Cyclopropanes. XXXVIII. Effect of 1-Substituents on the Stereochemical Stability of the Cyclopropyl Radical[1]

H. M. Walborsky* and P. C. Collins

Department of Chemistry, Florida State University, Tallahassee, Florida 32306

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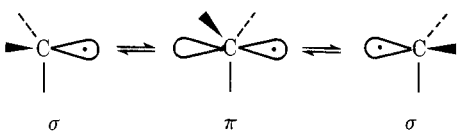
The *tert*-butyl peresters of chiral 1-X-2,2-diphenylcyclopropanecarboxylic acids (X = F, Cl, OCH_3) were prepared. The peresters were decomposed in tetrahydrofuran at 100 °C to yield, inter alia, 1-X-2,2-diphenylcyclopropane. The stereochemical results showed that the effect of the 1-substituent in stabilizing the σ radical was in the order of F > OCH_3 > Cl. This order follows what would be predicted by the Pauling–Walsh model based on the electronegativity of the substituent.

The stereochemistry of free radicals and the question of their geometry, whether they are planar or not, has been the subject of a number of reviews.[2] The consensus is that most acyclic hydrocarbon radicals (sp^3) are planar or π radicals. Cyclic hydrocarbons, if not strained, also fit into this category. The highly strained cyclopropyl ($sp^{2.3}$) radical and the vinyl (sp^2) radical are bent σ radicals.[3] Delocalizing substituents (π systems) attached to the radical site will convert the σ radical into a π radical. In contrast, electronegative substituents (O, F) attached to the radical site have a tendency to convert what would ordinarily be a π radical into a σ radical.[4]



σ π σ

Unless constrained, σ radicals such as cyclopropyl will invert configuration rapidly ($\sim 10^8$–10^{10} s^{-1}), with the inversion proceeding through a π-radical transition state or intermediate. In general, increasing the s character of the orbital containing the unpaired electron will result in stabilizing the σ radical.[4] Thus, both cyclopropyl and vinyl radicals are bent σ radicals and their inversion barriers are larger than those of their acyclic or saturated counterparts.[5]

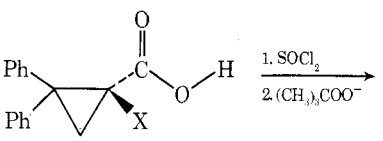
Two theories have been advanced to explain why electronegative substituents tend to cause the radical to be a σ radical. Pauling and Walsh[6] propose that the effect is due to a difference in electronegativity which would cause the orbital occupied by the odd electron to have a greater amount of s character and hence tend to be pyramidal. Any highly electronegative substituent attached to the free-radical center would therefore enhance the nonplanarity of the radical and the substituent effect would be F > OCH_3 > Cl. Dewar[7] argues that the electronegativity of the substituents is not the factor which accounts for the increased configurational stability of the free radicals and that the stabilization in, for example, the vinyl and cyclopropyl radicals is due to an antibonding interaction between the nonbonding electrons of the substituent and the MO's arising from interactions between the singly occupied carbon AO and the MO's of adjacent carbon bonds. Based on MINDO/3 calculations it was predicted that the barrier to inversion, caused by a substituent at the radical site, should increase in the order O < Cl < F. Clearly, the two theories are in conflict and it is the purpose of this paper to provide an experimental test of these two concepts.

Results and Discussion

Syntheses and Decomposition of *tert*-Butyl Peresters. The syntheses, resolution, and establishment of the absolute configurations of 1-X-2,2-diphenylcyclopropanecarboxylic acids **1** (X = F, **a**; Cl, **b**; Br, **c**; OCH_3, **d**) have previously been described.[8]

Table I. Percentage Yields of Decomposition Products

X	1	5	6	8	9	10
F	35.1	19.0		7.0		0.5
OCH_3	11.5	6.7	0.8			0.04
Cl	63.7	13.3				0.8
Br	56.3				1.3	1.2



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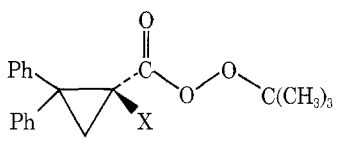
X = F, **a**, (−)-(*S*)
X = Cl, **b**, (+)-(*S*)
X = Br, **c**, (+)-(*S*)
X = CH_3O, **d**, (−)-(*S*)



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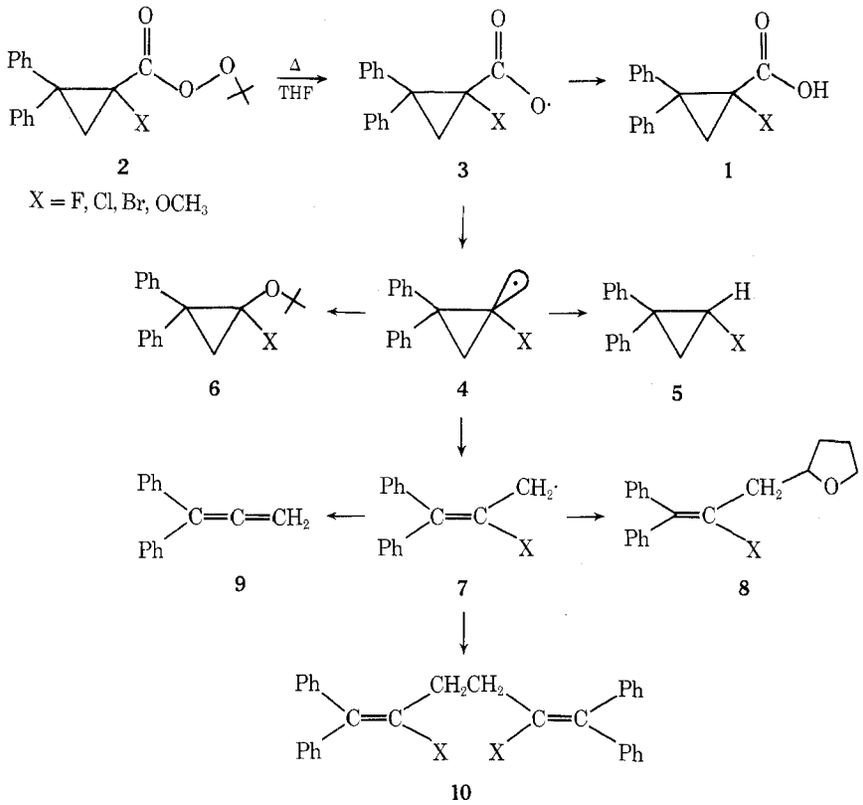
X = F, **a**, (−)-(*S*)
X = Cl, **b**, (+)-(*S*)
X = Br, **c**, (+)-(*S*)
X = CH_3O, **d**, (−)-(*S*)

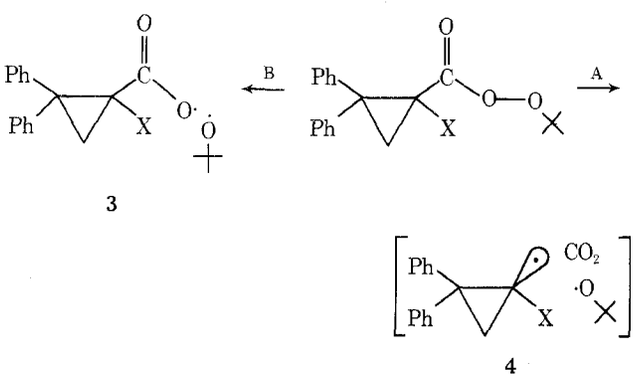
The *tert*-butyl peresters **2a–d** were prepared by converting the acids to their corresponding acid chlorides, using thionyl chloride, and adding them to a suspension of the sodium salt of *tert*-butyl hydroperoxide at −5 °C in diethyl ether.[9] The peresters are all quite stable and may be stored for prolonged periods at ambient temperature. Heating an approximately 0.05 M solution of the perester in tetrahydrofuran for 48–70 h at 100 °C caused complete decomposition to give a variety of products as shown in Scheme I. The percentage yields of the products are given in Table I. It may be assumed, based on the findings of DeTar and Weis,[10] that there is little induced decomposition taking place since the most concentrated solution of any perester was 0.07 M.

There are two possible mechanisms for the homolytic decomposition of the perester. One involves the concerted cleavage of the O–O bond along with the carboxy carbon–cyclopropyl ring bond to initially give the cyclopropyl radical **4**, a carbon dioxide molecule, and a *tert*-butoxy radical in the solvent cage (A). The other mechanism is a stepwise cleavage in which the O–O bond breaks first to give the cy-

Scheme I. Products from Perester Decomposition

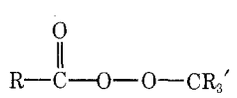


clopropylcarboxy radical 3 and a *tert*-butoxy radical (B). The cyclopropylcarboxy radical then loses carbon dioxide to give the cyclopropyl radical.



As has been shown,[11-13] the concerted cleavage mechanism would be expected to give very little, if any, of the acid **1**. On the other hand, the stepwise decomposition mechanism would be expected to give a significant yield of acid **1** since the rate of cage breakdown would be at least as fast, if not faster, than decarboxylation. This would allow the abstraction of a hydrogen atom from the solvent by the acyloxy radical **3** to become competitive with decarboxylation to give the cyclopropyl radical **4**.

In all the peresters studied there was a substantial yield of cyclopropylcarboxylic acid (**1**); thus the decomposition is probably proceeding by a stepwise mechanism. Using the arguments of Pryor[14] it is possible to understand why the cyclopropyl perester decomposes in a stepwise mechanism. Pryor pointed out that in peresters of the form



the less stable the R radical, the more stable the perester. This is because in the concerted mechanism some of the odd electron density is localized on the R group in the transition state. As the stability of R· increases, the probability of a rapid concerted scission of two bonds increases. However if R· is unstable then the perester is extremely stable and decomposes by a slow O–O bond scission in which none of the odd electron density is localized on the R group.

All the cyclopropyl peresters in this study are very stable, and since it is known that the cyclopropyl σ radical is the least stable of all the cycloalkyl radicals,[11] it is reasonable to suppose that the peresters decompose in a stepwise mechanism.

In Table I there appears to be an anomaly when X = OMe. Here the yield of recovered acid is substantially lower than in the other three cases. In addition, in only this case was the *tert*-butyl ketal **6** isolated. This ketal, resulting from the combination of a *tert*-butoxy radical with the cyclopropyl radical **4**, could be formed in a number of ways.

The simplest mechanism would be a combination of the *tert*-butoxy radical and the cyclopropyl radical in the bulk solvent. However, it has been shown[2a,12] that a *tert*-butyl ether is often the result of an in-cage combination of the two radicals immediately after their formation. In most cases where the decomposition of a *tert*-butyl perester is used to generate the radical pair the decomposition proceeds by the concerted expulsion of carbon dioxide. The lower yield of acid and the presence of the ketal **6** may be an indication that when X = OMe the perester is decomposing by a concerted cleavage mechanism or a combination of concerted and stepwise mechanisms. On the other hand, there are a number of examples in which the decomposition proceeds by a purely stepwise mechanism and still gives cage coupling products. For example, acetyl peroxide[2a] decomposes to give a 3% yield of ethane, the product of an in-cage combination of two methyl radicals.

Table II. Optical Purity of Products Resulting from Hydrogen Atom Abstraction by the Various Cyclopropyl Radicals

X	% optical purity[a]	% retention of configuration[a]
F	46.8	73.5
OMe	8.4	54.2
Cl	0.0	50.0
Br		
CH_3[b]	0.0	50.0

[a] Average of at least three separate experiments. [b] Reference 12.

Koenig[15] has shown that the in-cage recombination product, 2-butyl *tert*-butyl ether, obtained from the thermolysis of (+)-(*S*)-*tert*-butylperoxy 2-methylbutyrate or from the thermolysis of (*S*)-*N*-nitroso-*N*-(α-methyl)butanoyl-*O*-*tert*-butylhydroxylamine showed from 1.8 to 2.4% retention of optical activity. In Koenig's system the intermediate radical is known to be a π radical so that the retention is the result of cage trapping. Thus the optical purity of the ketal **6** may be used as a test as to whether it is a cage or bulk combination product. If **6** results from combination in the bulk solvent then the optical purity would be expected to be approximately the same as that of the cyclopropyl ether **5**. If the ketal **6** results from an in-cage combination then the optical purity of **6** would be expected to be much higher than that of **5**. The ketal **6** isolated was found to be optically active, $[\alpha]^{24}_{Hg}$ −63° (*c* 0.34, $CHCl_3$). Although the optical purity of **6** has not been established[16] the high rotation observed indicates a substantial retention of optical activity and suggests that **6** probably results largely from a cage recombination reaction.

Aside from the cage recombination of the σ radical **4** with a *tert*-butoxy radical and the abstraction of a hydrogen atom from solvent, the radical may also ring open[11] to give the allyl π radical **7**. Since this radical is stabilized by delocalization it dimerizes to give **10**. As can be seen in Table I the yield of the dimer increases in the order F < Cl < Br. This is due to the ability of Cl, and especially Br, to stabilize the allyl radical. When X = Br the stabilization increases the propensity of **4** to ring open even before hydrogen atom abstraction, thus preventing the formation of hydrocarbon **5**. Moreover, when X = Br a product was isolated which gave an ir and NMR compatible with the structure 1,1-diphenylallene (**9**). This is a reasonable product considering the stability of the allyl radical **7** and the large size of bromine. These factors would combine to make the elimination of a bromine atom from **7** to give **9** very facile.[17] An alternative mechanism for the formation of **9** could be the elimination of a bromine atom from **7** to yield a 2,2-diphenylcyclopropyl carbene as an intermediate which then rearranges to allene **9** as previously demonstrated by Jones[18] in the decomposition of *N*-nitroso-*N*-(2,2-diphenylcyclopropyl)urea with base. At this time, no decision can be made between these alternatives. It is also noteworthy that only when X = F does radical **7** react with a tetrahydrofuranyl radical.

Effect of Substituent on the Stereochemistry of the Cyclopropyl σ Radical. The average optical purity and average percent retention of configuration of the substituted cyclopropyl hydrocarbons **5** are presented in Table II.

It can be seen that the optical purity decreases in the order F > OMe > Cl. Since this is the first study involving a single system where only the substituent is varied[19] and one which yields unambiguously free radicals, it is possible to make some comments as to whether the Walsh–Pauling[6] or the Dewar[7] theory on stereochemical stabilization of a free radical is the more viable.

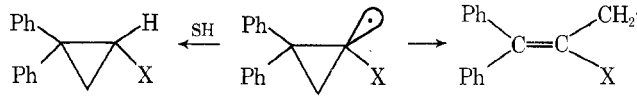
Table III. Mutually Consistent Group Electronegativities

Group	Empirical electronegativities	Group	Empirical electronegativities
F	3.95	OCH_3	3.70
Cl	3.03	CH_3	2.30
Br	2.80	H	2.28
I	2.47		

The Walsh–Pauling model is based on electronegativity; the more electronegative a substituent the more σ type is the radical to which the substituent is attached. Wells[20] has published a critical review on group electronegativities; a portion of his compilation of mutually consistent group electronegativities is presented in Table III. The electronegativity decreases in the order F > OMe > Cl, the same order as the decrease in the percent optical purity of the hydrocarbon **5**. This is also the same order that Kampmeier[21] observed for vinyl radicals. Kampmeier concluded, as do we, that this order can best be correlated with the electronegativity differences of the substituents. Clearly the order predicted by Dewar,[7] F > Cl > OCH_3, is not obtained.

Perhaps the electronegativity stabilizing argument is not the whole answer. It could be argued that the observed retention of configuration may be due to the increase in the rate of hydrogen abstraction from solvent by the radical (**4**). Should this be the case then, based on our observations, the radical reactivity order would be F > OCH_3 > Cl.

In an earlier study[11] we established the reactivity of **4** (X = CH_3) toward hydrogen atom donating solvents by determining the ratio of cyclopropyl hydrocarbon (**5**) to the sum of the products derived from **7** formed in the reaction. In



5 4 7

tetrahydrofuran the ratio of **4** (X = CH_3) was unity. As can be seen from Table I the ratios of **5** to the products derived from **7** for X = F, OCH_3, and Cl are 2.5, 188, and 17.[22] This would indicate that these radicals are reacting with solvent at a faster rate than when X = CH_3 and would establish the order of reactivity as CH_3O > Cl > F. On this basis one would conclude that this should also be the order of retention of configuration. This does not correlate with order observed and we conclude that the increase in the rate of hydrogen abstraction is not the determining factor for retention of configuration.

Experimental Section

Infrared spectra were obtained with a Perkin-Elmer Model 257 grating infrared spectrophotometer. Solution spectra were run on 3% solutions of either carbon tetrachloride or chloroform in a 0.5-mm sodium chloride cell. Ultraviolet spectra were run on a Perkin-Elmer Model 202 ultraviolet–visible spectrophotometer.

Rotations were measured at the 546.1-nm line of mercury on a Bendix-Ericson Model 987 ETL/NPC polarimeter. The estimated error limits of the rotations measured using the Bendix-Ericson polarimeter were calculated using the previously determined value of 0.002° for the standard deviation in recorded values of the rotation.

Nuclear magnetic resonance spectra were obtained on a Varian Associates A-60 or a Brucker 90-MHz spectrometer using tetramethylsilane as an internal standard. Mass spectra were obtained from an AEI Picker high-resolution mass spectrometer. Melting points were determined in capillary tubes using a Mel-Temp apparatus; the melting points are uncorrected. Vapor phase chromatography (VPC) was conducted on a Hewlett-Packard Model 5710A

programmed temperature gas chromatograph with a thermistor detector, using helium as a carrier gas. Silica gel $PF_{254+366}$ was used for preparative thin layer chromatography.

High-pressure liquid phase chromatography (HPLPC) was conducted on a Waters Model 6000 liquid chromatograph equipped with a differential uv detector. The column used was a 4 ft × 2 mm analytical column packed with Corasil 11. The solvent system was a 60:40 mixture of hexane–methylene chloride. The detector was calibrated by injection of known concentrations of previously identified compounds and, using the cut-and-weigh technique, relating the peak areas to the amount of sample injected. After calibration, the percentage yield was determined by injecting a weighed sampled of the neutral fraction of the decomposition products and relating the peak areas to those of the known concentrations.

Elemental analyses were run by J. Beller's Microanalytisches Laboratorium, Göttingen, Germany.

(±)-1-Methoxy-2,2-diphenylcyclopropanecarbonyl Chloride. A 2.68-g (0.094 mol) sample of the racemic acid[8] was dissolved in 1 ml of thionyl chloride and 2 drops of dimethylformamide were added. The reaction was stirred overnight after which the thionyl chloride was evaporated under vacuum and the residual oil recrystallized from high-boiling petroleum ether. Three recrystallizations gave 2.30 g (80%) of the acid chloride: mp 111–113 °C; ir ($CHCl_3$) 3005, 2930 (s, CH), 2830 (s, CH_3O), 1770 (s, C=O), 1600 (w, phenyl), 1500, 1450 cm^{-1} (s; phenyl); NMR (CCl_4) δ 7.5–7.0 (m, 10, phenyl), 3.25 (s, 3 H, CH_3O–), 2.45 (d, 1 H, cyclopropyl), 1.9 ppm (d, 1 H, cyclopropyl).

Anal. Calcd for $C_{17}H_{15}O_2Cl$: C, 71.20; H, 5.37. Found: C, 71.09; H, 5.51.

(−)-(*S*)-1-Methoxy-2,2-diphenylcyclopropanecarbonyl Chloride. In a similar manner to that used in the preparation of the racemic acid chloride 2.68 g (0.094 mol) of the optically active acid, $[\alpha]^{24}_{Hg}$ −75.9° (*c* 1.04, $CHCl_3$), was treated with thionyl chloride and dimethylformamide to give 2.75 g (97%) of acid chloride: mp 142–144 °C; $[\alpha]^{24}_{Hg}$ −120 ± 1.30° (*c* 0.380, $CHCl_3$); ir ($CHCl_3$) and NMR ($CDCl_3$) were identical with those of the racemic product.

Anal. Calcd for $C_{17}H_{15}O_2Cl$: C, 71.20; H, 5.37. Found: C, 71.28; H, 5.51.

***tert*-Butyl (±)-1-Methoxy-2,2-diphenylcyclopropanepercarboxylate.** *tert*-Butyl hydroperoxide was purified by twice extracting 5 g of the commercial product into 30 ml of cold 15% potassium hydroxide. The aqueous extract was saturated with ammonium chloride and the hydroperoxide separated as a clear, colorless liquid which was distilled under reduced pressure, bp 58 °C (20 mm).

To a suspension of 4.1 g of 52% sodium hydride oil dispersion (2.1 g pure, 0.09 mol) in 200 ml of anhydrous ether was added a solution of 9.0 g (0.01 mol) of purified *tert*-butyl hydroperoxide in 50 ml of anhydrous ether and the mixture stirred overnight. The white sodium salt of *tert*-butyl hydroperoxide was filtered off, washed three times with dry ether, and dried in a vacuum oven at 30 °C (5 mm) for 5 h.

A solution of 2.86 g (0.010 mol) of (±)-1-methoxy-2,2-diphenylcyclopropanecarbonyl chloride in 50 ml of anhydrous ether was added dropwise, over the course of 1 h, to a suspension of 2.24 g (0.020 mol) of the sodium salt to *tert*-butyl hydroperoxide in 200 ml of anhydrous ether at −5 °C. After hydrolyses with ice water, the ether layer was washed three times with saturated sodium chloride and dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was recrystallized from a 3:1 pentane–ether solution at −30 °C as white needles: 1.73 g (51%); mp 101–103 °C (effervescence); ir (CCl_4) 3080–2940 (w, CH), 2840 (s, CH_3O–), 1772 (s, C=O), 1610, 1500, 1455 (phenyl), 1030 cm^{-1} (cyclopropyl); NMR ($CDCl_3$) δ 7.0–7.5 (m, 10 H, phenyl), 3.28 (s, 3 H, CH_3O–), 2.28 (d, 1 H, cyclopropyl), 1.80 (d, 1 H, cyclopropyl), 1.11 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.13; H, 7.03.

***tert*-Butyl (−)-(*S*)-1-Methoxy-2,2-diphenylcyclopropanepercarboxylate.** In a manner similar to that used for the preparation of the racemic perester 2.86 g (0.010 mol) of (−)-(*S*)-1-methoxy-2,2-diphenylcyclopropanecarbonyl chloride, $[\alpha]^{24}_{Hg}$ −120°, was allowed to react with the sodium salt of *tert*-butyl hydroperoxide to give 1.70 g (50%) of the perester: mp 115–116 °C (effervescence); $[\alpha]^{24}_{Hg}$ −110 ± 0.9° (*c* 0.540, $CHCl_3$); ir (CCl_4) and NMR (CCl_4) spectra were identical with those of the racemic perester.

Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.19; H, 7.01.

Procedure for the Thermal Decomposition of the Perester 2d. Run 1. A 0.534-g (1.6 mmol) sample of *tert*-butyl (−)-(*S*)-1-methoxy-2,2-diphenylcyclopropanepercarboxylate was dissolved in 100 ml of tetrahydrofuran that had been distilled under nitrogen from lithium aluminum hydride. A glass tube containing the solution was flushed with nitrogen for 10 min, sealed, and heated at 100 °C for 24 h. After the tube was cooled the solvent was removed under vacuum, and the residual oil dissolved in ether and washed three times with sodium bicarbonate. The aqueous extract was acidified to give recovered 1-methoxy-2,2-diphenylcyclopropanecarboxylic acid: 0.071 g (0.26 mmol, 16.8%), $[\alpha]^{24}_{Hg}$ −76.8 ± 0.49° (*c* 1.02, $CHCl_3$), complete retention of configuration.[8]

The neutral fraction was analyzed by preparative TLC using 50% methylene chloride–50% hexane. The fraction at R_f 0.50–0.56 was found to be 1-methoxy-2,2-diphenylcyclopropane by comparison of the ir and NMR spectra with those of an authentic sample: 0.21 g (0.092 mmol, 5.9%); $[\alpha]^{24}_{Hg}$ +4.58 ± 1.2° (*c* 0.414, $CHCl_3$); optical purity 6.17%; retention of configuration.[8]

Run 2. In a similar manner to that used in run 1, a 0.776-g (2.3 mmol) sample of the perester was decomposed. The recovered acid weighed 0.086 g (0.32 mmol, 13.9%), $[\alpha]^{24}_{Hg}$ −72.3 ± 0.46° (*c* 1.09, $CHCl_3$). The isolated 1-methoxy-2,2-diphenylcyclopropane weighed 0.056 g (0.25 mmol, 10%), $[\alpha]^{24}_{Hg}$ +8.27 ± 0.44° (*c* 1.12, $CHCl_3$), optical purity 11.2%, retention of configuration.[8]

Run 3. In a similar manner to that used in run 1, a 0.60-g (1.7 mmol) sample of the perester was decomposed. The recovered acid weighed 0.017 g (0.063 mmol, 3.7%), $[\alpha]^{24}_{Hg}$ −75.5 ± 0.88° (*c* 0.340, $CHCl_3$). The isolated 1-methoxy-2,2-diphenylcyclopropane weighed 0.018 g (0.071 mmol, 4.2%), $[\alpha]^{24}_{Hg}$ +5.94 ± 1.42° (*c* 0.352, $CHCl_3$), optical purity 7.95%, retention of configuration.[8]

Isolation of 1-Methoxy-1-*tert*-butoxy-2,2-diphenylcyclopropane. The band at R_f 0.58–0.61 of the preparative TLC was collected as a yellow oil: ir (CCl_4) 3180, 3160, 3020 (m, CH aromatic), 2980, 2930 (s, CH allyl), 3890 (m, CH_3O–), 1600, 1500, 1450 (m, C–C aromatic), 1390, 1370, 1260, 1215 (m, *tert*-butyl), 1150 cm^{-1} (s, C–O–C–O–C); NMR (CCl_4) δ 7.3–7.1 (m, 10 H, phenyl), 2.05 (s, 3 H, CH_3O–), 1.95 (d, 1 H, cyclopropyl), 1.85 (d, 1 H, cyclopropyl), 1.15 (s, 9 H, *tert*-butyl); mass spectra *m/e* (rel intensity) 296 (≪1) ($P.^+$); 240 (16.1), 239 (27.8), 180 (100), 167 (71.0).

Anal. Calcd for $C_{20}H_{24}O_2$: *m/e* 296.1776. Found: *m/e* 296.1783 (deviation 0.7 mmu).

Unfortunately, there was insufficient material collected in the first three runs to give an accurate rotation on the polarimeter. In a fourth run, 2.51 g of the perester was dissolved in 180 ml of tetrahydrofuran and decomposed. After purification by TLC 0.017 g (0.058 mmol, 0.79%) of the ketal was collected, $[\alpha]^{24}_{Hg}$ −63.4 ± 1.45° (*c* 0.344, $CHCl_3$).

In an attempt to determine the optical purity of the recovered optically active ketal a sample of the racemic ketal was dissolved in carbon tetrachloride and placed in an NMR tube. The solution was deoxygenated by a freeze–pump–thaw cycle under a nitrogen atmosphere. In a glove bag, under a nitrogen atmosphere, tris[(3-heptafluoropropylhydroxymethylene)-*d*-camphorato]europium-(III) was added in 5-mg increments. After each addition the NMR of the solution was taken. The shift reagent was added beyond a 1:1 molar ratio up to the limit of line broadening without any significant shift being observed.

Isolation of 1,1,6,6-Tetraphenyl-2,5-dimethoxyl-1,5-hexadiene. The band at R_f 0.50–0.47 of the preparative TLC of the fourth run was collected as a yellow, amorphous solid: mp 135–137 °C; ir (CCl_4) 3070, 3030 (m, C–H aromatic), 2950, 2850 (w, C–H aliphatic), 1625 cm^{-1} (m, C=C stretch); NMR (CCl_4) δ 7.5–7.0 (m, 20, phenyl), 3.32 (s, 6, –OMe), 2.50 (s, 4, allylic); mass spectra *m/e* (rel intensity) 223 (100) (monomer), 208 (7.6) (monomer − CH_3), 191 (29.4) (monomer − HOMe).

Anal. Calcd for $C_{32}H_{30}O_2$: *m/e* 446.2246. Found: *m/e* 446.2247 (deviation 1.1 mmu).

The actual amount of the dimer was too small to accurately determine; this necessitated the use of an approximation method. By use of the HPLPC chromatograph the yields of **5**, **6**, and **10** were determined to be 47, 32, and 0.2% of that part of the neutral fraction that eluted off the column. On a relative basis the dimer yield would be 0.4% of the cyclopropyl hydrocarbon yield. Since the average percentage yield of **5** in the first two runs was 8%, the percentage yield of the dimer based on the starting perester was approximately 0.04%.

Other Possible Products. The total percentage yield of the four products **1**, **5**, **6**, and **10** was 24%. The rest was an intractable tar that gave a broad continuum of bands below R_f 0.5 on the preparative TLC and would not elute off the HPLPC column even after extensive flushing.

(±)-1-Chloro-2,2-diphenylcyclopropanecarbonyl Chloride. A 1.0-g (0.0037 mol) sample of the racemic acid[8] was dissolved in 2 ml of thionyl chloride and 2 drops of dimethylformamide were added. The reaction mixture was stirred for 4 h after which the thionyl chloride was evaporated under vacuum and the residual oil recrystallized from a 1:1 mixture of benzene–hexane. Three recrystallizations gave 1.0 g (95%) of the acid chloride: mp 83–89 °C; ir ($CHCl_3$) 3090, 3070, 3040 (m, C–H), 1778 (s, C=O), 1600, 1495, 1450 cm^{-1} (m, phenyl); NMR (CCl_4) δ 7.5–7.0 (m, 10, phenyl), 2.75 (d, 1, J = 6 Hz, ring H trans to C=O), 2.05 (d, 1, J = 6 Hz, ring H cis to C=O).

Anal. Calcd for $C_{16}H_{12}OCl_2$: m/e 290.0265. Found: m/e 290.0275 (deviation 1.0 mmu).

(+)-(*S*)-1-Chloro-2,2-diphenylcyclopropanecarbonyl Chloride. In a similar manner to that used in the preparation ofthe racemic acid chloride 9.0 g (0.033 mol) of the optically active acid was treated with thionyl chloride and dimethylformamide to give 9.5 g (99%) of acid chloride: mp 90–93 °C; $[\alpha]_{Hg}^{24}$ +51.0 ± 0.4° (c 1.262, $CHCl_3$); ir ($CHCl_3$) and NMR ($CDCl_3$) were identical with those of the racemic product.

Anal. Calcd for $C_{16}H_{12}OCl_2$: m/e 290.0265. Found: m/e 290.0257 (deviation 0.7 mmu).

***tert*-Butyl (±)-1-Chloro-2,2-diphenylcyclopropanepercarboxylate.** A solution of 1.0 g (3.4 mol) of (±)-1-chloro-2,2-diphenylcyclopropanecarbonyl chloride in 50 ml of anhydrous ether was added dropwise over the course of 1 h to a suspension of 0.78 g (7.0 mmol) of the sodium salt of *tert*-butyl hydroperoxide in 200 ml of anhydrous ether at −5°. After hydroxysis with ice water, the ether layer was washed three times with saturated sodium chloride and dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure. The residue was recrystallized from a 3:1 pentane–ether solution at −30 °C as white needles: 0.90 g (76%); mp 115–117 °C; ir (CCl_3) 3050, 3030, 2985, 2940, 2880 (m, C–H), 1775 (s, C=O), 1600, 1495, 1450 cm^{-1} (m, phenyl); NMR (CCl_4) δ 7.5–7.0 (m, 10 H, phenyl), 2.60 (d, J = 6 Hz, ring H trans to C=O), 1.90 (d, 10, J = 6 Hz, ring H cis to C=O), 1.20 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{20}H_{21}O_3Cl$: C, 69.66; H, 6.14; Cl, 10.28. Found: C, 69.55; H, 6.18; Cl, 10.14.

***tert*-Butyl (+)-(*S*)-1-Chloro-2,2-diphenylcyclopropanepercarboxylate.** In a manner similar to that used in the preparation of the racemic perester 9.60 g (0.033 mol) of (−)-1-chloro-2,2-diphenylcyclopropanecarbonyl chloride was allowed to react with the sodium salt of *tert*-butyl hydroperoxide to give 8.90 g (79%) of the perester: mp 125–127 °C; $[\alpha]_{Hg}^{24}$ +2.15 ± 0.82° (c 0.612, $CHCl_3$); ir (CCl_4) and NMR (CCl_4) spectra were identical with those of the racemic perester.

Anal. Calcd for $C_{20}H_{21}O_3Cl$: C, 69.66; H, 6.14; Cl, 10.28. Found: C, 69.67; H, 6.19; Cl, 10.23.

Procedure for the Thermal Decomposition of the Perester 2b. Run 1. A 1.20-g (3.45 mmol) sample of *tert*-butyl (+)-(*S*)-1-chloro-2,2-diphenylcyclopropanepercarboxylate was dissolved in 100 ml of freshly distilled tetrahydrofuran, placed in a glass tube, flushed with nitrogen for 10 min, sealed, and heated at 100 °C for 24 h. After the tube was cooled the solvent was removed under vacuum, and the residual oil dissolved in ether and washed three times with sodium bicarbonate. The aqueous extract was acidified to give recovered 1-chloro-2,2-diphenylcyclopropanecarboxylic acid: 0.610 g (2.24 mmol, 65%); $[\alpha]_{Hg}^{24}$ +85.0 ± 0.4° (c 1.12, $CHCl_3$); complete retention of configuration.[8]

The neutral fraction was analyzed by preparative TLC using 50% methylene chloride–50% hexane. The fraction at R_f 0.90–0.85 was found to be 1-chloro-2,2-diphenylcyclopropane by comparison of the ir and NMR spectra with that of an authentic sample: 0.119 g (0.52 mmol, 15.1%); $[\alpha]_{Hg}^{24}$ +0.073 ± 0.209° (c 2.39, $CHCl_3$); racemic.

Run 2. In a similar manner to that used in run 1, a 1.25-g (3.62 mmol) sample of the perester was decomposed. The recovered acid weighed 0.563 g (2.07 mmol, 56.9%), $[\alpha]_{Hg}^{24}$ +85.9 ± 0.5° (c 1.066, $CHCl_3$). The isolated 1-chloro-2,2-diphenylcyclopropane weighed 0.090 g (0.39 mmol, 10.9%), $[\alpha]_{Hg}^{24}$ +0.070 ± 0.280° (c 1.79, $CHCl_3$), racemic.

Run 3. In a similar manner to that used in run 1, a 1.19-g (3.47 mmol) sample of the perester was decomposed. The recovered acid weighed 0.648 g (2.41 mmol, 69.4%), $[\alpha]_{Hg}^{24}$ +83.8 ± 0.4° (c 1.13, $CHCl_3$). The recovered hydrocarbon weighed 0.111 g (0.486 mmol, 14%), $[\alpha]_{Hg}^{24}$ +0.079 ± 0.225° (c 2.22, $CHCl_3$), racemic.

Isolation of 1,1,6,6-Tetraphenyl-2,5-dichloro-1,5-hexadiene. In order to determine the other possible products a 2.03-g (5.87 mmol) sample of the racemic perester was decomposed for 50 h at 100 °C in tetrahydrofuran. The preparative TLC of the neutral fraction using 50% methylene chloride–50% hexane showed three bands with R_f 0.90–0.85, 0.84–0.79, and 0.53–0.37.

The band at R_f 0.84–0.79 was collected as colorless prisms: 0.020 g (0.75%); mp 94–96 °C; ir (CCl_4) 3070, 3040 (w, C–H aromatic), 2970, 2910 (s, C–H aliphatic), 1601 cm^{-1} (w, C=C stretch); NMR (CCl_4) δ 7.5–7.0 (m, 20, phenyl), 2.83 (s, 4, allylic); mass spectra m/e (rel intensity) 454 (8.3) (parent), 227 (100) (monomer), 191 (54.7) (monomer − HCl).

Anal. Calcd for $C_{30}H_{24}Cl_2$: m/e 454.1254. Found: m/e 454.1227 (deviation 2.7 mmu).

Other Possible Products. The band from the TLC with R_f 0.53–0.37 defied characterization. The NMR of the fraction showed numerous broad multiplets and when a sample was injected into the HPLPC it failed to elute. Further TLC did not isolate any distinguishable products.

(±)-1-Bromo-2,2-diphenylcyclopropanecarbonyl Chloride. A 1.0-g (3.2 mmol) sample of the racemic acid was dissolved in 1 ml of thionyl chloride and 2 drops of dimethylformamide were added. The reaction mixture was stirred overnight after which the thionyl chloride was evaporated under vacuum and the residual oil recrystallized from 1:1 benzene–hexane. Three recrystallizations gave 0.70 g (75%) of the acid chloride: mp 59–61 °C; ir ($CHCl_3$) 3090, 3060, 3030 (m, C–H), 1772 (s, C=O), 1600, 1580, 1475 cm^{-1} (m, phenyl); NMR (CCl_4) δ 7.5–7.0 (m, 10, phenyl), 2.85 (d, 1, J = 6 Hz, ring H trans to C=O), 2.18 (d, 1, J = 6 Hz, ring H cis to C=O).

Anal. Calcd for $C_{16}H_{12}OBrCl$: m/e 333.9761. Found: m/e 333.9776 (deviation 1.5 mmu).

***tert*-Butyl (±)-1-Bromo-2,2-diphenylcyclopropanepercarboxylate.** A solution of 1.0 g (3.0 mmol) of (±)-1-bromo-2,2-diphenylcyclopropanecarbonyl chloride in 50 ml of anhydrous ether was added dropwise over the course of 1 h to a suspension of 0.67 g (6.0 mmol) of the sodium salt to *tert*-butyl hydroperoxide in 200 ml of anhydrous ether at −5 °C. After hydrolysis with ice water, the ether layer was washed three times with saturated sodium chloride and dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was recrystallized from a 3:1 pentane–ether solution at −30 °C as white needles: 0.90 g (77%); mp 132–134 °C; ir (CCl_3) 3090, 3060, 3030, 2990, 2940, 1772 (s, C=O), 1600, 1580, 1495, 1450 cm^{-1} (m, phenyl); NMR ($CDCl_3$) δ 7.0–7.5 (m, 10, phenyl), 2.68 (d, 1, J = 6 Hz, ring H trans to C=O), 1.93 (d, 1, J = 6 Hz, ring H cis to C=O), 1.20 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{20}H_{21}O_3Br$ (mol wt 389.29): C, 61.71; H, 5.44; Br, 20.52. Found: C, 61.61; H, 5.44; Br, 20.58.

***tert*-Butyl (−)-(*R*)-1-Bromo-2,2-diphenylcyclopropanepercarboxylate.** In a manner similar to that used in the preparation of the racemic perester (6.83 g (0.020 mol) of (−)-1-bromo-2,2-diphenylcyclopropanecarbonyl chloride was allowed to react with the sodium salt of *tert*-butyl hydroperoxide to give 6.29 g (79.4%) of the perester: mp 112–114 °C; $[\alpha]_{Hg}^{24}$ −36.9 ± 1.01° (c 0.494, $CHCl_3$); ir (CCl_4) and NMR (CCl_4) spectra were identical with those of the racemic perester.

Anal. Calcd for $C_{20}H_{21}O_3Br$ (mol wt 389.29): C, 61.71; H, 5.44; Br, 20.5. Found: C, 61.73; H, 5.41; Br, 20.55.

Procedure for the Thermal Decomposition of the Perester 2c. Run 1. A 2.789-g (7.17 mmol) sample of *tert*-butyl (±)-1-bromo-2,2-diphenylcyclopropanepercarboxylate was dissolved in 100 ml of freshly distilled tetrahydrofuran, placed in a glass tube, flushed with nitrogen for 10 min, sealed, and heated at 100 °C for 24 h. After the tube was cooled the solvent was removed under vacuum, and the residual oil dissolved in ether and washed three times with sodium bicarbonate. The aqueous extract was acidified to give recovered 1-bromo-2,2-diphenylcyclopropanecarboxylic acid: 1.281 g (4.04 mmol, 56.3%), $[\alpha]_{Hg}^{23}$ −132° (c 1.1, $CHCl_3$), complete retention of configuration.

The neutral fraction was analyzed by preparative TLC using 50% methylene chloride–50% hexane. Four bands were found: R_f 0.87–0.83, R_f 0.82–0.78, R_f 0.77–0.70, and a broad continuum from R_f 0.58 to the baseline.

Isolation of 1,1,6,6-Tetraphenyl-2,5-dibromo-1,5-hexadiene. The band from the TLC with R_f 0.77–0.70 was collected as a white, amorphous solid: 0.045 g (1.2%); mp 161–164 °C; ir ($CHCl_3$) 3080, 3020 (w, C–H aromatic), 2940, 2860 (w, C–H aliphatic), 1600 cm^{-1} (m, C=C stretch); NMR ($CHCl_3$) δ 7.3–6.9 (m, 20, phenyl), 2.83 (s, 4, allylic); mass spectra m/e (rel intensity) 542 (0.9) (parent), 273 and 271 (23.0) (monomer), 191 (54.1) (monomer − HBr).

Anal. Calcd for $C_{30}H_{24}Br_2$: m/e 544.0226. Found: m/e 544.0215 (deviation 1.1 mmu).

Isolation of 1,1-Diphenyl-1,2-propadiene. The band from the TLC with R_f 0.87–0.83 was collected as a yellow oil which weighed

0.0278 g. Analysis by LPC showed that the product was 56% pure, while analysis by VPC showed that the product was 73% pure although in neither case was it possible to calibrate the detector. A 1–2-mg portion was preparatively separated on the VPC using a 6 ft × 0.125 in. column packed with 5% W-98 silicone oil on 70–80 mesh Anakrom Q: ir (CCl_4) 3100, 3070, 3040 (w, C–H aromatic), 2970 (w, C–H vinylic), 1930 (m, C=C stretch, allene), 1600, 1500, 1460, 1450 cm^{-1} (m, C=C stretch phenyl); NMR (CCl_4) δ 7.4–7.2 (m, 10, phenyl), 5.2 (s, 1, vinyl).

Attempted Isolation of 1-Bromo-2,2-diphenylcyclopropane. No trace of the hydrocarbon **5** could be found in any of the TLC fractions of the decomposition products when the decomposition solvent was tetrahydrofuran. Changing the solvent to diethyl ether, chloroform, or thiophenol still did not produce any of the bromohydrocarbon.

Other Possible Products. The second band with R_f 0.77–0.70 showed a strong absorption in the NMR (CCl_4) from δ 7.3 to 7.0 but no other peaks. The ir (CCl_4) showed many phenyl absorption peaks but also a strong C–H vinylic absorption at 2970 and 2910 cm^{-1}. It is most likely that this fraction is a polymeric decomposition product of the allene.

(−)-(*S*)-1-Fluoro-2,2-diphenylcyclopropanecarbonyl Chloride. To a solution of 2.7 g (0.011 mol) of (−)-(*S*)-1-fluoro-2,2-diphenylcyclopropanecarboxylic acid,[8] $[\alpha]_{Hg}^{24}$ −147°, in 12 ml of thionyl chloride was added 0.5 ml of *N,N*-dimethylformamide and the reaction mixture stirred at ambient temperature for 4 h. The excess thionyl chloride was evaporated under reduced pressure and the residue dissolved in benzene. Recrystallization from benzene yielded 2.2 g (75%) of product: mp 100–104 °C; $[\alpha]_{Hg}^{24}$ −121.2° (*c* 0.52, acetone); ir (CCl_4) 3035, 3065, 3088 (m, C–H), 1793 (s, C=O), 1248 cm^{-1} (s, C–F); NMR ($CDCl_3$) δ 7.6–7.1 (m, 10, H), 2.2 (dd, 1, J_{FH} = 22.5, J_{H-H} = 6.0 Hz, cis ring H–F), 2.4 (dd, 1, J_{FH} = 15.0, J_{H-H} = 6.0 Hz, trans ring H–F).

Anal. Calcd for $C_{16}H_{12}OFCl$: *m/e* 274.0560. Found: *m/e* 274.0550 (deviation 1 mmu).

***tert*-Butyl (−)-(*S*)-1-Fluoro-2,2-diphenylcyclopropanepercarboxylate (2a).** *tert*-Butyl hydroperoxide was purified by first extracting 5 g of the commercial hydroperoxide twice into 30 ml of cold 15% potassium hydroxide. The aqueous extract was saturated with ammonium chloride; the hydroperoxide separated as a clear, colorless liquid which was distilled under reduced pressure, bp 58 °C (20 mm).

To a suspension of 4.1 g of a 52% NaH oil dispersion (2.1 g pure, 0.09 mol) in 200 ml of anhydrous ether there was added a solution of 9.0 g (0.10 mol) of purified *tert*-butyl hydroperoxide in 50 ml of anhydrous ether and the mixture was stirred overnight. The white sodium salt of *tert*-butylhydroperoxide was filtered off, washed three times with dry ether, and dried in a vacuum oven at 30 °C (5 mm) for 5 h.

A solution of 3.62 g (0.013 mol) of (−)-1-fluoro-2,2-diphenylcyclopropanecarbonyl chloride in 50 ml of anhydrous ether was added dropwise over the course of 1 h to a suspension of 3.0 g (0.013 mol) of the purified sodium salt of *tert*-butyl hydroperoxide in 200 ml of anhydrous ether at −5 °C. After addition was complete the solution was stirred for an additional 1 h at −5 °C and then hydrolyzed with ice water. The ethereal layer was washed three times with saturated sodium chloride and dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was recrystallized from ethyl ether at −30 °C as white needles: 0.814 g (19%); mp 105–106 °C; $[\alpha]_{Hg}^{24}$ −186° (*c* 0.58, $CHCl_3$); ir (CCl_4) 3080, 2870 (w, C–H), 1780 (s, C=O), 1605, 1490, 1450 (m, phenyl), 1248 cm^{-1} (s, C–F); NMR (CCl_4) δ 7.5–7.0 (m, 10, phenyl), 2.03 (dd, 1, J_{FH} = 36.5, J_{HH} = 7.0 Hz, trans ring H to F), 1.16 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{20}H_{21}O_3F$: C, 73.14; H, 6.44; F, 5.78. Found: C, 73.04; H, 6.43; F, 5.7.

Thermal Decomposition of 2a. The perester was dissolved in 100 ml of anhydrous THF and placed in a thick-walled Pyrex decomposition tube. The sample was flushed with nitrogen for 10 min and then placed in an oven and heated at 100 °C for 44 h. After the tube was cooled the THF was removed under vacuum and the residual oil taken up in ether. The ether was washed three times with a 10% sodium bicarbonate solution and twice with a saturated sodium chloride solution and then dried over anhydrous sodium sulfate. The oily neutral residue remaining after the ether was removed under vacuum was initially purified by preparative TLC on silica gel using a 50% benzene–50% chloroform solution as the eluent. The developed TLC showed three bands: R_f 0.94–0.81, 0.76–0.69, 0.56–0.38. The recovered acid weighed 0.7821 g, 35.1%; $[\alpha]_{Hg}^{23}$ − 144° (*c* 1.1, acetone); complete retention of configuration.

In order to determine the identity and percentage composition of the reaction products, a 2.524-g (0.008 mol) sample of the racemic perester was decomposed. The total weight of the purified neutral fraction was 0.534 g. The isolation and identification of the reaction products are detailed below.

Isolation of 1-Fluoro-2,2-diphenylcyclopropane (5a). The uppermost band from the preparative TLC plate was extracted with chloroform and analyzed by VPC using an 8-ft column packed with 20% EGIP on 80/100 mesh Chromosorb P/AW at 200 °C. The 1-fluoro-2,2-diphenylcyclopropane was identified by comparison of the retention time with that of an authentic sample. A sample was collected and the ir was found to be identical with that of an authentic sample.[8] The average optical purity[8] (four runs), $[\alpha]_{Hg}^{24}$ −11.3, −8.10, −9.1, −12.7°, is 46.8%.

Isolation of 1,1-Diphenyl-2-fluoro-3-(2-tetrahydrofuranyl)-1-propene (8a). The second compund from the VPC analysis of the third band on the TLC plate was collected as a yellow oil: ir (CCl_4) 2980, 2770 (s, C–H THF), 1669 (s, tetrasubstituted C=C stretch), 1600, 1580, 1500, 1450 cm^{-1} (m, phenyl); NMR (CCl_4) δ 6.1–6.7 (m, 10, phenyl), 2.7–4.2 (m, 3, H on 2 and 5 positions of THF), 2.25–2.28 (m, 2, allyl), 1.7–2.2 (m, 4, H on 3 and 4 position of THF); uv (CH_3OH) λ_{max} 246 nm (ϵ 8970); mass spectra *m/e* (rel intensity) 282 (13.7) ($P\cdot^+$), 211 (5.1) ($P\cdot^+$ − THF), 191 (6.7) (211 − HF).

Anal. Calcd for $C_{19}H_{19}OF$: *m/e* 282.1419. Found: *m/e* 282.1419 (deviation 0.1 mmu).

Isolation of 1,1,6,6-Tetraphenyl-2,5-difluoro-1,5-hexadiene (10a). The uppermost band from the preparative TLC plate was extracted with chloroform and analyzed by VPC using an 8-ft column packed with 20% Apiezon L on Chromosorb P at 200 °C. The collected dimer was a yellow oil: ir (CCl_4) 3060, 3020 (w, C–H aromatic), 2920, 2860 (s, C–H aliphatic), 1669 cm^{-1} (m, aromatic C=C stretch); NMR (CCl_4) δ 7.5–7.0 (m, 20, phenyl), 2.2–2.0 (d, 4, allylic); uv (CH_3OH) λ_{max} 250 nm (ϵ 2820); mass spectra *m/e* (rel intensity) 422 (0.1) ($P\cdot^+$), 211 (45.8) (monomer), 191 (12.1) (monomer − HF).

Anal. Calcd for $C_{30}H_{24}F_2$: *m/e* 422.18604. Found: *m/e* 422.184965 (deviation 0.4 mmu).

Determination of Percentage Composition. The percentage composition of the neutral fraction was determined by taking a small sample of the unpurified neutral products, purifying it by preparative TLC, and extracting all but the baseline from the plate. A portion of this mixture was then analyzed on the VPC using the EGIP column. By a cut-and-weigh technique the relative areas of **5a**, **8a**, and **10** to each other were determined. The data are summarized in Table I.

Registry No.—(−)-(*S*)-**1a**, 30745-01-8; (±)-**1b**, 57719-61-6; (+)-(*S*)-**1b**, 57793-31-4; (±)-**1c**, 57719-62-7; (±)-**1d**, 30724-80-2; (−)-(*S*)-**1d**, 30745-02-9; (−)-(*S*)-**2a**, 57761-85-0; (±)-**2b**, 57719-63-8; (+)-(*S*)-**2b**, 57793-32-5; (±)-**2c**, 57719-64-9; (−)-(*R*)-**2c**, 57793-33-6; (±)-**2d**, 57719-65-0; (−)-(*S*)-**2d**, 57793-34-7; (−)-(*S*)-**5a**, 57719-66-1; (±)-**5b**, 57793-35-8; (*S*)-**5d**, 57793-36-9; **6d**, 57719-67-2; **8a**, 56701-23-6; **9**, 14251-57-1; **10a**, 57719-68-3; **10b**, 57719-69-4; **10c**, 57719-70-7; **10d**, 57719-71-8; (±)-1-methoxy-2,2-diphenylcyclopropanecarbonyl chloride, 57719-72-9; (−)-(*S*)-1-methoxy-2,2-diphenylcyclopropanecarbonyl chloride, 57793-37-0; *tert*-butyl hydroperoxide, 75-91-2; (±)-1-chloro-2,2-diphenylcyclopropanecarbonyl chloride, 57719-73-0; (+)-(*S*)-1-chloro-2,2-diphenylcyclopropanecarbonyl chloride, 57793-38-1; (±)-1-bromo-2,2-diphenylcyclopropanecarbonyl chloride, 57719-74-1; (−)-1-bromo-2,2-diphenylcyclopropanecarbonyl chloride, 57793-39-2; (−)-(*S*)-1-fluoro-2,2-diphenylcyclopropanecarbonyl chloride, 57719-75-2.

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Radical Chain Reactions of Halomethyldimethylsilanes

Il Nam Jung and William P. Weber*

Department of Chemistry, University of Southern California, Los Angeles, California 90007

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Chloromethyldimethylsilyl or bromomethyldimethylsilyl radicals have been generated by photolysis of the corresponding silanes in the presence of mercury or thermolysis with di-*tert*-butyl peroxide. No products of coupling of the silyl radicals [XCH_2–$\dot{S}i(CH_3)_2$] were observed. The products of radical reactions of chloromethyldimethylsilane are time dependent. At short reaction time trimethylsilane and chloromethyldimethylchlorosilane are the major products, while the major product at long reaction time is trimethylchlorosilane. The radical reactions of bromomethyldimethylsilane are faster than those of chloromethyldimethylsilane. No time dependence of the products of radical reaction of bromomethyldimethylsilane was observed. Trimethylbromosilane was the major product of radical reaction of bromomethyldimethylsilane. These results can be explained by two consecutive radical chain processes rather than by a 1,2-halogen shift in the radical intermediates.

The hydrosilation reaction is perhaps the best studied example of a radical chain process involving silyl radicals as intermediates. Thus, the addition of trichlorosilane to 1-octene catalyzed by acetyl peroxide yields trichloro-*n*-octylsilane.[1] This reaction has been proposed to occur by the following mechanism.[1-4]

$$Cl_3Si\text{-}H + In\cdot \rightarrow Cl_3Si\cdot + In\text{-}H$$

$$Cl_3Si\cdot + R\text{-}CH{=}CH_2 \rightarrow Cl_3Si\text{-}CH_2\text{-}\dot{C}H\text{-}R$$

$$Cl_3Si\text{-}CH_2\text{-}\dot{C}H\text{-}R + Cl_3Si\text{-}H \rightarrow Cl_3Si\text{-}CH_2\text{-}CH_2\text{-}R + Cl_3Si\cdot$$

We should like to report a new radical chain process involving silyl radicals as intermediates. The reaction is the conversion of chloromethyldimethylsilane into trimethylchlorosilane under radical initiation. At first this reaction might appear to be a 1,2-radical rearrangement. Few examples of 1,2-radical rearrangements are known in organosilicon chemistry.[5-11] However, on examination this reaction appears to occur by two consecutive radical chain processes both of which involve silyl radical intermediates. The reaction was discovered quite by accident.

Photolysis of trimethylsilane in the vapor phase in the presence of mercury yields hexamethyldisilane and hydrogen.[12] The reaction is believed to involve silyl radicals formed by homolytic cleavage of the Si–H bond. Despite numerous possible complications, both the chemical and quantum yields for the reaction are high. In fact, the reaction has proved a valuable synthetic method to prepare disilanes.[13,14] However, if chloromethyldimethylsilane is photolyzed in the gas phase in the presence of mercury, the products are not the expected disilane, but rather trimethylchlorosilane, trimethylsilane, chloromethyldimethylchlorosilane, and small amounts of hexamethyldisiloxane and chloromethylpentamethyldisiloxane. A small amount of mercury is converted to mercuric chloride. The possibility that mercuric chloride, a weak Lewis acid, catalyzed these transformations was eliminated by control experiments. Thus, chloromethyldimethylsilane was recovered unchanged after refluxing with mercuric chloride. The alternative possibility that this reaction involved a free-radical process was supported by the following experiment. Heating chloromethyldimethylsilane at 136 °C in the presence of a catalytic amount of di-*tert*-butyl peroxide (2%) leads to a similar product mixture. Di-*tert*-butyl peroxide has been previously used to generate silyl radicals by hydrogen abstraction from silanes.[15-17]

The ratio of products is time dependent. (See Figure 1 and Table I). After 20 min at 136° the reaction of chloromethyldimethylsilane initiated by di-*tert*-butyl peroxide (2%) has already consumed almost 40% of the starting material. At this time, the major products were trimethylsilane (~20%) and chloromethyldimethylchlorosilane (~20%). Trimethylchlorosilane was present in small amount (1%). However, if the reaction mixture was heated for longer periods of time, the amounts of trimethylsilane and chloromethyldimethylchlorosilane decreased while the yield of trimethylchlorosilane increased. These results can be explained by a sequence of two radical chain reactions.

The reaction is initiated by abstraction of a hydrogen atom from the Si–H bond by a *tert*-butoxy radical to form the chloromethyldimethylsilyl radical. Abstraction of a chlorine atom from the starting material by this radical leads to chloromethyldimethylchlorosilane and the dimeth-