOAr–X)₂, are reported. A quantitative study of the decomposition for seven of these compounds in chloroform (0.008–0.030 *M*) at 28–38° has been undertaken. Under these conditions the reaction is kinetically of the first order and yields iodoxybenzene (identified as a new polymorphous modification), benzoic acid, dibenzoyl peroxide, and hexachloroethane as the major products. A Hammett plot of the rates of decomposition of meta- and para-substituted compounds vs. σ values gives a ρ of −0.29 (*r* = 0.93). The effect of substituents on decomposition is discussed in terms of increased or decreased electron densities on the peroxidic oxygens. A unimolecular free-radical mechanism, with a transition state in which some rotational restrictions appear (partial ionic character), is proposed to be the major reaction path. *The explosive properties of compounds under investigation are pointed out.*

The chemistry of compounds ArI(OCOAr)₂, usually formed in the reaction of iodobenzene with peroxy acid,² has received intensive study in the past and is now rather well understood mainly by the efforts of Leffler and co-workers.³,⁴ On the other hand, compounds of the type ArI(OOR)₂ have been only scarcely investigated. Milas et al. reported the results of a study of the reaction of iodosobenzene with *tert*-butyl hydroperoxide in methylene chloride,

and proposed ArI(OOBu-*t*)₂ to be an intermediate of short lifetime below −80°.⁵

As a part of our continuing interest in organic polyvalent iodine compounds, we wish to report in the present paper details concerning the preparation and characterization of symmetrically substituted *I,I*-dibenzoyldioxyiodobenzenes together with the results of the thermal decomposition in chloroform.

Scheme I

$$C_6H_5I(OOCOC_6H_4X)_2 \longrightarrow$$
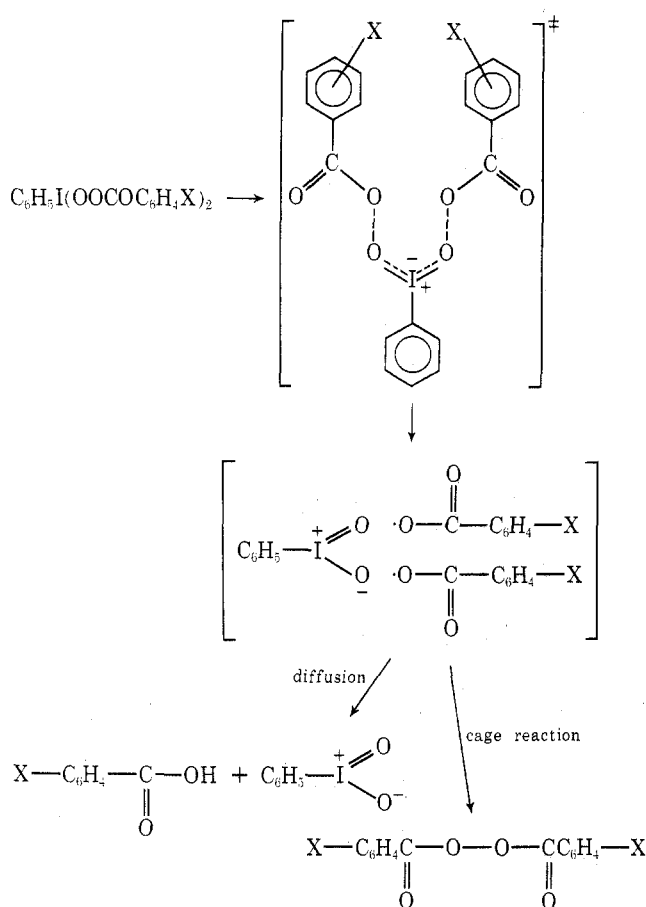
I,I-Dibenzoyldioxyiodobenzenes are the first class of compounds with peroxide functional groups directly bound to iodine. Aromatic peroxides with iodine as a substituent in the ortho position have already been reported to decompose rather quickly owing to the anchimerically assisted cleavage.[6-8]

Results and Discussion

Preparation and Characterization. *I,I*-Dibenzoyldioxyiodobenzenes were prepared from iodosobenzene and substituted peroxybenzoic acids in chloroform (or methylene chloride) at −5°, eq 1, in yields ranging from 60 to

$$Y = F, Cl, CH_3; \quad X = F, Cl, Br, NO_2, t\text{-Bu}$$
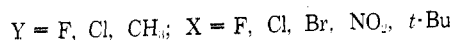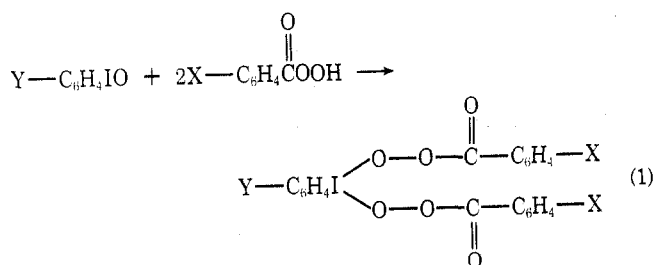
70%. Derivatives of aliphatic peroxy acids could not be isolated; i.e., iodoxybenzene was identified as the major product in the reaction of iodosobenzene with peroxyacetic acid.

I,I-Dibenzoyldioxyiodobenzenes possess three "active" oxygens per molecule as determined by iodometric titration. Iodobenzene and benzoic acid are the end products of this reduction.

The infrared spectra of compounds under investigation show some similarities with those of the corresponding parent peroxybenzoic acid. Carbonyl stretching frequencies

Table I
Rate Constants and Activation Parameters for the Decomposition of *I,I*-Dibenzoyldioxyiodobenzenes, ArI(OOCOArX)₂, in Chloroform

Substituent, X	Concn, M	Temp, °C	$k \times 10^5$, sec^{-1} [a]	ΔH^+, kcal/mol	ΔS^+, eu
4-*t*-Bu	{0.025	28.0	1.94 (±0.06)		
	{0.026	38.0	5.15 (±0.04)	17.5	−21.8
4-F	0.025	38.0	3.80 (±0.03)		
4-Cl	{0.025	28.0	1.35 (±0.07)		
	{0.025	38.0	3.80 (±0.04)	18.6	−19.0
3-Cl	0.022	38.0	3.08 (±0.05)		
4-Br	0.026	38.0	3.96 (±0.06)		
3-NO₂	0.019	38.0	2.49 (±0.09)		
4-NO₂	0.022	38.0	2.70 (±0.08)		

[a] Average of at least three runs with standard deviations rentheses.

Table II
Products of Decomposition of *I,I*-Dibenzoyldioxyiodobenzenes, ArI(OOCOArX)₂, in Chloroform

Substituent, X	Concn, M	Temp, °C	Products, mol/mol of peroxide[a]		
			ArIO₂	X−ArCO₂H	(X−ArCOO)₂[b]
4-Cl	0.010	28.0	0.85	1.60	0.15
	0.030	38.0	0.80	1.70	0.10
4-Br	0.025	38.0	0.83	1.65	0.08

[a] Hexachloroethane was determined qualitatively in all decompositions by mass spectrometry. [b] The correct value for diaroyl peroxide (X = 4-NO₂) in ref 1 is 0.15.

are located a little higher but with the same type of splitting of the carbonyl band (ca. 20 cm⁻¹), indicating a covalent rather than ionic structure.[9] Attempts to obtain some stereochemical data on *I,I*-dibenzoyldioxyiodobenzenes by a dipole moment study met with no success.[10] Nevertheless, it seems reasonable to assume, on the basis of only one signal for *tert*-butyl protons (−60 to 30°) in the 60-MHz ¹H NMR (CDCl₃) spectrum of $C_6H_5I(OOCOC_6H_4\text{-}t\text{-Bu})_2$, centered at δ 1.37 (18 H) (aromatic multiplet, 13 H, δ 7.19–8.30), that these compounds appear in solution in a single conformation,[11] most probably a symmetrical (C_{2v}) one, with both functional groups in a mirror position (Scheme I).[12]

Kinetics and Products of Decomposition. The decomposition in chloroform at 28–38° obeys a first-order rate law over a concentration range 0.008–0.030 M. Each reaction was followed for at least 2 half-lives of the starting material. The rate constants and activation parameters are listed in Table I.

As can be seen from Table I, electron-repelling substituents increase the rate of decomposition whereas electron-attracting groups retard. A plot of the rates of decomposition against Hammett σ constants gives a reasonable correlation ($r = 0.93$) with ρ −0.29 (Figure 1). The products under various conditions for two representative compounds are summarized in Table II.

The decomposition products and first-order kinetics are in accord with an unimolecular free-radical decomposition as the predominant reaction path as proposed in Scheme I. The effect of substituents could be explained as being due to an inductive effect removing or adding the excess of electron density on the peroxidic oxygens, stabilizing or destabilizing in this way both peroxidic bonds with respect to homolytic cleavage (dipole–dipole repulsion).[13] The low enthalpy of activation together with a rather large negative
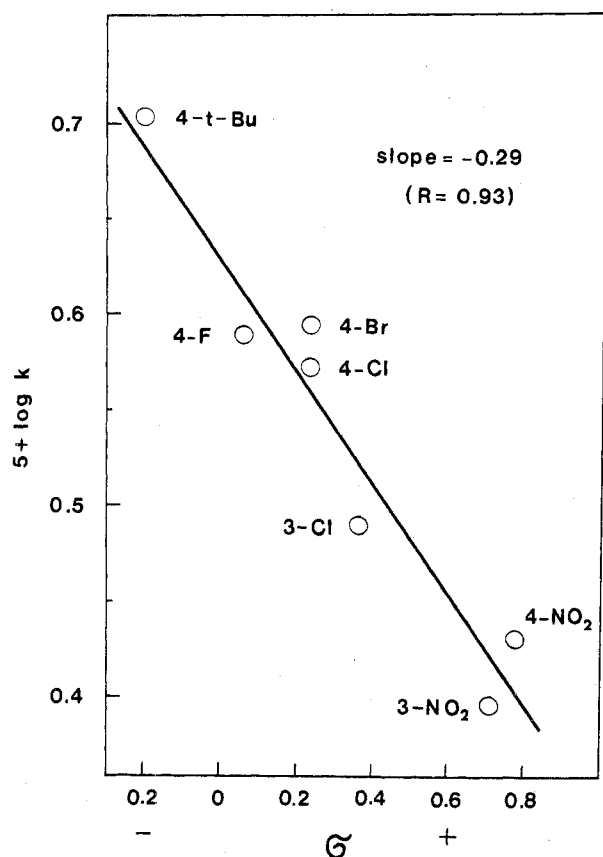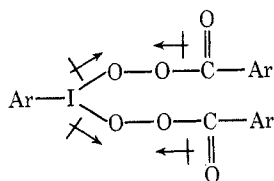
Figure 1. Plot of the logarithms of the rates of decomposition (38°) of *I,I*-dibenzoyldioxyiodobenzenes, ArI(OOCOArX)$_2$, against Hammett σ values of the substituents.

entropy of activation seem to indicate considerable rotational restrictions in, as well as a partially ionic character of, the transition state.[14-16]

Some comments regarding the decomposition products are appropriate. Iodoxybenzene (B) formed in the decomposition had a sharp melting point (223°), i.e., much lower than that of the authentic sample (A), mp 236–237° (lit.[17] 230°), prepared by two independent methods.[17] Infrared spectra of both compounds also differ considerably, especially in the ν C–H, C=C, and I–O regions of the spectrum (Figure 2). The presence of symmetric and asymmetric I–O stretching bands in the ir spectra of both compounds (710–770 cm^{-1}), together with the fact that B can be transformed to A by recrystallization from water, indicate that A and B are polymorphous modifications of the same compound.[18] It is interesting to mention that 4F-C$_6$H$_4$I-(O$_2$COC$_6$H$_4$-4Cl)$_2$ decomposes in chloroform to give *p*-fluoroiodoxybenzene (B), mp 214° (authentic sample, mp 248°), with A and B showing the same general features in the infrared spectra.[19] The formation of iodoxybenzene in the decomposition of *I,I*-dibenzoyldioxyiodobenzenes indicates that both reported synthetic methods which are in use for the preparation of iodoxybenzene, i.e., the reaction of iodobenzene with excess of peroxyacetic acid[17] and peroxybenzoic acid,[20] proceed via corresponding *I,I*-diacyl- or *I,I*-dibenzoyldioxyiodobenzenes as intermediates. The mechanism of these reactions was believed previously to involve the nucleophilic attack of the iodine lone electron
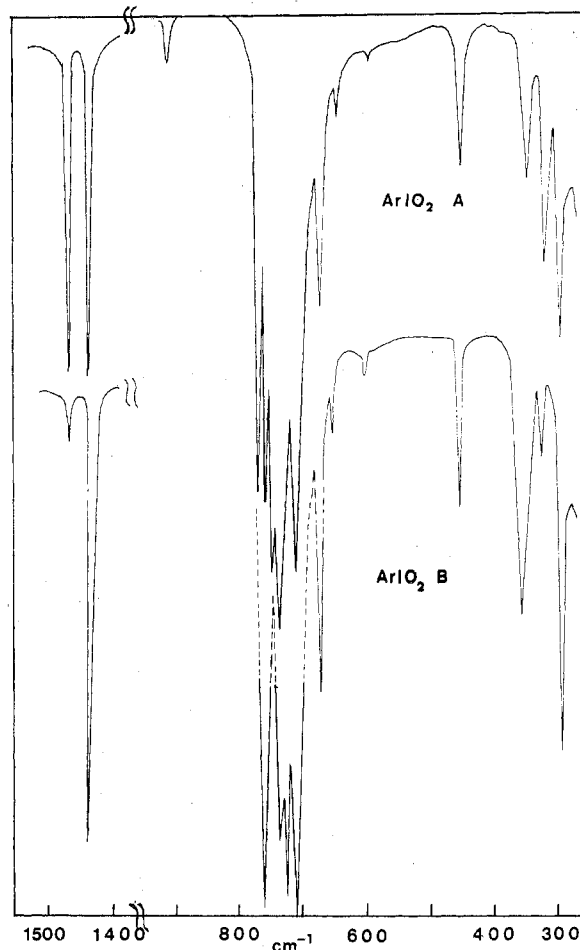
Figure 2. Segments of the infrared spectra of iodoxybenzene A and B.

pair in iodobenzene and iodosobenzene (which is formed first) at the electrophilic oxygen of the peroxy acid.[21] Benzoyloxy radicals formed initially in the decomposition appear to have sufficient lifetime under conditions investigated to be rapidly trapped by the abstraction of hydrogen from the solvent.[22-26] Absence of any products which would indicate the abstraction of chlorine is rather surprising, but is in accord with the findings reported previously for the decomposition of dibenzoyl peroxides in the same solvent.[27]

Relatively small amounts of dibenzoyl peroxides formed in the decomposition, most probably as a result of geminate recombination, could be explained with a rather great initial distance of benzoyloxy radicals formed as well as with a low viscosity of the solvent used.[28,29]

The study of decomposition in other conventional solvents requires higher initial temperatures owing to a low solubility of peroxides investigated. For example, decomposition in CCl$_4$ (79.9°) does not follow the first-order law well; small amounts of benzoic acids are formed in this solvent, indicating induced (or free-radical and polar) decomposition. These reactions are not well understood at present and additional work is being done to clarify them.

Experimental Section

Chloroform was shaken with sulfuric acid and washed with sodium hydrogen carbonate solution and water. After successive 24-hr periods of drying over anhydrous MgSO$_4$ it was fractionally distilled and kept over 3A molecular sieves.

Substituted peroxybenzoic acids were prepared by direct oxidation of the corresponding benzoic acids by 95% hydrogen peroxide in methanesulfonic acid,[30] and were found to be over 99% pure by iodometry (recrystallization from chloroform–hexane).

Iodosobenzene was made by hydrolysis of the iodobenzene dichloride with 5% sodium hydroxide solution.[31] Iodometric titration showed this product to be over 99.5% pure. Owing to its tendency to disproportionate the iodosobenzene was prepared freshly before use.

Iodoxybenzene (A) was prepared by two independent methods, i.e., direct oxidation of iodobenzene by 40% peroxyacetic acid[17b] and by disproportionation of iodosobenzene.[17a] The crude product was recrystallized from water, giving white needles, mp 236–237° (100% pure by iodometry).

Iodoxybenzene (B) obtained in the decomposition had mp 223°.

Anal. Calcd for $C_6H_5IO_2$: C, 30.50; H, 2.12; O, 13.55. Found: C, 30.48; H, 2.13; O, 13.55.

I,I-Dibenzoylidoxyiodobenzenes. In a typical preparation, iodosobenzene (20 mmol) was suspended under magnetic stirring in 60 ml of chloroform at −5°. Peroxybenzoic acid (45 mmol) was added slowly within a few minutes. Stirring was continued for about 15 min. The reaction mixture was then filtered and the solvent removed on a rotary evaporator below room temperature. The crude product was washed several times with small portions of diethyl ether and dried in vacuo over P_2O_5. All peroxides were found to be over 97% pure by iodometry. See Table III.

Table III
Melting Points and Ir (NMR) Data for
I,I-Dibenzoyldioxyiodobenzenes

	$YC_6H_4I(OOCOC_6H_4X)_2$			
	Y	X	Mp, °C[a]	Ir[b] (NMR)[c]
I[d]	H	3-Cl	96–98 dec	1744, 1725
II[d]	H	4-Cl	89–90 dec	1740, 1723
III[d]	H	3-NO$_2$		
IV[d]	H	4-NO$_2$	114–116 dec	1749, 1729
V[d]	H	3-Br	95–96 dec	1738, 1720
VI[d]	H	4-Br	93–95 dec	1740, 1722
VII[d]	H	4-F	77–78 dec	1745, 1720
VIII[d]	H	4-t-Bu	99–101 dec	(CDCl$_3$) δ 1.37 (s, 18 H), 7.19–8.30 (m, 13 H)
IX[d]	2-CH$_3$	3-Cl	61–63 dec	
X[d]	3-CH$_3$	3-Cl	67–69 dec	
XI[d]	4-CH$_3$	3-Cl	74–76 dec	
XII[d]	4-F	3-NO$_2$	93–94 dec	
XIII[d]	4-Cl	3-NO$_2$	90–91 dec	
XIV[d]	4-F	4-t-Bu	88–89 dec	(CDCl$_3$) δ 1.36 (s, 18 H), 7.07–8.27 (m, 12 H)

[a] Melting points were taken on a Kofler micro hot stage and are not corrected. [b] Infrared spectra were recorded on Perkin-Elmer Models 521 and 180 spectrometers (Nujol). [c] The nuclear magnetic resonance spectra were obtained with a Varian Model A-60 and Jeol JNM-C-60HL spectrometers (CDCl$_3$, Me$_4$Si). [d] Satisfactory analytical data for C, H, and "active" O (iodometric) were provided for these compounds. Ed.

Caution. Although this procedure was repeated several times without incident, the use of safety shielding is strongly recommended. Particular caution should be observed when solvent is removed on a rotary evaporator and in handling pure, dry materials. For example, a small sample of I detonated when it was touched by a metal spatula, although previous samples had been handled in the same way without incident.

Kinetic experiments were carried out in sealed, degassed tubes, and the remaining peroxide was determined (after removal of the unsoluble iodoxybenzene) by an iodometric titration already described.[32] First-order rate constants and correlation coefficients were obtained from a linear least-squares program. Activation parameters were calculated by the usual methods.

Product Analysis. The products were determined by a combination of techniques. Iodoxybenzene was removed by filtration. Benzoic acids were extracted with bicarbonate or determined by infrared in the decomposition mixture prior to any work-up procedure. Diaroyl peroxides were determined by infrared[33] and by thin

layer chromatography.[34] The quantities reported are probably good within 7% of their reported values. The presence of hexachloroethane in the reaction mixture (prior to any work-up procedure) was confirmed by mass spectrometry.

In a typical run, approximately 0.025 M solution was decomposed, and the solution was subjected to the analysis described. The absence of other volatile products was confirmed by gas–liquid chromatography.

Registry No.—I, 30242-75-2; II, 56391-39-0; III, 56391-40-3; IV, 30030-30-9; V, 56391-41-4; VI, 56391-42-5; VII, 56391-43-6; VIII, 56391-44-7; IX, 56391-45-8; X, 56391-46-9; XI, 56391-47-0; XII, 56391-48-1; XIII, 56391-49-2; XIV, 56391-50-5; iodosobenzene, 536-80-1; iodoxybenzene, 696-33-3; 3-chloroperoxybenzoic acid, 937-14-4; 4-chloroperoxybenzoic acid, 937-22-4; 3-nitroperoxybenzoic acid, 2453-41-0; 4-nitroperoxybenzoic acid, 943-39-5; 3-bromoperoxybenzoic acid, 5106-10-5; 4-bromoperoxybenzoic acid, 13020-00-3; 4-fluoroperoxybenzoic acid, 1514-03-0; 4-$tert$-butylperoxybenzoic acid, 1711-40-6.

References and Notes

(1) (a) A portion of this work was introduced in preliminary form; see B. Plesničar and G. A. Russell, *Angew. Chem., Int. Ed. Engl.*, **9**, 797 (1970); *Angew. Chem.*, **82**, 834 (1970). (b) International Symposium on Organic Free Radicals, Sirmione, Italy, June 1974.

(2) D. F. Banks, *Chem. Rev.*, **66**, 243 (1966).

(3) J. E. Leffler and L. J. Story, *J. Am. Chem. Soc.*, **89**, 2333 (1967), and references cited therein.

(4) J. E. Leffler, D. C. Ward, and A. Burduroglu, *J. Am. Chem. Soc.*, **94**, 5339 (1972).

(5) N. A. Milas and B. Plesničar, *J. Am. Chem. Soc.*, **90**, 4450 (1968).

(6) J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos, *J. Am. Chem. Soc.*, **80**, 5435 (1958).

(7) W. G. Bentrude and J. C. Martin, *J. Am. Chem. Soc.*, **84**, 1561 (1962).

(8) J. C. Martin and M. M. Chau, *J. Am. Chem. Soc.*, **96**, 3319 (1974).

(9) R. Kavcic, B. Plesničar, and D. Hadri, *Spectrochim. Acta, Part A*, **23**, 2483 (1967).

(10) Decomposition was observed in benzene and dioxane during the measurements (O. Exner and B. Plesničar, unpublished results).

(11) The NMR argument holds for the case that the barriers to rotation about I-O bonds are higher than ca. 10–12 kcal/mol; otherwise an "apparent" single conformation would be seen even at −60° in the 60-MHz NMR spectrum.

(12) Even if dipole moments had been measured, the interpretation would be difficult. On the other hand, the principle of estimating conformation part by part, according to simpler model compounds, might be quite promising. The dihedral angle ∠O=C-O-O is almost certainly ∼0–30°, according to esters and peroxy esters [F. D. Verderame and J. G. Miller, *J. Phys. Chem.*, **66**, 2185 (1962)]; the dihedral angle ∠C-O-O-I is very probably ∼100–120°, according to peroxides; and ∠O-O-I-C is perhaps ∼180°, according to I,I-diacyloxyiodobenzenes [O. Exner and B. Plesničar, *J. Org. Chem.*, **39**, 2812 (1974)].

(13) For similar interpretation of the effect of substituents on the decomposition of dibenzoyl peroxides, see C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950),

(14) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).

(15) P. D. Bartlett and D. M. Simons, *J. Am. Chem. Soc.*, **82**, 1753 (1960).

(16) J. P. Lorand and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 3294 (1966).

(17) H. J. Lukas and E. R. Kennedy, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 485; J. G. Sharefkin and H. Saltzman, *Org. Synth.*, **43**, 65 (1963).

(18) C$_6$H$_5$IO$_2$ (infrared studies): C. Furlani and G. Sartori, *Ann. Chim. (Rome)*, **47**, 124 (1957); R. Bell and K. J. Morgan, *J. Chem. Soc.*, 1209 (1960); G. P. Baker, F. G. Mann, N. Sheppard, and A. J. Tetlow, *J. Chem. Soc.*, 3721 (1965).

(19) The same phenomenon is observed also in the case of 3-BrC$_6$H$_4$IO$_2$ (A, mp 233–234; B, mp 226°) and 4-ClC$_6$H$_4$IO$_2$ (A, mp 242–245°; B, mp 232–233°).

(20) J. Boeseken and E. Wicherlich, *Recl. Trav. Chim. Pays-Bas*, **55**, 936 (1936).

(21) S. O. Lawesson and G. Schroll in "The Chemistry of Carboxylic Acids and Esters", S. Patai, Ed., Wiley-Interscience, New York, N.Y., 1969, Chapter 14, and references cited therein.

(22) G. S. Hammond and L. M. Soffer, *J. Am. Chem. Soc.*, **72**, 4711 (1950).

(23) H. J. Shine, J. A. Waters, and D. M. Hoffman, *J. Am. Chem. Soc.*, **85**, 3613 (1963).

(24) R. L. Huang, H. H. Lee, and S. H. Ong, *J. Chem. Soc.*, 3336 (1962).

(25) D. F. DeTar, *J. Am. Chem. Soc.*, **89**, 4058 (1967).

(26) C. Walling and J. C. Azar, *J. Org. Chem.*, **33**, 3885 (1968).

(27) J. I. Cadogan, D. H. Hey, and P. G. Hibbert, *J. Chem. Soc.*, 3939 (1965).

(28) T. Koenig, M. Deinzer, and J. A. Hoobler, *J. Am. Chem. Soc.*, **93**, 938 (1971).
(29) E. Niki and Y. Kamiya, *J. Am. Chem. Soc.*, **96**, 2129 (1974).
(30) L. S. Silbert, E. Siegel, and D. Swern, *J. Org. Chem.*, **27**, 1336 (1962).

(31) H. Saltzmann and J. G. Sharefkin, *Org. Synth.*, **43**, 60 (1963).
(32) T. T. Wang and J. E. Leffler, *J. Org. Chem.*, **36**, 1531 (1971).
(33) W. H. T. Davison, *J. Chem. Soc.*, 2456 (1951).
(34) R. Kavcic, B. Plesnicar, and A. Perdih, *J. Chromatogr.*, **66**, 321 (1972).

Successful Direct Fluorination of Oxygen-Containing Hydrocarbons

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New methods which have been recently developed for direct fluorination have enabled practical syntheses in high yields of oxygen-containing perfluorocarbons from their hydrocarbon analogs. These syntheses have been successful on several important classes of oxygen-containing hydrocarbons and most functional groups survive these gentle fluorinations. The syntheses of perfluoro-1,2-dimethoxyethane, perfluorobis(2-methoxyethyl) ether, perfluoro-1,2-diethoxyethane, perfluoro-1,4-dioxane, perfluoroethyl acetate, perfluorodimethylmalonyl difluoride, and perfluoropivaloyl fluoride from their hydrocarbon analogs are discussed. The monohydro species α-hydrotetrafluoroethyl trifluoroacetate, monohydroctafluoropivaloyl fluoride, and 1-hydrononafluoro-2,5-dioxahexane have also been prepared and characterized.

A substantial body of oxygen-containing and functional perfluoroorganic compounds have been prepared and characterized over the last 30 years and their physical properties investigated. Some have been prepared by fluorination using fluorinating agents such as cobalt trifluoride, but the majority have been prepared by the industrially important hydrogen fluoride electrochemical cell techniques pioneered by Simons.[1b] Relatively few successful syntheses of such species have been reported using elemental fluorine as the fluorinating agent. For example: "Fluorination by fluorine is unlikely to be used in normal organic syntheses".[2] A new technique for direct fluorination developed by Lagow and Margrave[3] has led to practical methods[4-7] for the synthesis of oxygen-containing perfluorocarbons from their hydrocarbon analogs. These new direct fluorination techniques for preparing functional and oxygen-containing fluorocarbons promise to develop into an important synthetic method yielding many unreported fluorocarbon compounds and better syntheses for many known compounds. In addition, direct fluorination is particularly valuable for preparing fluorocarbon compounds which are impossible or difficult to obtain by methods such as the cobalt trifluoride or electrochemical methods. The use of direct fluorination to prepare fluorocarbon species such as esters and some ethers whose hydrocarbon analogs are spontaneously decomposed in the hydrogen fluoride solvent used in the electrochemical cell establishes that there are many unique applications for such synthetic techniques.

Several new fluorocarbon compounds which are perfluoro analogs of structurally basic hydrocarbon species are reported in this paper (see Figure 1). Every synthesis reported in this paper represents the highest yield of perfluoro analog yet obtained with any method involving fluorination of the respective starting materials. The yields obtained for the present syntheses of perfluoro-1,4-dioxane, perfluoro-1,2-dimethoxyethane, perfluorobis(2-methoxyethyl) ether, perfluoro-1,2-diethoxyethane, perfluorodimethylmalonyl difluoride, and perfluoropivaloyl fluoride are the highest obtained by any synthetic method.

Experimental Section

Mass spectra were measured on a Hitachi RMU6B mass spectrometer at 70 eV. NMR spectra were taken on a Perkin-Elmer R20-B spectrometer at 70 MHz for protons and 56.466 MHz for

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fluorine. Gas chromatography separations were made using either a Varian Moduline 2700 or a Bendix Model 2300 gas chromatograph. Either a 10% SE-30 or Chromosorb P on a fluorosilicone QF1-0065 10% on Chromosorb P column (10 m × 0.375 in.) was used; however, the fluorosilicone column generally provided better separation.

Molecular weight determinations were performed on 20–50-mg samples sealed in preweighed capillaries and broken into a 66-cm³ bulb attached to a manometer calibrated for volume change with pressure. Precision was about 0.5%.

Carbon, hydrogen, and fluorine analyses were done by Schwarzkopf Microanalytical Laboratory on 4–10-mg samples sealed under nitrogen into preweighed capillaries. Precision using this technique usually was 0.2–0.3% for fluorine analyses.

The reactor system used is illustrated in Figure 2, except that for the fluorination of pivaloyl fluoride and dimethylmalonyl difluoride a six-zone cryogenic reactor was used. The dimensions of the reactor have been previously described.[4] Physical properties of reactants are important in the cryogenic fluorination reactor. An ideal compound should have a reasonably high vapor pressure in the solid state. The combination of volatility and exposure in the solid phase, except during transfer, permits the renewal of the reactant surface as the more volatile products are produced and the dissipation of heat into the lattice and ultimately to the supporting copper turnings, walls, and cooling system in the reactor. A large initial surface area formed by sublimation of the reactant into the reactor permits fluorine at very low concentrations (less than 2%) to react with a large percentage of the hydrocarbon molecules.

Initial fluorination of a hydrocarbon decreases the volatility of the species. At about 50% fluorination, a maximum boiling point or minimum vapor pressure occurs. Under such conditions, hydrogen bonding and other associative interactions are at a maximum. After such a minimum vapor pressure of the reactant is obtained, each successive substitution of a fluorine for a hydrogen atom increases the vapor pressure. If at this point a temperature gradient is produced in the reactor, the more highly fluorinated products will be volatilized, exposing less highly fluorinated, less volatile species to interaction with fluorine. By repeating the above procedure, essentially complete fluorination of the hydrocarbon can occur under conditions which maintain a slow controllable rate of reaction. In the initial stages of the reaction, this rate of reaction is controlled by a high dilution of the fluorine and by cryogenic temperatures which reduce the reaction rate. As the reaction proceeds and more protons have been replaced by fluorine, the concentration of fluorine is increased and the temperature gradient applied to maintain a more constant rate of reaction. The amount of fluorine used is carefully controlled and is usually between 30 and 150 mmol/day. Should combustion occur, all the fluorine in the reactor is consumed and the reaction terminates until more fluorine is delivered. Therefore, the only adverse effect is an unsuccessful reaction. This is an important safety factor.

Perfluoro-1,2-dimethoxyethane. 1,2-Dimethoxyethane (4.015