Table III. Downfield Shifts of ^{1}H NMR Absorptions of Polyethers in the Presence of Diethylmagnesium in Diethyl Ether

polyether	downfield shift, 10^2 ppm: polyether alone[a]	polyether in presence of 15-C-5[b]	15-C-5 in presence of polyether[b]
15-crown-5	12.3		
12-crown-4	4.0	0.5	11.8
4	18.0[c]	10.3[c]	3.5
1	17.8[c]	14.5[c]	3.7

[a] The concentrations of Et_2Mg and polyether were 0.17 M. [b] The concentrations of Et_2Mg, polyether, and 15-crown-5 were 0.17 M. [c] This is the shift of a broad singlet due to the methylene hydrogens.

then the unique action of 15-crown-5 must reside in its being considerably more able than the other polyethers to coordinate to Mg^{2+} or to $EtMg^+$. On the basis of two suggestive but inconclusive pieces of evidence, we favor eq 3. First, a recent study has shown that in acetone, 15-crown-5 is better able than acyclic polyethers or other crown ethers to complex the Mg^{2+} of $Mg(SCN)_2$.[14] Second, we observed that in pyridine, the equilibrium shown in eq 5 lies to the right.[15] The ^{1}H NMR spectrum of the

$$2(Fl^-EtMg^+\cdot(15\text{-C-}5)) \rightleftarrows (Fl^-)_2Mg^{2+}\cdot(15\text{-C-}5) + Et_2Mg + 15\text{-C-}5 \quad (5)$$

solution prepared from 1:1:1 amounts of fluorene, diethylmagnesium, and 15-crown-5 exhibited an absorption characteristic of diethylmagnesium and two equal absorptions for the crown ether, one of which is characteristic of uncomplexed crown ether. By contrast, the equilibrium was to the left when the polyether was 18-crown-6 or **1**.

An "ate" species such as Et_3Mg^- would reasonably react more rapidly than Et_2Mg in reactions in which some kinds of mechanistic steps are rate determining. By comparison to Et_2Mg, for example, the alkyl groups of Et_3Mg^- should be more basic and nucleophilic, and Et_3Mg^- should be a better electron-transfer agent.[16,17] Analysis of the kinetics of addition of diethylmagnesium to pyridine assisted by 15-crown-5 is more difficult, and we do not know if the rate law is similar to that observed for fluorene metalation.

Acknowledgment. We are grateful to the National Science Foundation for support of this research and for aiding in the purchase of the NMR spectrometers that were used. We thank B. J. Wakefield for a helpful discussion.

Registry No. 1, 112-49-2; **4**, 143-24-8; fluorene, 86-73-7; pyridine, 110-86-1; 15-crown-5, 33100-27-5; 12-crown-4, 294-93-9; Et_2Mg, 557-18-6.

(13) A species that formally contains $(Li^+)_2Ph_6Mg_2^{2-}$ has been prepared, but its crystal structure shows Mg-Ph-Li bridge bonding: Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3726. Species with the composition R_3MgM where M is a group 1A metal have been prepared but not structurally characterized: Seitz, L. M.; Brown, T. L. *J. Am. Chem. Soc.* **1967**, *89*, 1602. Malpass, D. B.; Eastham, J. F. *J. Org. Chem.* **1973**, *38*, 3718. A species that formally contains $(Li^+)_2Me_4Mg^{2-}$ has been isolated, but its crystal structure shows Mg-Me-Li bridge bonding: Greiser, T.; Kopf, J.; Weiss, E. *Chem. Ber.* **1981**, *114*, 209.

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(16) Electron transfer from an organomagnesium compound to the substrate has been suggested as a step in the metalation of some hydrocarbons: Shirley, D. A.; Hendrix, J. P. *J. Organomet. Chem.* **1968**, *11*, 217. However, also see: Shirley, D. A.; Harmon, T. E.; Cheng, D. F. *Ibid.* **1974**, *69*, 237.

(17) Formation of 4-alkylpyridines rather than of 2-alkylpyridines predominates in reaction of an alkyl halide, magnesium, and pyridine.[18,19] The pyridine radical anion has been suggested[18] to be an intermediate in these reactions. It is interesting that large amounts of 4-alkylpyridines are formed in reactions of pyridine with allylmagnesium bromide [Gilman, H.; Eisch, J.; Soddy, T. *J. Am. Chem. Soc.* **1957**, *79*, 1245] or benzylmagnesium compounds [Benkeser, R. A.; Holton, D. S. *Ibid.* **1951**, *73*, 5861].

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On Cyclopropenyl, Dimethylcyclopropenyl, and Trimethylcyclopropenyl Radicals[1]

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The cyclopropenyl radical[4] has been the subject of considerable theoretical interest.[5-10] In 1974 an EPR spectrum, which was attributed to the cyclopropenyl radical, was obtained by photolysis of di-*tert*-butyl peroxide and cyclopropene.[11] The spectral parameters (viz.,[11] at 163 K, $g = 2.0061$, four broad lines, $\Delta H_{pp} \approx 7.5$ G, assigned to three equivalent hydrogen atoms, $a^H = 13.5$ G) have generally[9,12,13] been regarded with some scepticism. We now report that this spectrum is actually a poorly resolved spectrum of the known 1-chloroallyl radical.[14,15] It is readily obtained when unpurified cyclopropene prepared by the method of Closs and Krantz[16] is photolyzed with di-*tert*-butyl peroxide. This radical is formed by H atom abstraction from allyl chloride,[15] which, being the reagent used to prepare cyclopropene,[16] is generally a contaminant. Purification of cyclopropene by VPC produced, in our hands, some isomerization to methyl acetylene, and on photolysis with di-*tert*-butyl peroxide, the known propargyl radical[17] was obtained. Incompletely purified cyclopropene gave a spectrum having $g = 2.0032$, $a^H = 60.0$ G (1 H, $\partial a^H/\partial T = -0.036$ G K^{-1}), 22.0 G (2 H), 1.0 G (1 H) at 153 K, which we could not identify. Cyclopropene, which had been carefully purified by trap-to-trap distillation (<0.3% allyl chloride) did not give an EPR spectrum in a similar experiment.

We also attempted to prepare 3-chlorocyclopropene in order to try to generate the cyclopropenyl radical by a chlorine abstraction reaction. The reported synthesis[18] involves the reaction of tetrachlorocyclopropene with tri-*n*-butyltin hydride. By making use of preparative VPC, we were eventually able to obtain pure trichlorocyclopropene (1,2,3- to 1,3,3- in a 1:9 ratio) and pure dichlorocylcopropene (1,3- to 3,3- in a 1:1 ratio) both of which yielded some interesting radicals.[19] However, we were quite unable to obtain 3-chlorocyclopropene even when starting with the purified dichloro compound.

Although our attempts to generate an authentic spectrum of cyclopropenyl were unsuccessful, it is certain that the spectrum previously reported is not due to the cyclopropenyl radical.

We were also unsuccessful in our attempts to generate a me-

(1) Issued as NRCC No. 20510.
(2) NRCC research associate 1979-1981.
(3) NRCC visiting scientist, 1981.
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(18) Breslow, R.; Ryan, G.; Groves, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 988-993.
(19) Photolysis at low temperatures in cyclopropane of the following: C_3Cl_4, alone, no radicals; with *t*-BuOO-*t*-Bu, cyclopropyl (from solvent); with *t*-BuOO-*t*-Bu + Me_3SiH, a radical with $g = 2.0053$, $a = 25.7$ G (1 ^{35}Cl), 21.2 G (1 ^{37}Cl) at 169 K; C_3HCl_3, alone, no radicals; with *t*-BuOO-*t*-Bu, a radical with $g = 2.0017$, $a = 4.8$ G (1 ^{35}Cl), 4.0 G (1 ^{37}Cl) at 173 K; with *t*-BuOO-*t*-Bu + Me_3SiH, a radical with $g = 2.0011$, $a = 5.0$ G (1 ^{35}Cl), 4.1 G (1 ^{37}Cl) at 150 K; $C_3H_2Cl_2$, no radicals under any of these conditions.

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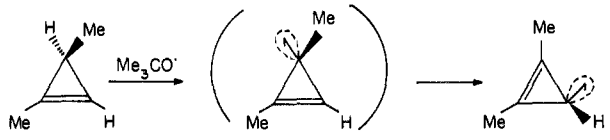
thylcyclopropenyl radical. Photolysis at 138 K with di-*tert*-butyl peroxide of trap-to-trap distilled 1-methylcyclopropene[20] and 3-methylcyclopropene[21] gave radicals having $g = 2.0028$, $a^H = 59.5$ G ($\partial a^H/\partial T = -0.033$ G K^{-1}), 22.0 G (2 H), and $g = 2.0030$, $a^H = 61.3$ G (1 H, $\partial a^H/\partial T = -0.040$ G K^{-1}), 22.0 G (2 H), 1.0 G (1 H), respectively, which could not be identified. In both cases, incompletely purified materials gave the corresponding methyl-substituted chloroallyl radicals.

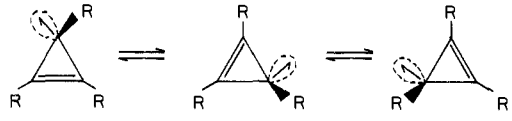
The work outlined above was initiated after we succeeded in identifying an "impurity" radical that had been observed[22] during the photolysis of 3-methylcyclobutene and di-*tert*-butyl peroxide in cyclopropane at low temperatures. This radical, which has $g = 2.0028$, $a^H = 37.0$ G (1 H), 3.25 G (6 H), $\Delta H_{pp} = 0.4$ G, invariant with temperature in the range 123–173 K, is the 2,3-dimethylcyclopropen-1-yl radical, **2**. It can be readily produced by photolysis of pure 1,3-dimethylcyclopropene[23] and di-*tert*-butyl peroxide.[24]



1 2

The large magnitude of a^H for the Hα of **2** implies a *positive* sign and indicates that the C–H$_\alpha$ bond is bent much further out of the cyclopropene plane than the cyclopropyl radical's C–H$_\alpha$ bond is bent out of the cyclopropane ring. (For the latter radical $a^H_\alpha = 6.6$ G and the out-of-plane angle is 30–35°.)[26] It is clear that **2** is a σ radical like the tri-*tert*-butylcyclopropenyl radical, **3**.[13,27] There must be a substantial preference for the secondary alkyl radical structure, **2**, since there was no sign of the tertiary alkyl radical, **1**.[28] This conformational preference may be due to the greater thermodynamic stability of alkyl substituted C=C double bonds[29] and/or to the bending at the radical center being sufficient to produce a steric repulsion between the α-Me group and the cyclopropene ring in **1**, which is relieved by an isomerization to **2**. Indeed relief of strain could provide a driving force for the H atom abstraction.[24]

At the temperature at which it was generated (328 K), radical **3** exists as three rapidly equilibrating and energetically equivalent



3, R = Me$_3$C 4, R = Me

σ radicals.[13] For trimethylcyclopropenyl, **4**, we thought that it might be possible to freeze out a similar equilibrium. In the event, photolysis of di-*tert*-butyl peroxide and 1,2,3-trimethylcyclopropene in cyclopropane at 240 K gave an equilibrating mixture of the three equivalent σ radicals, **4**, $g = 2.0026$, $a^H = 6.0$ G (9 H), $\Delta H_{pp} = 0.4$ G, while at 113 K (in propane) a localized σ radical is obtained with the same g value and $a^H = 3.0$ G (6 H), 11.9 G (3 H) (see Figure 1).[30] At this low temperature the center lines due to the quartet from the unique CH_3 group have less than their expected intensity relative to the outer lines (3:1), while at 104 K the spectrum shows that these three hydrogens yield a quartet of lines of approximately equal intensity with the central lines noticeably broadened. Rotation of the α-methyl group must therefore be restricted at low temperatures, a phenomenon that has been observed previously in other nonplanar, α-methyl-substituted carbon radicals.[31]

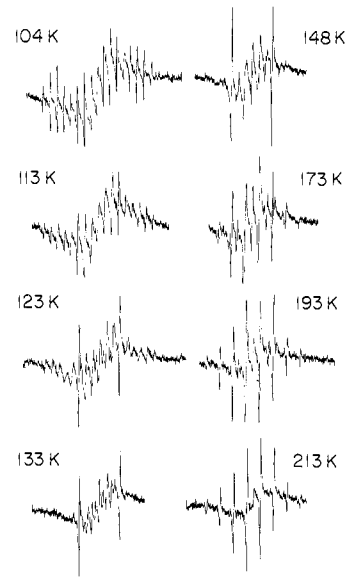


Figure 1. Experimental EPR spectra for the trimethylcyclopropenyl radical in cyclopropane or propane at different temperatures.

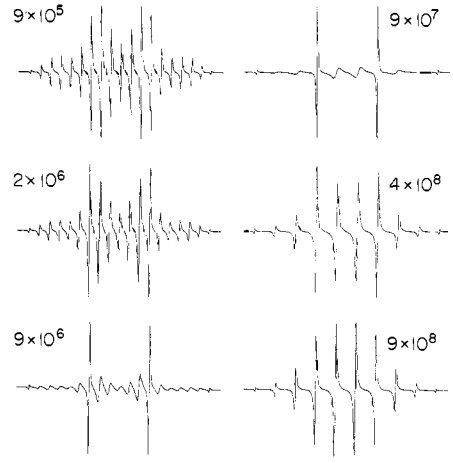


Figure 2. Some simulated EPR spectra for the trimethylcyclopropenyl radical using $a^H = 3.0$ G (6 H), 12.0 G (3 H), $\Delta H_{pp} = 0.25$ G, and a three-jump exchange process. Rate constants for exchange are given in s^{-1} units.

Since the spectral parameters for the α-Me and two β-methyl groups at the slow exchange limit are known, an attempt was made to simulate spectra at intermediate and high temperatures with a three-jump exchange process with interchange of the three sets of CH_3 group hyperfine splittings using QCPE program 209.[32] The spectrum at 213 K and the most characteristic feature at intermediate temperatures, i.e., the broadening of all but two of the visible[33] lines in the spectrum could be reproduced (see Figure

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(29) Whangbo, M. H.; Stewart, K. R. *J. Org. Chem.* **1982**, *47*, 736–738 and references cited.
(30) After submission of this manufscript a matrix EPR spectrum of a trimethylcyclopropenyl radical was reported which had $a^H = 3.5$ G (6 H), 12.5 G (3 H) at 120 K; see: Closs, G. L.; Evanochko, W. T.; Norris, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 350–352.
(31) Gaze, C.; Gilbert, B. C. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1161–1168.
(32) Heinzer, J. Quantum Chemistry Program Exchange, Indiana University, Program 209.
(33) The intensities of the two outermost lines were too low for them to be observed experimentally.

2). However, extensive effort failed to yield a precise simulation of the observed spectral pattern in the 17-G "gap" between the two sharp lines. We are inclined to attribute this failure, which is not unique,[34] to the influence of a slightly restricted rotation of the α-methyl group at all temperatures below 213 K, the QCPE program being unable to deal with intermediate exchange rates for two separate motions. Although the possibility that an "impurity" radical produces some of these sharp "extra" lines cannot be entirely ruled out, it seems improbable since extra lines do not appear to be present at high or low temperatures.

In summary, a great deal of labor has yielded EPR spectra for only two cyclopropenyl radicals, the 2,3-dimethyl- and the trimethylcyclopropenyls. The parent cyclopropenyl radical remains as elusive as ever.

Acknowledgment. We are deeply indebted to an anonymous referee for some very helpful comments on the work described above.

Registry No. 2, 82246-53-5; **3**, 60528-80-5; **4**, 60528-77-0; 1-chloroallyl radical, 40905-10-0; cyclopropene, 2781-85-3; 1,3-dimethylcyclopropene, 82190-83-8; 1,2,3-trimethylcyclopropene, 34785-53-0.

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Origin of Oxonitine: A Potassium Permanganate Oxidation Product of Aconitine

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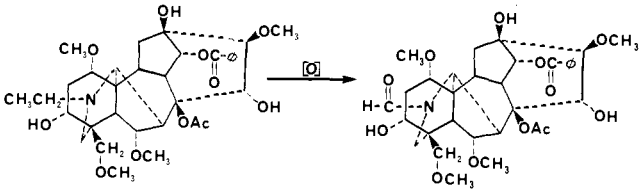
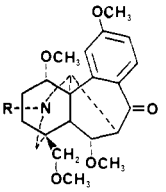
Since Carr's report in 1912,[1] oxonitine, one of the permanganate oxidation products of aconitine (**1**), has been repeatedly studied,



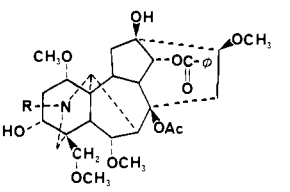
Aconitine (1) Oxonitine (2)

and various proposals have been suggested for its molecular formula, chemical structure, and origin.[2-4] Thus the molecular formulas $C_{32}H_{41}NO_{12}$,[3] $C_{33}H_{43}NO_{12}$,[4] and $C_{34}H_{45}NO_{12}$[2] have been suggested for oxonitine. Though oxonitine is known to possess an amide group and to lack the *N*-ethyl group,[5] there has been little agreement as to its mode of formation from aconitine. Several investigators have favored a lactam-type structure.[6-10] The problem is rendered difficult by the highly insoluble, polyfunctional nature of oxonitine.

In 1960, Jacobs and Pelletier,[11] as well as Turner and coworkers,[12] independently demonstrated that purified oxonitine, mp 285-292 °C, contains an *N*-formyl group instead of the earlier suggested *N*-acetyl group. Turner's group[12] also concluded on the basis of oxidation of labeled aconitine ($N-^{14}CH_2CH_3$) that the formyl group of oxonitine (**2**) is not derived from the *N*-ethyl group of aconitine. In 1971, Wiesner and Jay[13] reported that the mass and proton NMR spectra of the *N*-acyl aromatization product **3** prepared from oxonitine proved it to be a mixture of



3 R=Mixture of -CHO and -COCH$_3$



4 R=CH$_3$ Mesaconitine

5 R=H N-Desethylaconitine

6 R=CH$_2$OH

the *N*-formyl and *N*-acetyl derivatives. They suggested that since aconitine (**1**) is known to contain varying amounts of mesaconitine as an impurity, the differing *N*-acyl groups result from oxidation of the *N*-methyl group of mesaconitine (**4**) and the *N*-ethyl group of aconitine (**1**). In this communication, we report our results on the origin of the *N*-formyl group of oxonitine and establish the mechanism for its formation.

Oxidation of pure aconitine,[14] mp 196-203 °C, with $KMnO_4$ in acetone and acetic acid for 5 h at 25 °C afforded oxonitine, mp 281-282 °C, $[\alpha]^{20}_D$ -48.5° (*C* 0.4, $CHCl_3$) in 20-25% yield.[15] When a similar oxidation was carried out with 5% methanol in acetone, the yield of oxonitine was increased to 45-65%. Spectral data including ^{13}C NMR analysis[16] revealed that oxonitine contains the *N*-formyl group but no *N*-acetyl group, confirming the earlier proposed structure **2** for oxonitine.[11,12] Mesaconitine (**4**),[17] mp 200-207 °C, was resistant to oxidation when it was treated with $KMnO_4$ in acetone and acetic acid or 5% methanol in acetone and acetic acid, at 25 °C for 5 h. However, when this reaction was performed at 50 °C for 48 h, mesaconitine afforded crude oxonitine, mp 267-269 °C, in 75% yield. These results demonstrate that mesaconitine is resistant to oxidation under conditions that oxidize aconitine to oxonitine and that oxidation of aconitine with $KMnO_4$ affords oxonitine *in the absence of any mesaconitine impurity*. Thus, the previous explanations about the origin of oxonitine are not valid. Our results reveal that the source of the *N*-formyl group of oxonitine must be solvents (e.g., acetone, methanol, or acetic acid) used during oxidation or the *N*-ethyl group of aconitine.

In 1964, Marion and co-workers[18] reported the formation of *N*-desethylaconitine (**5**) as a major product by treatment of aconitine with $KMnO_4$ in aqueous acetone for 10 min. In our hands, treatment of aconitine with $KMnO_4$ under these conditions afforded *N*-desethylaconitine (**5**): mp 180-182 °C; ^1H NMR ($CDCl_3$) δ 1.36 (3 H, s, CH_3CO), 3.23, 3.35, 3.37, and 3.76 (each

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(13) Wiesner, K.; Jay, L. *Experientia* **1971**, *27*, 758.

(14) The purity of aconitine was checked by TLC and ^1H and ^{13}C NMR spectra. It contained no detectable amount of mesaconitine. Aconitine and mesaconitine can be separated easily on alumina TLC using 2% methanol in ether.

(15) Earlier investigators were unable to get consistent yields of oxonitine. During several experiments we also observed that oxonitine is formed in erratic yields. We have, therefore, reported yields as a range. Formation of oxonitine depends on the pH of the reaction mixture, the rate of addition of oxidant, and concentration. Oxonitine is usually accompanied by a certain amount of the *N*-acetyl derivative (**7**) and requires several recrystallizations to free it from this impurity.

(16) The ^{13}C NMR spectrum of oxonitine in $CDCl_3$ with a few drops of CD_3OD revealed the following signals: 172.5, 166.4, 163.7, 133.8, 129.8, 129.8, 128.9, 90.2, 90.2, 83.0, 79.5, 79.5, 78.6, 74.4, 73.3, 68.6, 61.1, 59.1, 58.3, 57.9, 55.6, 51.1, 48.7, 47.5, 43.2, 42.4, 40.5, 38.6, 34.4, 33.9, 21.3 ppm.

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