Similar model building with ferrioxamine B and D_1 shows that only in the case of Δ(orΛ)-N-cis,cis the trihydroxamate chain is twist-free, and this is the isomer ferrioxamine D_1 assumes in the crystal structure. One can, therefore, conclude that the most probable isomer of **4** is Δ-C-trans,trans and that of ferrioxamine B and D_1 is Δ(or Λ)-N-cis,cis. Following the same line of argument, it can be proposed that the second most probable isomer for **4** would be Δ-N-cis,cis, because this isomer requires a single twist in the chain end containing only a methyl group. Similarly, for ferrioxamine B (or D_1), the second most probable isomer is Δ(or Λ)-N-cis,trans. This may explain why only two isomers could be identified in the case of Cr^{3+} and also of Ga^{3+} complexes of ferrioxamine B.[44-46]

Structure-activity relationships have been investigated for coprogens in *Neurospora crassa*. The number of *trans*-anhydromevalonoyl groups in these siderophores have been found to be an important determinant in the iron-uptake process. As these groups are replaced gradually by acetyl groups, the uptake activity reduces proportionally (i.e., iron-uptake rate is in the order, coprogen > neocoprogen I > neocoprogen II).[12]

The molecular structures of the ligands in the coprogen family are very different from the ones observed in the ferrichrome family. Furthermore, coprogens assume predominantly a Δ-trans coordination geometry, while all the members of the ferrichrome family show a Λ-cis geometry. Yet the two groups of siderophores reveal competition with each other during iron transport process in *N. crassa*. A shared transport system with separate receptor proteins has been proposed for coprogen and ferrichromes.[48] Neither the uptake of coprogen nor its competition with ferrichromes has been observed in *Penicillium parvum* indicating that this fungus lacks the coprogen receptor system and does not recognize this siderophore. Recent studies have revealed that the immediate surrounding of the iron atom in ferrichromes is involved in the process of coprogen uptake inhibition.[12] The members of the ferrichrome family that have *trans*-anhydromevalonic acid groups as their *N*-acyl moiety exert maximum inhibition on coprogen uptake in *N. crassa*.

Another shared uptake system has been recognized in *Escherichia coli*, in which a common outer membrane receptor, fhuE, is used by coprogen, ferric rhodotorulate, and ferrioxamines (B and D_1).[14,15,49] Ferrioxamine D_1 exists as a mixture of Λ-cis and Δ-cis isomers in the crystal structure,[34] while all coprogens exist predominantly as the Δ-trans optical isomer. It has been mentioned earlier that the molecules of **4** and ferrioxamine D_1 (Δ-form), in their respective crystal structures, superpose quite well (Figure 4). The orientation of the hydroxamate groups (cis or trans) seems to have little influence on the activity of these siderophores in this system. An analogous observation has been made in the case of retroferrichrome, in which the orientation of all three hydroxamate groups of ferrichrome is reversed (i.e, the C=O groups takes the position of N-O groups and vice versa). Such a reversal of the hydroxamate groups was found to have little effect on the iron transport activity.[50] Chirality of the iron atom (Λ or Δ), on the other hand, seems to be far more important in relation to uptake activity.[51]

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Supplementary Material Available: A packing diagram, atomic parameters, and bond distances for neocoprogen I (8 pages). Ordering information is given on any current masthead page.

(47) The nomenclature for the iron coordination of the diastereoisomers of coprogen is based on the rules outlined by Leong and Raymond.[44] (i) Viewed down the C_3 axis, the chelate rings 1, 2, and 3 are arranged clockwise for Λ isomers and counterclockwise for Δ isomers. (ii) If ring 1 has the carbon atom of the hydroxamate group below the nitrogen, it is denoted "C". If the reverse is true it is called "N". (iii) For rings 2 and 3, each is called "cis" or "trans", depending upon whether it has the same or opposite relative orientation with respect to the C_3 axis as does ring 1. (iv) The ring nearest to the free amino terminus (in ferrioxamine B) is designated as ring 1. Because in the coprogens there is no unique N-terminus (as in ferrioxamine B or D_1), we propose that the chelate rings are designated such that the diketopiperazine ring be placed between rings 1 and 2. The resulting isomer designations (Figure 5) are applicable to all members of the coprogen family and constitute a correction of the nomenclature used in a recent review.[2]

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Kinetics of Cyclopropyl Radical Reactions. 3. Study of Some 1-Substituted Cyclopropyl Radicals by EPR Spectroscopy. The Inversion Barrier for 1-Methylcyclopropyl[1]

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Abstract: The 1-methyl-, 1-ethoxy-, and 1-chlorocyclopropyl radicals have been observed by low-temperature EPR spectroscopy in "frozen" configurations in which the ring hydrogens that are syn and anti to the unpaired electron's orbital have different hyperfine splittings. The $a^H(syn)/a^H(anti)$ ratios are 1.5 (CH_3), 1.8 (EtO), and 1.9 (Cl), all considerably lower than the ratio of ca. 3.3 found by Kawamura et al.[25] for methyl-substituted 1-fluorocyclopropyl radicals. The out-of-plane angles of the 1-substituent have been calculated from measured a^{13C_α} values to be 22.5° (cyclopropyl), 22.9° (CH_3), 29.1° (EtO), and 5.8° (Me_3Si). These angles are considerably smaller than those that have been calculated for some of these radicals by ab initio and other methods. Variable-temperature EPR spectroscopy on 1-methylcyclopropyl yields the following Arrhenius equation for its inversion: $\log (k_{inv}/s^{-1}) = (13.1 \pm 0.3) - (3.1 \pm 0.2)/2.3RT$ kcal/mol. For 1-ethoxycyclopropyl the rate constant for rotation about the C–OEt bond can be represented by $\log (k_{rot}/s^{-1}) = (12.5 \pm 0.2) - (5.8 \pm 0.2)/2.3RT$. The barrier to inversion of this radical is ≥9 kcal/mol. The 1-chlorocyclopropyl radical could only be observed at very low temperatures.

In Part 1[3] we reported the first absolute rate constants for some reactions of the cyclopropyl radical in solution.[4] In Part 2[5] we described how a combination of absolute rate data, stereospecific deuterium labeling of appropriate radical precursors, and chemical

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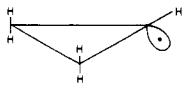
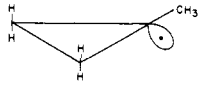
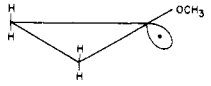
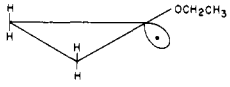
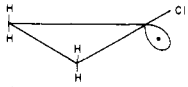
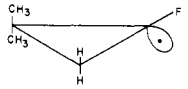
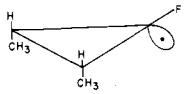
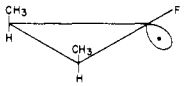
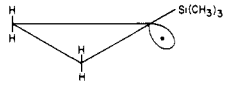
Table I. EPR Parameters for Cyclopropyl and Substituted Cyclopropyl Radicals[a]

radical	T (K)	a^H(syn)	a^H(anti)	a^H(syn)/a^H(anti)	a^H(ring, averaged)	a^{other}	a^{13C_α}	g	ref
	203				23.5 (4 H)	6.7 (1 H)	95.9	2.0028[b]	5
	92	24.85 (2 H)	16.55 (2 H)	1.50	20.7 (4 H)[c]	19.5 (3 H)[d]		2.0027[e]	*f*
	203				20.7 (4 H)[g]	19.5 (3 H)	98		5
	173	16.4 (1 H) 13.6 (1 H)	8.5 (1 H) 7.7 (1 H)	1.93 1.77	11.55 (4 H)[c]	1.6 (3 H)		2.0034	*f*
	173	16.5 (1 H) 13.5 (1 H)	8.6 (1 H) 7.8 (1 H)	1.92 1.73	11.6 (4 H)[c]	1.9 (2 H)	137	2.0033[h]	*f*
	277	15.0 (2 H)	8.25 (2 H)	1.83	11.6 (4 H)[c]	1.75 (2 H)			*f*
	173	20.3 (2 H)	10.7 (2 H)	1.90	15.5 (4 H)[c]	7.3 (1 Cl)		2.0059	*f*
	165	16.3 (1 H)	5.0 (1 H)	3.26	10.65 (2 H)[c]	77.0 (1 F) 2.4 (3 H)		2.0039	25
	165		5.53 (2 H)			74.8 (1 F)		2.0040	25
	165	15.6 (2 H)				77.6 (1 F) 2.43 (6 H)		2.0040	25
	203				27.0 (4 H)		40.9	2.0023	26

[a] Hfs are in gauss. [b] At 179 K, see: Chen, K. S.; Edge, D. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7036–7043. [c] Calculated. [d] Broadened very severely, see Figure 1D. [e] At 151 K. [f] This work. [g] A value of 21 G which was based on a spectrum of rather poor quality was given in ref 5. [h] At 203 K.

trapping with CCl_3Br could be used to estimate the rate constants for inversion of cyclopropyl, viz., ca. 10^{12} s^{-1} at 344 K, and 1-methylcyclopropyl, viz., $(2.1 \pm 0.8) \times 10^{11}$ s^{-1} at the same temperature. Our long-standing interest in radical inversions[6] has led us to undertake the present EPR spectroscopic study of 1-methyl-, 1-alkoxy-, and 1-chlorocyclopropyl radicals.

Results

The 1-Methylcyclopropyl Radical. From our earlier chemical trapping studies we concluded that quantum-mechanical tunneling played a major role in the inversion of the cyclopropyl radical but that tunneling must be relatively unimportant for 1-methylcyclopropyl.[5] By assuming that the Arrhenius preexponential factor for inversion would have a "normal" value of 2×10^{13} s^{-1} we calculated from the measured rate constant for inversion at 344 K that the barrier to inversion should be 3.1 kcal/mol. At 203 K the EPR spectrum of this radical had hyperfine splittings (hfs): $a^H(3H) = 19.5$ G and $a^H(4H) = 21$ G.[5] It subsequently occurred to us that if the pairs of hydrogens on the cyclopropane ring that are syn and anti to the unpaired electron had different hfs (as one would intuitively expect) then a barrier of 3.1 kcal/mol should, in the absence of tunneling, allow these two pairs of hydrogens to be resolved. On further cooling, the EPR spectrum of 1-methylcyclopropyl should therefore show first a classic line-broadening phenomenon of the 1:4:6:4:1 quintet pattern due to the four ring hydrogens which, at still lower temperatures, should resolve into two (1:2:1) triplets. Such proved to be the case, but the spectral changes (see Figure 1) were somewhat more complicated than anticipated because rotation of the methyl group also becomes slow on the EPR time scale at very low temperatures—a phenomenon that has been observed previously for CH_3 groups[14-19] and CF_3 groups[14,19-21] that are directly attached to nonplanar radical centers.

The 1-methylcyclopropyl radical was generated by direct photolysis in the EPR cavity of a mixture containing 1-bromo-

(1) Issued as NRCC No. 27767.
(2) Canada–France Postdoctoral Exchange Fellow.
(3) Johnston, L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 4877–4881.
(4) For an excellent review of cyclopropyl radical chemistry, see: Walborsky, H. M. *Tetrahedron* **1981**, *37*, 1625–1651.
(5) Johnston, L. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1986**, *108*, 2343–2348.
(6) For some previous work from this laboratory on the inversion of carbon-centered radicals see ref 7–9 and on the inversion of heteroatom-centered radicals see ref 10–13.
(7) Griller, D.; Ingold, K. U.; Krusic, P. J.; Fischer, H. *J. Am. Chem. Soc.* **1978**, *100*, 6750–6752.
(8) Malatesta, V.; McKelvey, R. D.; Babcock, B. W.; Ingold, K. U. *J. Org. Chem.* **1979**, *44*, 1872–1873.
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(16) Itzel, H.; Fischer, H. *Helv. Chim. Acta* **1976**, *59*, 880–901.
(17) Gaze, C.; Gilbert, B. C. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1161–1168.
(18) Sutcliffe, R.; Lindsay, D. A.; Griller, D.; Walton, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1982**, *104*, 4674–4676.
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(20) Meaken, P.; Krusic, P. J. *J. Am. Chem. Soc.* **1973**, *95*, 8185–8188.
(21) Chatgilialoglu, C.; Ingold, K. U. *J. Phys. Chem.* **1982**, *86*, 4372–4375.

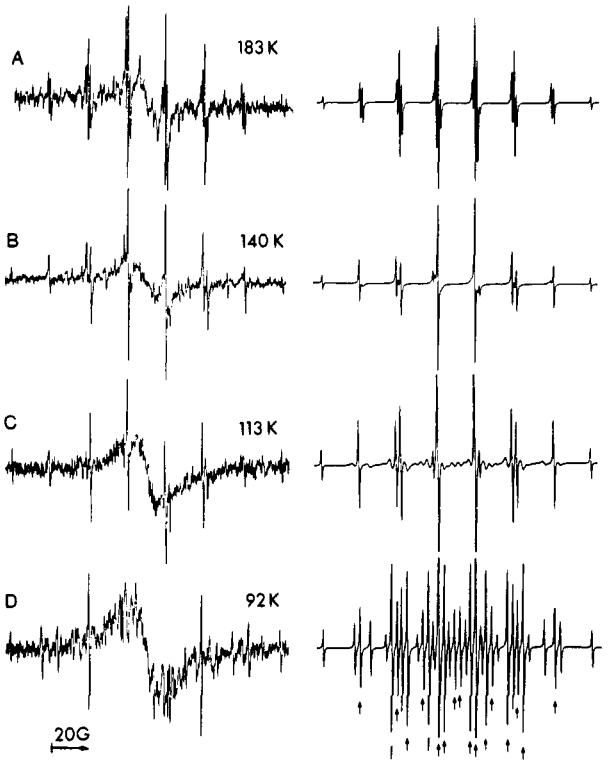


Figure 1. EPR spectra of the 1-methylcyclopropyl radical at four temperatures. Left, experimental spectra; right, simulated spectra (see text). Radicals were generated by bromine atom abstraction from 1-bromo-1-methylcyclopropane with $Et_3Si^{\bullet}$ radicals (formed by photolysis of $Me_3COOCMe_3$ in the presence of Et_3SiH) in cyclopropane ($T \geq 137$ K) or ethane ($T < 137$ K) as solvent. The arrows on the 92 K simulated spectrum indicate the central lines in the methyl hydrogens' quartet pattern that, in the experimental spectrum, are broadened almost to invisibility at this temperature.

1-methylcyclopropane, triethylsilane, and di-*tert*-butyl peroxide in cyclopropane ($T \geq 137$ K) or ethane ($T < 137$ K) as solvent. At 183 K both inversion and methyl rotation are rapid and the spectrum (Figure 1A) shows a quintet (from four equivalent ring hydrogens) of quartets (from three equivalent methyl hydrogens). At 140 K there is severe line broadening that is associated only with the quintet splitting (Figure 1B). This indicates that inversion at the radical center is becoming slow on the EPR time scale and that the syn and anti ring hydrogens have different hfs. Although inversion is slow at 140 K the methyl group is still rotating freely. It is clear, therefore, that the process of inversion is not coupled to the methyl rotation.[22] The experimental spectrum can be readily simulated[23] (vide infra) both at 183 K and at 140 K. As the temperature is further reduced to 113 K the lines of the quintet patterns that were visibly broadened at 140 K become so broad that they can no longer be observed (Figure 1C), which indicates a further slowing of the inversion process. In addition, the central lines of the methyl hydrogens' 1:3:3:1 quartet patterns have started to broaden (i.e., to lose intensity). The simulated spectrum matched to the experimental 113 K spectrum takes account only of the changes associated with inversion (vide infra) and does not reproduce the broadening due to the hindered methyl rotation. Finally, at 92 K the central lines of the quartet patterns (marked by arrows in the simulation, Figure 1D) have broadened almost beyond detection. However, the "missing" lines from the four ring hydrogens now "reappear" in the form of two 1:2:1 triplet patterns corresponding to nonequivalent syn and anti pairs of hydrogens.

(22) By way of contrast, methyl rotation and inversion appear to be quite strongly coupled in the case of the *tert*-butyl radical. See, e.g., ref 7; see also: Yoshimine, M.; Pacansky, J. *J. Chem. Phys.* **1981**, *74*, 5168–5173. Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 5046–5049. Paddon-Row, M. N.; Houk, K. N. *J. Phys. Chem.* **1985**, *89*, 3771–3774. Pacansky, J.; Yoshimine, M. *Ibid.* **1986**, *90*, 1980–1983.

(23) Heinzer, J. *QCPE* **1972**, No. 209.

Table II. Rate Constants for Inversion of the 1-Methylcyclopropyl Radical Obtained from a Comparison of Measured and Simulated EPR Spectra

T, K	k_{inv}, s^{-1}	T, K	k_{inv}, s^{-1}
92	5.0×10^5	145	3.0×10^8
103	5.0×10^6	148	4.0×10^8
113	2.0×10^7	153	5.0×10^8
136	1.3×10^8	159	7.0×10^8
140	2.0×10^8	161	8.0×10^8

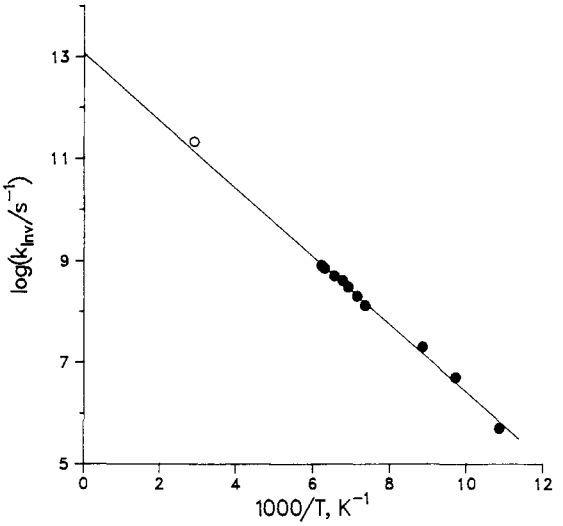
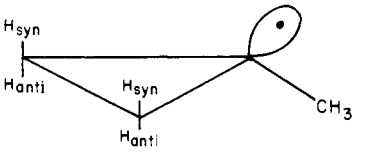


Figure 2. Inversion of the 1-methylcyclopropyl radical. Filled circles obtained by spectral simulation. Open circle by chemical trapping, see ref 5.

Kawamura et al.[24,25] have shown that in the configurationally "locked" (*E*,*E*)- and (*Z*,*Z*)-1-fluoro-2,3-dimethylcyclopropyl radicals the two ring hydrogens that are syn to the unpaired electron (in the *Z*,*Z* radical) have hfs of 15.6 G, while those that are anti to the unpaired electron (in the *E*,*E* radical) have hfs of 5.53 G (see also Table I). Following this lead, for the configurationally "locked" 1-methylcyclopropyl radical at 92 K we assign the larger of the two triplet hfs (24.85 G) to the two syn ring hydrogens and the smaller triplet hfs (16.55 G) to the two anti ring hydrogens. These hfs, together with other spectral parameters for this and related radicals, are given in Table I.



The lowest temperature we could reach without solidifying the reactant mixture was 92 K which was still not low enough for us to determine the individual hfs of the nonequivalent methyl hydrogens (see Figure 1D). We could not, therefore, determine the barrier to methyl rotation nor properly simulate this motion. The simulations[23] presented in Figure 1 therefore take account only of the exchange of the syn and anti pairs of ring hydrogens. Simulated spectra calculated with appropriate rate constants for this exchange process[23] were matched with experimental spectra recorded at temperatures from 92 to 161 K. These data are presented in Table II and have been plotted in the Arrhenius form in Figure 2.

1-Methoxycyclopropyl and 1-Ethoxycyclopropyl Radicals. In our earlier work[5] we failed to detect the EPR spectrum of the 1-methoxycyclopropyl radical on photolysis of the *tert*-butyl

(24) Kawamura, T.; Tsumura, M.; Yonezawa, T. *J. Chem. Soc., Chem. Comm.* **1977**, 373–374.

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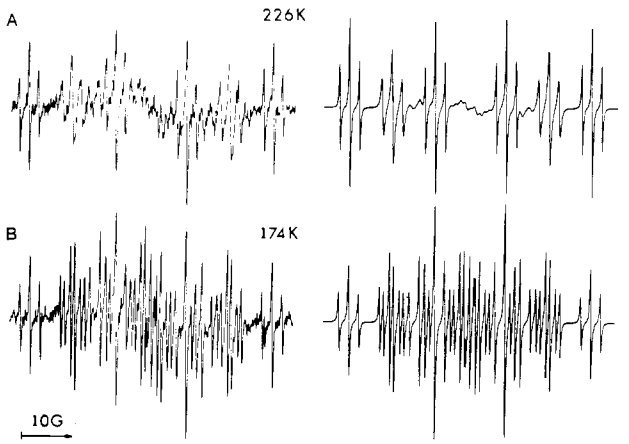


Figure 3. EPR spectra of the 1-ethoxycyclopropyl radical at two temperatures. Left, experimental spectra; right, stimulated spectra. Radicals were generated by bromine atom abstraction from 1-bromo-1-ethoxycyclopropane in cyclopropane solvent.

Table III. Rate Constants for Motional Averaging[a] of the 1-Ethoxycyclopropyl Radical As Obtained from a Comparison of Measured and Simulated EPR Spectra

T, K	k_{rot}, s^{-1}	T, K	k_{rot}, s^{-1}
203	2.0×10^6	261	5.0×10^7
211	4.0×10^6	277	1.0×10^8
226	1.0×10^7		

[a] Rotation about the $\dot{C}_\alpha$–O bond, see text.

perester of 1-methoxycyclopropanecarboxylic acid. We attribute this failure to complications (i.e., other radical species) arising from the simultaneous formation of *tert*-butoxyl radicals. We have now found that excellent EPR spectra of 1-alkoxycyclopropyl radicals can be obtained by photolysis of mixtures containing 1-alkoxy-1-bromocyclopropane, triethylsilane, and di-*tert*-butyl peroxide in cyclopropane solvent. The EPR parameters for 1-methoxycyclopropyl and 1-ethoxycyclopropyl are summarized in Table I. Detailed study of the temperature-dependent behavior of the EPR spectra was restricted to 1-ethoxycyclopropyl since a few measurements showed that the 1-methoxycyclopropyl radical's spectrum behaved in essentially the same way as the 1-ethoxycyclopropyl radical's spectrum.

At 174 K the EPR spectrum of 1-ethoxycyclopropyl shows that it has *four* nonequivalent ring hydrogens plus two equivalent hydrogens from the ethoxyl group (see Table I and Figure 3B). At 226 K the spectrum has collapsed to a simpler pattern, which indicates that the four nonequivalent ring hydrogens are becoming two nonequivalent pairs of hydrogens, $a^H(2H) = 15.0$ G and $a^H(2H) = 8.2$ G (Figure 3A). At the highest temperature at which this radical could still be observed (~277 K) this process is almost complete (i.e., the two new triplets have intensities close to 1:2:1). However, there is still no sign of that broadening, which would indicate that all four ring hydrogens are about to become magnetically equivalent. Simulations of spectra measured at temperatures from 203 to 277 K yielded the rate constants for the exchange process that are listed in Table III.

The 1-Chlorocyclopropyl Radical. This radical was generated by photolysis of 1-bromo-1-chlorocyclopropane/triethylsilane/di-*tert*-butyl peroxide in cyclopropane with the hope that some of the problems encountered with the 1-alkoxycyclopropyl radicals would be less severe. Unfortunately, this was not the case. The spectrum could not be obtained at temperatures above 170 K. At this and at lower temperatures inversion at the radical center is completely "frozen", the ring hydrogens appearing as two nonequivalent pairs of hydrogens (see Figure 4 and Table I).

Discussion

EPR Spectra of 1-Substituted Cyclopropyl Radicals. a^H(syn), a^H(anti), and Their Ratio. For those 1-substituted cyclopropyl radicals in which the four ring hydrogens appear as two non-

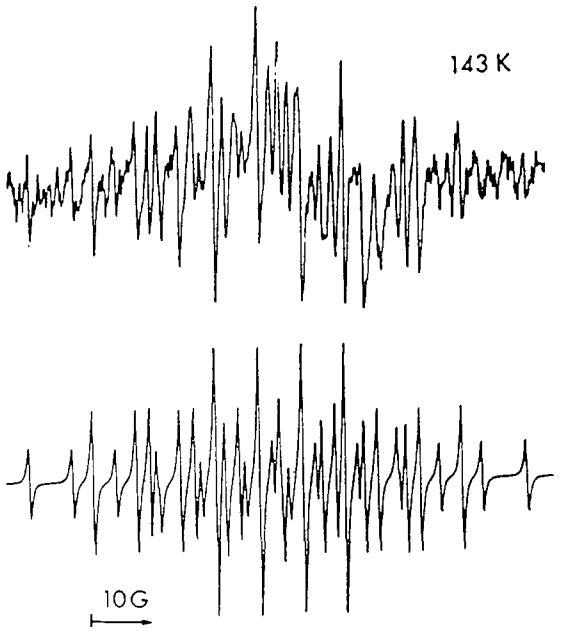


Figure 4. EPR spectra of the 1-chlorocyclopropyl radical at 143 K. Top, experimental spectrum; bottom, simulated spectrum. Radicals were generated by bromine atom abstraction from 1-bromo-1-chlorocyclopropane in cyclopropane solvent.

equivalent pairs of hydrogens we follow Kawamura's pioneering study of various "frozen" methyl-substituted 1-fluorocyclopropyl radicals[24,25] (see Table I). Specifically, we identify the pair of hydrogens with the larger hfs as being in the syn position with respect to the unpaired electron and the pair with the smaller hfs as being in the anti position (see Table I).

The ratio $a^H(syn)/a^H(anti)$ shows an interesting trend that more or less parallels the electronegativity of the 1-substituent.[26] Presumably, an increase in the electronegativity of the 1-substituent either causes[28-30] or, more or less, parallels[28,31-33] an increase in bending at the radical center, and this directly influences both the magnitudes of $a^H(syn)$ and $a^H(anti)$ and the ratio of these two quantities. Thus for a planar, or nearly planar, 1-substituted cyclopropyl radical such as the 1-(trimethylsilyl)-cyclopropyl,[34,35] the terms syn and anti have no meaning. That is, for a planar radical $a^H(syn)/a^H(anti) = 1.0$. For Kawamura's 2,2-dimethyl-1-fluorocyclopropyl radical,[24,25] which must be extremely bent, $a^H(syn)/a^H(anti) = 3.26$. Our radicals have $a^H(syn)/a^H(anti)$ ratios that fall between these two extremes and increase in the order CH_3, 1.50 < CH_3CH_2O, 1.83 ≤ Cl, 1.90. (This order does not exactly parallel the electronegativities of these substituents, viz.,[26,27] CH_3, 2.30 < Cl, 3.03 < CH_3O, 3.70.) We

(26) According to Wells[27] mutually consistent group electronegativities (empirical values) for the substituents of interest to this work are the following: F, 3.95; CH_3O, 3.7; Cl, 3.03; CH_3, 2.3; H, 2.28.

(27) Wells, P. R. *Prog. Phys. Org. Chem.* **1968**, *6*, 111–145.

(28) Two theories have been advanced to explain why electronegative substituents induce bending at a radical center. Pauling[29] and Walsh[30] have suggested that the effect is due to a difference in electronegativity which would cause the singly occupied molecular orbital (SOMO) to have a greater amount of s character and hence cause C_α to become pyramidal. Normal et al.,[31] Dewar et al.,[32] and others[33] have suggested that the effect is due to an antibonding interaction between the nonbonding electrons of the substituent and the SOMO, $\ddot{X}$–$\dot{C}_\alpha \leftrightarrow \dot{X}^+$–$\ddot{C}_\alpha^-$, which introduces carbanionic character to C_α and hence causes its pyramidalization.

(29) Pauling, L. *J. Chem. Phys.* **1969**, *51*, 2767–2769.

(30) Walsh, A. D. *Discuss. Faraday Soc.* **1947**, *2*, 21–25.

(31) Dobbs, A. J.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc. A* **1971**, 124–135.

(32) Bingham, R. C.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1973**, *95*, 7180–7182, 7182–7183.

(33) Krusic, P. J.; Bingham, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 230–232. Bernardi, F.; Epiotis, N. D.; Cherry, W.; Schlegel, H. B.; Wangbo, M. H.; Wolfe, S. *Ibid.* **1976**, *98*, 469–478.

(34) Paquette, L. A.; Hoppe, M.; Johnston, L. J.; Ingold, K. U. *Tetrahedron Lett.* **1986**, *27*, 411–414.

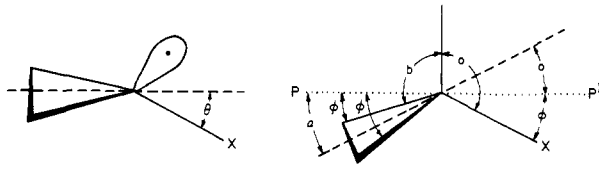
(35) The planarity, or otherwise, of a cyclopropyl radical can be most reliably judged by the magnitude of its $\alpha^{13}C$ hfs.

use the general similarities in the a^H(syn)/a^H(anti) ratios for these three radicals to conclude that the motion that remains "frozen" in 1-alkoxycyclopropyl radicals at the highest attainable temperatures is inversion at the radical center (vide infra). Furthermore, we suggest that if the cyclopropyl radical could itself be "frozen" the a^H(syn)/a^H(anti) ratio would have a value of 1.50 ± 0.10.[36]

The absolute values of a^H(syn), a^H(anti), and a^H(ring, averaged) appear to reflect both changes in bending at the radical center and the extent of electron delocalization into the 1-substituent.[38] For example, the 1-(trimethylsilyl)cyclopropyl radical, which is planar or nearly so,[34,35] has an a^H(ring, averaged) value larger than that for cyclopropyl, viz., 27.0 G vs. 23.5 G, despite the fact that there must be appreciable delocalization of the unpaired electron into the Me_3Si group. Another example is provided by a comparison of 1-methylcyclopropyl with cyclopropyl, two radicals that appear to be approximately equally nonplanar at their radical centers[5,35] (vide infra). The 1-methylcyclopropyl radical has appreciable spin density in the methyl group (a^H(3H) = 19.5 G) and hence has a significantly lower a^H(ring, averaged) value, viz., 20.7 G vs. 23.5 G.

a $^{13}C_\alpha$. The absolute magnitude of the $^{13}C_\alpha$ hfs provides the most reliable evidence as to whether a carbon-centered radical is planar or bent. Thus, we have previously concluded[34] that the 1-(trimethylsilyl)cyclopropyl radical with a^{13C_α} = 40.9 G is nearly, but probably not exactly, planar. In contrast, cyclopropyl and 1-methylcyclopropyl, which have similar $^{13}C_\alpha$ hfs, viz., 95.9 and 98 G, respectively,[5] are certainly bent and are probably bent to a rather similar degree. The 1-methoxycyclopropyl radical has a considerably larger $^{13}C_\alpha$ hfs, viz., 137 G, and must be even more bent.

We have made use of our $^{13}C_\alpha$ hfs to calculate the out-of-plane angle, θ, for the 1-substituent, X. The geometries of carbon-



centered radicals are generally calculated from the relation[42,43]

$$a^{13C_\alpha}(\phi) = a^{13C_\alpha}(0) + A(n \tan^2 \phi)$$

where ϕ is the angle between the three bonds and a plane, PP′, normal to the (nominally) threefold symmetry axis. For 1-substituted cyclopropyl radicals the out-of-plane angle, θ, is related to ϕ by

$$\theta = \phi + \alpha$$

where α is the angle between the bisector of the cyclopropane ring and PP′. We assume that the cyclopropane ring remains an equilateral triangle in the radical and therefore

$$\sin \alpha = \sin \phi / \sin 60°$$

We have chosen to taken $a^{13C_\alpha}(0)$ (which is the $^{13}C_\alpha$ hfs for a hypothetical "planar"[44] cyclopropyl radical) to be 37.1 G since this is the value obtained by Griller and Preston[45] for the hypothetical "planar"[44] isopropyl radical via a careful study of the temperature dependence of the $^{13}C_\alpha$ hfs of this radical.[46] We have taken A = 1348 G from Morton and Preston's[47] compilation of isotropic hyperfine interactions.[46] This quantity corresponds to the hfs for unit spin density in the α-carbon's 2s orbital. Finally, we have taken the normalizing factor, n, to be 1.27.[46] This value is based on the geometry of cyclopropane (∠HCH = a = 115.1°, ∠HCC = b = 117.7°)[48] and the conclusion, initially based on $J_{^{13}C-H}$ spin–spin coupling constants,[49a] that the C–H bond in cyclopropane has about 32% s character (i.e., the C–H bond is much more nearly sp^2 hybridized than sp^3 hybridized).[49] Therefore, if a hydrogen atom is removed from cyclopropane with no change in geometry, θ will be = $^1/_2 \times 115.1° = 57.6°$ and the unpaired electron will reside in an orbital having 32% s character; that is, $n \tan^2 \phi$ = 0.32. For θ = 57.6, calculation yields ϕ = 26.5° and hence n = 1.29.

Values of θ, calculated as described above from the experimental $^{13}C_\alpha$ hfs, are compared in Table IV with θ values recently calculated by Lien and Hopkinson[50] at the RHF 3-21G level of theory. It is clear that their computational procedure gives θ values that are much larger than those we calculate from the $^{13}C_\alpha$ hfs. Of course, our own calculations take no account of electron delocalization into the 1-substituent and θ will therefore be underestimated for X = CH_3, $(CH_3)_3Si$, and particularly C_2H_5O. For the cyclopropyl radical itself (X = H) our θ value should be moderately reliable. However, we note that three other theoretical studies of cyclopropyl also yield rather large θ values, viz., 41°,[37] 30°–35°,[51] and 39.3°.[52] Moreover, in two of these studies values of the $^{13}C_\alpha$ hfs were also calculated and these values are in satisfactory agreement with our own experimental value of 95.9 G, viz., 138.8 G,[37] 94.5 G (for θ = 30°),[51] and 108.7 G (for θ = 35°).[51] A direct determination of θ for cyclopropyl and/or 1-methylcyclopropyl by, for example, electron diffraction,[53] would seem to be a worthwhile goal.

Table IV. Comparison of Experimental and Theoretical Out-of-Plane Angles, θ, and Inversion Barriers, B, for 1-Substituted Cyclopropanes

	experimental			theoretical[a]	
substituent	a^{13C_α}(G)	θ^b (deg)	B (kcal/mol)	θ (deg)	B (kcal/mol)
None (H)	95.9	22.5	<3.0[c]	42.7	5.5
CH_3	98	22.9	3.1 ± 0.2	43.4	6.1
OCH_2CH_3	137	29.1	≥9.0	48.4[d]	15.0[d]
$Si(CH_3)_3$	40.9	5.8			

[a] From ref 50. [b] Calculated from a^{13C_α}, see text. [c] Estimate, see text. [d] For the OH substituent.

(36) This predicted ratio can be compared with a ratio of 1.53 calculated for the minimum energy geometry of cyclopropyl by Ellinger et al.[37] with use of ab initio methods. However, their calculated values of a^H(syn) and a^H(anti), viz., 14.65 and 9.58 G, respectively, are clearly too small. We would predict values of ca. 28.2 and 18.8 G, respectively.

(37) Ellinger, Y.; Subra, R.; Levy, B.; Millie, P.; Bertheir, G. *J. Chem. Phys.* **1975**, *62*, 10–29.

(38) Ring-strain effects must also be important for cyclopropyl radicals that are 2,3-fused into another ring system. Thus, in the 2-bicyclobutyl radical[39] and in the *exo*-tricyclo[3.2.1.$0^{2,4}$]octan-3-yl radical[25] the equivalent pair of hydrogens on the cyclopropane ring have been identified as lying anti to the unpaired electron: their hfs are 4.40 and 9.52 G, respectively (cf. our estimate that a^H(anti) is ca. 18.8 g in "frozen" cyclopropyl).[36] It is clear that these polycyclic radicals are not good models for cyclopropyl, a fact that is also indicated by their H_α hfs (viz., 12.64 G[39] and 7.76 G[25]). Indeed, we have suggested[40] that 2-bicyclobutyl is so much more bent than cyclopropyl that its H_α hfs is positive (+12.64 G) whereas that for cyclopropyl is known to be negative[41] (−6.51 G).

(39) Krusic, P. J.; Jesson, J. P.; Kochi, J. K. *J. Am. Chem. Soc.* **1969**, *91*, 4566–4568.

(40) Ingold, K. U.; Walton, J. C. *Acc. Chem. Res.* **1986**, *19*, 72–77.

(41) Kaptein, R. In *Chemically Induced Magnetic Polarization*; Lepley, A. R., Closs, G. L., Eds.; Wiley: New York, 1973; Chapter 4.

(42) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1965**, *43*, 2704–2712.

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

(44) No radical will ever assume a planar structure since even at very low temperatures each radical will have zero point vibrational energy.

(45) Griller, D.; Preston, K. F. *J. Am. Chem. Soc.* **1979**, *101*, 1975–1979.

(46) Values of $a^{13C_\alpha}(0)$ = 30 G, of A = 1190 G, and of n = 2 were used in ref 34 and 35.

(47) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577–582.

(48) Bastiansen, O.; Fritsch, F. N; Hedberg, K. *Acta Crystallogr.* **1964**, *17*, 538–543.

(49) (a) Patel, D. J.; Howden, M. E. H.; Roberts, J. D. *J. Am. Chem. Soc.* **1963**, *85*, 3218–3223. (b) See also: Randič, M.; Maksič, Z. *Theor. Chim. Acta* **1965**, *3*, 59–68. Watts, V. S.; Goldstein, J. H. *J. Chem. Phys.* **1967**, *46*, 4165–4166. Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 5962–5963. Bernett, W. A. *J. Chem. Educ.* **1967**, *44*, 17–24. Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311–365.

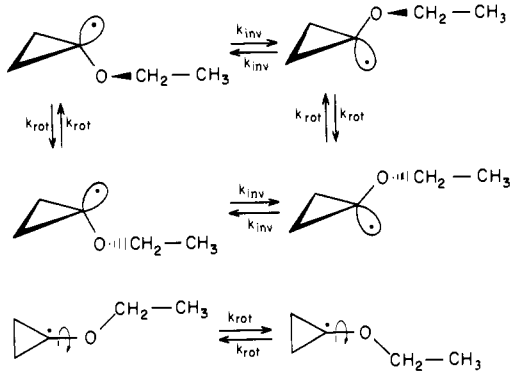
(50) Lien, M. H.; Hopkinson, A. C. *J. Comput. Chem.* **1985**, *6*, 274–281.

(51) Kochi, J. K.; Bakuzis, P.; Krusic, P. J. *J. Am. Chem. Soc.* **1973**, *95*, 1516–1526.

(52) Dupuis, M.; Pacansky, J. *J. Chem. Phys.* **1982**, *76*, 2511–2515.

(53) See, e.g.: Vajda, E.; Tremmel, J.; Rozsondai, B. Hargittai, I.; Maltsev, A. K.; Kagramanov, N. D.; Nefedov, O. M. *J. Am. Chem. Soc.* **1986**, *108*, 4352–4353.

Scheme I



Other Spectral Parameters. The hfs by hydrogens on the 1-substituent (X = CH_3, OCH_3, OC_2H_5) and by the 1-substituent itself (X = Cl, F) serve to confirm the identities of the various radicals. This is also true of the *g* factors that increase as expected along the series X = H, CH_3 < OCH_3, OC_2H_5 < F < Cl.

Inversion of 1-Substituted Cyclopropyl Radicals. The rate constants, k_{inv}, for the inversion of the 1-methylcyclopropyl radical that were obtained by spectral simulation (Table II) have been plotted against $1/T$ in Figure 2. They yield the Arrhenius relationship

$$\log (k_{inv}/s^{-1}) = (13.1 \pm 0.3) - (3.1 \pm 0.2)/2.3RT \text{ kcal/mol}$$

where the errors represent two standard deviations. It is this Arrhenius line that is drawn in the figure. The unique point shown in Figure 2 as an open circle was obtained previously at 344 K by a chemical trapping procedure.[5] Since it lies virtually on the line defined by the EPR spectral data we have confidence in the reliability of each of the two independent techniques we have employed to measure absolute rates for this radical inversion. The slope of this line yields 3.1 kcal/mol as the barrier to inversion, *B*. This value is significantly smaller than the value of 6.1 kcal/mol calculated by Lien and Hopkinson[50] for the 1-methylcyclopropyl radical. The Arrhenius preexponential factor has the expected value (ca. $10^{13.3}$ s^{-1}) for a simple inversion.[54]

The $^{13}C_\alpha$ hfs for cyclopropyl is slightly smaller than that for 1-methylcyclopropyl and therefore the former radical is probably slightly less "bent" on average than the latter.[55] The barrier to cyclopropyl inversion is, however, expected to be significantly lower than the 3.1 kcal/mol found for 1-methylcyclopropyl because of zero-point energy and mass effects. Certainly, the barrier to inversion for cyclopropyl must be appreciably lower than Lien and Hopkinson's[50] estimate of 5.5 kcal/mol, and somewhat lower than other theoretical estimates, viz., *B* = 3.8,[37] 3.2,[51] and 3.0 kcal/mol.[52] Of course, these calculated *B* values refer to the "classical" barrier to cyclopropyl inversion. As we[5] and others[56] have pointed out, quantum-mechanical tunneling must play a very important role in the inversion of cyclopropyl, and it is for this reason that it is difficult to "freeze" the cyclopropyl inversion on the EPR time scale.

For 1-ethoxycyclopropyl (and 1-methoxycyclopropyl) it is necessary to decide whether the motion that can be "unfrozen" is inversion (rate constants, k_{inv}, barrier height, *B*) or rotation about the C–O bond (rate constant, k_{rot}, barrier height, *R*, see Scheme I). Since the a^H(syn)/a^H(anti) ratios for the "unfrozen" 1-alkoxycyclopropyls lie between the values found for the "frozen" 1-methylcyclopropyl and 1-chlorocyclopropyl radicals (see Table I), we presume that it is rotation that can be unfrozen at high temperatures. Spectral simulation for the 1-ethoxycyclopropyl radical yields the Arrhenius equation

$$\log (k_{rot}/s^{-1}) = (12.5 \pm 0.2) - (5.8 \pm 0.2)/2.3RT \text{ kcal/mol}$$

The barrier to ethoxy group rotation, *R*, of 5.8 kcal/mol is comparable to the rotation barriers found in related alkoxyalkyl radicals, e.g., $HOCH_2^\bullet$, 4.6 kcal/mol;[57] $CH_3OCH_2^\bullet$, 5.3 kcal/mol;[57,58] $CH_3CH_2OCH_2^\bullet$, 5.7 kcal/mol.[58] Certainly this barrier is appreciably below the 15.0 kcal/mol calculated for the inversion of 1-hydroxycyclopropyl.[50] From the absence of detectable line broadening attributable to inversion at the highest attainable temperature (277 K) we estimate that $B \geq 9.0$ kcal/mol for the 1-ethoxycyclopropyl radical.

Walborsky and Collins[59] have used a chemical trapping method to show that the inversion barrier for 1-chloro-2,2-diphenylcyclopropyl is almost certainly smaller than that for 1-methoxy-2,2-diphenylcyclopropyl and that it is considerably smaller than that for 1-fluoro-2,2-diphenylcyclopropyl.[60,61] They conclude that the increase in barrier height along the series Cl < CH_3O < F follows the predictions of the Pauling[29]–Walsh[30] model, i.e., the barrier increases with the electronegativity of the substituent. Unfortunately, as Walborsky and Collins[59] are careful to point out, their results *could be* interpreted as indicating differences in the rates of trapping of their 1-substituted cyclopropyl radicals. Although this is rather unlikely,[59] our somewhat unexpected failure to measure the inversion barrier for 1-chlorocyclopropyl by EPR (we estimate that $B \geq 5.3$ kcal/mol from the absence of line broadening at 143 K) means that final confirmation of Walborsky and Collins' results and conclusions will have to wait on chemical trapping/absolute rate measurement experiments of the type we previously employed.[5] Until this has been done, no detailed analyses of the effect of 1-substituents on *B* and on $^{13}C_\alpha$ hfs would appear to be worthwhile.

Experimental Section

EPR Spectroscopic Measurements. Spectra were recorded on a Varian E 104 EPR spectrometer. Radicals were generated by UV photolysis with a 1000-W mercury–xenon lamp of samples containing the appropriate cyclopropyl bromide, triethylsilane, and di-*tert*-butyl peroxide in cyclopropane or ethane as solvent. For the calculation of *g* values the magnetic field was calibrated with the tetracene radical cation.

Synthetic Procedures. General. Yields refer to isolated pure compounds. ^1H NMR spectra were recorded on a Varian EM 360A, 60-MHz instrument. The GC and GC/MS analyses were carried out on a Hewlett Packard 5995 instrument with an HP-Ultra I fused silica capillary column (10 m × 0.2 mm i.d., OV-101 type, cross-linked, bonded phase). Certain samples were purified on a Varian 920 Preparative GC equipped with a 10 ft × $^3/_8$ in. column (Al, 5% OV 101 on chromosorb P, AW DMCS 45–60 mesh). A short-path (minimum hold-up) apparatus equipped with a 13-cm Vigreaux column was used for fractional distillations.

Methylenecyclopropane was obtained from Fluka. Ethyl 3-chloropropionate, methyl 3-bromopropionate, ethylenechlorohydrin, cyclopropanecarboxylic acid chloride, chlorotrimethylsilane, and *N*-chlorosuccinimide were obtained from Aldrich and sodium cyanide-^{13}C (99 atom % ^{13}C) from MSD Isotopes.

1-Bromo-1-methylcyclopropane. Following the general procedure described by Anderson[63] methylenecyclopropane (5 mL, 64.8 mmol) was dissolved in ahydrous ether (35 mL), cooled to −70 °C, and treated with cooled HBr (6.5 mL, 222 mmol). The reaction mixture was warmed slowly to room temperature and allowed to stand at this temperature for 1 h. It was then poured into an excess $NaHCO_3$ solution containing ice,

(54) This provides a second reason for believing that inversion and methyl rotation are not coupled.

(55) If θ were the same for cyclopropyl and 1-methylcyclopropyl the latter radical might be expected to have only a very slightly lower $^{13}C_\alpha$ hfs because of electron delocalization into the methyl group. See: Griller, D.; Marriott, P. R.; Preston, K. F. *J. Chem. Phys.* **1979**, *71*, 3703–3707.

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

(57) Krusic, P. J.; Meakin, P.; Jesson, J. P. *J. Phys. Chem.* **1971**, *75*, 3438–3453.

(58) Biddles, I.; Hudson, A.; Whiffen, J. T. *Tetrahedron* **1972**, *28*, 867–874.

(59) Walborsky, H. M.; Collins, P. C. *J. Org. Chem.* **1976**, *41*, 940–946.

(60) MNDO calculated barriers of 4.6 kcal/mol for the inversion of 1-chlorocyclopropyl[32] and 5.9 kcal/mol for the inversion of 1-fluorocyclopropyl[32] would both appear to be too low.

(61) The 2,2-dichloro-3-methyl-1-methoxycyclopropyl radical has also been shown to be configurationally less stable than the 2,2-dichloro-3-methyl-1-fluorocyclopropyl radical.[62]

(62) Ando, T.; Ishihara, T.; Yamashita, A.; Matsumoto, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3873–3874.

(63) Anderson, B. C. *J. Org. Chem.* **1962**, *27*, 2720–2724.

extracted with ether (×3), dried over Na_2SO_4, and fractionally distilled to yield 5.0 g of low-purity (76% by GC analysis) 1-bromo-1-methylcyclopropane (bp 78–80 °C (lit.[63] bp 72–85 °C)). Further purification by preparative GC gave 1.89 g (20.9% yield) of material with 99.98% purity. ^{1}H NMR: Me_2SO, $(CH_3)_4Si$ (int), δ 0.75–1.1 (m, 4 H, ring *H*), 1.7 (s, 3 H, C–C*H*$_3$). MS: *m/e* (relative intensity) 55 (100), 134 (3.22, M^+, ^{79}Br), 136 (3.10, M^+, ^{81}Br).

1-Bromo-1-ethoxycyclopropane. Ethyl 3-chloropropionate (6.83 g, 50 mmol) and sodium (2.3 g, 100 mmol) in diethyl ether (Bouveault–Blanc condensation) in the presence of trimethylchlorosilane (5.43 g, 50 mmol) gave on distillation 1-ethoxy-1-(trimethylsilyloxy)cyclopropane[64] (1.15 g, 6.6 mmol, 13.2% yield). The last named compound was reacted with PBr_3 as described by Gadwood[65] to give 1-bromo-1-ethoxycyclopropane. Preparative GC of this compound gave 0.55 g (6.7% yield based on ethyl 3-chloropropionate) of material with 90.2% purity. ^{1}H NMR: $CDCl_3$, $(CH_3)_4Si$ (int), δ 1.15 (m, 7 H, ring *H* and CH_2CH_3), 3.60 (q, 2 H, OCH_2CH_3, J = 7 Hz) in agreement with the literature.[65] MS: *m/e* (relative intensity) 57 (100), 164 (15.7, M^+, ^{79}Br), 166 (15.5, M^+, ^{81}Br).

1-Bromo-1-methoxycyclopropane. This compound was prepared from methyl 3-bromopropionate following the procedure outlined above for the ethoxy derivative.[64,65] Preparative GC gave 1-bromomethoxycyclopropane (0.5 g, 10% yield based on starting methyl 3-bromopropionate) with 97.0% purity. ^{1}H NMR: $CDCl_3$, $(CH_3)_4Si$ (int), δ 1.3 (s, 4 H, ring *H*), 3.4 (s, 3 H, OCH_3). MS: *m/e* (relative intensity) 41 (100), 150 (13.6, M^+, ^{79}Br), 152 (13.6, M^+, ^{81}Br).

(1-^{13}C)-1-Bromo-1-ethoxycyclopropane. Reaction of $Na^{13}CN$ with ethylenechlorohydrin by a literature procedure[66] gave ethylenecyanohydrin-^{13}*C* which was then hydrolyzed with concentrated HCl[67] to form (1-^{13}C)-3-chloropropionic acid. This acid was esterified in refluxing ethanol with *p*-toluenesulfonic acid as catalyst. The resultant (1-^{13}C)-3-chloropropionate was converted[64,65] as described above to (1-^{13}C)-1-bromo-1-ethoxycyclopropane. Preparative GC gave a product (0.1 g, 6.6% yield based on ethylenechlorohydrin) with 89.5% purity. ^{1}H NMR: $CDCl_3$, $(CH_3)_4Si$ (int), δ 1.1 (m, 7 H, ring *H* and CH_2CH_3), 3.6 (m, 2 H, $^{13}COCH_2CH_3$). MS: *m/e* (relative intensity) 58 (100), 165 (12.0), 167 (11.2).

1-Bromo-1-chlorocyclopropane. Cyclopropanecarboxylic acid chloride (57 g, 548 mmol) was treated at 135 °C (oil bath) for 1.5 h with *N*-chlorosuccinimide (144 g, 1082 mmol). 1-Chlorocyclopropane-1-carboxylic acid chloride was formed in 14% yield (7.9 g, GC analysis). Since trial experiments had shown that reaction for a longer time gave only over-chlorinated products, the crude reaction mixture was fractionally distilled (32–34 °C (10 mmHg)) to obtain 53.5 g of a mixture containing 10% (GC analysis) 1-chlorocyclopropane-1-carboxylic acid chloride and 90% cyclopropanecarboxylic acid chloride. This mixture was cooled to 0 °C and then treated dropwise with cooled (0 °C) acetone (136 mL). This was followed by the dropwise addition of a solution containing 98 g (1166 mmol) of $NaHCO_3$ in 700 mL of water, the internal temperature of the reactants being maintained at <7 °C. The solutiuon was cooled to 0 °C, and concentrated HCl (90 mL) was added dropwise (internal temperature <5 °C). Extraction with CH_2Cl_2 (3 × 300 mL), drying over Na_2SO_4, and removal of solvent at 25 °C gave 38 g of a colorless liquid containing (GC analysis) 10% 1-chlorocyclopropanecarboxylic acid and 90% cyclopropanecarboxylic acid. Fractional distillation gave 3.6 g of 76% pure 1-chlorocyclopropane-1-carboxylic acid: bp 102–104 °C (10 mm Hg), mp 70–72 °C (lit.[68] bp 206 °C (760 mmHg), mp 70–71 °C); yield 6.3% (based on cyclopropanecarboxylic acid chloride). MS: *m/e* (relative intensity) 85 (100), 120 (72.5, M^+, ^{35}Cl), 122 (23.7 M^+, ^{37}Cl). This material (3.6 g, 30 mmol) was dissolved in $CHBr_3$ (36 mL) and treated with HgO (6.4 g, 30 mmol) with stirring at room temperature for 1 min and cooled to 0 °C, and Br_2 (6.1 g, 38 mmol) was added dropwise maintaining the internal temperature <12 °C. The yellow reaction mixture was then allowed to warm to room temperature, and stirring was continued for a further 16 h. The now colorless reaction mixture was suction filtered, and the filtrate was fractionally distilled to give 1-bromo-1-chlorocyclopropane (1.8 g, 76% purity, bp 25 °C (50 mmHg)). Preparative GC gave 0.58 g (0.68% yield based on cyclopropanecarboxylic acid) of this compound with 99.3% purity. ^{1}H NMR: $CDCl_3$, $(CH_3)_4Si$ (int), δ 1.44 (s, 4 H, ring *H*). MS: *m/e* (relative intensity) 75 (100), 154 (6.9, M^+, ^{35}Cl, ^{79}Br), 156 (9.5, $(M + 2)^+$).

Registry No. 1-Bromo-1-methylcyclopropane, 50915-27-0; 1-bromo-1-ethoxycyclopropane, 95631-62-2; 1-bromo-1-methoxycyclopropane, 72282-90-7; 1-bromo-1-chlorocyclopropane, 108817-33-0; (1-^{13}C)-1-bromo-1-ethoxycyclopropane, 108817-34-1; methylenecyclopropane, 6142-73-0; ethyl 3-chloropropionate, 623-71-2; chlorotrimethylsilane, 75-77-4; 1-ethoxy-1-(trimethylsiloxy)cyclopropane, 27374-25-0; methyl 3-bromopropionate, 3395-91-3; cyclopropanecarbonyl chloride, 4023-34-1; 1-chlorocyclopropanecarbonyl chloride, 73492-25-8; 1-chlorocyclopropanecarboxylic acid, 108817-35-2; 1-methylcyclopropyl radical, 65338-31-0; 1-methoxycyclopropyl radical, 108817-36-3; 1-ethoxycyclopropyl radical, 108834-54-4; 1-chlorocyclopropyl radical, 33272-69-4; 1-methylcyclopropane, 594-11-6; 1-ethoxycyclopropane, 5614-38-0; cyclopropyltrimethylsilane, 930-40-5.

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Mechanistic Diagnosis of Aminium Salt Initiated Diels–Alder Cycloadditions in the Diene/Diene Format

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Abstract: The aminium salt catalyzed Diels–Alder reaction has been subjected to mechanistic scrutiny. Eight discrete reaction systems in the diene/diene Diels–Alder format, including both dimerizations and cross additions, and also one cyclobutanation reaction, have been examined on the basis of as many as five distinct mechanistic criteria. The previously proposed cation radical chain mechanism is specifically confirmed and, among others, a Brønsted acid catalyzed mechanism ruled out in every instance except one. As previously proposed by another laboratory, the cyclodimerization of 2,4-dimethyl-1,3-pentadiene is found to proceed via a Brønsted acid catalyzed mechanism. These results support and further broaden similar conclusions based upon detailed kinetic studies on two cycloaddition systems, previously reported by this laboratory. Experimental procedures for performing these reactions and isolating and characterizing the cycloadducts are also reported.

Aminium salt initiation has been found to represent a powerful and highly stereoselective protocol for Diels–Alder[1–3] and other[4,5] cycloadditions and cyclodimerizations of ionizable substrates. The cation radical chain mechanism invoked for these reactions

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