Our results show that oxidation of carbomultianions offers a valuable method for preparation and characterization of hydrocarbon multiradicals in solution. Even greater in size and higher spin multiplicity hydrocarbon multiradicals can be made more stable by introducing steric hindrance at all para sites. It remains to be seen if such ferromagnetic *microdomains* will lead to ferromagnetic order at $T \gg 4$ K.

Finally, the quintet state for $\mathbf{1}^{4\bullet}$ in conjunction with the uniformly charged triarylmethyl anion fragments in $\mathbf{1}^{4-},4\mathrm{Li}^+$ suggests a relationship between spin multiplicity and electron density distribution.

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The Elusive Methyleneoxirane: Preparation and Characterization by Flash-Vacuum Pyrolysis and Neutralization-Reionization Mass Spectrometry

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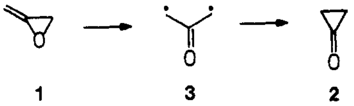
Typifying the interesting chemistry of strained small-ring compounds, e.g., methylenecyclopropane,[1] -cyclopropene,[2] -aziridine,[3] and -thiirane,[4] methyleneoxirane (allene oxide, **1**) was predicted by Hoffmann[5] to isomerize readily to cyclopropanone (**2**) via electrocyclic ring opening involving oxyallyl intermediate **3** (eq 1). While **1** has been studied intensively by theory,[6] it has been elusive in experimental investigations, such as its role in the oxidation of allene[7] (although bulky substituents can make eq 1 observable).[8] Here we report on the first preparation and characterization of $\mathbf{1}^{\bullet+}$ and **1**.



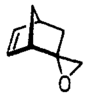
1 **3** **2** (1)

Table I. Collisionally Activated Dissociation (O_2, 50% T[a]) and $^+$NR$^+$ (Hg, 70% T/O_2, 50% T) Mass Spectra[b,c]

	CAD				$^+$NR$^+$			
m/z	$\mathbf{1}^{\bullet+}$	$\mathbf{6}^{\bullet+}$	$\mathbf{7}^{\bullet+}$	$\mathbf{8}^{\bullet+}$	$\mathbf{1}^{\bullet+}$	$\mathbf{6}^{\bullet+}$	$\mathbf{7}^{\bullet+}$	$\mathbf{8}^{\bullet+}$
56					69	100	3	63
55	(11)	(22)	(20)	(233)	3.5	7.5	0.8	100
54	15	12	3	18	4	3	0.2	13
53	15	14	11	15	11	3.5	0.3	12
42	100	3	24	<0.5	22	0.5	4.5	1
41	17	24	11	4	8	8	2.5	6.5
39	22	5.5	4	9.5	5.5	2.5	1.5	15
30	11	<0.5	<0.5	<0.5	5.5	<0.5	<0.5	1.5
29	40	5.5	6	44	23	3	<0.5	57
28	(122)	(87)	(181)	(76)	100	40	100	79
27	69	100	100	100	44	32	24	90
15	<0.5	1.5	<0.5	<0.5	<0.5	0.8	0.6	0.5
14	6.5	2	3.5	1.5	8	1	3	7
$\sum_{\mathrm{ions}}$	560	455	500	625	420	275	235	635

[a] Transmittance. [b] Integrated peak areas. Intensities in parentheses include dissociations of metastable ions. [c] From ionization of the following: $\mathbf{6}^{\bullet+}$, 2,2,5-trimethyl-1,3-dioxane-4,6-dione; $\mathbf{7}^{\bullet+}$, succinnic anhydride; and $\mathbf{8}^{\bullet+}$, acrolein.

In unsuccessful attempts to generate $\mathbf{1}^{\bullet+}$, ionized spiro[norborn-2-ene-5,2'-oxirane][9] (**4**), 1-(phenylsulfinyl)-2,3-epoxypropane, and 5,6-epoxyhexan-2-one[10] yield only $C_5H_6^{\bullet+}$, $PhSOH^{\bullet+}$, and $CH_3C(OH){=}CH_2^{\bullet+}$, respectively. However, the γ-hydrogen rearrangement (eq 2) of ionized glycidol benzoates (**5**) produces $C_3H_4O^{\bullet+}$ (17% abundance for Ar = 4-$NO_2C_6H_4$); its collisionally activated dissociation (CAD) spectrum[11] is strikingly different from those of the isomers $CH_3CH{=}C{=}O^{\bullet+}$ (**6**),[12] $^{\bullet}CH_2CH_2CO^+$ (**7**),[13] and $CH_2{=}CHCH{=}O^{\bullet+}$ (**8**)[13] (Table I). Structure $\mathbf{1}^{\bullet+}$ is supported by the favored formation of its structural subunits $C_2H_2O^{\bullet+}$ (m/z 42), $CH_2O^{\bullet+}$ (m/z 30), and $CH_2^{\bullet+}$ (m/z 14). Its isomerization to $CH_2{=}C^+OCH_2^{\bullet}$ should be quite endothermic,[14]



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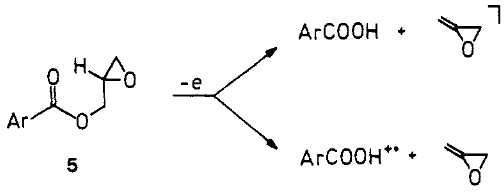

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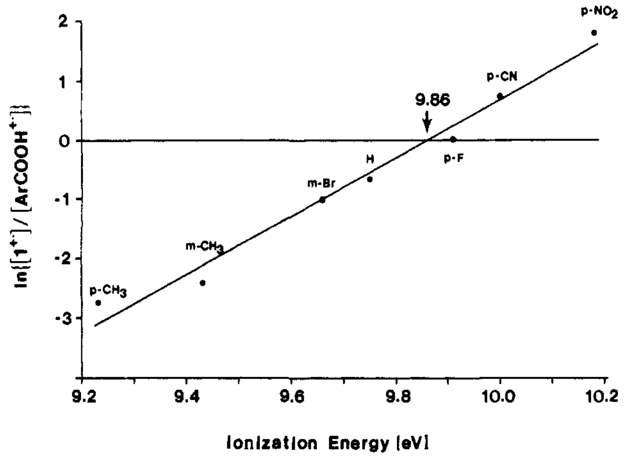

Figure 1. Plot of ln {$[1^{\cdot+}]/[\text{ArCOOH}^{\cdot+}]$} from ionized glycidol benzoates vs IE(ArCOOH).

while isomerization to $2^{\cdot+}$ or $3^{\cdot+}$ is inconsistent with the predominant loss of CH_2 (84%; CHD, 3%; CD_2, 13%) from methylene-d_2-oxirane$^{\cdot+}$ (1-$d_2^{\cdot+}$).[17]

Neutralization of the mass-analyzed beam of $C_3H_4O^{\cdot+}$ yields a beam of fast neutrals; their reionization ~10^{-6} s later produces the $^+$NR$^+$ mass spectra[11,18] of Table I. For $1^{\cdot+}$, 16% of the products are undissociated, reflecting relatively high stabilities (especially versus 7) for both the neutral and the reionized species. It is conceivable that this results from rearrangement of the newly formed 1 neutrals to a more stable isomer; however, no low-energy isomer[19] appears to be logical. The $^+$NR$^+$ spectrum of $8^{\cdot+}$ shows H loss 30× that of $1^{\cdot+}$. For $6^{\cdot+}$, CAD (He, 30% transmittance) of its neutrals ~10^{-6} s after formation, followed by reionization,[11,18e] doubles the abundance of *m/z* 28 with little effect on *m/z* 53, while the same CAD of neutrals from $1^{\cdot+}$ doubles *m/z* 53 without affecting *m/z* 28. Further, the $^+$NR$^+$ spectrum of $1^{\cdot+}$ is similar to that from CAD (favored *m/z* 42, 30, 14), with 1-d_2 losses of 79% CH_2, 1% CHD, and 20% CD_2 inconsistent with isomerization to 2 or 3. Thus these products appear to arise mainly from dissociation, after reionization, of the long-lived methyleneoxirane (1).

An independent effort to generate 1 utilized flash-vacuum pyrolysis mass spectrometry.[20] Pyrolysis of 1-(phenylsulfinyl)-2,3-epoxypropane (500–650 °C) and of glycidol acetate and trifluoroacetate (750–850 °C) afforded no C_3H_4O. However, pyrolysis of 4 (800 °C) gave C_3H_4O (~1% yield) of ionization energy (IE, inverse convolution method)[21] 9.81 ± 0.05 eV. Using an independent method,[2c] we find that the log plot of the relative intensities of $\text{ArCOOH}^{\cdot+}$ and $1^{\cdot+}$ from esters 5 against IE(ArCOOH)[22] (Figure 1) is linear (correlation coefficient, 0.990) with the intercept at 9.86 eV. These values are further supported by $-\epsilon_{\text{HOMO}}$ from MNDO[23] (9.85 eV) and ab initio[16] (9.70 eV) calculations and differ substantially from those reported for isomers.[24] The high ionization energy of 1 versus linear enol ethers[24] is likely due to Coulombic factors imposed by the hybridization of the ring σ-bond framework.[25]

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Ab Initio Bond Strengths in Ethylene and Acetylene

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Accurate determinations of bond dissociation energies (BDEs) are essential for quantifying the thermodynamics of chemical reactions. The sequential C–H and C–C bond strengths in simple unsaturated hydrocarbons are very poorly known.[1] For instance, even measurements of the first C–H BDEs in ethylene and acetylene are still controversial: reports of $D_0(H_2CCH{-}H)$ range in value from 100 to 116.7 ± 1.2 kcal/mol,[1-7] while $D_0(HCC{-}H)$ ranges from <126.647 ± 0.002 to 132 ± 5 kcal/mol.[8-12] Further, dramatic differences in estimated[3] strengths of the four C–H bonds in C_2H_4 require a theoretical explanation.

Recently, Ervin et al. measured the gas-phase acidities of HCCH, C_2H_4, and C_2H_3 radical and electron affinities of C_2H, C_2H_3, and H_2CC in order to derive $D_0^{\text{exp}}(HCC{-}H)$ = 131.3 ± 0.7 kcal/mol, $D_0^{\text{exp}}(H_2CCH{-}H)$ = 109.7 ± 0.8 kcal/mol, and $D_0^{\text{exp}}(H_2CC{-}H)$ = 81.0 ± 3.5 kcal/mol.[3] Other C–H and C–C BDEs in C_2H_4 and C_2H_2 have not been measured directly. Ervin et al. derived the other C–H and C–C BDEs in C_2H_4 and C_2H_2 using current literature values for the heats of formation of C, C_2, CH, and CH_2. It is difficult to assess error bars for such derived BDEs, since the data are from a variety of sources.

A number of ab initio calculations of $D_0(HCC{-}H)$ and $D_0(H_2CCH{-}H)$ have been performed,[14-17] but few included high

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