Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XVIII. Persistent Vinyl, Alkyl, and Allyl Radicals[1]

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Abstract: Five 1,2-disubstituted, $R_1\dot{C}{=}CHMR_n$, and fifteen trisubstituted, $R_1\dot{C}{=}C(R_2)MR_n$, vinyl radicals were prepared at room temperature in solution by addition of a variety of radicals, $\cdot MR_n$, to a number of mono- and disubstituted acetylenes. For steric reasons many of these vinyls are relatively long lived. Some decay with first-order and some with second-order kinetics. Their EPR spectra are discussed in terms of "linear" and "bent" structures. It is concluded that only $Me_3Si\dot{C}{=}C(SiMe_3)_2$ is truly "linear". In certain systems prolonged reaction leads to the formation of various highly persistent alkyl radicals. The EPR spectra of these alkyls and some of their decay kinetics are also reported. Ten "perpendicular" allyls, $(Me_3C)_2\dot{C}C(MR_n){=}CR_1R_2$, of great persistence were prepared by addition of $\cdot MR_n$ to two di-*tert*-butylvinylidenecyclopropanes. The EPR spectra of these allyls are compared with those of the corresponding $(Me_3C)_2\dot{C}CH_2MR_n$ radicals, since the two types of radicals have similar structures. It is pointed out that in gaining persistence the allyl radicals lose their stabilization.

Much of our recent work has been concerned with studies of carbon centered radicals that have exceptionally long lifetimes in solution.[4,5] Choosing an appropriate adjective to describe these radicals was not easy.[5] *Stable* is unsatisfactory because this word is generally used to describe a radical such as benzyl which forms a weaker bond to hydrogen than does methyl or some other arbitrarily defined alkyl radical.[6] Despite its greater "stability", benzyl is normally no longer lived in solution than methyl because both radicals can undergo their bimolecular self-reactions (combinations) at rates approaching the diffusion-controlled limit. Both benzyl and methyl are therefore *transient* radicals. As a further illustration of the fact that "stability" and longevity are not necessarily related is our observation[8] that even the destabilized[9] phenyl can have a considerable lifetime in solution if the radical center is sterically protected. We have therefore proposed[5] that *PERSISTENT be used to describe a radical that has a lifetime significantly greater than methyl under the same conditions and that STABILIZED be used to describe the bond-strength aspect of a radical's properties.*

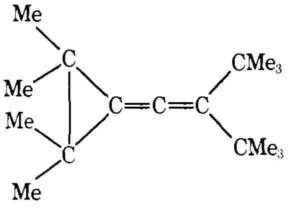
The vinyl radical, $CH_2{=}\dot{C}H$, is destabilized and the allyl radical, $CH_2{=}CH\dot{C}H_2$, is stabilized. Both radicals are *transient*. In this paper we describe the EPR spectra and the kinetic properties of vinyl and allyl radicals which have been made *persistent* by the presence of bulky substituents adjacent to the radical center. While unhindered allyl radicals have a planar structure[10] and are stabilized by resonance[11] ($CH_2{=}CH\dot{C}H_2 \leftrightarrow \dot{C}H_2CH{=}CH_2$), the persistent allyls are twisted so that the principal axis of the π orbital of the double bond is orthogonal to that of the p orbital containing the unpaired electron.[12] There is, therefore, no resonance stabilization of these radicals. That is, in becoming persistent these radicals lose stabilization.

The vinyl radicals were less persistent than the allyls. In some vinyl systems prolonged reaction led to the formation of persistent alkyl radicals which are also described.

Experimental Section

Our general technique has been adequately described in previous papers from this laboratory.[1,15]

Materials. Bis(trimethylsilylacetylene) was prepared by the method of Merker and Scott.[16] 1,1,2,2-Tetra(trimethylsilyl)ethane was prepared by reaction of bis(trimethylsilylmethyl chloride) with lithium metal.[17] The di-*tert*-butylvinylidenecyclopropanes[18] **1** and **2** were the generous gift of Dr. H. D. Hartzler. All other compounds were commercial materials that were generally purified before use.



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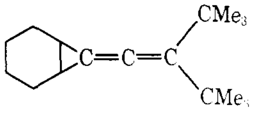

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Radical Generation. Vinyl and allyl radicals were generated by addition of a reagent radical, $\cdot MR_n$, to the acetylenes and to the di-*tert*-butylvinylidenecyclopropanes, respectively. The $\cdot MR_n$ were generated by the photolytic routes previously described.[19] "Blank" experiments were always carried out to ensure that the observed radicals did indeed arise by addition of $\cdot MR_n$ to the acetylene or allene. Persistent alkyl radicals were occasionally formed via multiple additions of $\cdot MR_n$ to the acetylenes. In general attempts were made to react $\cdot MR_n$ ($\cdot MR_n$ = $Me_3Si\cdot$, $Cl_3Si\cdot$, $(EtO)_2\dot{P}O$, $\overline{OCH_2CH_2O}\dot{P}\overline{OCH_2CH_2O}$, $Me_3CO\dot{P}(OEt)_3$, $C_6H_5\cdot$, $C_6F_5\cdot$, $Me_3\dot{C}$, $\dot{C}F_3$, $\dot{C}Cl_3$, $Me_3CO\cdot$, $CF_3O\cdot$, $CF_3S\cdot$, $Me_3Sn\cdot$, and $Me_2N\cdot$), with each of the following acetylenes: $Me_3CC{\equiv}CH$, $Me_3SiC{\equiv}CH$, $Me_3CC{\equiv}CCMe_3$, $Me_3SiC{\equiv}CSiMe_3$, $CF_3C{\equiv}CH$, $CF_3C{\equiv}CCF_3$, $PhC{\equiv}CH$, and $PhC{\equiv}CPh$. Often no EPR signal or only very weak unidentifiable EPR signals were obtained; such was the case with $PhC{\equiv}CH$ and $PhC{\equiv}CPh$. *Only* those radicals that were unequivocally identified are discussed below.

Results

Radical Additions to Acetylenes. (i) EPR Spectra of Vinyl Radicals. The EPR parameters for the vinyl radicals[20] formed by addition of $\cdot MR_n$ to the acetylenes are given in Table I.[21] All of the vinyl radicals were present as soon as photolysis was begun. Because of their persistence, high concentrations of the vinyl radicals could often be obtained and as a consequence, hyperfine couplings to isotopes of low natural abundance (e.g., ^{29}Si) could be detected. In many instances the major lines of the spectra showed small but resolvable hyperfine splittings due to the large numbers of atoms on groups attached to both C_α and C_β. No attempt was made to identify these splittings by computer simulation since this procedure is not only very expensive but can lead to multiple "solutions".[22] The information so obtained is therefore of little value. In some systems persistent alkyl radicals were formed by prolonged photolysis (see below).

Table I. EPR Parameters for Some Vinyl Radicals in Solution at 25° (Hyperfine Splittings in Gauss)

Radical	g^a	$a^{H\gamma a}$	$a^{^{29}Si\beta}$	$a^{^{29}Si\gamma a}$	$a^{H\delta,\epsilon b}$	$a^{other\,a}$
$Me_3C\dot{C}{=}C(H)SiMe_3$	2.0020	67.6		(22.8)^c	0.34	
$Me_3Si\dot{C}{=}C(H)SiMe_3$	2.0023	72.4	*d*	*d*	*e*	
$Me_3C\dot{C}{=}C(CMe_3)SiMe_3$	2.0025			*d*	0.26	
$Me_3Si\dot{C}{=}C(SiMe_3)_2$	2.0022		8.5	49.7^f	0.25	$a^{^{13}C\alpha} = 28.1$
$Me_3C\dot{C}{=}C(CMe_3)SiCl_3$	2.0030			83.4	0.52	
$Me_3Si\dot{C}{=}C(SiMe_3)SiCl_3$	2.0033		*e*	113.4^g 39.1	0.25	
$Me_3C\dot{C}{=}C(CMe_3)[P(O)(OEt)_2]$	2.0021				0.57	$a^{^{13}C\alpha} = 65.1$, $a^{^{31}P} = 132.7$
$Me_3Si\dot{C}{=}C(SiMe_3)[P(O)(OEt)_2]$	2.0023		13.7	34.8	*e*	$a^{^{31}P} = 164.1$
$Me_3C\dot{C}{=}C(CMe_3)[\overline{P(OCH_2CH_2O})_2]$	2.0024				*e*	$a^{^{31}P} = 176.5$
$Me_3Si\dot{C}{=}C(SiMe_3)[\overline{P(OCH_2CH_2O})_2]$	2.0023		7.2	36.6	0.23	$a^{^{31}P} = 201.0$
$Me_3C\dot{C}{=}C(CMe_3)[P(OEt)_3OCMe_3]$	2.0023				0.55	$a^{^{31}P} = 133.2$
$Me_3Si\dot{C}{=}C(SiMe_3)[P(OEt)_3OCMe_3]$	2.0022		7.5	34.6	*e*	$a^{^{31}P} = 164.8$
$Me_3C\dot{C}{=}C(H)(C_6H_5)$	2.0021	53.3			*e*	
$Me_3Si\dot{C}{=}C(H)(C_6H_5)$	2.0018	54.7	*d*		*e*	
$Me_3C\dot{C}{=}C(CMe_3)CF_3$	2.0024				0.67	$a^F = 4.6$ (3 F)
$Me_3Si\dot{C}{=}C(SiMe_3)CF_3{}^h$	2.0025		10.0	28.2	0.42	$a^{^{13}C\alpha} = 47.7^i$
$Me_3Si\dot{C}{=}C(H)CCl_3$	2.0037	47.6	*d*		*d, e*	
$Me_3Si\dot{C}{=}C(SiMe_3)CCl_3$	2.0038		*e*	24.5	0.19	$a^{^{13}C\alpha} = 69.2$
$Me_3C\dot{C}{=}C(CMe_3)OCF_3$	2.0024				0.70	$a^F = 6.8$ (3 F)
$Me_3Si\dot{C}{=}C(SiMe_3)OCF_3$	2.0021		12.1	19.0	0.37	$a^F = 12.4$ (3 F)
$H\dot{C}{=}CH_2{}^j$	2.0022	68.0 34.0				$a^{H\alpha} = 16.0$, $a^{^{13}C\alpha} = 107.5$

[a] Corrected as necessary using the Breit–Rabi equation. [b] Data quoted are line spacings in the hyperfine splitting patterns that are produced by both δ and ϵ hydrogens (see text). [c] Tentative assignment (weak signal). [d] Too weak for detection. [e] Not resolved. [f] Due to two equivalent silicons. [g] Assigned to Si of the $SiCl_3$ group. [h] Fluorine splittings not identified; they are presumably a multiple of $a^{H\delta,\epsilon}$. [i] Assigned to C_α. [j] From ref 31.

(ii) **Kinetic Studies on Vinyl Radicals.** Although kinetic studies could not be made on many vinyls because of the relatively rapid generation of persistent alkyl radicals, it was clear that our vinyls fell into two classes. Those containing a γ hydrogen, such as $Me_3C\dot{C}{=}C(H)SiMe_3$, were not persistent but the vinyls that had three bulky substituents were quite persistent, having half-lives at 25° ranging from ca. 0.1 sec to hours.

The vinyls derived from $Me_3CC{\equiv}CCMe_3$ were considerably less persistent than those obtained from $Me_3SiC{\equiv}CSiMe_3$. For example, a solution of $Me_3C\dot{C}{=}C(CMe_3)CF_3$ (ca. 10^{-6} *M*) decays at 25° by a *first*-order process. The half-life for the reaction, $\tau_{1/2}$, is 0.092 sec which corresponds to a first-order rate constant of 7.5 sec^{-1}. In contrast, a solution of $Me_3Si\dot{C}{=}C(SiMe_3)CF_3$ (5.7×10^{-5} *M*) decays at the same temperature by a *second*-order process with a rate constant of 2.9×10^3 M^{-1} sec^{-1}. Under these conditions its half-life is 5.3 sec. Similarly, $Me_3C\dot{C}{=}C(CMe_3)OCF_3$ (ca. 10^{-6} *M*) decays by a first-order process with $\tau_{1/2}$ = 2.3 sec at −60°, while its counterpart $Me_3Si\dot{C}{=}C(SiMe_3)OCF_3$ decays by a second-order process at the same temperature. A 1.2×10^{-5} *M* solution of the latter radical has a half-life of 530 sec at −60°. Over the temperature range +25 to −60° the decay of $Me_3Si\dot{C}{=}C(SiMe_3)OCF_3$ can be represented by

$$2Me_3SiC{=}C(SiMe_3)OCF_3 \xrightarrow{k} \text{nonradical products}$$

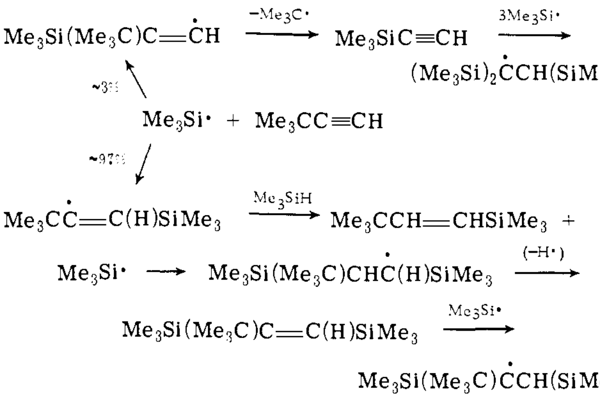
with

$$\log (2k/M^{-1}\ sec^{-1})\ (7.8 \pm 1.3) - (5.5 \pm 1.4)/\theta$$

where $\theta = 2.3RT$ kcal/mol.

(iii) **Formation of Persistent Alkyl Radicals.** During the course of our investigations of vinyl radicals, spectra due to a variety of highly persistent alkyl radicals were also detected. Some of these spectra were not interpretable. Those we could interpret have their EPR parameter listed in Table II.

(a) **From $Me_3Si\cdot$.** The reaction of $Me_3Si\cdot$ with $Me_3CC{\equiv}CH$ has been reported in less detail elsewhere.[22] The following radicals were detected sequentially on continuous irradiation: $Me_3C\dot{C}{=}CHSiMe_3$ (see Table I), $Me_3Si(Me_3C)CH\dot{C}HSiMe_3$, and finally $Me_3Si(Me_3C)\dot{C}CH(SiMe_3)_2$. At 50° the half-life of a 3×10^{-6} *M* solution of the last named radical was 23 hr. Storage in the dark for many hours at 50° of a much more concentrated solution of this radical left a "residue" of $(Me_3Si)_2\dot{C}CH(SiMe_3)_2$ (about 3% based on the initial concentration of $Me_3Si(Me_3C)\dot{C}CH(SiMe_3)_2$):



$$Me_3Si(Me_3C)C{=}\dot{C}H \xrightarrow{-Me_3C\cdot} Me_3SiC{\equiv}CH \xrightarrow{3Me_3Si\cdot} (Me_3Si)_2\dot{C}CH(SiMe_3)_2$$

$$Me_3Si\cdot + Me_3CC{\equiv}CH \xrightarrow{\sim 3\%} Me_3Si(Me_3C)C{=}\dot{C}H$$

$$Me_3Si\cdot + Me_3CC{\equiv}CH \xrightarrow{\sim 97\%} Me_3C\dot{C}{=}C(H)SiMe_3 \xrightarrow{Me_3SiH} Me_3CCH{=}CHSiMe_3 + Me_3Si\cdot \longrightarrow Me_3Si(Me_3C)CH\dot{C}(H)SiMe_3 \xrightarrow{(-H\cdot)} Me_3Si(Me_3C)C{=}C(H)SiMe_3 \xrightarrow{Me_3Si\cdot} Me_3Si(Me_3C)\dot{C}CH(SiMe_3)_2$$

Reaction of $Me_3Si\cdot$ with $Me_3SiC{\equiv}CH$ gave $Me_3Si\dot{C}{=}CH(SiMe_3)$ (Table I) followed by $(Me_3Si)_2CCH(SiMe_3)_2$, presumably by a similar reaction sequence.

Although no vinyls were detected in the reaction of $Me_3Si\cdot$ with $CF_3C{\equiv}CH$ or $CF_3C{\equiv}CCF_3$ both acetylenes gave persistent alkyls. Thus, $CF_3C{\equiv}CH$ gave $CF_3(Me_3Si)\dot{C}CH(SiMe_3)_2$ on prolonged photolysis

$$CF_3C{\equiv}CH \xrightarrow{Me_3Si\cdot} [CF_3\dot{C}{=}C(H)SiMe_3] \xrightarrow{2Me_3Si\cdot} CF_3(SiMe_3)\dot{C}CH(SiMe_3)_2$$

and $CF_3C{\equiv}CCF_3$ gave an intense EPR signal due to $CF_3(Me_3Si)\dot{C}CH(SiMe_3)CF_3$ even without photolysis

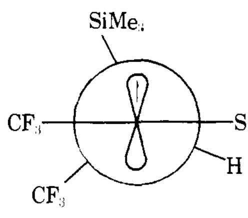
Table II. EPR Parameters for Some Persistent Alkyl Radicals in Solution at 25° (Hyperfine Splittings in Gauss)

Radical	g	$a^{29}\mathrm{Si}_\beta$	$a^{29}\mathrm{Si}_\gamma$	a^{H_γ}	$a^{\mathrm{H}_\delta,\epsilon}$ [a]	a^{other}
$Me_3Si\dot{C}HCH(SiMe_3)CMe_3$	2.0026		*b*	≤ 1.5 [c]	0.17	$a^{\mathrm{H}_\beta} = 20.0$
$Me_3Si(Me_3C)\dot{C}CH(SiMe_3)_2$	2.0023	14.8	29.1 [d]	≤ 2.0 [c]	0.30	$a^{13}C_\alpha \leq 29$ [c]
$(Me_3Si)_2\dot{C}CH(SiMe_3)_2$	2.0024	13.7 [d]	27.6 [d]	≤ 0.2 [e]	0.14	$a^{13}C_\gamma = 4.9$ (6 C), $a^{13}C_\alpha \leq 29$ [c]
$CF_3(Me_3Si)\dot{C}CH(SiMe_3)_2$	2.0023	13.1	27.2 [d]	≤ 1.7	*c*	$a^{13}C_\alpha \simeq 35$ [f], $a^F = 30.9$ (3 F)
$CF_3(Me_3Si)\dot{C}CH(SiMe_3)CF_3$ [g]	2.0023	*b*	*b*	6.1	0.30	$a^F = 28.1$ (3 F)
$CF_3(Me_3Si)\dot{C}CH(SiMe_3)CF_3$ [g]	2.0023	*b*	*b*	1.54	0.26	$a^F = 26.8$ (3 F)
$Me_3C\dot{C}HCH(SiCl_3)_2$	2.0037		~53 [d,h]	≤ 2.9	0.72	$a^{\mathrm{H}_\beta} = 20.9$
$CF_3(Cl_3Si)\dot{C}CH(SiCl_3)_2$	2.0031	*c*	~42 [d,h]	≤ 5.5	*c*	$a^F = 22.1$ (3 F)
$CF_3(Cl_3Si)\dot{C}CH(SiCl_3)CF_3$	2.0032	*c*	*c*	≤ 5.6	0.60	$a^F = 21.1$ (3 F)

[a] Minimum hyperfine spacing; see text. [b] Signal too weak to allow detection. [c] Not resolved. Where preceded by ≤ hyperfine splitting listed is the maximum possible value; for a^{H_γ} the figure listed is ΔH_{pp} of the major EPR lines. [d] Due to two equivalent silicon atoms. [e] See ref 22. [f] Partially resolved. [g] 3 or 4. [h] Weak signal.

$$CF_3C{\equiv}CCF_3 \xrightarrow{Me_3SiH} CF_3(Me_3Si)C{=}C(H)CF_3 \xrightarrow{Me_3Si\cdot} CF_3(Me_3Si)\dot{C}CH(SiMe_3)CF_3$$

The EPR spectrum of the last named radical showed that it exists in two conformers, **3** and **4**, that are present in approximately equal concentration.



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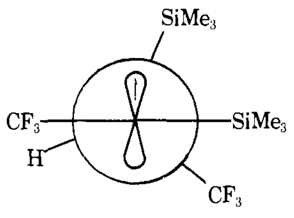

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Addition of $Me_3Si\cdot$ to $Me_3CC{\equiv}CCMe_3$ and to $Me_3SiC{\equiv}CSiMe_3$ gave first the expected vinyls, viz., $Me_3C\dot{C}{=}C(CMe_3)SiMe_3$ and $Me_3Si\dot{C}{=}C(SiMe_3)_2$, respectively. However, after prolonged photolysis *both* systems showed the EPR spectrum of $(Me_3Si)_2\dot{C}CH(SiMe_3)_2$.

$$Me_3CC{=}CCMe_3 \xrightarrow{Me_3Si\cdot} Me_3C\dot{C}{=}C(CMe_3)SiMe_3 \xrightarrow{-Me_3\dot{C}}$$

$$Me_3CC{\equiv}CSiMe_3 \xrightarrow{Me_3Si\cdot} Me_3Si(Me_3C)C{=}\dot{C}SiMe_3 \xrightarrow{-Me_3\dot{C}}$$

$$Me_3SiC{\equiv}CSiMe_3 \xrightarrow{Me_3Si\cdot} Me_3Si\dot{C}{=}C(SiMe_3)_2 \xrightarrow{Me_3SiH}$$

$$Me_3Si(H)C{=}C(SiMe_3)_2 + Me_3Si\cdot \longrightarrow (Me_3Si)_2CH\dot{C}(SiMe_3)_2$$

As we have noted previously,[22] $(Me_3Si)_2CHC(SiMe_3)_2$ is extremely persistent though its lifetime does depend on the reaction medium or method of formation. In general, alkyl radical persistence appears to be greatest in reaction media that do not contain readily abstractable hydrogen atoms.[23] The identification of $(Me_3Si)_2CH\dot{C}(SiMe_3)_2$ was confirmed by its preparation from the parent ethane[17] by hydrogen atom abstraction with *tert*-butoxy radicals.

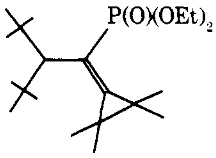
$$(Me_3Si)_2CHCH(SiMe_3)_2 + Me_3CO\cdot \rightarrow (Me_3Si)_2CH\dot{C}(SiMe_3)_2 + Me_3COH$$

(b) From $Cl_3Si\cdot$. No radical was produced from $Me_3SiC{\equiv}CH$ and no vinyl was observed with $Me_3CC{\equiv}CH$. However, after several minute's photolysis of the $Me_3CC{\equiv}CH$ system the spectrum of $Me_3C\dot{C}HCH(SiCl_3)_2$ was obtained. The half-life of this radical at room temperature is ca. 1 sec. Prolonged photolysis gave a single line spectrum with a g value of 2.00371 and $\Delta H_{pp} \sim 8$ G. The radical did not decay significantly after three days at room temperature which suggests that it is $Cl_3Si(Me_3C)\dot{C}CH(SiCl_3)_2$.

Both $CF_3C{\equiv}CH$ and $CF_3C{\equiv}CCF_3$ reacted with $Cl_3Si\cdot$ in the same manner as they reacted with $Me_3Si\cdot$ except that with $CF_3C{\equiv}CCF_3$ there was no signal prior to photolysis and there was no evidence that $CF_3(Cl_3Si)\dot{C}CH(SiCl_3)CF_3$ existed as more than one conformer.

Radical Additions to Vinylidenecyclopropanes. (i) EPR Spectra of Persistent Allyl Radicals. Addition of a variety of $\cdot MR_n$ to the two di-*tert*-butylvinylidenecyclopropanes, **1** and **2**, yielded a number of persistent allyls, the EPR parameters for which are listed in Table III. While most of the "blank" experiments gave no EPR spectra, photolysis of **1** and **2** in di-*tert*-butyl peroxide gave weak single-line EPR spectra (g = 2.0026), which are probably due to radicals formed by addition of $Me_3CO\cdot$. These signals were too weak for hyperfine couplings to be detected.

(ii) Kinetic Studies on Allyl Radicals. The persistent allyls in Table III had half-lives of at least an hour at room temperature. One of the least persistent was radical **8** which decays by a first-order process at low concentrations but by a second-order process at high concentration. At 25° the rate constant for the second-order decay

2 

$\xrightarrow{k}$ nonradical products

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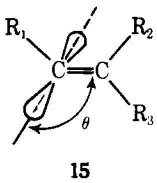
is given by $2k = 1.2\ M^{-1}\ \mathrm{sec}^{-1}$, which at typical concentrations (ca. $3 \times 10^{-4}\ M$) corresponds to a half-life of about 1 hr. The corresponding radical formed by addition of $Cl_3Si\cdot$ (i.e., **6**) was one of the most persistent allyls. A $2 \times 10^{-4}\ M$ solution showed no sign of decay after 1 month at 25°.

Discussion

Vinyl Radicals. (i) Structure from EPR Spectra. Information regarding the structure of vinyl radicals can be obtained more easily by EPR spectroscopy than by any other method.[24] By this technique it has been shown that vinyls can be classified as either "bent" **15** or "linear" **16**. Struc-



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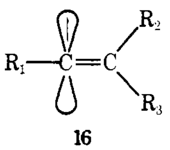

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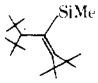
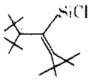
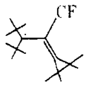
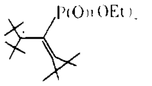
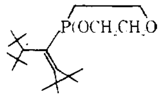
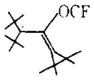
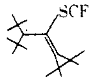
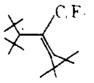
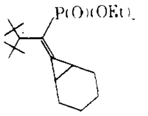
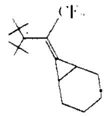
Table III. EPR Parameters for Some Persistent Allyl Radicals in Solution at 25° (Hyperfine Splittings in Gauss)

Radical	g	$a^{^{13}C_\alpha}$	$a^{^{13}C_\gamma}$[a]	$a^{^{13}C_\gamma}$[b]	$a^{H_{\delta,\epsilon}}$[c]	a^{other}
 **5**	2.0026	42.8	10.6	*d*	*d*	a^{29Si} = 23.9 (1 Si)
 **6**	2.0028	*d*	*d*	*d*	0.31	a^{29Si} = 55.2 (1 Si)
 **7**	2.0025	43.9	10.2	*d*	*d*	a^F = 4.1 (3 F)
 **8**	2.0025[e]	44.0	10.4	21.0	0.28	a^{31P} = 75.9[e] (1 P)
 **9**	2.0027	*f*	*f*	*f*	*d*	a^{31P} = 79.38 (1 P)
 **10**	2.0025	39.0	9.0[g]	*d*	0.31	a^F = 3.2 (3 F)
 **11**	2.0024	43.8	10.0[g]	*d*	0.12	a^F = 4.1 (3 F)
 **12**	2.0026	*f*	*f*	*d*	0.17	a^F = 2.8 (2 F)
 **13**	2.0025[e]	42.7	10.3	21.2	*d*	a^{31P} = 71.4[e] (1 P)
 **14**	2.0027	43.0	10.7	*d*	0.35	a^F = 3.8 (3 F)

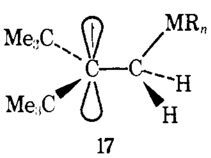
[a] Due to six equivalent carbon atoms of the two *tert*-butyl groups. [b] Due to a single carbon atom in the olefinic part of the structure. [c] See footnote *b*, Table I. [d] Not resolved. [e] Corrected using the Breit–Rabi equation. [f] Signal too weak for detection. [g] Partially resolved.

ture **15**, in which the unpaired electron is in an orbital with substantial s character, is adopted by vinyl and 1-methylvinyl, with $\theta \sim 140$-150°.[28-33] Structure **16** has previously only been identified for vinyls having α substituents (R_1) capable of delocalizing the unpaired electron, e.g., C_6H_5,[33-36] C≡N,[37] and COOH.[35,38]

Both $Me_3C\dot{C}{=}C(H)SiMe_3$ and $Me_3Si\dot{C}{=}C(H)SiMe_3$ have values of a^{H_γ} close to that reported for the γ-H of vinyl that is trans to the unpaired electron (viz., 68 G).[29] It would appear, therefore, that these radicals adopt structure **15** with R_2 = H. As one would expect, the two bulky substituents take up a trans conformation with respect to one another.

The radicals $Me_3C\dot{C}{=}C(H)C_6H_5$, $Me_3Si\dot{C}{=}C(H)C_6H_5$, and $Me_3Si\dot{C}{=}C(H)CCl_3$ have values of a^{H_γ} which are close to the average value for the two H_γ hyperfine splittings in vinyl itself, viz., 51 G.[28,29] If taken at face value, these data would suggest "linear", **16**, or close to "linear" structures for these three vinyls. However, this seems improbable for steric reasons and, for the reasons outlined below, we believe that these radicals are indeed "bent".

In a study of persistent ethyl radicals of the type $(Me_3C)_2\dot{C}CH_2MR_n$, **17**, it was found that the hyperfine splittings due to the two methylene hydrogens, H_γ (and to M), were strongly dependent on the electronegativity of MR_n.[19] However, for reasons that were discussed in detail,[19] it was concluded that these hyperfine splittings did not reflect the ability of MR_n to bond (via the unpaired electron) with the α carbon, nor did they accurately reflect the geometry at the β carbon. These persistent ethyls have the MR_n group eclipsed by the C_α $2p_z$ orbital, i.e.,



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The MR_n group therefore has the same geometry (relative to the orbital containing the unpaired electron) in **17** as in

Table IV. Hyperfine Splitting Ratios for Vinyl- and 1,1-Di-*tert*-butyl-2-Substituted Ethyl Radicals

Radical	$a^{\mathrm{H}\gamma}$	$a^{^{29}\mathrm{Si}\gamma}$ [a]	$a^{\mathrm{H}\text{“ethyl”}}$ [b]	$a^{\mathrm{H}\gamma}/a^{\mathrm{H}\text{“ethyl”}}$	$a^{^{29}\mathrm{Si}\gamma}/a^{\mathrm{H}\text{“ethyl”}}$
$\mathrm{Me_3C\dot{C}{=}C(H)SiMe_3}$	67.6		15.8	4.3	
$\mathrm{Me_3Si\dot{C}{=}C(H)SiMe_3}$	72.4		15.8	4.6	
$\mathrm{Me_3Si\dot{C}{=}C(SiMe_3)_2}$		49.7	15.8		3.2
$\mathrm{Me_3Si\dot{C}{=}C(SiMe_3)SiCl_3}$		39.1	15.8		2.7
$\mathrm{Me_3Si\dot{C}{=}C(SiMe_3)[P(O)(OEt)_2]}$		34.8	14.0		2.5
$\mathrm{Me_3Si\dot{C}{=}C(SiMe_3)[\overline{P(OCH_2CH_2O})_2]}$		36.6	13.1		2.8
$\mathrm{Me_3C\dot{C}{=}C(H)(C_6H_5)}$	53.3		13.0	4.1	
$\mathrm{Me_3Si\dot{C}{=}C(H)(C_6H_5)}$	54.7		13.0	4.2	
$\mathrm{Me_3Si\dot{C}{=}C(SiMe_3)CF_3}$		28.2	12.2		2.3
$\mathrm{Me_3Si\dot{C}{=}C(H)CCl_3}$	47.6		10.7	4.5	
$\mathrm{Me_3Si\dot{C}{=}C(SiMe_3)CCl_3}$		24.5	10.7		2.3
$\mathrm{Me_3Si\dot{C}{=}C(SiMe_3)OCF_3}$		19.0	7.2		2.6

[a] ^{29}Si hyperfine splitting due to SiMe$_3$ groups. [b] Taken from ref 19.

“bent” **15,** and “linear” **16,** vinyls. The steric and electronic effects of MR$_n$ should therefore be rather similar in both the ethyl and the vinyl radicals.

A simple way to correct for the electronic effect of MR$_n$ on $a^{\mathrm{H}\gamma}$ in vinyls of the type $\mathrm{R\dot{C}{=}C(H)MR}_n$ is to divide $a^{\mathrm{H}\gamma}$ by the γ-hydrogen splitting, $a^{\mathrm{H}\text{“ethyl”}}$, for the appropriately substituted **17.** If the resulting ratios are similar for all 1,2-disubstituted vinyls it must be concluded that these vinyls are all isostructural. From the data listed in Table IV it can be seen that $a^{\mathrm{H}\gamma}/a^{\mathrm{H}\text{“ethyl”}} = 4.35 \pm 0.25$, over a range of $a^{\mathrm{H}\gamma}$ values from 48 to 72 G. Since $\mathrm{Me_3C\dot{C}{=}C(H)SiMe_3}$ and $\mathrm{Me_3Si\dot{C}{=}C(H)SiMe_3}$ are most probably “bent” (see above) the other three 1,2-disubstituted vinyls must also be “bent” and their “low” $a^{\mathrm{H}\gamma}$ values must be a consequence of the electronic influences of the various MR$_n$ groups.

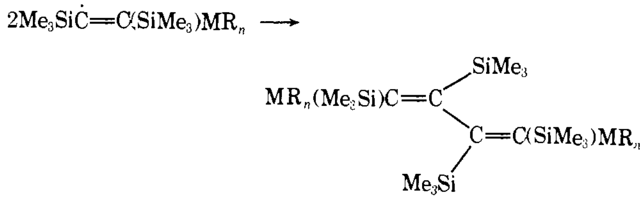
A similar approach can be applied to those trisubstituted vinyls that have an Me$_3$Si group attached to the β carbon. Division of $a^{^{29}\mathrm{Si}\gamma}$ by $a^{\mathrm{H}\text{“ethyl”}}$ should once again correct for the electronic effects of the *other* group on the β carbon (see Table IV). All but one of the vinyls yield $a^{^{29}\mathrm{Si}\gamma}/a^{\mathrm{H}\text{“ethyl”}}$ values in the range 2.55 ± 0.25 which implies that they are isostructural. However, with $\mathrm{Me_3Si\dot{C}{=}C(SiMe_3)_2}$ this ratio has the much larger value of 3.2. Since the two γ silicons in this radical are magnetically equivalent not only at room temperature, but also at −130°, it seems certain that this radical is a “linear” vinyl. A “linear” structure for $\mathrm{Me_3Si\dot{C}{=}C(SiMe_3)_2}$ is also implied by its $a^{^{13}\mathrm{C}\alpha}$ value of 28.1 G, which is typical of a planar alkyl radical (e.g., $a^{^{13}\mathrm{C}\alpha} = 38.3$ G for $\mathrm{\dot{C}H_3}$[31] and 26 ± 3 for $\mathrm{(Me_3Si)_3\dot{C}}$[39]), whereas for (“bent”) vinyl itself, $a^{^{13}\mathrm{C}\alpha} = 107.6$ G.[31] If $\mathrm{Me_3Si\dot{C}{=}C(SiMe_3)_2}$ is the “odd man out” with a “linear” structure, it implies that *all* of the remaining vinyls adopt a “bent” structure, **15.** Such a conclusion is also supported by the values of $a^{^{13}\mathrm{C}\alpha}$ obtained for $\mathrm{Me_3C\dot{C}{=}C(CMe_3)[P(O)(OEt)_2]}$, 65 G; $\mathrm{Me_3Si\dot{C}{=}C(SiMe_3)CF_3}$, 48 G; and $\mathrm{Me_3Si\dot{C}{=}C(SiMe_3)CCl_3}$, 69 G since these values are intermediate between those found for methyl and for vinyls and indicate that the unpaired electron is in an orbital with considerable s character. Presumably the degree of bending depends very much on the physical size of the three groups on the vinyl. A truly “linear” form would seem to require either delocalization of the unpaired electron into the α substituent[34-38] or a high degree of symmetry and steric hindrance.

***(ii)* Persistence.** Although almost all major types of carbon centered radicals have been extensively studied in solution by EPR spectroscopy, the observation of destabilized radicals such as vinyl[40] is always difficult. This is because the destabilization of vinyls makes hydrogen abstraction by them from other components of the solution very favorable thermodynamically. Detectable concentrations of vinyls are, therefore, seldom attained. Fessenden and Schuler[28] overcame this observational problem by generating the radicals extremely rapidly at low temperatures. The EPR spectra of vinyl and 1-methylvinyl were obtained in this way and were formerly the only neutral vinyls that had been detected in solution.[43] An alternative approach to the generation of a significant concentration of destabilized radicals is to use bulky groups to sterically protect the radical center.[4,5] As the preceding results show, this method can be applied to vinyl radicals.

None of the 1,2-disubstituted vinyls listed in Table I were really persistent but their Me$_3$C and Me$_3$Si groups did reduce vinyl reactivity sufficiently for them to be easily detected.[45] This was not the case with smaller groups, that is, no vinyls were detected in the radical additions to $\mathrm{CF_3C{\equiv}CH}$ (or even $\mathrm{CF_3C{\equiv}CCF_3}$).

Trisubstituted vinyls are generally much more persistent. Those derived from $\mathrm{Me_3SiC{\equiv}CSiMe_3}$ decayed by second-order processes and were considerably longer lived than the vinyls obtained from $\mathrm{Me_3CC{\equiv}CCMe_3}$, which decayed by first-order processes. Presumably the $\mathrm{Me_3C\dot{C}{=}C(CMe_3)MR}_n$ decay by elimination of *tert*-butyl.[46] The corresponding elimination of trimethylsilyl must be unfavorable and so a bimolecular self-reaction is preferred.

$$\mathrm{Me_3C\dot{C}{=}C(CMe_3)MR}_n \longrightarrow \mathrm{Me_3CC{\equiv}CMR}_n + \mathrm{Me_3C^{\cdot}}$$

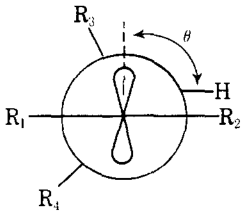


$$2\mathrm{Me_3Si\dot{C}{=}C(SiMe_3)MR}_n \longrightarrow \mathrm{MR}_n\mathrm{(Me_3Si)C{=}C(SiMe_3)\text{–}C(SiMe_3){=}C(SiMe_3)MR}_n$$

The Arrhenius parameters for self-reaction of $\mathrm{Me_3Si\dot{C}{=}C(SiMe_3)OCF_3}$ indicate that this radical's persistence is due mainly to the existence of a significant activation energy for the dimerization reaction. Of course, the (presumed) butadiene product is likely to be nonplanar for steric reasons.

Persistent Alkyl Radicals. The EPR spectra and kinetic behavior of persistent alkyl radicals have been discussed by us in some detail previously.[15b,19,21,22,23,47] The observation of $\mathrm{Me_3Si(Me_3C)CH\dot{C}HSiMe_3}$ and $\mathrm{Me_3C\dot{C}HCH(SiCl_3)_2}$ (Table II) increases the number of known persistent secondary alkyl radicals to five.[48] The highly persistent $\mathrm{(Me_3Si)_2\dot{C}CH(SiMe_3)_2}$ radical has now been identified as a product of the reaction of $\mathrm{Me_3CO\cdot}$ with $\mathrm{(Me_3Si)_2CH_2}$,[22] and of $\mathrm{Me_3Si\cdot}$ with $\mathrm{Me_3CCH{=}CHCMe_3}$,[22] $\mathrm{MeC{\equiv}N}$,[22] $\mathrm{Me_3C{\equiv}CH}$,[22] $\mathrm{Me_3SiC{\equiv}CH}$, $\mathrm{Me_3CC{\equiv}CCMe_3}$, and $\mathrm{Me_3SiC{\equiv}CSiMe_3}$. Presumably the extraordinary persistence of the radical ensures its detection (by the patient observer)[49] even when it is formed with very low efficiency. Since we have now also formed this radical by hydrogen abstraction from $\mathrm{(Me_3Si)_2CHCH(SiMe_3)_2}$ there can no longer be any doubt about the validity of the EPR spectral assignment.

Persistent alkyl radicals adopt conformations which minimize steric interactions. Values of a^{H_γ} (and $a^{^{29}Si_\gamma}$) for 1,1,2,2-tetrasubstituted ethyl radicals indicate that in the optimum conformation the hydrogen attached to the β carbon lies in or near the nodal plane of the orbital containing the unpaired electron,[22] **18**, i.e., $\theta \sim 90°$.



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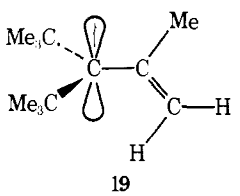
With one exception (see below) all the radicals listed in Table II have a^{H_γ} values that are less than the line width of the principal EPR lines. That is, from the usual empirical equation,[50] $a^{H_\gamma} = A + B \cos^2 \theta$, since $\theta = 90°$, $a^{H_\gamma} = A$, and A must be quite small. In cases where R_1 and R_2 are different the radical can, in principle, exist in two conformers (though there should be a preference for **18** if R_1 is much smaller than R_2). Only $CF_3(Me_3Si)\dot{C}CH(SiMe_3)CF_3$ actually exists in two conformations (**3** and **4**) and, interestingly, one of these shows an appreciable splitting (6.1 G) by H_γ, implying that this conformer has $\theta < 90°$.

It seems probable that $a^{^{29}Si_\gamma}$ will show a similar angular dependence on θ, i.e., $a^{^{29}Si_\gamma} = A^{^{29}Si} + B^{^{29}Si} \cos^2 \theta$. The $(Me_3C)_2\dot{C}CH_2SiMe_3$ radical[19] adopts conformation **17** with $\theta^{SiMe_3} = 0°$. Since $a^{^{29}Si_\gamma}$ for this radical is 35.0 G,[19] $B^{^{29}SiMe_3}$ will also be ca. 35 G provided $A^{^{29}SiMe_3}$ is negligible. There are three persistent alkyls listed in Table II that have observable $a^{^{29}Si_\gamma}$ due to γ-Me_3Si groups. These splittings are in the range 28 ± 1 G which yields $\theta^{SiMe_3} \sim 27 \pm 2°$ in excellent agreement with the assigned conformation, **18.** A similar calculation for the two persistent alkyls having γ-$SiCl_3$ groups (for which $B^{^{29}Si} = 77$ G)[19] yields $\theta = 34°$ for $Me_3C\dot{C}HCH(SiCl_3)_2$ and 42° for $CF_3(Cl_3Si)\dot{C}CH(SiCl_3)_2$.[51]

Hyperfine splittings from fluorine in the CF_3 groups are in agreement with the values found in related radicals. That is, they are either unresolved or very small for a CF_3 attached to the β carbon (cf.[19] 0.90 G in $(Me_3C)_2\dot{C}CH_2CF_3$ and 0.33 G in $\dot{C}H_2CH_2CF_3$) and are ca. 25 G for CF_3 attached to the α carbon (cf.[52] 29.9 G in $\dot{C}H_2CF_3$).

The small magnitude of $a^{^{13}C_\alpha}$ (detected, or estimated maximum values, Table II) implies that these persistent alkyls are, as we would expect,[19] planar (or close to it) at the α carbon.

Allyl Radicals. (i) **Structure from EPR Spectra.** The persistent allyl radicals listed in Table III all have the "perpendicular" structure first described by Ragenstein and Berndt[13] for 1,1-di-*tert*-butyl-2-methylallyl, **19**, in which the principal axis of the π orbital of the double bond is at right angles to the C_α $2p_z$ direction.



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These radicals therefore have a structure that is similar to that of $(Me_3C)_2\dot{C}CH_2MR_n$ radicals, **17**, and indeed the two types of radicals have similar EPR parameters. Thus, values of $a^{^{13}C_\alpha}$ (ca. 43 G, Table III, and 46 G for **19**[13]) are similar to those found for various **17** (ca. 46 G)[19] and the values of $a^{^{13}C_\gamma}$ (6 C, the Me groups of the two α-Me_3C) are ca. 11 G for both types of radical. In two cases (**8, 13**) hyperfine splittings of 21 G from the γ carbon in the olefinic moiety were resolved. A similar splitting (18 G) was reported for **19**[13] but was assigned to two equivalent β carbons (which seems rather unlikely since $a^{^{13}C_\beta}$ is 11 G in $(Me_3C)_2\dot{C}H$ and in $(Me_3C)_3C\cdot$[19]).

The magnitudes of the hyperfine splittings due to the M of the MR_n group in **5**, **6**, **8**, **9**, and **13** are 67 ± 5% of the magnitudes found for the corresponding splittings in $(Me_3C)_2\dot{C}CH_2MR_n$ radicals. This reduction in a^{M_γ} is presumably a consequence of the greater C_α-M_γ distance and greater $C_\alpha C_\beta M_\gamma$ angle in the allyls compared with the ethyls. Another consequence of the increased C_α-M_γ distance is apparent in **12** which shows splitting by two equivalent fluorines (presumable ortho), whereas $(Me_3C)_2\dot{C}CH_2C_6F_5$ shows a very much larger (17.6 G)[19] splitting by *one* ortho fluorine. Clearly, in the allyl there is either rotation[53] of the C_6F_5 group or it is locked at right angles to the $C_\alpha C_\beta M_\gamma$ plane, but in the ethyl the C_6F_5 group is unable to rotate and it is locked in the $C_\alpha C_\beta M_\gamma$ plane.

(ii) **Persistence.** The structure of these allyls implies that they will be at least as long lived as the corresponding 1,1-di-*tert*-butylethyl radicals. In fact, the absence of γ hydrogens suggests they will be even more persistent since a bimolecular disproportionation[23] is not possible. The limited kinetic data available support these conclusions.

Destabilized vinyl radicals can be made persistent by steric protection of the radical center. Although allyl radicals can also be made persistent, the steric requirements are such that they then lose their stabilization.

Acknowledgment. The authors would like to express their gratitude to Dr. H. D. Hartzler for providing the precursors from which the persistent allyl radicals were generated.

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Carbon-13 Fourier Transform CIDNP. Kinetics and Mechanism of the Photochemical Decomposition of Benzoyl Peroxide in Chloroform[1]

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Abstract: Pulsed Fourier transform NMR was used to study ^{13}C CIDNP arising from the photolysis of benzoyl peroxide in chloroform. The most intense ^{13}C CIDNP signals were those of benzene (emission) and of the phenoxy carbon of phenyl benzoate (enhanced absorption). Weak CIDNP signals were observed from CO_2 and hexachloroethane. CKO radical-pair theory was applied to explain the signs of the polarizations and provide mechanistic insight. Analysis of the time dependence of the CIDNP signals to yield rate constants and enhancement factors required incorporation of the effects of the pulse technique into the CIDNP kinetic expressions. Good agreement was obtained between rate constants derived from CIDNP data and those from chemical analysis.

The phenomenon of chemically induced dynamic nuclear polarization (CIDNP) has great potential for the mechanistic and kinetic elucidation of liquid phase radical reactions.[3] A majority of the CIDNP work has centered around the use of proton NMR spectroscopy although ^{13}C NMR offers several distinct advantages. For example, since the ^{13}C chemical shift range is quite large and since carbon nuclei are very sensitive to substituent and subtle conformational effects, it is often possible to unambiguously identify individual ^{13}C signals without the complication of overlapping lines as usually occurs in proton spectra. In addition, the spectrum can be simplified by eliminating carbon–hydrogen spin–spin splitting through the use of proton noise decoupling. Polarizations of carbons which do not bear protons can, of course, be studied directly. Finally, the utilization of pulse Fourier transform (FT) NMR methods enables the entire spectrum to be recorded in a matter of seconds, a highly desirable feature in studying the time dependence of polarized NMR signals. Carbon-13 FT CIDNP does not suffer from the disadvantage of proton FT CIDNP in which line intensities depend on the pulse flip angle because of homonuclear spin–spin couplings.[4] To judge the practicality of ^{13}C FT CIDNP as a tool for in situ material degradation studies, we have embarked on an examination of polarized ^{13}C nuclei produced during photolytic and thermal decomposition of organic compounds.

This report concerns the use of ^{13}C FT CIDNP and analytical techniques to study the photolytic decomposition of benzoyl peroxide (BPO) in chloroform. The mechanistic and kinetic conclusions obtained from the CIDNP data are compared with those obtained from product analyses. The CIDNP kinetic analysis scheme for the pulsed NMR experiment is presented for the case of a 90° flip angle, which was used in this study; the generalized treatment will appear elsewhere.[5] The thermal chemistry of BPO has been extensively studied[6] but its photochemistry has received relatively little attention.[7] CIDNP during the thermal reaction has been examined by proton[8] and ^{13}C[9a,b] CW NMR and ^{13}C FT NMR.[9c]

Results

A typical ^{13}C FT CIDNP spectrum obtained during the photolysis of 0.82 *M* BPO in chloroform is shown in Figure 1. Although the CIDNP signal enhancements are large, it