Kinetics of Cyclopropyl Radical Reactions. 2. Studies on the Inversion of Cyclopropyl and 1-Methylcyclopropyl Radicals and on the Kinetics of Some Addition and Abstraction Reactions of 1-Methylcyclopropyl and 1-Methoxycyclopropyl Radicals[1]

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Abstract: Laser flash photolytic studies have shown that the 1-methylcyclopropyl radical has a reactivity similar to that of the cyclopropyl radical toward styrene, β-methylstyrene, 1,4-cyclohexadiene, CCl_3Br, and n-Bu_3SnH but that it is more reactive toward CCl_4. Chemical trapping with CCl_3Br of these two radicals stereospecifically labeled with deuterium yields rate constants for their inversion at 71 °C of $(2.1 \pm 0.8) \times 10^{11}$ s^{-1} for c-C_3H_4•CH_3 and ca. 10^{12} s^{-1} for c-C_3H_5•. EPR spectra of ^{13}C-labeled radicals confirm that they are nonplanar: $a^{^{13}C_\alpha} = 98$ and 95.9 G for c-C_3H_4•CH_3 and c-C_3H_5•, respectively. The similar magnitudes of these splittings implies that there is also a similar degree of deviation from planarity. The barrier to inversion is probably ca. 3 kcal/mol for both radicals but the c-C_3H_5• inverts more rapidly possibly because of hydrogen tunneling. 1-Methoxycyclopropyl is less reactive toward styrene and 1,4-cyclohexadiene than the other two radicals. The EPR spectrum of this radical could not be obtained.

In part 1[3] we reported the first absolute rate constants for some addition and abstraction reactions of the cyclopropyl radical in solution at ambient temperatures. These kinetic data, which were obtained by laser flash photolysis, showed that cyclopropyl was less reactive than phenyl but more reactive than primary alkyl radicals.[3] In subsequent work on certain hydrogen-abstraction reactions we showed[4] that at ambient temperatures radical reactivities decreased along the following series: Ph• > $Me_2C{=}CH$• > c-C_3H_5 > CH_3• > RCH_2CH_2•. Our results largely confirmed Walborsky's conclusion,[5] which had been based on studies of relative reactivities, that "the cyclopropyl radical behaves as a rapidly inverting σ radical of high reactivity".

A large number of experiments have been performed in attempts to determine the extent to which a variety of substituted cyclopropyl radicals are capable of maintaining their original configuration.[6] Most of these studies have involved chemical trapping in which the products formed from appropriately substituted cyclopropyl radicals were used to determine the extent to which the radicals retain their stereochemical identity.[5-7] The results have varied through the entire spectrum of possibilities, from complete inversion, through partial inversion, complete configurational equilibration, and partial retention, all the way to complete retention.[7] Fortunately, the detailed picture is not quite as confusing as this summary might suggest. Inversion appears always to be due to steric constraints on the trapping process. Equilibration is observed for cyclopropyls α-substituted with groups such as cyano that can delocalize the unpaired electron and, by so doing, partially or completely flatten the radical center. Retention occurs most readily with an α-fluorine and, indeed, the EPR spectrum of each inversion isomer of 1-fluoro-2,3-*cis*-dimethylcyclopropyl can be separately observed at −108 °C.[8] Retention occurs somewhat less readily with an α-chlorine or α-methoxy substituent. For cyclopropyl radicals having a hydrogen atom or an alkyl group at the α-position there would appear to be few, if any, authentic examples of intermolecular trapping by a molecular reagent that occur with retention of configuration.[5,9]

Although there have been a very large number of investigations of the inversion process in appropriately substituted cyclopropyl radicals[5,6] there have been no serious attempts to measure the rate of any such process. One possible approach to such measurements would be to combine the results of chemical trapping product studies with absolute kinetic data measured by laser flash photolysis. We have, indeed, employed this approach in estimating the rates of inversion of triorganosilyl[12] and triorganogermyl[13] radicals. It therefore occurred to us that CCl_3Br might be able to trap cyclopropyl radicals before they could invert since this compound is an extremely efficient cyclopropyl trap ($k_1 = 2.8 \times 10^9$ M^{-1} s^{-1} at 298 K).[3,14]

$$\text{c-}C_3H_5\text{•} + CCl_3Br \rightarrow \text{c-}C_3H_5Br + CCl_3\text{•} \qquad (1)$$

To investigate this possibility we decided to use the same stereospecific pattern of deuterium labeling of the cyclopropyl radical that had been previously employed by Kobayashi and Lambert[15] in their (unsuccessful) attempt to trap cyclopropyl before it could invert. These workers generated their labeled radicals from the corresponding labeled cyclopropane carboxylic acid in the Hunsdiecker reaction. The Kobayashi and Lambert[15] synthesis of a stereospecifically deuterium labeled cyclopropane carboxylic acid suited our requirements because our preferred source of cyclopropyl radicals has been the derived diacyl peroxide.[3,4] Deuterium labeling has a particular advantage over "labeling" with an organic group (or groups) attached to one (or more) of

(1) Issued as NRCC No. 25481.
(2) NSERC Postdoctoral Fellow 1983-1984.
(3) Johnston, L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 4877-4881.
(4) Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickrema, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594-4596.
(5) Walborsky, H. M. *Tetrahedron* **1981**, *37*, 1625-1651.
(6) (a) Most of this work is very clearly summarized in Walborsky's excellent review.[5] For later work not included in that review, see: (b) Ando, T.; Ishihara, T.; Yamashita, A.; Matsumoto, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3873-3874. (c) McKinney, M. A.; Anderson, S. W.; Keyes, M.; Schmidt, R. *Tetrahedron Lett.* **1982**, *23*, 3443-3446. (d) Paquette, L. A.; Uchida, T.; Gallucci, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 335-340. See also ref 17b.
(7) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed., Academic Press: New York, 1980; pp 161-310.
(8) (a) Kawamura, T.; Tsumura, M.; Yonezawa, T. *J. Chem. Soc., Chem. Commun.* **1977**, 373-374. (b) Kawamura, T.; Tsumura, M.; Yokomichi, Y.; Yonezawa, T. *J. Am. Chem. Soc.* **1977**, *99*, 8251-8256.
(9) A claim to the contrary[10] has been shown to be in error.[11]
(10) Jacobus, J.; Pensak, D. *J. Chem. Soc., Chem. Commun.* **1969**, 400-401.
(11) Boche, G.; Schneider, D. R.; Wintermayr, H. *J. Am. Chem. Soc.* **1980**, *102*, 5697-5699. See also: Boche, G.; Schneider, D. R. *Tetrahedron Lett.* **1978**, 2327-2330.
(12) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123-5127.
(13) Ingold, K. U.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 343-348.
(14) CCl_3Br is a better trap for c-C_3H_5• than is n-Bu_3SnH, for which $k = 8.5 \times 10^7$ M^{-1} s^{-1} at 30 °C.[4]
(15) Kobayashi, K.; Lambert, J. B. *J. Org. Chem.* **1977**, *42*, 1254-1256.

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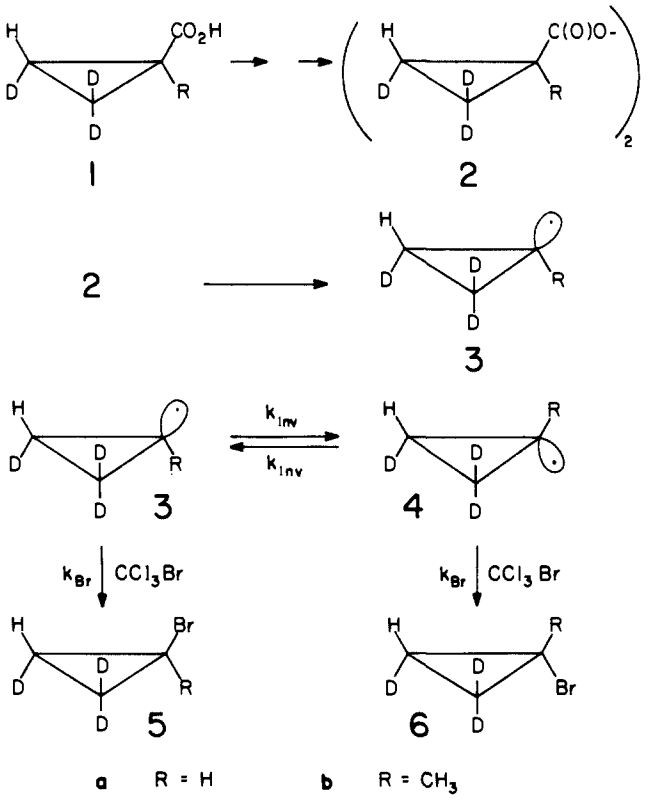
Scheme I



the other positions in the cyclopropane ring, since it is known that large groups at the 2 (and 3) positions can "flatten" the radical center. For example, at their radical centers 2,2-di-*tert*-butyl-3,3-difluorocyclopropyl is planar[16] whereas 2,2-dimethylcyclopropyl is nonplanar.[8] Even relatively small groups at the 2 position may well exert a sufficient steric effect to reduce the inversion barrier relative to the barrier for the unsubstituted radical.[17]

As we report below, inversion of the cyclopropyl radical is so rapid that only a very rough estimate could be made of the inversion rate with use of the CCl_3Br trap. However, in an extension of these studies we have found that the 1-methylcyclopropyl radical can be fairly readily trapped with neat CCl_3Br before it has completely lost its stereochemical identity. We have undertaken kinetic studies on 1-methylcyclopropyl and have been able to obtain a fairly reliable estimate of the inversion rate. Both cyclopropyl and 1-methylcyclopropyl radicals have also been examined by EPR spectroscopy and it is concluded that they are approximately equally "bent" at the radical center. An attempt to extend our studies to 1-methoxycyclopropyl was not very successful, though some kinetic data are reported.

Results

The Cyclopropyl Radical. (i) Reaction of a Stereospecifically Deuterium Labeled Radical with Bromotrichloromethane. Cyclopropane-*trans*-2,2,3-d_3-carboxylic acid (**1a**)[15] was converted to the corresponding bis(cyclopropylformyl) peroxide (**2a**),[3,18] which was thermolyzed in CCl_3Br/C_6H_6 mixtures and in neat CCl_3Br to >98% conversion at 71 ± 1 °C in vacuum degassed, sealed tubes (see Scheme I). The initially formed cyclopropyl radical, **3a**, can invert to **4a** and both **3a** and **4a** can react with CCl_3Br to form the bromides **5a** and **6a**, respectively. The bromides were separated from the reaction mixture by preparative gas chromatography and were then analyzed by 500-MHz NMR spectroscopy. In CCl_4 as solvent the two isomeric bromides, **5a** (retention) and **6a** (inversion), could be readily distinguished (see Figure 1). In this figure the low field signal is due to the 1-proton and is identical for the two isomers. However, the signals due to the 3-proton differ. We assign the signal at δ 1.02 to isomer **5a** and that at δ 1.12 to isomer **6a** both on the basis of the larger H–H coupling for **6a** and in agreement with Lambert's earlier assignments.[15] Note that the lines are broadened by unresolved deuterium couplings so that the smaller H–H trans coupling in **5a** is not resolved in our experiments. The NMR spectrum in C_6D_6 is also shown in Figure 1. Interestingly, the positions of the two 3-protons are reversed in this solvent with the **5a** isomer now appearing to low field of the **6a** isomer. An examination of the NMR spectrum in CCl_4/C_6D_6 solvent mixtures confirmed this crossover in the relative positions of the two 3-proton signals.

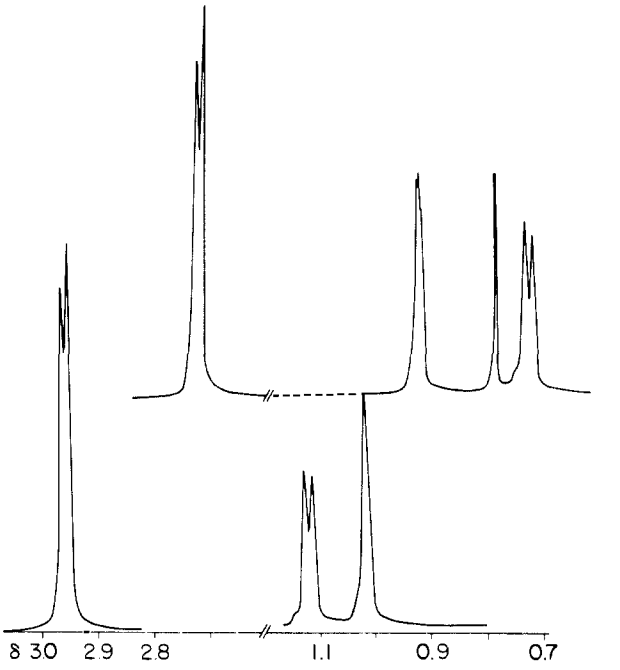


Figure 1. 500-MHz NMR spectra of mixtures of **5a** and **6a**. Top: in C_6D_6, isolated from thermolysis of 0.14 M **2a** in 0.5 M CCl_3Br in C_6D_6. Bottom: in CCl_4, isolated from thermolysis of 0.14 M **2a** in neat CCl_3Br.

Table I. Retention/Inversion Ratios for the Cyclopropyl Radical[a]

solvent	5a/6a
0.1 M CCl_3Br/benzene	1.0_0
0.5 M CCl_3Br/benzene	1.0_1[b]
9.8 M CCl_3Br[c]	1.0_7[d]
2.9 M CBr_4/CCl_3Br	1.1_1

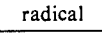
[a] On the basis of a 500-MHz NMR determination of the relative yields of bromides, **5a**/**6a**, produced by the thermolysis of the stereospecifically deuterated peroxide **2a** at 71 ± 1 °C. [b] Mean of two separate experiments: 1.0_0 and 1.0_3. [c] Neat CCl_3Br. [d] Mean of two separate experiments: 1.0_3 and 1.1_1.

The degree to which the initially formed cyclopropyl radical retains its configuration is indicated for each experiment in Table I by the retention/inversion ratios of the cyclopropyl bromides, i.e., by **5a**/**6a**. It is clear that at 71 °C inversion is very rapid relative to trapping by CCl_3Br.

(ii) EPR Spectroscopy. (a) Measurement of Hydrogen Hyperfine Splittings at 4 K. The EPR spectrum of the cyclopropyl radical[19,20] shows a small (negative)[21] α-hydrogen hyperfine splitting (hfs), a^{H_α}(1 H) ~−6.7 G, and four equivalent (positive)[21] β-H hfs, a^{H_β}(4 H) ~+23.5 G. The small magnitude of the α-H hfs[22] provides the evidence that the cyclopropyl radical in its

(16) Malatesta, V.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1978**, *100*, 7073–7074.
(17) (a) See, e.g.: Ishihara, T.; Ohtani, E.; Ando, T. *J. Chem. Soc., Chem. Commun.* **1975**, 367–368. (b) Ando, T.; Ishihara, T.; Ohtani, E.; Sawada, H. *J. Org. Chem.* **1981**, *46*, 4446–4450.
(18) Singer, L. A.; Kong, N. P. *J. Am. Chem. Soc.* **1966**, *88*, 5213–5219.
(19) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147–2195.
(20) Chen, K. S.; Edge, D. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7036–7043.
(21) Kaptein, R. In "Chemically Induced Magnetic Polarization"; Lepley, A. R., Closs, G. L., Eds.; Wiley-Interscience: New York, 1973; pp 137–196.

Table II. Hfs's in Gauss for Cyclopropyl and 1-Methylcyclopropyl Radicals in Cyclopropane at −70 °C

radical	a^H	$a^{^{13}C_\alpha}$
	6.7 (1 H); 23.5 (4 H)	95.9
	19.5 (3 H); 21 (4 H)	98

equilibrium configuration is nonplanar, i.e., H_α does not lie in the plane defined by the three carbon atoms. INDO calculations on cyclopropyl suggest an out-of-plane angle for the C_α–H_α bond, θ, of ca. 30–35° and a barrier to inversion of 3.2 kcal/mol.[23] More recent ab initio calculations give θ = 41°[24a] and 39.3°[24b] with inversion barriers of 3.8[24a] and 3.0[24b] kcal/mol.[24c] The INDO calculated hfs for the syn and anti β-H's were nearly equal to each other for all values of θ,[23,25] indicating that rapid pyramidal inversion at the radical center is not necessarily required to explain the apparent magnetic equivalence of the four β-H's at temperatures as low as 77 K.[26] Nevertheless, it did seem worthwhile to examine the EPR spectrum of cyclopropyl at still lower temperatures because ab initio calculations[24a] have indicated that the β-H's that are syn to the unpaired electron should have significantly larger hfs's than the β-H's that are anti to the unpaired electron. More importantly, Kawamura et al.[8] have found that in various substituted cyclopropyl radicals containing β-H's, those that are syn to the unpaired electron have hfs's that are about three times larger than those that are anti.[27] These workers have suggested[8b] that the INDO method is unsatisfactory for cyclopropyl radicals and that a "frozen" cyclopropyl would have a^{H_β}(syn) > 30 G and a^{H_β}(anti) ≤9.5 G.

The cyclopropyl radicals were prepared on the surface of a rotating cryostat at 77 K.[28] Three separate molecular beams, cyclopropyl bromide, sodium atoms, and cyclopropane (as an inert matrix), were co-condensed onto the cryostat.

$$c\text{-}C_3H_5Br + Na \rightarrow c\text{-}C_3H_5^{\bullet} + NaBr$$

The condensate was scraped off and fell directly into an EPR tube held at 77 K. This tube was sealed under vacuum and transferred to the spectrometer, the sample never being allowed to warm above the temperature of liquid nitrogen. The EPR spectrum at 77 K had very broad lines and was poorly resolved but was undoubtedly that of the cyclopropyl radical. The spectrum did not change appreciably on cooling the sample to 4 K. It does not, therefore, appear possible to produce an EPR observable "freezing-out" of the cyclopropyl inversion, at least in a cyclopropane matrix.

(b) Measurement of α-^{13}C Hfs. This quantity provides the most definitive information about the degree of nonplanarity of a carbon-centered radical.[29] Values of $\alpha^{^{13}C_\alpha}$ for cyclopropyl radicals appear to be confined to species having substituents which make them planar, or nearly so, at the radical center.[30] We therefore decided to measure $a^{^{13}C_\alpha}$ for the unsubstituted cyclopropyl radical. This was accomplished by direct UV photolysis in the cavity of the EPR spectrometer of ^{13}C-labeled bis(cyclopropylformyl) peroxide in cyclopropane as solvent at ca. −70 °C. The observed H and ^{13}C hfs's are given in Table II; the former are in agreement with the results of earlier workers,[19,20] while the latter are in satisfactory agreement with values calculated by INDO (viz.[23] 94.5 G for θ = 30°, 108.7 G for θ = 35°) but in poor agreement with the ab initio calculated value[24a] of 138.8 G (for θ = 41°). The limited quantity of labeled peroxide precluded attempts to measure $a^{^{13}C_\alpha}$ over a range of temperatures.[29]

Table III. Rate constants for the Reactions of Cyclopropyl, 1-Methylcyclopropyl, and 1-Methoxycyclopropyl Radicals with Various Substrates at 298 ± 2 K in Benzene

substrate	k,[a] M^{-1} s^{-1}		
	c-$C_3H_4^{\bullet}$-H[b]	c-$C_3H_4^{\bullet}$-CH_3	c-$C_3H_4^{\bullet}$-OCH_3
styrene	(1.5 ± 0.3) × 10^7	(1.3 ± 0.2) × 10^7	(4.3 ± 0.6) × 10^6
β-methylstyrene	(2.0 ± 0.5) × 10^6	(3.8 ± 0.3) × 10^6	
1,4-cyclohexadiene	(7.9 ± 0.3) × 10^6	(8.6 ± 1.0) × 10^6	(2.1 ± 0.3) × 10^6
CCl_4	(1.5 ± 0.2) × 10^6	(1.1 ± 0.3) × 10^7	
CCl_3Br	(2.8 ± 0.5) × 10^9	(3.7 ± 1.4) × 10^9	
n-Bu_3SnH	(1.1 ± 0.1) × 10^8[c]	(9.6 ± 1.1) × 10^7	

[a] Total rate constant for the reaction, including all paths and reaction sites. [b] From ref 3 and 4. [c] A vaue of 8.5 × 10^7 M^{-1} s^{-1} at 30 °C given previously in n-pentane[4] (not benzene as incorrectly indicated in this reference).

Table IV. Retention/Inversion Ratios for the 1-Methylcyclopropyl Radical[a]

solvent	**5b**/**6b**
0.2 M CCl_3Br/*tert*-butylbenzene	1.0_0
1.0 M CCl_3Br/*tert*-butylbenzene	1.0_3
9.8 M CCl_3Br[b]	1.4_7[c]

[a] On the basis of a 500-MHz NMR determination of the relative yields of bromides, **5b**/**6b**, produced by the thermolysis of the stereospecifically deuterated peroxide **2b** at 71 ± 1 °C. [b] Neat CCl_3Br. [c] Mean of three separate experiments: 1.3_2, 1.5_0, and 1.5_9.

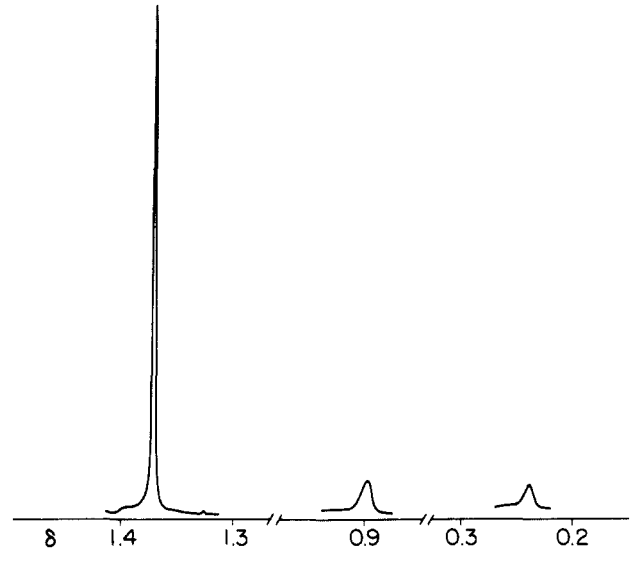


Figure 2. 500-MHz NMR spectrum in C_6D_6 of a mixture of **5b** and **6b** isolated from thermolysis of 0.14 M **2b** in neat CCl_3Br.

The 1-Methylcyclopropyl Radical. (i) Absolute Rate Constants for Some Addition and Abstraction Reactions. The kinetics of some

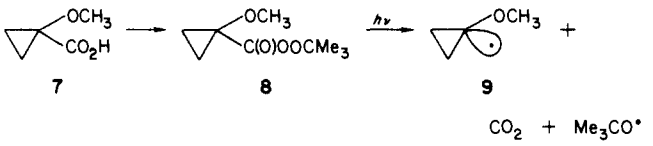
(22) Relative to the −23 G of the H's in the $CH_3^{\bullet}$ radical.
(23) Kochi, J. K.; Bakuzis, P.; Krusic, P. J. *J. Am. Chem. Soc.* **1973**, *95*, 1516–1526.
(24) (a) Ellinger, Y.; Subra, R.; Levy, B.; Millie, P.; Berthier, G. *J. Chem. Phys.* **1975**, *62*, 10–29. (b) Dupuis, M.; Pacansky, J. *J. Chem. Phys.* **1982**, *76*, 2511–2515. (c) **Note Added in Proof**: Even more recent ab initio calculations[24d] give θ = 42.7° and an inversion barrier of 5.5 kcal/mol for the cyclopropyl radical and θ = 43.4° with an inversion barrier of 6.1 kcal/mol for the 1-methylcyclopropyl radical. (d) Lien, M. H.; Hopkinson, A. C. *J. Comput. Chem.* **1985**, *6*, 274–281.
(25) See also ref 8b.
(26) Greatorex, D.; Kemp, T. J. *Trans. Faraday Soc.* **1971**, *67*, 1576–1586. Trofimov, V. I.; Blumenfeld, A. L.; Kostyanovsky, R. G.; Chkheidze, I. I. *Tetrahedron Lett.* **1971**, 3267–3270.
(27) For example,[8] in the configurationally "frozen" 2,2-dimethyl-1-fluorocyclopropyl, a^{H_β}(syn) = 16.3 G and a^{H_β}(anti) = 5.0 G.
(28) Bennett, J. E.; Mile, B.; Thomas, A.; Ward, B. *Adv. Phys. Org. Chem.* **1970**, *8*, 1–77.
(29) Accurate measurements of $a^{^{13}C_\alpha}$ made over a range of temperatures can provide information about the vibrational properties of the radical, see, e.g.: Griller, D.; Ingold, K. U.; Krusic, P. J.; Fischer, H. *J. Am. Chem. Soc.* **1978**, *100*, 6750–6752. Griller, D.; Preston, K. F. *Ibid.* **1979**, *101*, 1975–1979. Griller, D.; Marriott, P. R.; Preston, K. F. *J. Chem. Phys.* **1979**, *71*, 3703–3707. Griller, D.; Ingold, K. U.; Krusic, P. J.; Smart, B. E.; Wonchoba, E. R. *J. Phys. Chem.* **1982**, *86*, 1376–1377 and references cited therein.
(30) (a) $\underline{CH_2CH_2}\dot{C}CO_2H$, $a^{^{13}C_\alpha}$ = 49 G: Kikuchi, M.; LeRay, N.; Roncin, J. *Chem. Phys. Lett.* **1975**, *34*, 395–397. (b) $\underline{C(CMe_3)_2CF_2}\dot{C}F$, $a^{^{13}C_\alpha}$ = 51.5 G: ref 16. (c) $\underline{CH_2CH_2}\dot{C}Si(CH_3)_3$, $a^{^{13}C_\alpha}$ = 40.9 G: Paquette, L. A.; Hoppe, M.; Johnston, L. J., Ingold, K. U. *Tetrahedron Lett.* **1986**, *27*, 411–414.

reactions of the 1-methylcyclopropyl radical were measured by laser flash photolysis using the same procedures as those employed in our earlier studies of cyclopropyl radical kinetics.[3,4] The radical was generated from bis((1-methylcyclopropyl)formyl)peroxide with 308-nm excitation from an excimer laser. Growth of the signal due to the radical formed by reaction with 1-methylcyclopropyl was monitored when possible, while for substrates which did not yield optically detectable radicals we used the probe technique[31] with β-methylstyrene as our probe. The results of these kinetic experiments are summarized in Table III. Rate constants for reaction of the same substrates with the cyclopropyl radical have been included for comparison.

(ii) **Reaction of a Stereospecifically Deuterium Labeled Radical with Bromotrichloromethane.** 1-Methylcyclopropane-*trans*-2,2,3-d_3-carboxylic acid (**1b**) was prepared by essentially the same procedure as **1a**. Conversion to the diacyl peroxide, **2b**, was followed by thermolysis at 71 ± 1 °C in the presence of CCl_3Br in vacuum degassed, sealed tubes (see Scheme I). The bromides **5b** and **6b** were separated by preparative GC and analyzed by 500-MHz NMR spectroscopy. In C_6D_6 the methyl signal for both bromides is at δ 1.38 but the 3-proton in **5b** and **6b** appears as two well-separated singlets at δ 0.90 and 0.23, respectively (see Figure 2). This assignment was confirmed by the observation of a nuclear Overhauser effect for the δ 0.23 proton, this proton and the methyl group being syn to each other in **6b**. Further confirmation was provided by the fact that the δ 0.23 proton has a shorter relaxation time, T_1 (because of the proximity of the methyl group), than the δ 0.90 proton; 65 s vs. 108 s. The retention/inversion ratios as measured by the ratio of 1-methylcyclopropyl bromides, **5b/6b**, are given in Table IV. In neat CCl_3Br the degree of retention of configuration is greater for the 1-methylcyclopropyl radical than for the cyclopropyl radical (Table I). It should be noted that our product ratios are consistent with the small degrees of retention of configuration found by Walborsky and Chen[32] on decomposition of optically pure (−)-(*R*)-1-methyl-2,2-diphenylcyclopropionyl peroxide in thiophenol as solvent (3.22% retention) and in the reduction of (−)-(*R*)-1-bromo-1-methyl-2,2-diphenylcyclopropane[33] in tri-*n*-butyltin hydride as solvent (≲1% retention). The order of trapping ability for the cyclopropyl radical of these reagents is CCl_3Br < PhSH > *n*-Bu_3SnH, with the last named compound having only about 3% of the trapping ability of CCl_3Br (see Table III).

(iii) **EPR Spectroscopy.** The proton and α-^{13}C hfs for 1-methylcyclopropyl at −70 °C are given in Table III. They were obtained as described above for the cyclopropyl radical. Once again, the limited quantity of ^{13}C-labeled peroxide prevented a detailed study of the temperature dependence of the $^{13}C_\alpha$ hfs.[29]

The 1-Methoxycyclopropyl Radical. We prepared 1-methoxycyclopropyl carboxylic acid (**7**) but were unable to convert this compound to the desired bis((1-methoxycyclopropyl)formyl) peroxide by any of the usual methods. The acid **7** was therefore converted to its acid chloride which was then reacted with *tert*-butyl hydroperoxide to give the *tert*-butyl perester **8**. This compound had perforce to serve as our source of 1-methoxycyclopropyl radicals, **9**. For kinetic purposes we carried out the laser flash photolysis of **8** in benzene/triethyl phosphite, 9:1 (v/v), as solvent ($[(EtO)_3P]$ = 0.58 M). The phosphite serves as a very active trap for the *tert*-butoxyl radicals that are generated simultaneously with **9**,[36] but it is probably rather unreactive towards **9**. Kinetic measurements on the 1-methoxycyclopropyl radical were nevertheless much more difficult to carry out than had been the measurements with the cyclopropyl and 1-methylcyclopropyl radicals. Only two substrates gave reasonably reliable data,[37] styrene and 1,4-cyclohexadiene. The rate constants for these two substrates are given in Table III.



Photolysis of **8** in cyclopropane in the cavity of the EPR spectrometer at temperatures from −110 to 0 °C gave rather complex spectra in which we could not identify **9**. The main features were two triplets which clearly belonged to different radicals, $a^H(2\ H) \approx 18.0$ G and $a^H(2\ H) = 21.2$ G, which we tentatively attribute to the radicals formed by hydrogen abstraction from the OCH_3 group and the $C(CH_3)_3$ group of **8**, respectively. Addition of triethyl phosphite eliminated these radicals and left in their place the *tert*-butyl radical spectrum.[39] We do not understand why **9** could not be observed.

Finally, all our varied and strenuous attempts to synthesize **7** with stereospecific deuterium labeling were unsuccessful. Further work on the 1-methoxycyclopropyl radical was therefore abandoned.

Discussion

Although the measurement of the relative yields of bromides **5a/6a** by 500-MHz NMR cannot be very precise there can be no doubt that inversion of the cyclopropyl radical is extremely rapid relative to its trapping by CCl_3Br (see Table I). For the latter reaction, $k_{Br} = 2.8 \times 10^9\ M^{-1}\ s^{-1}$ at 25 °C and so a value of ca. $4 \times 10^9\ M^{-1}\ s^{-1}$ would appear reasonable at 71 °C, the temperature of the inversion studies. The rate constant for inversion is given by[12]

$$k_{inv} = k_{Br}[CCl_3Br]\left(\frac{[5] + [6]}{[5] - [6]} - 1\right) \qquad (I)$$

If we take the data listed in Table I at face value we obtain $k_{inv} = 4.0 \times 10^{11}\ s^{-1}$ for 0.5 M CCl_3Br, $k_{inv} = 1.1 \times 10^{12}\ s^{-1}$ for 9.8 M CCl_3Br, and, assuming that CBr_4 is four times as reactive on a molar basis as CCl_3Br,[40] $k_{inv} = 1.3 \times 10^{12}\ s^{-1}$. We therefore come up with a value for k_{inv} for cyclopropyl that is certainly $>10^{11}\ s^{-1}$ and is probably ca. $10^{12}\ s^{-1}$.

It is interesting to compare the rate of inversion of cyclopropyl with the rate of inversion of ammonia. The inversion barrier for ammonia is ca. 5.9 kcal/mol,[41] i.e., about twice as high as the barrier calculated for cyclopropyl.[23,24] In its ground state the average time taken for an ammonia molecule to invert is 2.5 ×

(31) Paul, H.; Small, R. D.; Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520–4527.

(32) Walborsky, H. M.; Chen, J.-C. *J. Am. Chem. Soc.* **1971**, *93*, 671–675. See also footnote 22 in this reference.

(33) Altman et al.[34a] have reported a slight perference for inversion of configuration in the reduction of this bromide in neat Ph_3SnH (and also of optically active 1-bromo-1-carbomethoxy-2,2-diphenylcyclopropane).[34b] These workers attributed their results to "blocking" of the front side of the cyclopropyl ring by the departing Ph_3SnBr. Since Ph_3SnH is only a slightly better trap for alkyl radicals than *n*-Bu_3SnH[35] the difference between Altman's results[34a] and those of Walborsky and Chen[32] (and our own) would, if confirmed, have to be attributed to the high viscosity of neat Ph_3SnH.

(34) (a) Altman, L. J.; Nelson, B. W. *J. Am. Chem. Soc.* **1969**, *91*, 5163–5164. See also: Altman, L. J.; Erdman, T. R. *Tetrahedron Lett.* **1970**, 4891–4894. (b) The 1-carbomethoxy-2,2-cyclopropyl radical is probably planar, or close to it; see ref 30a.

(35) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047–7055.

(36) For the reaction: $Me_3CO^\bullet + (EtO)_3P \rightarrow (EtO)_3\overset{+}{P}OCMe_3$, $k = 1.7 \times 10^9\ M^{-1}\ s^{-1}$ at 301 K, see: Roberts, B. P.; Scaiano, J. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 905–911. The effective pseudo-first-order rate constant for *tert*-butoxy trapping by the phosphite is therefore ca. $1 \times 10^9\ s^{-1}$.

(37) There will be essentially no interference by the *tert*-butoxyl radicals on the measured rates of reaction of **9** with these substrates. At room temperature, $k \sim 2 \times 10^6\ M^{-1}\ s^{-1}$ for $Me_3CO^\bullet$ + styrene → products (this work; a value of $1.0–1.5 \times 10^6\ M^{-1}\ s^{-1}$ can be estimated from data given in ref 38) and $k = 5.4 \times 10^7\ M^{-1}\ s^{-1}$ for $Me_3CO^\bullet$ + 1,4-cyclohexadiene → products (ref 31).

(38) Howard, J. A.; Scaiano, J. C. In "Landolt-Börnstein, New Series, Radical Reaction Rates in Liquids"; Fischer, H.; Ed.; Springer-Verlag: Berlin, 1984; Vol. 13d.

(39) Formed by the following reaction: $Me_3CO^\bullet + (EtO)_3P \rightarrow Me_3C^\bullet + (EtO)_3P{=}O$.

(40) That is we *assume* $k_{Br} = 1.6 \times 10^{10}\ M^{-1}\ s^{-1}$ for CBr_4 at 71 °C. In this experiment the CCl_3Br concentration would have been ca. 6.7 M.

(41) Herzberg, G. "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules"; Van Nostrand: New York, 1945; pp 221–224.

10^{-11} s and this process involves quantum-mechanical tunneling through the potential barrier.[41] Thermally activated processes leading to an increase in the rate of inversion are relatively unimportant except at very high temperatures.[42] The principal vibrational mode for ammonia inversion[41,42] has a frequency (950 cm^{-1}) which is not very much greater than the calculated pyramidal bending frequency for the cyclopropyl radical, viz.,[24b] 713 cm^{-1}.

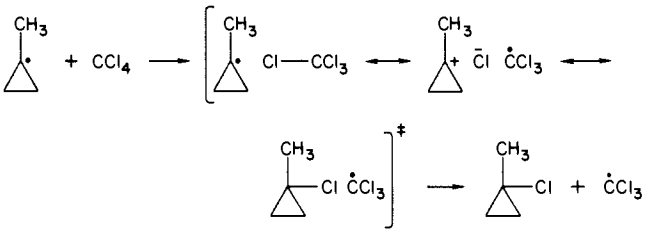
We presume that the cyclopropyl inversion also occurs largely by tunneling at ambient temperatures. If this is correct, it would seem unlikely that inversion could be "frozen-out" by going to low temperatures. Our failure to observe any major change in the EPR spectrum of cyclopropyl between 77 and 4 K can therefore be readily understood, though it must be admitted that the spectrum was so poorly resolved that a relatively minor change might well have been masked. Certainly this result sheds no light on the difference between Kochi et al.'s[23] conclusion that the syn and anti β-H hfs's are approximately equal and Kawamura et al.'s[8b] conclusion that the former will be about three times as large as the latter.

We turn now to the inversion of the 1-methylcyclopropyl radical. This process is unquestionably slower, relative to trapping by CCl_3Br, than the cyclopropyl inversion (cf. Tables I and IV). The trapping rate constant for 1-methylcyclopropyl is $(3.7 \pm 1.4) \times 10^9$ M^{-1} s^{-1} at 25 °C (see Table III) and so a value for k_{Br} of $(5.0 \pm 1.5) \times 10^9$ M^{-1} s^{-1} would seem appropriate at 71 °C. From eq I, k_{inv} is calculated to be 3.3×10^{11} s^{-1} for 1.0 M CCl_3Br and, much more reliably, $(2.1 \pm 0.8) \times 10^{11}$ s^{-1} from the results in neat CCl_3Br.

Inversion by tunneling must be relatively unimportant in the 1-methylcyclopropyl radical because of the methyl group's mass. A slower inversion for 1-methylcyclopropyl than for cyclopropyl is therefore to be expected,[43] *particularly* at low temperatures. It can reasonably be assumed that the Arrhenius preexponential factor for inversion will have a normal value of ca. 2×10^{13} s^{-1}, in which case the barrier to inversion can be calculated[45] to be ca. 3.1 kcal/mol. This barrier height is in excellent agreement with the barrier heights calculated for cyclopropyl inversion[23,24] and it implies that the potential functions for the inversion of these two radicals are rather similar. This seems eminently reasonable both on intuitive grounds and because the $^{13}C_\alpha$ hfs's—which provide a rough measure of the degree of pyramidality at the radical centers[46]—are so similar for cyclopropyl and 1-methylcyclopropyl, viz., 95.9 and 98 G, respectively. We think it highly probable that the inversion of 1-methylcyclopropyl could be frozen (relative to fast chemical trapping or to the EPR time scale) at low temperatures.[47]

It is interesting to note that the hfs's due to the CH_3 group's protons are essentially identical for 1-methylcyclopropyl (19.5 G, Table II) and 1-methylvinyl (19.48 G).[19] However, the $^{13}C_\alpha$ hfs's of 96–98 G found for cyclopropyl radicals are slightly lower than the 107.5 G found for vinyl,[48] which is also a "bent" σ-radical. There is, therefore, somewhat more s-character in the semioccupied orbital in the vinyl radical[49] than in the cyclopropyl radical. Similarly, the H_α hfs in cyclopropyl is negative[21] (−6.7 G), whereas that in vinyl is positive[48,50] (+13.4 G), which also implies that vinyl is more "bent" than cyclopropyl.[51] Certainly the barrier to inversion for vinyl appears to be appreciably greater than for cyclopropyl since this process can be frozen-out on the EPR time scale for 1-methylvinyl and even for vinyl at low temperatures.[19,50a,52,53] For vinyl at −180 °C k_{inv} has been estimated to lie between 3×10^7 and 3×10^9 s^{-1} and 1-methylvinyl inverts somewhat more slowly.[19]

Finally, the kinetic data summarized in Table III show that 1-methylcyclopropyl and cyclopropyl have very similar reactivities except toward carbon tetrachloride. For this particular substrate the rate constant for 1-methylcyclopropyl is about an order of magnitude larger than for cyclopropyl. We attribute this rate enhancement to a strong polar contribution to the transition state for reaction of the tertiary radical, i.e.,



On the basis of the only two successful rate measurements the 1-methoxycyclopropyl radical would appear to be somewhat less reactive than the unsubstituted or methyl-substituted radicals.

Experimental Section

General. Standard ^1H NMR spectra were recorded on a Varian EM-360 instrument, but all cyclopropyl bromide mixtures obtained in the radical inversion studies were analyzed on a Bruker AM-500 NMR spectrometer. Prepartive gas chromatography was done on a Varian 920 Chromatograph equipped with a 10 ft × $^3/_8$ in. 5% OV-101 column. Analytical gas chromatography was done on a Varian 6000 gas chromatograph equipped with a 30-m DB1 30-W 0.25-μm capillary column and mass spectrometry on a Hewlett Packard 5995 GC/MS with a 10-m Ultra 1 (OV-101) capillary column.

Benzene was washed with concentrated H_2SO_4, water, and aqueous $NaHCO_3$ and then dried and distilled from CaH_2. Carbon tetrachloride was distilled from P_2O_5. *tert*-Butylbenzene, styrene, β-methylstyrene, 1,4-cyclohexadiene, triethyl phosphite and bromotrichloromethane were distilled before use.

Cyclopropane-*trans*-2,2,3-d_3-carboxylic Acid (1a). This compound was prepared from *trans*-β-bromostyrene by the procedure of Kobayashi and Lambert.[15] NMR analysis indicated an isomeric purity >95%: NMR (CCl_4) δ 1.2 (br d, 1 H), 1.5 (d, 1 H).

Cyclopropane-*1*-^{13}C-carboxylic Acid. Acetophenone-α-^{13}C (0.02 mol, Merck Sharp and Dohme, 90 atom % ^{13}C) was reduced to α-methylbenzyl alcohol with $LiAlH_4$. This alcohol was dehydrated to styrene by addition over a 30-min period to 15 mL of a benzene solution of 0.021 mol of (carboxysulfamoyl)triethylammonium hydroxide, inner salt, methyl ester and 0.002 mol of *tert*-butylcatechol (to prevent polymerization) under a dry argon atmosphere at room temperature.[54] After this mixture was heated for 1 h at 65 °C, 20 mL of water was added and the benzene layer separated and dried. Solvent removal and distillation gave $C_6H_5{}^{13}CH{=}CH_2$ in ca. 50% yield.

The styrene-α-^{13}C was converted to cyclopropane-1-^{13}C-carboxylic acid with use of essentially the same procedure that was employed to prepare **1a**, i.e.,[15] the dichlorocyclopropane obtained by treatment of the labeled styrene with chloroform and 50 mL of aqueous NaOH was hydrodehalogenated with sodium in aqueous methanol and the product was ozonized.

1-Methylcyclopropanecarboxylic Acid. Essentially the same procedure was employed as that used to prepare **1a**. That is, starting with α-methylstyrene, reaction with dichlorocarbene gave 1,1-dichloro-2-methyl-2-phenylcyclopropane which was treated with Na and wet methanol to give 1-methyl-1-phenylcyclopropane. Ozonolysis[15] followed by vacuum distillation gave 1-methylcyclopropanecarboxylic acid as a low-melting, white solid: mp 31–33 °C (lit.[55] mp 32–34 °C); NMR (CCl_4) δ 0.5–0.7

(42) In this regard, the most important normal mode vibration in NH_3 is ν_2 which more or less corresponds to a one-dimensional oscillation of the N atom against the H_3 plane.[41] The ν_2 frequency is 950 cm^{-1} and only the ν_2 levels 0, 1, and 2 lie below the barrier. At 71 °C we calculate that the average time for an inversion would be ca. 1.1×10^{-11} s.

(43) Nearly 20 years ago Dewar and Harris[44] pointed out that cyclopropyl radicals having an α-H would invert more rapidly than those having an α-alkyl (or similar) group because of hydrogen tunnelling. The analogous situation for vinyl and 1-methylvinyl had been pointed out even earlier.[19]

(44) Dewar, M. J. S.; Harris, J. M. *J. Am. Chem. Soc.* **1969**, *91*, 3652–3653.

(45) That is, $\log (2.1 \times 10^{11}) = \log (2.0 \times 10^{13}) - (E/2.3R \times 344)$.

(46) "Rough" because vibrational averaging effects[29] have been ignored.

(47) For example, k_{inv} can be calculated to be ca. 3×10^6 s^{-1} at 100 K.

(48) Fessenden, R. W. *J. Phys. Chem.* **1967**, *71*, 74–83.

(49) Estimated to be 6.5% in vinyl.[48]

(50) See also: (a) Cochran, E. L.; Adrian, F. J.; Bowers, V. A. *J. Chem. Phys.* **1964**, *40*, 213–220. (b) Kasai, P. H.; Whipple, E. B. *J. Am. Chem. Soc.* **1967**, *89*, 1033–1034.

(51) The $C_\beta{=}C_\alpha{-}H_\alpha$ angle in vinyl has been estimated to be 151° (see ref 48 and 50a).

(52) Nagai, S.; Ohnishi, S.; Nitta, I. *Chem. Phys. Lett.* **1972**, *13*, 379–381.

(53) In some matrices, however, the two β-H's of vinyl appear to be magnetically equivalent even at 4 K.[50b]

(54) Burgess, E. M.; Penton, H. R., Jr.; Taylor, E. A. *J. Org. Chem.* **1973**, *38*, 26–31.

(m, 2 H), 1.15–1.35 (m, 2 H), 1.25 (s, 3 H).

1-Methylcyclopropane-*trans*-2,2,3-d_3-carboxylic Acid (1b). This acid was also prepared by a minor modification of the stereospecific route used for acid **1a**.[15] (E)-1-Methyl-2-bromostyrene was prepared by bromination of α-methylstyrene, followed by dehydrobromination of the resulting dibromide.[56] NMR analysis showed contamination by ca. 10% of the corresponding *Z* isomer which was removed by column chromatography.[56] α-Methylstyrene-*trans*-β-*d* was prepared by D_2O hydrolysis of the Grignard reagent of the above bromide. Analysis by NMR indicated an isomeric purity ≥95%. The d_3-labeled acid, **1b**, was then prepared by the standard procedure[15] and was purified by vacuum distillation: mp 32–34 °C; NMR (C_6D_6) δ 1.05 (s, 3 H), 1.1 (br s, 1 H).

1-Methylcyclopropane-1-^{13}C-carboxylic Acid. Acetophenone-α-^{13}C (0.02 mol) was converted to α,α-dimethylbenzyl-α-^{13}C alcohol by reaction with 1.05 equiv of methylmagnesium iodide. This alcohol was then dehydrated with use of the procedure outlined above[54] in the preparation of cyclopropane-1-^{13}C-carboxylic acid, but with a reaction temperature of 50 °C. The α-methylstyrene-α-^{13}C was reacted with diethyl zinc/diiodomethane (as outlined below for acid **7**) to yield 1-methyl-1-phenylcyclopropane-1-^{13}C, ozonolysis[15] of which gave the desired carboxylic acid.

1-Methoxycyclopropanecarboxylic Acid (7). α-Methoxystyrene was prepared from acetophenone dimethyl ketal with use of a literature procedure.[57] A mixture of freshly distilled α-methoxystyrene (6.5 g, 0.0485 mol) and diethyl zinc (44 mL of a 15 wt % solution in toluene, 0.049 mol) was heated to ca. 65 °C and diiodomethane (7.9 mL, 0.098 mol) was added dropwise over a 30-min period.[58] The mixture was stirred at 65 °C for an additional 5 h and was then poured slowly into 3% HCl (50 mL). The organic layer was separated, washed with 5% $NaHCO_3$ and water, and then dried. Unreacted CH_2I_2 was removed by heating the crude material obtained after solvent removal at 70 °C with 25 g of NaOH in 200 mL of methanol for 10 h. The resulting mixture was poured into water and extracted with *n*-hexane and the organic extract was washed and dried. 1-Methoxy-1-phenylcyclopropane was obtained as a colorless oil (70% yield) after solvent removal and distillation: NMR (CCl_4) δ 0.8–1.15 (m, 4 H), 3.1 (s, 3 H), 7.2 (s, 5 H).

Ozonolysis[15] of the 1-methoxy-1-phenylcyclopropane (5.2 g, 0.035 mol) followed by distillation of the crude material gave 2.4 g (60% yield) of **7** as a viscous oil which solidified at $T < 20$ °C: NMR (CCl_4) δ 1.05–1.3 (m, 4 H), 3.3 (s, 3 H), 11.0 (br s, 1 H).

Preparation of Diacyl Peroxides. These compounds were prepared from the corresponding acids with use of the *N*,*N*-carbonyldiimidazole/H_2O_2 method.[18] Purification methods and spectral data for each are listed below: Bis(cyclopropyl-*trans*-2,2,3-d_3-formyl) peroxide (**2a**) was purified by recrystallization from pentane: white crystals; mp 80–81 °C; NMR (CCl_4) δ 0.43 (d, J = 4 Hz, 1 H), 0.98 (d, J = 4 Hz, 1 H). Bis(cyclopropyl-1-^{13}C-formyl) peroxide was purified in the same way: white crystals; mp 80–81 °C; NMR ($CDCl_3$) δ 1.0–1.3 (m, 3 H), 1.7 (dm, $J(^{13}C-H)$ = 164 Hz, 1 H). Bis((1-methylcyclopropyl)formyl) peroxide was purified by chromatography on silica gel (4% ethyl acetate/hexane): colorless oil; NMR (C_6D_6) δ 0.31, 1.28 (A_2B_2 multiplet, 4 H), 1.10 (s, 3 H). Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.78; H, 7.12. Bis(1-methylcyclopropyl-*trans*-2,2,3-d_3-formyl) peroxide (**2b**) was purified in the same manner: colorless oil; NMR (C_6D_6) δ 1.05 (s, 3 H), 1.22 (br s, 1 H). Bis((1-methylcyclopropyl-1-^{13}C)formyl) peroxide was purified in the same manner: colorless oil; NMR (CCl_4) δ 0.6–0.85 (m, 2 H), 1.3 (d, $J(^{13}C-H)$ = 5 Hz, 3 H), 1.2–1.4 (m, 2 H).

tert-Butyl 1-Methoxycyclopropanepercarboxylate (**8**) was prepared by converting the corresponding acid, **7**, to its acid chloride with thionyl chloride.[59] Pyridine (0.0075 mol) was then slowly added to a mixture of the acid chloride (0.58 g, 0.005 mol) and *tert*-butyl hydroperoxide (0.54 g, 0.006 mol) in diethyl ether at 0 °C.[60] After being stirred for 1 h the mixture was warmed to room temperature, washed with 10% HCl, 10% Na_2CO_3, and saturated aqueous NaCl, and dried. Purification of the crude material on silica gel (3% ethyl acetate/hexane) gave a 60% yield of **8**: colorless oil; NMR (C_6D_6) δ 0.82, 1.12 (A_2B_2 multiplet, 4 H), 1.15 (s, 9 H), 3.15 (s, 3 H). Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.52; H, 8.60.

Thermolysis of Peroxides 2a and 2b. The peroxides (0.14–0.15 M) were dissolved in the appropriate solvent (see Tables I and IV), degassed by the freeze–thaw technique, sealed under vacuum, and then thermolyzed at 71 ± 1 °C to >98% conversion. The required bromocyclopropanes, **5** and **6**, were first identified by GC/MS and were then separated from the reaction mixture by preparative GC. They were then redissolved in CCl_4 or C_6D_6 and analyzed by 500-MHz NMR spectroscopy.

The two 1-bromocyclopropanes-2,2,3-d_3 **5a** and **6a** derived from **2a** were identified on the basis of the larger coupling of the 3-proton in **5a** (see Figure 1), as previously assigned:[15] NMR (CCl_4) δ 1.02 (3-proton, coupling not resolved, **6a**), 1.12 (3-proton, $J \sim 7$ Hz, **5a**), 2.95 (1-proton, **5a** and **6a**); (C_6D_6) δ 0.72 (3-proton, $J \sim 8$ Hz, **5a**), 0.92 (3-proton, coupling not resolved, **6a**), 2.72 (1-proton, **5a** and **6a**).

The two 1-bromo-1-methylcyclopropanes-2,2,3-d_3 **5b** and **6b** were readily distinguishable (see Figure 2): NMR (C_6D_6) δ 0.23 (br s, 3-proton, **6b**), 0.90 (br s, 3-proton, **5b**), 1.38 (s, CH_3, **5b** and **6b**). This stereochemistry was assigned on the basis: (i) observation of a nuclear Overhauser effect for the δ 0.23 proton which in **6b** is cis with respect to the CH_3 group; (ii) the shorter relaxation time for the δ 0.23 proton (T_1 = 65 s) compared with the δ 0.90 proton (T_1 = 108 s), a difference that can be assigned to the closer proximity of the 3-proton and the methyl group in **6b** relative to **5b**.

EPR Spectra. The hfs's recorded in Table II were measured on a Varian E-104 EPR spectrometer. The radicals were generated at −70 °C by UV photolysis (1000-W high-pressure Hg lamp) of solutions of the diacyl peroxides (0.1–0.2 M) in cyclopropane which had been degassed and sealed under vacuum. The cyclopropyl radicals generated on the rotating cryostat[28] by reaction of c-C_3H_5Br with Na atoms in a cyclopropane matrix at 77 K were examined on a Varian E-12 EPR spectrometer equipped with an Oxford Instruments ESR-9 Liquid Helium Cryostat.

Laser Flash Photolysis Experiments. Peroxides (0.2 M) in benzene solution held in 7 × 7 mm quartz cells were deoxygenated by purging with nitrogen. A Lumonics TE-860-2 excimer laser (Xe–HCl, 308 nm, ~5-ns pulse, ≤80 mJ/pulse) was used for sample excitation. Details of the apparatus[61] and of the measurements of rate constants for reactions of the cyclopropyl radical[3] have been reported previously.

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Registry No. 1a, 61377-11-5; **1b**, 100683-06-5; **2a**, 100683-09-8; **2b**, 100700-83-2; **5a**, 61377-12-6; **5b**, 100700-84-3; **6a**, 61377-13-7; **6b**, 100683-13-4; **7**, 100683-08-7; **8**, 100683-12-3; $(Bu)_3SnH$, 688-73-3; $C_6H_5{}^{13}CH{=}CH_2$, 31124-35-3; CCl_4, 56-23-5; CCl_3Br, 75-62-7; 1-methylcyclopropyl radical, 65338-31-0; cyclopropane-1-^{13}C-carboxylic acid, 100683-05-4; 1-methylcyclopropanecarboxylic acid, 6914-76-7; 1-methylcyclopropane-1-^{13}C-carboxylic acid, 100683-07-6; bis(cyclopropyl-1-^{13}C-formyl)peroxide, 100683-10-1; bis((1-methylcyclopropyl)-formyl)peroxide, 100683-11-2; acetophenone-α-^{13}C, 10383-88-7; α-methylbenzyl alcohol, 98-85-1; 1,1-dichloro-2-methyl-2-phenylcyclopropane, 3591-42-2; 1-methyl-1-phenylcyclopropanecarboxylic acid, 2214-14-4; cyclopropyl radical, 2417-82-5; styrene, 100-42-5; β-methylstyrene, 637-50-3; 1,4-cyclohexadiene, 628-41-1; α-methylstyrene, 98-83-9; dichlorocarbene, 1605-72-7.

Supplementary Material Available: Tables V–XIV giving detailed laser flash kinetic data (11 pages). Ordering information is given on any current masthead page.

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