

Persistent Carbon-Centered Radicals¹

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*"When I use a word it means just what I choose it to mean—neither more nor less."*²

If a physical chemist is asked to name a carbon-centered radical he is likely to mention methyl, while an organic chemist or historian would probably choose triphenylmethyl.

In their behavior these two radicals are poles apart. Methyl radicals decay extremely rapidly unless they are immobilized in a solid. In the gas or liquid phase they normally decay either by reaction with a second methyl radical (i.e., $\cdot\text{CH}_3 + \cdot\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$) or by reaction with a molecule in the surrounding medium (e.g., $\cdot\text{CH}_3 + \text{RH} \rightarrow \text{CH}_4 + \text{R}\cdot$). Methyl, and related species, can accurately be described as *transient* radicals.

Triphenylmethyl, on the other hand, is anything but transient. In solution it exists in equilibrium with its dimer. Since triphenylmethyl is rather unreactive in atom abstraction and in addition to unsaturated molecules, a solution of the radical usually survives for several days in the absence of oxygen. Because of its relatively long lifetime this radical is generally referred to as a *stable* radical.

Unfortunately, the adjective³ *stable* is also commonly applied to all carbon-centered radicals that are derived from compounds having weaker C-H bonds than methane or than some other arbitrarily defined alkane. On this basis, benzyl and allyl would be correctly described as *stable* radicals since the primary C-H bonds in toluene and propylene are significantly weaker than the primary C-H bonds in alkanes. However, under most conditions benzyl and allyl have as *transient* an existence as methyl since they undergo their bimolecular self-reactions at rates similar to the $\cdot\text{CH}_3 + \cdot\text{CH}_3$ reaction, i.e., at rates approaching the encounter-controlled limit.

There is no doubt that the lax use of "*stable*" has introduced a freedom into discussion such that an author almost has the possibility, like Humpty Dumpty,² to make "*stable*" mean just what he chooses. Sometimes within a single exposition the word expands or contracts to harmonize with the enlargement or diminution of ideas. Despite its lack of precision, the widespread use and popularity of the term indicate that it fills an obvious gap and that it conveys a generally accepted though variable meaning.

However, there remains the danger that the imprecision of the word may introduce a corresponding diffuseness in thought.

To ameliorate this situation we propose that the adjective "*persistent*" be used to describe a radical that has a lifetime significantly greater than methyl under the same conditions and that "*stabilized*" should be used to describe a carbon-centered radical, *R*·, when the R-H bond strength is less than the appropriate C-H bond strength in an alkane. The word *stable* should only be used to describe a radical so persistent and so unreactive to air, moisture, etc., under ambient conditions that the *pure* radical can be handled and stored in the lab with no more precautions than would be used for the majority of commercially available organic chemicals.

The persistence of a radical depends on its environment. That is, the lifetime of a radical is sometimes dramatically decreased by minor "impurities" in the surrounding medium, e.g., a trace of oxygen or a radical scavenger. However, under specified experimental conditions the persistence of a radical can be quantitatively described by the rate constant for the bimolecular or unimolecular process by which the radical decays. If the decay kinetics are unknown, or if decay involves reaction with a second material, the half-life of the radical gives a measure of its persistence.

An intrinsic property of a radical is the extent to which it is stabilized or destabilized. Benson and co-workers⁴ have defined a radical "stabilization energy", E_s , as the difference between the strength of the appropriate (i.e., primary, secondary, or tertiary) alkane C-H bond and the C-H bond to the radical in question. Thus, the stabilization energy of benzyl is defined as $D[\text{CH}_3\text{CH}_2\text{-H}] - D[\text{C}_6\text{H}_5\text{CH}_2\text{-H}] = 13$ kcal/mol. Quantifying the extent to which a radical is stabilized in this way has the advantages of (i) simplicity, (ii) the fact that many C-H bond strengths have been measured, and (iii) that steric effects are minimized since hydrogen is the smallest substituent that can be attached to the radical.

We can examine some representative carbon-centered radicals with a view to classifying them according to whether they are stabilized or destabilized and according to their transience or persistence (Figure 1). Ethyl, isopropyl, and *tert*-butyl are *transient* and are not stabilized since, for each radical, $E_s = 0$ by

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(1) Issued as N.R.C.C. Publication No. 14931.

(2) H. Dumpty, as quoted by L. Carroll in "Through the Looking-Glass", Chapter 6.

(3) "Adjectives you can do anything with"²

(4) See, e.g., S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968; D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969); H. E. O'Neal and S. W. Benson in "Free Radicals", Vol. II. J. K. Kochi, Ed., Wiley, New York, N.Y., 1973.

definition.⁴ Vinyl and phenyl are transient and destabilized because E_s is negative. Allyl, benzyl, 1-phenylethyl, cyclohexadienyl, and cumyl are transient, stabilized radicals, while triphenylmethyl is persistent and stabilized. Why is triphenylmethyl unique?

The persistence of triphenylmethyl cannot be attributed to electronic effects since delocalization of the unpaired electron produces a stabilized radical, *not* a persistent radical. Thus, the transient cyclohexadienyl radical, for example, is more stabilized than the persistent triphenylmethyl radical (i.e., $E_s^{\text{C}_6\text{H}_7} > E_s^{\text{Ph}_3\text{C}}$). It therefore seems most reasonable to attribute the persistence of triphenylmethyl to steric factors. This was, in fact suggested by Gomberg in 1900,^{5,6} but *generalization* of this concept to other types of carbon-centered radicals did not occur for 73 years.¹¹ However, once it was appreciated that *persistent carbon-centered radicals were produced primarily by steric and not by electronic factors*, the number and variety of such radicals underwent explosive growth.¹²

In this Account we present a systematic discussion of carbon-centered radicals (other than those of the triphenylmethyl type) which have been made persistent by suitable arrangement of bulky groups around the radical center. These radicals range from alkyls which have no stabilization energy, through the destabilized (E_s negative) phenyls and vinyls, to the stabilized (E_s positive) benzyls, allyls, and cyclohexadienyls.

The radicals have been studied in solution at room temperature by electron paramagnetic resonance (EPR) spectroscopy. They have been generated by atom abstraction from a parent molecule, by photolytic decomposition of suitable precursors, and by radical addition to molecules containing multiple bonds. The persistent radicals have half-lives varying from seconds to years whereas, under similar conditions, transient radicals would have half-lives of less than 10^{-3} sec. Since the persistent radicals can easily be prepared in relatively high concentrations, their structural and chemical properties can be examined with an ease and accuracy impossible to attain with transient radicals. However, it must be emphasized that just because a persistent radical can be prepared in fairly high concentration in a deoxygenated solu-

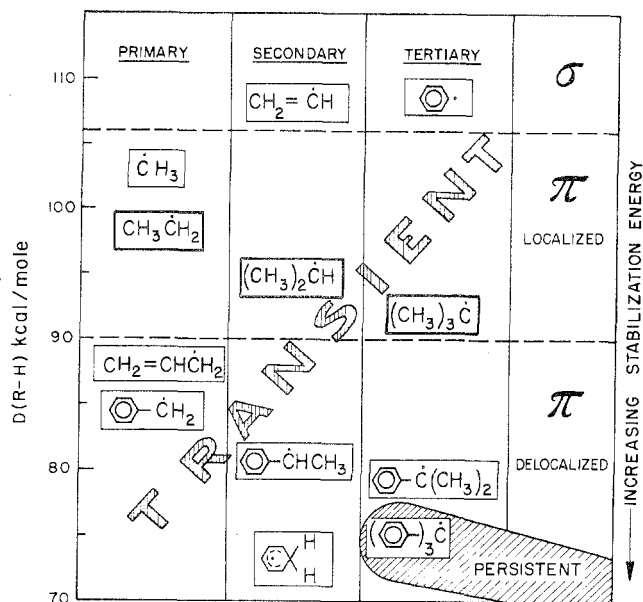


Figure 1. Some representative carbon-centered radicals ranked in terms of their stabilization energy and type. Destabilized radicals are of the σ type and have their unpaired electron in a localized orbital with considerable s character. Radicals that are not stabilized are of the π type and have their unpaired electron in a localized p orbital. Stabilized radicals are also of the π type, but the unpaired electron can be delocalized into adjacent systems of π bonds.

tion, this does not imply that the radical could be isolated and "put in a bottle" on display.

Persistent Alkyl Radicals

The simplest test of the "steric" hypothesis is to begin with the transient methyl radical and monitor the effect of successive substitutions of hydrogen by bulky groups such as *tert*-butyl and trimethylsilyl. The result can be seen in Table I which lists half-lives, $\tau_{1/2}$, for a variety of alkyl radicals under standard conditions (25° , $[\text{radical}] = 10^{-5} M$). A single substitution by *tert*-butyl, 2, or trimethylsilyl, 3, does not confer persistence,¹³ nor do two trimethylsilyl groups, 5.¹¹ However, substitution by two *tert*-butyls, 4, does produce a persistent radical,^{11,14} as does substitution by three *tert*-butyls, 9,^{11,14} and three trimethylsilyls, 10.^{11,14,15} Attempts to prepare other primary, secondary, and tertiary alkyl radicals and the information that they can yield once produced are described below.

Primary Alkyls. There is, at present, no known persistent primary alkyl, presumably because it is too difficult to protect the $\cdot\text{CH}_2$ moiety with a single group. For example,¹³ radicals 2 and 3 are not significantly longer lived than methyl. Even the stabilized 2,4,6-tri-*tert*-butylbenzyl radical, 22, is not persistent but dimerizes to the bibenzyl at a rate approaching the diffusion-controlled limit.¹⁶

Secondary Alkyls. A few representative examples, 4, 6, and 7 (Table I), have been prepared by hydrogen abstraction with *tert*-butoxy from the parent hydrocarbon. The 2,2,4,4,6,6-hexamethylcyclohexyl radical, 7,^{14,17} is significantly more persistent than 2,2,4,6,6-

(5) M. Gomberg, *J. Am. Chem. Soc.*, **22**, 757 (1900).

(6) The fact that the triphenylmethyl dimer is a "head-to-tail" dimer⁷ rather than the long-postulated "head-to-head" hexaphenylethane⁸ serves to show just how strongly the simple coupling is hindered. If the para positions on the three rings are blocked by suitable substituents the radicals do not dimerize.^{9,10}

(7) W. Lankamp, W. Th. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968); H. A. Staab, H. Brettschneider, and H. Brunner, *Chem. Ber.*, **103**, 1101 (1970).

(8) For an enlightening history of "hexaphenylethane", see J. M. McBride, *Tetrahedron*, **30**, 2009 (1974).

(9) See, e.g., K. Ziegler and E. Boye, *Justus Liebigs Ann. Chem.*, **458**, 248 (1927); P. W. Selwood and R. M. Dobres, *J. Am. Chem. Soc.*, **72**, 3860 (1950).

(10) For a recent review of radicals of the triphenylmethyl type, see V. D. Sholle and E. G. Rozantsev, *Russ. Chem. Rev.*, **42**, 1011 (1973).

(11) G. D. Mendenhall and K. U. Ingold, *J. Am. Chem. Soc.*, **95**, 3422 (1973).

(12) It should be noted that steric factors not only influence the persistence of radicals but frequently also influence the rate of their formation. See, e.g., C. Ruchardt et al., "XXIII I.U.P.A.C. Congress, Special Lectures", Vol. 4, Butterworths, London, 1971, p 233 ff; H. D. Beckhaus and C. Ruchardt, *Tetrahedron Lett.*, 1971 (1973); W. Duisman and C. Ruchardt, *ibid.*, 4517 (1974).








(13) G. B. Watts and K. U. Ingold, *J. Am. Chem. Soc.*, **94**, 491 (1972).

(14) G. D. Mendenhall, D. Griller, D. Lindsay, T. T. Tidwell, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 2441 (1974).

(15) A. R. Bassindale, A. J. Bowles, M. A. Cook, C. Eaborn, A. Hudson, R. A. Jackson, and A. E. Jukes, *Chem. Commun.*, 559 (1970).

(16) D. Griller, L. R. C. Barclay, and K. U. Ingold, *J. Am. Chem. Soc.*, **97**, 6151 (1975).

Table I
Persistent and Transient Carbon-Centered Radicals

Radical	Persistent	Log ($\tau_{1/2}/\text{sec}$) ^a	Decay kinetics ^b	Ref
Primary alkyls				
1 Me·	No	-4.7	2	13
2 Me ₃ C $\dot{\text{C}}\text{H}_2$	No	-4.3	2	13
3 Me ₃ Si $\dot{\text{C}}\text{H}_2$	No	-4.4	2	13
Secondary alkyls				
4 (Me ₃ C) ₂ $\dot{\text{C}}\text{H}$	Yes	1.8	1	14
5 (Me ₃ Si) ₂ $\dot{\text{C}}\text{H}$	No	-3.3	2	11
6 	Yes	2.4	1	14
7 	Yes	3.0	1	14
Tertiary alkyls				
8 (Me ₂ CH) ₃ C·	Yes	2.4	2	18
9 (Me ₃ C) ₃ C·	Yes	2.7	1	14
10 (Me ₃ Si) ₃ C·	Yes	5.3	1	14
11 (Me ₃ C) ₂ $\dot{\text{C}}\text{CH}_2\text{CF}_3$	Yes	<i>c</i>	<i>c</i>	14
12 (Me ₃ C) ₂ $\dot{\text{C}}\text{CH}_2\text{SiMe}_3$	Yes	<i>c</i>	<i>c</i>	14
13 (Me ₃ C) ₂ $\dot{\text{C}}\text{CH}_2\text{C}_6\text{H}_5$	Yes	3.9	1	14
14 (MeSi) ₂ $\dot{\text{C}}\text{CH}(\text{SiMe}_3)_2$	Yes	>7.0	<i>c</i>	29
15 (Me ₃ C) ₂ $\dot{\text{C}}\text{NHSiMe}_3$	No	<0	<i>c</i>	34
16 (Me ₃ Si) ₂ $\dot{\text{C}}\text{N}(\text{SiMe}_3)_2$	Yes	>6.5	<i>d</i>	34
Destabilized Radicals				
17 	Yes	-2.2	1	37
18 Me ₃ C $\dot{\text{C}}=\text{CHSiMe}_3$	No	<i>c</i>	<i>c</i>	30
19 Me ₃ C $\dot{\text{C}}=\text{C}(\text{CMe}_3)\text{CF}_3$	Yes	-1.0	1	30
20 Me ₃ Si $\dot{\text{C}}=\text{C}(\text{SiMe}_3)\text{CF}_3$	Yes	1.8	2	30
21 Me ₃ Si $\dot{\text{C}}=\text{C}(\text{SiMe}_3)_2$	Yes	<i>c</i>	<i>c</i>	30
Stabilized Radicals				
22 	No	-3.4	2	16
23 (Me ₃ C) ₂ $\dot{\text{C}}\text{C}(\text{SiCl}_3)=\text{CCMe}_2\text{CMe}_2$	Yes	>7.0	<i>c</i>	30
24 	Yes	2.6	1	42
25 	Yes	3.3	1	42
26 	Yes		1 ^e	42

^a Calculated at 25° and (for the second-order reactions) at a radical concentration of 10⁻⁵ M. ^b 1 = first order, 2 = second order. ^c Not measured. ^d Probably second order. ^e Pseudo first order. Decay involves a reaction of the radical with the parent phosphorin, with $k = 0.14 \text{ M}^{-1} \text{ sec}^{-1}$.

pentamethylcyclohexyl, 6, presumably because of the "buttressing" action of the remote extra methyl group in 7.

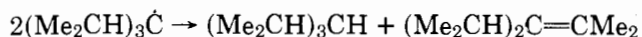
Radicals 4, 6, and 7 all decay with first-order kinetics.¹⁴ The decay reaction has not been identified. It may, in principle, be either an intramolecular 1,3 hydrogen transfer, e.g.



or a β scission, e.g.



Tertiary Alkyls. The largest class of persistent carbon radicals known at present consists of this type. The first to be discovered was tris(trimethylsilyl)methyl, 10,¹⁵ which is one of the most persistent. Many of these radicals (e.g., 9, 10, and 13) decay with first-order kinetics presumably also via intramolecular hydrogen transfers or β scissions. However, when there is hydrogen directly attached to the β carbon, second-order decay becomes more favored—particularly at low temperature and high radical concentrations,¹⁴ e.g.¹⁸



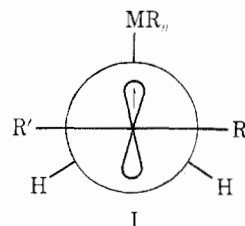
We have made use of the fact that relatively high concentrations of persistent tertiary alkyl radicals can be easily attained to study several problems of general interest that are related to the structure and conformation of more transient alkyl radicals. The utility of the persistent radicals, in this respect, arises from their intense EPR spectra. Because of the excellent signal-to-noise levels, measurements can be made of EPR hyperfine splittings from nuclei present in low natural abundance (e.g., ¹³C). As a consequence, a great deal of structural information is obtained. There follow a few examples of this application of persistent alkyls.

Example 1: Are Trialkylmethyl Radicals Planar? The EPR hyperfine splitting by the α carbon in an alkyl radical is related to the spin density and degree of s character in the α -carbon orbital that contains the unpaired electron. Thus, the planar, or nearly planar, methyl radical has $a^{13\text{C}} = 38.3$ G at -177° ,¹⁹ while the pyramidal $\cdot\text{CF}_3$ has $a^{13\text{C}} = 271.6$ G at -95° .²⁰ *tert*-Butyl has $a^{13\text{C}} \approx 46$ G at 50° , rising to 49.5 G when the temperature is decreased to -182° .²¹ This led to the suggestion²¹ that in $\text{Me}_3\text{C}\cdot$ the C-C-C angle was significantly less than the 120° required for a planar radical, a conclusion which was strongly disputed.²²

Our persistent trialkylmethyl radicals have $a^{13\text{C}\alpha}$ values varying, at room temperature, from ca. 45.5 G for the (relatively) unhindered $(\text{Me}_3\text{C})_2\dot{\text{C}}\text{H}_2\text{CF}_3$ and $(\text{Me}_3\text{C})_2\dot{\text{C}}\text{H}_2\text{OCF}_3$ radicals up to 51.1 G for the extremely hindered $(\text{Me}_3\text{C})_3\dot{\text{C}}\cdot$ radical.²³ For steric reasons, it seems to us unlikely that the last named

radical could be significantly nonplanar and we therefore conclude that the *tert*-butyl radical is also as close to planar as makes no difference. As we have pointed out in another connection,²³ free-radical structures cannot be deduced reliably by interpretations of small changes in hyperfine coupling constants.²⁴

Example 2: Does Hyperconjugation Determine the Conformation of β -Substituted Ethyl Radicals? The $\cdot\text{CH}_2\text{CH}_2\text{CF}_3$ radical is able to rotate quite freely about the $\text{C}_\alpha\text{-C}_\beta$ bond but, even at room temperature, the $\cdot\text{CH}_2\text{CH}_2\text{SiMe}_3$ radical adopts conformation I ($\text{R}' = \text{H}$, $\text{MR}_n = \text{SiMe}_3$). This conformation implies that there exists an attractive interaction between the silicon and the unpaired electron. There has been considerable debate as to whether the preference of $\cdot\text{CH}_2\text{CH}_2\text{SiMe}_3$ for conformation I is a consequence of homoconjugation (i.e., $p\pi\text{-}d\pi$ interaction),²⁵ of homo- plus hyperconjugation,²⁶ or of hyperconjugation alone.²⁷ We have used the following argument to conclude that any hyperconjugative attractive force is insufficient to determine conformation.²³



For steric reasons, all 1,1-di-*tert*-butylethyl radicals are forced to adopt conformation I (i.e., $\text{R}' = \text{Me}_3\text{C}$, various MR_n) irrespective of the ability or otherwise of MR_n to interact with the unpaired electron. The spin density at M, ρ_M , which arises by hyperconjugation can be calculated from the hyperfine splitting due to M. In the radicals $(\text{Me}_3\text{C})_2\dot{\text{C}}\text{H}_2\text{CF}_3$ and $(\text{Me}_3\text{C})_2\dot{\text{C}}\text{H}_2\text{SiMe}_3$ the two ρ_M values are virtually identical, which must mean that CF_3 and SiMe_3 groups have the same intrinsic capacity for hyperconjugation with the unpaired electron. However, since in the unhindered case ($\text{R}' = \text{H}$) only $\cdot\text{CH}_2\text{CH}_2\text{SiMe}_3$ adopts conformation I, we must conclude that this conformational preference of the SiMe_3 group is not entirely due to the effects of hyperconjugation to the silicon.

Example 3: "Invisible" Hydrogen. The hyperfine splitting due to hydrogen attached to the β carbon on an alkyl radical, $a^{\text{H}\beta}$, arises principally by hyperconjugative delocalization of the unpaired electron into the hydrogen 1s orbital (i.e., $\cdot\text{CH}_2\text{CH}_3 \leftrightarrow \text{CH}_2=\text{CH}_2\cdot\text{H}$). For a radical which is planar at the α carbon, such a mechanism can operate only if the β hydrogens are not located in the nodal plane of the C_α $2p_z$ orbital. The magnitude of $a^{\text{H}\beta}$ therefore depends on the dihedral angle, θ , between the $\text{C}_\beta\text{-H}$ bond and the C_α $2p_z$ direction. The angular dependence of $a^{\text{H}\beta}$ can

(17) D. Griller, E. C. Horswill, and K. U. Ingold, *Mol. Phys.*, **27**, 1117 (1974).

(18) D. Griller, S. Icgli, C. Thankachan, and T. T. Tidwell, *J. Chem. Soc., Chem. Commun.*, 913 (1974).

(19) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).

(20) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965).

(21) D. E. Wood, L. F. Williams, R. F. Sprecher, and W. A. Lathan, *J. Am. Chem. Soc.*, **94**, 6241 (1972); D. E. Wood and R. F. Sprecher, *Mol. Phys.*, **26**, 1311 (1973).

(22) M. C. R. Symons, *Tetrahedron Lett.*, 207 (1973).

(23) D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6715 (1974).

(24) In this connection, it is worth noting that for $\cdot\text{CD}_3$ $a^{13\text{C}}$ is 2.3 G less than for $\cdot\text{CH}_3$.¹⁹

(25) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **93**, 846 (1971).

(26) T. Kawamura and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 6481 (1972).

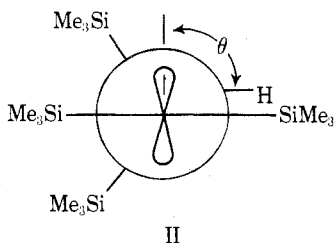
(27) A. R. Lyons and M. C. R. Symons, *Chem. Commun.*, 1068 (1971); *J. Chem. Soc., Faraday Trans. 2*, **68**, 622 (1972).

be represented by²⁸

$$a^{H\beta} = A + B \cos^2 \theta$$

and for the constants A and B values of 0–5 G and 40–50 G have been suggested.

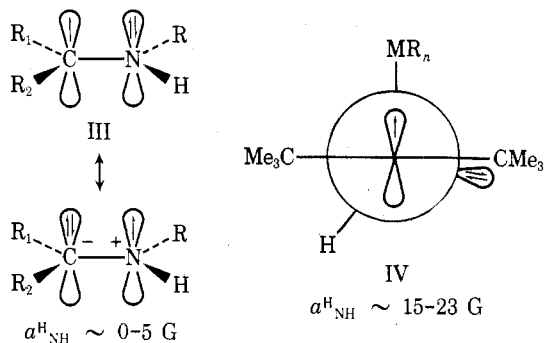
We have prepared the extremely persistent radical $(\text{Me}_3\text{Si})_2\dot{\text{C}}\text{CH}(\text{SiMe}_3)_2$, 14, by a large number of routes.^{29,30} The magnitude and the temperature independence of the hyperfine splittings due to the ^{29}Si atoms suggest that the radical adopts conformation II, i.e., $\theta = 90^\circ$, $B \cos^2 \theta = 0$; hence $a^{H\beta} = A$. Since no hyperfine splitting by the β hydrogen could be resolved, $a^{H\beta}$, and hence A , is less than, or equal to, the EPR line width of 0.27 G. A small value for A is supported by EPR data on many persistent 1,1,2,2-tetra-substituted ethyls,^{29,30} as well as by EPR data on some less hindered radicals.^{28,31}



II

Example 4: "Visible" Hydrogen. In persistent carbon-centered radicals steric effects frequently override the factors that produce stabilization energy. This is observed with persistent benzyls and allyls (see below) and with persistent α -aminoalkyl radicals.

Unhindered α -aminoalkyls, $\text{R}_1\text{R}_2\dot{\text{C}}\text{NHR}$, are probably planar at the α carbon and close to planar at nitrogen.³² They adopt conformation III because of the strong interaction of the unpaired electron with the lone pair on nitrogen. Since the amino hydrogen lies close to the C_α $2p_z$ nodal plane, $a^{H_{\text{NH}}}$ is always small and is sometimes invisible.³³ In contrast, persistent α -aminoalkyls formed by radical addition to 1,1-di-*tert*-butylimine (e.g., 15) are, for steric reasons, forced to adopt conformation IV, even though the



(28) See, e.g., H. Fischer in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 19.

(29) D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6203 (1974).

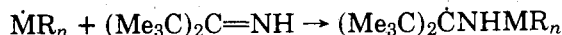
(30) D. Griller, J. W. Cooper, and K. U. Ingold, *J. Am. Chem. Soc.*, **97**, 4269 (1975).

(31) See, e.g., G. A. Russell, G. W. Holland, and K.-Y. Chang, *J. Am. Chem. Soc.*, **89**, 6629 (1967); K. W. Bowers, R. W. Giese, J. Grimshaw, H. O. House, N. H. Kolodny, K. Kronberg, and D. K. Roe, *ibid.*, **92**, 2783 (1970).

(32) A. R. Lyons and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, **68**, 502 (1972).

(33) See, e.g., D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, **52**, 3840 (1970); **53**, 3932 (1970); P. Neta and R. W. Fessenden, *J. Phys. Chem.*, **75**, 738 (1971).

odd-electron-lone-pair interaction is lost and the radical is no longer stabilized.³⁴

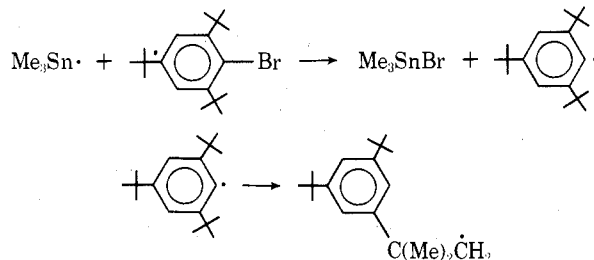


Since the amino hydrogen has now been twisted out of the nodal plane, $a^{H_{\text{NH}}}$ is dramatically increased, i.e., the amino hydrogen is "visualized" by steric effects.³⁴

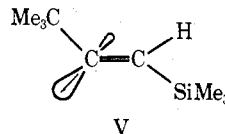
Persistent Destabilized Radicals

Destabilized radicals form much stronger bonds to hydrogen (and to other atoms) than do alkyl radicals. As a consequence, in solution destabilized radicals are normally destroyed by thermodynamically favorable reactions with molecules in the surrounding medium. This means that their lifetimes are, in general, even shorter than the lifetimes of simple alkyl radicals, which makes their detection extremely difficult. For this reason, destabilized radicals such as phenyls³⁵ and vinyls³⁶ have only been observed when rates of radical formation are very high indeed. Protection of the radical center with bulky groups does, however, make these destabilized radicals persistent and, therefore, easily detectable.

A Persistent Phenyl. The 2,4,6-tri-*tert*-butylphenyl radical, 17, can be prepared from the corresponding bromide using trimethyltin radicals to remove the bromine.³⁷ It is relatively persistent (Table I), but its destabilization leads to its decay by an intramolecular hydrogen abstraction from one of its own *tert*-butyl groups. The resulting 3,5-di-*tert*-butylneophyl radical is transient but can be observed, together with the hindered phenyl, in the EPR spectrometer. The intramolecular hydrogen abstraction has a large deuterium isotope effect. Thus, the lifetime of tri-*tert*-perdeuteriobutylphenyl at -30° is 50 times that of the undeuterated phenyl.³⁷



Persistent Vinyl Radicals. We have prepared a large number of vinyls by radical additions to acetylenes such as $\text{Me}_3\text{CC}\equiv\text{CH}$ and $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$.³⁰ Vinyls having a β hydrogen, e.g., $\text{Me}_3\text{CC}=\text{CHSiMe}_3$, 18, and $\text{Me}_3\text{SiC}=\text{CHC}_6\text{H}_5$, are rather transient, though they are sufficiently long-lived to be detected by EPR spectroscopy. Their spectra indicate that they are "bent", as in, e.g., V. That is, they are



V

(34) R. A. Kaba, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, **96** 6202 (1974).

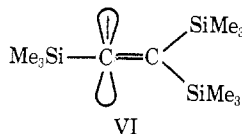
(35) A. L. J. Beckwith, *Intra-Sci. Chem. Rep.*, **4**, 127 (1970).

(36) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(37) L. R. C. Barclay, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 3011 (1974).

structurally similar to vinyl itself³⁶ and have the unpaired electron in an orbital with considerable s character. The two bulky groups are trans to one another.

Vinyls containing three bulky substituents were quite persistent, often having half-lives of minutes at room temperature. The majority of these radicals are also "bent", but $\text{Me}_3\text{SiC}=\text{C}(\text{SiMe}_3)_2$, **21**, is "linear", i.e., has structure VI. Such "linear" structures had previously only been observed in vinyls having an α substituent able to delocalize the unpaired electron, e.g., phenyl.³⁸ Presumably the "linear" structure of **21** is a consequence of large and symmetric steric effects.

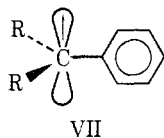


Persistent Stabilized Radicals

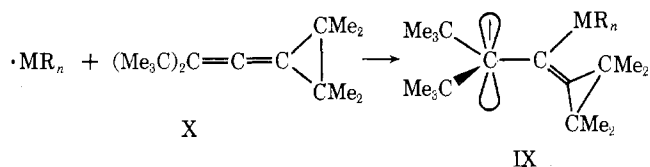
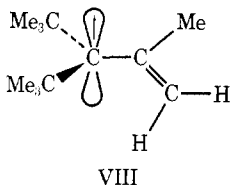
Benzyl, allyl, and cyclohexadienyl radicals are, for convenience, included in this class even when persistence is achieved at the expense of the radical's stabilization energy.

Benzyl Radicals. The 2,4,6-tri-*tert*-butylbenzyl radical, **22**, is not persistent (see above); but perchlorobenzyl is extremely persistent.³⁹ At room temperature it exists in solution in equilibrium with its dimer, the equilibrium mixture having a half-life of months.³⁹

For steric reasons, perchlorobenzyl has a "perpendicular" (or nearly "perpendicular") structure, VII, as does the persistent α,α -di-*tert*-butylbenzyl.⁴⁰ In this structure, the benzene ring has twisted through 90° so that it is no longer in conjugation with the unpaired electron. In achieving persistence these radicals sacrifice ca. 13 kcal/mol of stabilization energy,⁴ so they are no longer stabilized radicals.



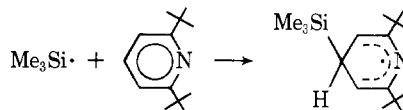
Allyl Radicals. Persistent allyls, like persistent benzyls, are not stabilized radicals. The 1,1-di-*tert*-butyl-2-methylallyl radical,⁴¹ VIII, has a "perpendic-



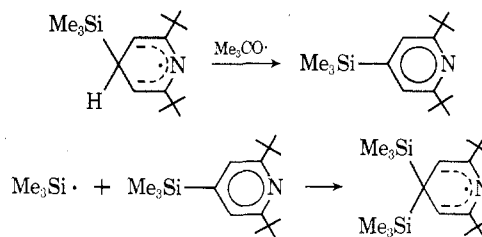
ular" structure, as do a large number of allyl radicals (IX) we have produced³⁰ by radical addition to alkenes such as di-*tert*-butylvinylidenetetramethylcyclopropane (X). Since these radicals lack a β hydrogen, some of them are extremely persistent (see Table I).

Cyclohexadienyls. These radicals are strongly stabilized ($E_s \sim 24$ kcal/mol)⁴ and can be made persistent with suitable blocking groups without losing their stabilization energy. They can be prepared by radical addition to suitably substituted benzenes, while nitrogen- and phosphorus-containing analogs can be prepared by addition to appropriate pyridines and phosphorins.⁴²

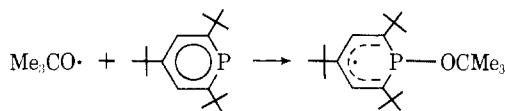
Radical additions to 1,3-di-*tert*-butylbenzene and 2,6-di-*tert*-butylpyridine occur readily, e.g.



A diadduct can also be formed which is much more persistent than the monoadduct, e.g.



Radical addition to 1,3,5-tri-*tert*-butylbenzene is not a facile process. However, the $\cdot\text{SiCl}_3$ radical adds to the nitrogen of 2,4,6-tri-*tert*-butylpyridine,⁴² and a wide variety of radicals add to the phosphorus of 2,4,6-tri-*tert*-butylphosphorin, e.g.



Conclusion

The reluctance of free-radical chemists to distinguish between the thermodynamic "stabilization" of a radical and its "persistence" in solution resulted in a very long delay between Gomberg's discovery of triphenylmethyl and the generation of persistent alkyl radicals that were not stabilized by p - π delocalization. However, once it was appreciated that persistence was principally a consequence of steric factors, it became a fairly simple matter to generate almost all types of carbon-centered radicals in persistent forms. These radicals are so new that their chemical behavior and the bulk of their physical properties are still unknown.

The general concept of sterically induced persistence has already been successfully extended to heteroatom-centered radicals such as, e.g., R_3Si ,⁴³

(38) J. E. Bennett and J. A. Howard, *Chem. Phys. Lett.*, **9**, 460 (1971).

(39) S. Olivella, M. Ballester, and J. Castaner, *Tetrahedron Lett.*, 587 (1974).

(40) K. Schreiner and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, **13**, 144 (1974).

(41) H. Ragenstein and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, **13**, 145 (1974).

(42) D. Griller, K. Dimroth, T. M. Fyles, and K. U. Ingold, *J. Am. Chem. Soc.*, **97**, 5526 (1975).

(43) J. D. Cotton, C. S. Cundy, D. H. Harris, A. Hudson, M. F. Lappert, and P. W. Lednor, *J. Chem. Soc., Chem. Commun.*, 651 (1974).

R_3Ge ,⁴³ R_3Sn ,⁴³ R_2N ,⁴⁴ $R_2C=N$,⁴⁵ and $R_2C=NO$ ⁴⁶ radicals. Its further extension to other areas of

(44) J. R. Roberts and K. U. Ingold, *J. Am. Chem. Soc.*, **95**, 3228 (1973).

(45) D. Griller, G. D. Mendenhall, W. Van Hoof, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6068 (1974).

chemistry where reactive intermediates are involved is a foregone conclusion.

(46) G. D. Mendenhall and K. U. Ingold, *J. Am. Chem. Soc.*, **95**, 2963 (1973); D. Lindsay, E. C. Horswill, D. W. Davidson, and K. U. Ingold, *Can. J. Chem.*, **52**, 3554 (1974).

Distinguishing between Concerted and Nonconcerted Eliminations

William H. Saunders, Jr.

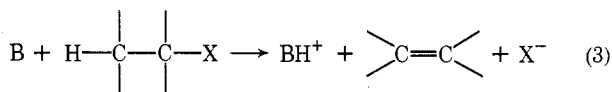
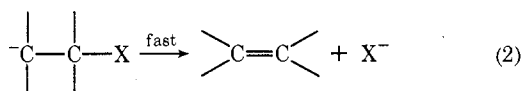
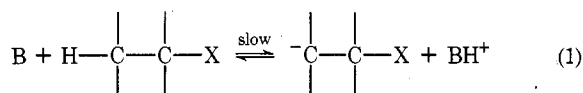
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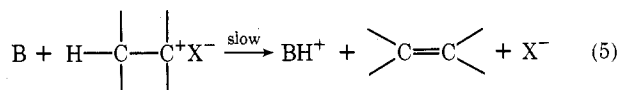
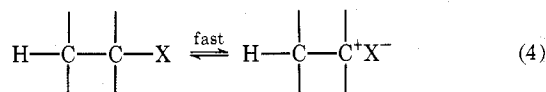
Recent articles by Bordwell have questioned the widely held view that concerted reactions in general¹ and concerted (E2) eliminations in particular² are quite common. He presents numerous examples of reactions for which there is evidence that they belong to the E1cB or ion-pair mechanisms, and then suggests that many more reactions formerly assigned to the E2 category may proceed by one of these mechanisms.

The scope of concerted processes is clearly a subject of wide interest. It is my aim in this Account to propose an operational definition of concerted elimination and to discuss evidence on the range of validity of the E2 mechanism.

Of the eight classes of elimination mechanisms cited by Bordwell,² there are three that show bimolecular kinetics and are particularly difficult to distinguish from each other: the irreversible carbanion mechanism (E1cB)_I, eq 1 and 2, the E2 mechanism, eq 3, and the (E2)_{ip} or ion-pair mechanism, eq 4–5.



E1cB and (E2)_{ip} mechanisms where the first and second steps happen to proceed at comparable rates will also show many of the characteristics of the E2 mechanism. Other types of bimolecular mechanisms are



readily distinguished from the above three. The (E1cB)_R mechanism, for example, in which the step shown in eq 1 is rapid and reversible, can be detected by isotopic exchange studies.

Before we can arrive at useful conclusions on the best ways of distinguishing the concerted E2 from the other two mechanisms, we must define precisely what we mean by the term "E2 mechanism". The basic definition, first proposed by Hanhart and Ingold in 1927,³ was a one-stage process in which base attacks the β hydrogen and removes it at the same time as the α -C-X bond is breaking and a carbon-carbon double bond is forming. These bond changes need not be precisely synchronous, and various workers have pointed out that C-X breaking may lag behind hydrogen transfer, or vice versa, at the transition state.³⁻⁸ This concept has become known as the "Variable Transition State Theory", and has been reviewed on numerous occasions, most recently by Saunders and Cockerill.⁹ Such a flexible concerted process can obviously mimic certain characteristics of the E1cB process at one extreme and the (E2)_{ip} process at the other.

Nonetheless, there is available, in principle, a clear operational distinction: for an E2 mechanism, the β

(1) F. G. Bordwell, *Acc. Chem. Res.*, **3**, 281 (1970).

(2) F. G. Bordwell, *Acc. Chem. Res.*, **5**, 374 (1972).

(3) W. Hanhart and C. K. Ingold, *J. Chem. Soc.*, 997 (1927).

(4) R. L. Letsinger, A. W. Schnizer, and E. Bobko, *J. Am. Chem. Soc.*, **73**, 5708 (1951).

(5) D. J. Cram, F. D. Greene, and C. H. DePuy, *J. Am. Chem. Soc.*, **78**, 790 (1956).

(6) C. H. DePuy and D. H. Froemsdorf, *J. Am. Chem. Soc.*, **79**, 3710 (1957).

(7) W. H. Saunders, Jr., and R. A. Williams, *J. Am. Chem. Soc.*, **79**, 3712 (1957).

(8) J. F. Bunnett, *Angew. Chem.*, **74**, 731 (1962); *Angew. Chem., Int. Ed. Engl.*, **1**, 225 (1962).

(9) W. H. Saunders, Jr., and A. F. Cockerill, "Mechanisms of Elimination Reactions", Wiley-Interscience, New York, N.Y., 1973, Chapter 2.

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