Stereochemical Studies on Some Reactions Proceeding via α-Fluoro- and α-Chlorocyclopropyl Radicals[1]

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The stereochemistry of the brominative decarboxylation of 7-*endo*-fluoro- (**1a**), 7-*exo*-fluoro- (**1b**), 7-*endo*-chloro- (**2a**), and 7-*exo*-chloronorcarane-7-carboxylic acid (**2b**), as well as the thermal decomposition of their *tert*-butyl peroxy esters in toluene, cumene, or bromotrichloromethane, has been examined. The degree of stereospecificity observed in these reactions has revealed that (i) the 7-fluoro-7-norcaryl radical is configurationally very stable and its bromine abstraction under the brominative decarboxylation conditions (0 or 77°) or from bromotrichloromethane (110°) occurs much more rapidly than its inversion of configuration, (ii) its hydrogen abstraction from toluene or cumene occurs less rapidly and can compete with its inversion, and (iii) the inversion of the 7-chloro-7-norcaryl radical occurs more rapidly than that of the corresponding fluoro radical, and as a result the stereospecificity of the reaction involving the chloro radical decreases. Similar reactions of 7-unsubstituted norcarane-7-carboxylic acids (**3a** and **3b**) and their peroxy esters have shown that the 7-norcaryl radical is configurationally unstable and behaves like a planar radical in these reactions.

Based on many spectrochemical data, ordinary alkyl radicals have been recognized either to have a pyramidal structure but be subject to rapid inversion of configuration, or to have a planar structure. For example, the trifluoromethyl radical has been proved to be pyramidal by ir[2] and ESR[3] spectroscopy and by photoionization studies.[4] The fluoro- and hydroxymethyl radicals are also considered to be pyramidal,[5] whereas electronic[6] and ESR[7] spectra have provided evidence supporting a planar structure for the methyl and unsubstituted alkyl radicals.

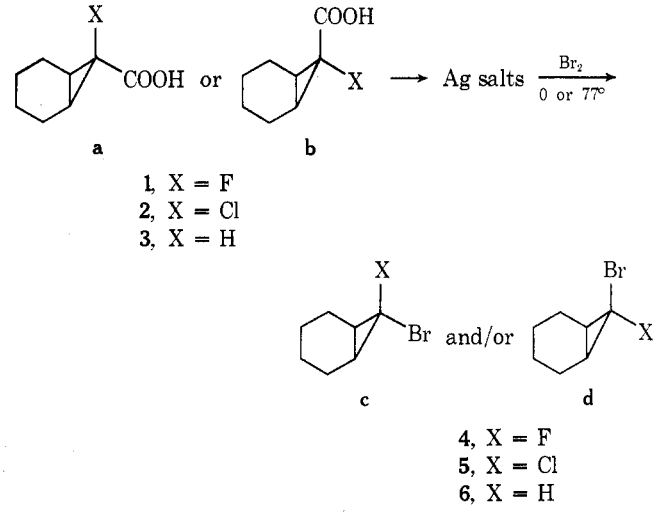
Recent chemical studies on the nature and, in particular, the configurational stability of vinyl[8] and cyclopropyl[9] radicals have favored a bent and a nonplanar configuration, respectively, at the tervalent carbon. Thus, we reported earlier that the reduction of some *gem*-halofluorocyclopropanes with tri-*n*-butyltin hydride proceeded with complete retention of configuration.[9a,b] The results were rationalized by postulating a pyramidal structure for the intermediate α-fluorocyclopropyl radical and the slow rate of its inversion relative to its hydrogen abstraction, which came from the high configurational stability, or the high energy barrier for inversion, of α-fluorocyclopropyl radicals.

The validity of this assumption has now been examined by studying the stereochemistry of some reactions which are believed to involve α-fluoro (or -chloro)cyclopropyl radicals, viz., the brominative decarboxylation (Hunsdiecker reaction) of 7-halonorcarane-7-carboxylic acids and the thermal decomposition of their peroxy esters.

Results

Brominative Decarboxylation of 7-Halonorcarane-7-carboxylic Acids (1, 2, and 3). Two isomers of 7-fluoronocarane-7-carboxylic acid (**1a** and **1b**) (Scheme I) were obtained by carbonation of 7-fluoro-7-norcaryllithium followed by fractional recrystallization. The configurational assignment to the isomers was made from their ^{19}F NMR spectra based upon the generalization that in fluorocyclopropanes the ring fluorine is more strongly coupled with cis than with trans hydrogen,[10] and that in alkyl- and aryl-substituted cyclopropanes the ring fluorine is shielded by cis and deshielded by trans substituents.[11] Isomers of 7-chloronorcarane-7-carboxylic acid (**2a** and **2b**) were prepared according to the method of Köbrich and Goyert.[12] The 7-unsubstituted acids, **3a** and **3b**, were prepared as follows: norcarane-7-*exo*-carboxylic acid (**3a**) was obtained by the reaction of ethyl diazoacetate with cyclohexene followed by alkaline hydrolysis and fractional recrystallization. Endo acid **3b** was obtained by the reduction of methyl 7-bromonorcarane-7-carboxylate with tri-*n*-butyltin hydride followed by hydrolysis. Their spectral data were in good agreement with the reported ones.[12,13,14]

Scheme I



The silver salts of the acids were separately prepared in the conventional manner and were allowed to react with bromine in carbon tetrachloride under the conditions indicated in Table I. The brominated cyclopropanes were identified by comparison of their retention times and spectral properties with those of an authentic sample of 7-bromo-7-fluoronorcarane, 7-bromo-7-chloronorcarane, or 7-bromonorcarane. The yields of these bromides were determined from their peak areas in GLC, calibrated against authentic sample solutions of known concentrations.

Thermal Decomposition of *tert*-Butyl Peroxy Esters (7 and 8). *tert*-Butyl 7-fluoro- and 7-chloronorcarane-7-peroxycarboxylates were prepared in good yields by treatment of the corresponding acid chloride with *tert*-butyl hydroperoxide in *n*-pentane at −20°. The peroxy esters were purified by chromatography on Kiesel gel prior to use. All four peroxy esters gave satisfactory spectral analyses. Two of the four peroxy esters were solids at room temperature (**7a**, mp 40.0–41.0°; **8a**, mp 46.5–47.5°), which minimized

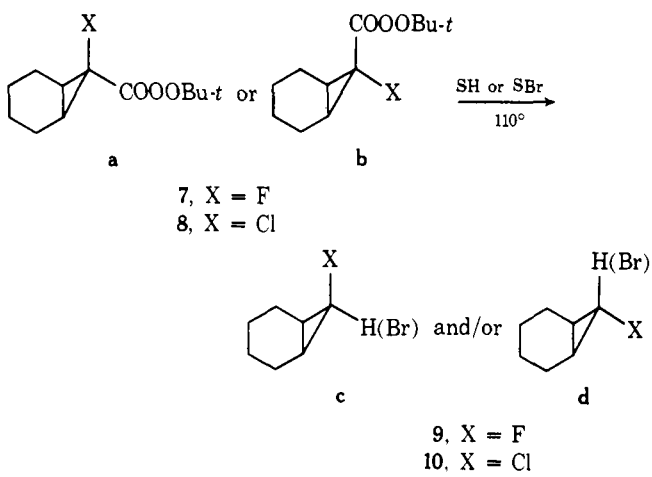
Table I
Brominative Decarboxylation of Acids 1, 2, and 3

Compd	Time, hr	Temp, °C	Yield, %	Isomer ratio retn:invn
1a	2	0	71	100:0
	2	77	75	100:0
1b	2	0	75	100:0
	2	77	71	100:0
2a	2	0	68	88:12
	2	77	73	72:28
2b	2	0	71	82:18
	2	77	74	43:57
3a	2	0	70	81:19
	2	77	73	84:16
3b	2	0	72	16:84
	2	77	76	15:85

contamination problems, and the others (**7b** and **8b**) were liquids at room temperature. The structural assignment of all peroxy esters was made on the basis of the stereochemistry of the starting acids.

Degassed solutions of the peroxy esters in toluene, cumene, or bromotrichloromethane as scavenging solvent were heated in sealed Pyrex ampoules at 110° for 24 hr (Scheme II). Infrared analysis revealed no remaining per-

Scheme II



oxy esters at the end of the reaction. The yields of the products are given in Table II together with the reaction conditions. The products formed by hydrogen (or bromine) abstraction, RH or RBr, were identified by comparison with authentic samples and their yields were measured by the internal standard method (GLC). Where only relative yields (isomer distributions) were desired, no internal standard was added. The yields of acids, RCOOH, were determined by calibration of the carboxyl absorption intensity against those of solutions of known concentrations. The isolated acids were found to have retained the geometry of the starting peroxy esters in all cases.

Discussion

As shown in Table I, the brominative decarboxylation of 7-fluoronorcarane-7-carboxylic acid (**1**) occurred with complete retention of configuration, whereas that of the chloro acid **2** occurred with only partial stereospecificity to give a mixture of two geometrical isomers. The high stereospecificity observed with the fluoro acid means that the inversion of configuration of the 7-fluoro-7-norcaryl radical oc-

Table II
Thermal Decomposition of Peroxy Esters 7 and 8

Compd	Solvent	Yield, %[a] RCOOH	Yield, %[a] RH or RBr	Isomer ratio retn:invn
7a	Toluene	13	61	94:6
	Cumene	15	65	96:4
	$CBrCl_3$		53	100:0
7b	Toluene	16	65	90:10
	Cumene	16	58	93:7
	$CBrCl_3$		49	100:0
8a	Toluene	17	64	78:22
	Cumene	18	56	80:20
	$CBrCl_3$		38	82:18
8b	Toluene	18	68	23:77
	Cumene	19	55	21:79
	$CBrCl_3$		47	18:82

[a] R stands for 7-fluoro- or 7-chloro-7-norcaryl group.

curs much more slowly than its bromine abstraction, and can be ascribed to the extremely high configurational stability of the α-fluorocyclopropyl radical intermediate as previously cited.[9b] On the other hand, the stereochemical behavior of the chloro acid suggests that the configurational stability of the 7-chloro-7-norcaryl radical is not so high as that of the corresponding fluoro radical, and that the inversion of the chloro radical occurs at a rate comparable to its bromine abstraction. Table I also shows that, as is the case in the reduction of cyclopropyl bromides with tri-*n*-butyltin hydride,[9b] the ratio of retention to inversion decreases as the temperature increases.

In the reaction of the corresponding 7-unsubstituted acid (**3**) under the same reaction conditions, the isomer distributions in the products were nearly identical in all runs, irrespective of the geometry of the starting acid. This indicates that the unsubstituted 7-norcaryl radical is either pyramidal but inverts its configuration so rapidly that it behaves like a planar radical, or in fact it is planar.

From the above-described results, it follows that both the α-fluoro and the α-chloro substituents can stabilize the pyramidal configuration of the cyclopropyl radical, but the effect of fluorine is much stronger than that of chlorine.

Further evidence supporting this view is provided by the thermal decomposition of the *tert*-butyl peroxy esters of 7-fluoro- and 7-chloronorcarane-7-carboxylic acid (**7** and **8**).

The significant yields of the acids suggest that a one-bond homolysis[15] operates with these peroxy esters. However, decarboxylation also occurs as indicated by the moderate to high yield of RH (Table II). As is clear from the data in Table II, the hydrogen abstraction of the 7-fluoro-7-norcaryl radical from toluene or cumene is not so rapid as the bromine abstraction from bromotrichloromethane and can compete with the inversion of configuration. It should be noted that the degree of stereospecificity is closely related to the bond-dissociation energy of the C–H or the C–Br bond in scavenger molecules.

In contrast to the fluoro peroxy esters, the isomer compositions of the products from the chloro peroxy esters are essentially the same, regardless of their stereochemistry. It means that, at least at this reaction temperature, the inversion of configuration of the chloro radical takes place much more rapidly than the hydrogen or bromine abstraction from the solvents, though more efficient scavenging systems might lead to partial or complete specificity. The preferential formation of *endo*-chloronorcarane and *endo*-chloro-*exo*-bromonorcarane (**10c**) is most easily explained

by stereoselectivity in the hydrogen or bromine abstraction step, i.e., the approach of the scavenging agent toward the 7 position from the exo side being sterically less hindered than that from the endo side.

A similar trend has been noted in studies on the 9-decalyl systems[16] where a change of solvent from cyclohexene to cumene leads to an increase in *cis*-decalin in the product mixture.

From the stereochemical results described herein, it may be concluded that in comparison with the α-fluorocyclopropyl radical, the configurational stability of the α-chloro radical is lower, but not so low as that of the α-unsubstituted one.

Generally, the configurational stability of free radicals can be regarded as being dependent upon the s character of the odd-electron orbital.[17] Thus, vinyl radicals are configurationally more stable than cyclopropyl radicals, since the odd-electron orbital of the former is sp^2 hybridized and that of the latter is $sp^{2.4}$ or $sp^{2.5}$ hybridized.[18] If the α hydrogen is replaced by an electronegative atom or group such as fluorine or chlorine, the s character of the carbon orbital forming the C–F or the C–Cl bond decreases relative to that of the C–H bond, and as a result the s character of the odd-electron orbital increases. It may be expected, therefore, that the more electronegative the α substituent is, the less rapidly the inversion of configuration will occur.

The results reported herein are in accordance with this expectation. An analogous tendency has been observed with α-substituted vinyl radicals,[8] and the calculation of the energy barrier for inversion of some cyclopropyl and vinyl radicals by CNDO/2[9c] or MINDO/3[19] also suggests the significance of the electronegativity effect of α substituents. The work of Altman et al.[9d] on the α-(trifluoromethyl)cyclopropyl radical reveals, however, that the electronegativity can not be the only factor that determines the configurational stability of cyclopropyl radicals. No doubt more work must be done, both theoretically and experimentally, in order to solve the problem.

Experimental Section

All boiling and melting points are uncorrected. Infrared spectra were taken on a Shimadzu IR-27 infrared spectrometer using a polystyrene film for calibration. Proton NMR spectra were measured for solutions in carbon tetrachloride with tetramethylsilane (Me_4Si) as an internal standard with a Varian Associates T-60 or A-60 or a Jeolco H-60 spectrometer. Fluorine NMR spectra were recorded on a Hitachi H-60 spectrometer (56.4 MHz) in carbon tetrachloride with trifluoroacetic acid (TFA) as an external reference. The proton and fluorine chemical shifts are expressed in parts per million downfield from Me_4Si and in parts per million upfield from TFA, respectively. Gas chromatographic (GLC) analyses were performed with a Shimadzu GC-2C or a Hitachi K23 gas chromatograph by use of a 3 m × 3 mm column with 7% Apiezon L or 7% Silicon DC 550 on 80–100 Celite 545, or a 45 m × 0.25 mm Golay column with Apiezon L or butanediol succinate (BDS). Isomer distributions were calculated from peak areas in gas chromatograms. The values of the isomer ratios listed in Tables I and II are accurate within ±2%.

Materials. All chemicals were reagent grade and used without further purification. Solvents were distilled (or vacuum distilled) through a 25-cm Vigreux column and, if necessary, were purified in the usual manner prior to use. Authentic samples were prepared as follows: 7-bromo-7-fluoronorcarane and 7-bromo-7-chloronorcarane were obtained by the reaction of cyclohexene with bromofluorocarbene[9a,20] and bromochlorocarbene,[21] respectively, generated by basic decomposition of the corresponding trihalomethane.

7-Fluoronorcarane-7-carboxylic Acid (1). To a solution of 29 g (0.15 mol) of 7-bromo-7-fluoronorcarane (mixture of isomers) in 200 ml of tetrahydrofuran–ether (1:1), cooled to −140° by immersing in a bath of liquid nitrogen and methylcyclohexane–*n*-hexane (4:1), was added, under nitrogen atmosphere, 200 ml of a 0.7 *N* solution of *n*-butyllithium in *n*-hexane at such a rate that the temperature should not rise above −130°. After the addition was over, the reaction mixture was stirred for 20 hr at −150 to −140°, and then an excess of solid carbon dioxide was carefully added. The mixture was warmed up to room temperature, poured onto ice water, and was worked up as usual. From the acid fraction, 2.1–2.5 g of 7-fluoronorcarane-7-carboxylic acid was obtained together with 3–4 g of *n*-valeric acid. The neutral fraction gave 6–7 g of unchanged 7-bromo-7-fluoronorcarane (*exo*-F:*endo*-F 9:1), ca. 2 g of 7-(2-tetrahydrofuryl)norcarane, and a small amount of some unidentified products. The crude acid thus prepared was fractionally recrystallized from petroleum ether to yield 1.4–1.7 g of the *exo*-fluoro isomer (**1b**), mp 99.0–99.5°, and 0.2–0.4 g of the *endo*-fluoro isomer (**1a**), mp 112.5–113.0°.

1a: ir (KBr) 1720 (vs), 1440 (s), 1308 (m), 1265 (s), 1250 (s), 1176 (s), 1122 (s), 1035 (m), 980 (m), 790 (m), 755 (m), 680 cm^{-1} (m); ^1H NMR δ 1.1–2.3 (complex m, 10 H) and 11.94 (s, 1 H); ^{19}F NMR δ_F 146.0 (J_{HF} = 5.9 Hz).

Anal. Calcd for $C_8H_{11}O_2F$: C, 60.75; H, 7.01; F, 12.01. Found: C, 61.02; H, 7.22; F, 12.02.

1b: ir (KBr) 1703 (vs), 1690 (vs), 1440 (vs), 1300 (s), 1220 (vs), 1195 (s), 1122 (s), 1095 (s), 1040 (m), 910 (s), 850 (m), 780 cm^{-1} (s); ^1H NMR δ 0.8–2.2 (complex m, 10 H) and 11.85 (s, 1 H); ^{19}F NMR δ_F 98.2 (J_{HF} = 22.3 Hz).

Anal. Calcd for $C_8H_{11}O_2F$: C, 60.75; H, 7.01; F, 12.01. Found: C, 60.83; H, 6.93; F, 12.14.

7-Chloronorcarane-7-carboxylic acid (2) was prepared according to the method of Köbrich and Goyert.[12]

2a: mp 92.0–92.5°; ir (KBr) 1680 (vs), 1440 (m), 1290 (s), 1170 (m), 1105 (m), 1000 (m), 900 (m), 780 (m), 728 cm^{-1} (m); ^1H NMR δ 1.0–2.2 (complex m, 10 H) and 12.63 (s, 1 H).

2b: mp 108.0–109.0°; ir (KBr) 1683 (vs), 1440 (s), 1310 (s), 1221 (s), 1170 (m), 1060 (m), 975 (m), 840 (m), 780 (m), 750 cm^{-1} (m); ^1H NMR δ 1.1–2.0 (complex m, 10 H) and 12.42 (s, 1 H).

Norcarane-7-carboxylic Acid (3). To 74 g (0.9 mol) of cyclohexene in the presence of ca. 0.5 g of anhydrous cupric sulfate was very carefully added, at room temperature, a solution of 34 g (0.3 mol) of ethyl diazoacetate which had been diluted with an equal volume of ether. After the addition, the mixture was stirred until the evolution of nitrogen ceased, and then was worked up as usual. Vacuum distillation of the organic layer afforded, together with ethyl maleate, an isomeric mixture of ethyl norcarane-7-carboxylate (exo ester:endo ester 9:1), bp 72–77° (3 mm), which was hydrolyzed with potassium hydroxide in 50% aqueous ethanol. After a usual work-up, the acid fraction was distilled in vacuo to give crude acid, bp 111–113° (3 mm). Recrystallization from petroleum ether gave 5.5 g of pure norcarane-7-*exo*-carboxylic acid (**3a**) in an overall yield of 13%: mp 95.0–96.0°; ir (KBr) 1673 (vs), 1450 (s), 1310 (s), 1233 (s), 1000 (m), 785 (m), 698 cm^{-1} (m); ^1H NMR δ 0.9–2.0 (complex m, 11 H) and 12.38 (s, 1 H). The reduction of 23 g (0.1 mol) of methyl 7-bromonorcarane-7-carboxylate with 35 g (0.12 mol) of tri-*n*-butyltin hydride at 0° gave 13.9 g of an isomeric mixture (endo ester:exo ester 13:1) in 90% yield, bp 93–94° (19 mm). By a similar treatment as above, 7.0 g of norcarane-7-*endo*-carboxylic acid (**3b**) was obtained as a crystalline solid: 51% yield; mp 77.0–78.0°; ir (KBr) 1690 (vs), 1450 (s), 1345 (m), 1205 (vs), 1170 (s), 1140 (m), 980 (m), 940 (m), 870 (m), 780 cm^{-1} (m); ^1H NMR δ 0.9–2.1 (complex m, 11 H) and 12.18 (s, 1 H).

Brominative Decarboxylation of Acids (1, 2, and 3). In a three-necked flask equipped with a thermometer, a dropping funnel, a stirrer bar, and a condenser with a drying tube at the top was placed 5–10 mmol of the silver salt of **1**, **2**, or **3** and 20 ml of carbon tetrachloride. This suspension was maintained at a constant temperature (0 or 77°) and a solution of 1.2 equiv of bromine in 10 ml of carbon tetrachloride was rapidly added with stirring. After being kept at the same temperature for 2 hr, the reaction mixture was brought to room temperature. The silver-containing precipitates were removed by filtration and washed with a small amount of carbon tetrachloride. The filtrate was concentrated by vacuum evaporation below 30°. The residue was carefully distilled under reduced pressure. The isomer composition of the product was determined by GLC prior to distillation and is shown in Table I.[22]

General Procedure for Preparation of *tert*-Butyl Peroxy Esters (7 and 8). A solution of pyridine (15 mmol) and the acid chloride (10 mmol), prepared by conventional methods from thionyl chloride, in 10 ml of *n*-pentane was cooled in an ice–salt bath, and to it was added a solution of 98% *tert*-butyl hydroperoxide (50 mmol) in 10 ml of *n*-pentane. The mixture was stirred for 3 hr at −15 to −20° and for 1 hr at room temperature. The organic layer was washed successively with cold 10% sulfuric acid, cold 10% aqueous sodium carbonate, and water. It was dried over anhydrous sodium sulfate and concentrated in vacuo to a slightly green oil.

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 (CCl_4 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 (CCl_4 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.

Registry No.—**1a,** 56403-11-3; **1b,** 56377-36-7; **2a,** 18688-20-5; **2b,** 18688-19-2; **3a,** 21448-77-1; **3b,** 21448-76-0; **4c,** 19144-91-3; **4d,** 19144-90-2; **7a,** 56403-13-5; **7b,** 56377-51-6; **8a,** 56377-52-7; **8b,** 56377-53-8.

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(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, $ArI(OOCOAr\text{-}X)_2$, 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 coworkers.[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 $ArI(OOBu\text{-}t)_2$ 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.