propyl-10-ethylidene-9,10-dihydroanthracene (**6b**) (42%). The latter structure was based on the nmr spectrum of the crude reaction product which showed a quartet at δ 6.09 (J = 7.5 Hz, vinylic) and a doublet at δ 2.12 ppm (J = 7.5 Hz, CH_3CH=) and formation of 9-isopropyl-10-ethylanthracene from acid-catalyzed rearrangement of the crude product. Isomerization took place under the conditions employed in the preceding example to afford a crude product (0.61 g) shown by glpc and nmr to contain 9-isopropyl-10-ethylanthracene (40%). Chromatography on alumina followed by crystallization from petroleum ether gave pure 9-isopropyl-10-ethylanthracene: mp 110–111°; nmr (CCl_4) δ 1.45 (t, 3, J = 7.5 Hz, CH_3CH_2), 1.75 (d, 6, J = 7.5 Hz, $(CH_3)_2CH$), 3.59 (q, 2, J = 7.5 Hz, CH_3CH_2), 4.53 (heptet, 1, J = 7.5 Hz, $(CH_3)_2CH$), 7.1–7.5 (m, 4, aromatic), and 8.1–8.5 ppm (m, 4, aromatic).

Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.81; H, 8.23.

Dehydrogenation of *trans*-9,10-Diisopropyl-9,10-dihydroanthracene (*trans*-5c). Similar reaction of *trans*-**5c** (0.66 g, 2.5 mmol) gave a crystalline product (0.65 g) shown to contain two components, *cis*-**5c** and 9-isopropyl-10-isopropylidene-9,10-dihydroanthracene (**6c**), in the ratio of 2:1 by nmr analysis in comparison with the authentic compounds.[35]

Epimerization of *trans*-5c to *cis*-5c. Similar reaction of *trans*-**5c** with the substitution of water (5 ml) for the cadmium salt afforded a product shown by nmr analysis to contain >95% *cis*-**5c**. Recrystallization from petroleum ether gave colorless crystals (0.55 g) of pure *cis*-**5c**: mp 114.5–115.5° (lit.[20,21] 116.5–117° and 109–110°); nmr (CCl_4) δ 0.99 (d, 12, J = 6 Hz, $(CH_3)_2CH$), 1.40–2.10 (m, 2, $(CH_3)_2CH$), 3.30 (d, 2, J = 9.5 Hz, benzylic), and 7.06 ppm (apparent s, 8, aromatic).

Acknowledgment. This research was supported by U. S. Public Health Service Grant CA 11968. The technical assistance of Mrs. Leticia Nazareno in the early part of this work is also gratefully acknowledged.

(35) In an earlier report[17b] from this laboratory the *cis*-**5c** structure was assigned to the product of reductive diisopropylation of anthracene with lithium and isopropyl chloride in liquid ammonia in analogy with the cis product shown to be obtained from reductive diethylation. However, it is now clear that the *trans*-**5c** structure is correct on the basis of the comparative nmr spectral analysis of both isomers by Zieger, *et al.*,[21] and by Redford.[20] The *trans*-**5c** isomer is also furnished in high yield from reduction of 9,10-diisopropylanthracene with lithium in ammonia by the procedure reported earlier.[17a]

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XIII. Di-*tert*-butylmethyl and Related Radicals[1]

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Abstract: Di-*tert*-butylmethyl, $B_2\dot{C}H$, and a wide variety of related radicals, *e.g.*, $B_3\dot{C}$, $B_2\dot{C}CH_2C_6H_5$, $B_2\dot{C}CH_2P$-(O)(OEt)$_2$, etc., are extremely long lived when compared with less highly substituted alkyl radicals. They show no sign of dimerizing even at low temperatures. At ambient temperatures these radicals decay with first-order kinetics and Arrhenius parameters for these reactions are reported. The decay mechanism could not be unequivocally established but it is believed to be either a β scission (*e.g.*, $B_2\dot{C}H \rightarrow B(H)C{=}CMe_2 + Me\cdot$) or a 1,3-intramolecular hydrogen atom transfer (*e.g.*, $B_2\dot{C}H \rightarrow BCH_2CMe_2\dot{C}H_2$). At low temperatures most $B_2\dot{C}CH_2R$ radicals decay with second-order kinetics, presumably yielding the disproportionation products, B_2CHCH_2R and $B_2C{=}CHR$.

It has recently been shown that nonconjugated carbon-centered radicals having bulky alkyl groups attached to the radical center possess remarkably long lives.[4] For example,[4] a 10^{-5} *M* solution of di-*tert*-butylmethyl prepared by hydrogen abstraction, by *tert*-butoxy, from the parent hydrocarbon has a half-life of about a minute at room temperature.[5] We now report in more detail on the decay kinetics of this radical and on the decay of a number of structurally related radicals containing the di-*tert*-butylmethyl moiety.

In this paper B is used to represent the *tert*-butyl group.

(1) Issued as N.R.C.C. No. 13,899. Part XII: D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 554 (1973).

(2) (a) N.R.C.C. Postdoctoral Fellow, 1971–1973. (b) N.R.C.C. Postdoctoral Fellow, 1973–1974.

(3) University of Toronto.

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

(5) In contrast, similar concentrations of less hindered carbon-centered radicals decay completely in a few milliseconds.[6]

(6) See, *e.g.*, G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 491 (1972).

Experimental Section

The general experimental technique has been adequately described in previous papers from this laboratory.[1,4,6]

Radical Generation. With one exception (*vide infra*), kinetic studies were carried out on radicals (R·) generated photolytically, directly in the cavity of a Varian E-3 epr spectrometer. The following methods were used.

A. Photolysis of a di-*tert*-butyl peroxide (BOOB) solution of RH.

$$BOOB \xrightarrow{h\nu} 2BO\cdot$$

$$BO\cdot + RH \longrightarrow BOH + R\cdot$$

B. Photolysis of a mixture of hexamethylditin and RCl.

$$Me_3SnSnMe_3 \xrightarrow{h\nu} 2Me_3Sn\cdot$$

$$Me_3Sn\cdot + RCl \longrightarrow Me_3SnCl + R\cdot$$

C. Photolysis of a mixture of BOOB, a trialkylsilane (generally Me_3SiH), and RCl.

$$BO\cdot + Me_3SiH \longrightarrow BOH + Me_3Si\cdot$$

$$Me_3Si\cdot + RCl \longrightarrow Me_3SiCl + R\cdot$$

D. Method A, B, or C carried out in the presence of 1,1-di-*tert*-butylethylene.[7]

$$R\cdot + B_2C{=}CH_2 \longrightarrow B_2\dot{C}CH_2R$$

E. Photolysis of a *tert*-butyl perester.

$$RC(O)OOB \xrightarrow{h\nu} R\cdot + CO_2 + BO\cdot$$

For all five methods an inert cosolvent such as benzene or cyclopropane was sometimes present.[8]

Method A was most suitable for kinetic studies but generally gave poorer epr spectra than the other methods (see below). This method rarely generated the radical cleanly and additional radicals could frequently be detected that arose from BO· attack on hydrogens other than those of interest. For example, with B_2CH_2 not only was $B_2\dot{C}H$ obtained but also a spectrum attributable to the $B_2CH_2CMe_2\dot{C}H_2$ radical. The latter radical (and other "secondary" radicals formed from other hydrocarbons) decayed almost instantly when the light was cut off[6] and so did not interfere with the decay of the long-lived radicals we wished to study.

Epr Spectra. The epr spectral parameters for the radicals studied in this work have been reported[4,7] and discussed in some detail[7] previously. We feel confident from these parameters that each radical has the structure assigned to it.[9]

One feature of the epr spectra that we are unable to account for with certainty is the very much poorer resolution obtained by method A than by any other method. Thus, with $B_2\dot{C}H$ the splittings due to the methyl protons are very readily detected at room temperature using methods B, C, and E, but method A gives only the two broad lines due to splitting by the α-H with small shoulders due to the methyl protons being just detectable. It is possible that this difference is due to a reduced rate of tumbling of $B_2\dot{C}H$ in the medium used in method A since a sample of B_2CH_2 in BOOB (under N_2) gave a weak but well-resolved spectrum of $B_2\dot{C}H$ on heating to 140°. The intensity of this signal could be improved by photolysis. Photolysis at room temperature yielded a much higher radical concentration but without the fine structure.

A similar effect was observed with $B_3\dot{C}$. That is, a strong, well-resolved spectrum was obtained by method B or C at room temperature. However, method A at room temperature gave a spectrum of three rather broad lines that might quite easily be mistaken for a 1:2:1 triplet. These broad lines could be readily resolved to show fine structure by heating the sample above 70°, photolysis no longer being necessary, and an excellent spectrum was obtained at 100°. At this temperature, it is quite obvious that the hyperfine splitting of the outer pair of lines is somewhat greater (0.68 G) than of the central line (0.51 G). On cooling to 40° the outer lines are destroyed and the inner line decays to about half its initial height in the first minute and then continues to decay at a similar rate. Clearly the inner line and outer pair of lines are due to different radicals. The epr parameters indicate that they are $B_3\dot{C}$ and $B_2\dot{C}H$, respectively. The process by which $B_2\dot{C}H$ is formed must be BO· attack on B_3CH, since no radicals were detectable when B_3CH was heated to 100° in benzene and photolyzed.

$$BO\cdot + B_3CH \longrightarrow B_3\dot{C}$$
$$BO\cdot + B_3CH \longrightarrow [B_2CHCMe_2\dot{C}H_2] \longrightarrow B_2\dot{C}H + Me_2C{=}CH_2$$

At −40° under continuous irradiation a very weak pair of lines outside those due to $B_2\dot{C}H$ were detectable which may well have been due to the intermediate $B_2CHCMe_2\dot{C}H_2$, $a_H \sim 21$ G.

Reagents. Carefully purified commercial materials were utilized except as noted below. In reporting ^1H and ^{13}C nmr spectra the chemical shifts are given in parts per million downfield from tetramethylsilane.

Di-*tert*-butylmethyl chloride, B_2CHCl, was prepared by the method of Kharasch, *et al.*[10] Reaction of B_2CHOH with phosgene yielded the chloroformate, $B_2COC(O)Cl$ ($n^{22.5}D$ 1.4382, lit.[10] $n^{20}D$ 1.4400), and this was decomposed thermally to the required chloride which was purified by preparative vpc ($n^{22}D$ 1.4470, lit.[10] $n^{20}D$ 1.4475; ^1H nmr, in isopentane, B_2CHCl, 3.55).

***tert*-Butylperoxy di-*tert*-butylacetate,** $B_2CHC(O)OOB$, was prepared as previously reported.[11]

1,1,3,3,5,5-Hexamethylcyclohexane, $(Me_2CCH_2)_3$, was prepared from 1,3,3,5,5-pentamethylcyclohexanol (Chemical Samples Co.) following literature procedures[12] and was purified by preparative vpc. The boiling point (183° at atmospheric pressure), freezing point (−13°), refractive index ($n^{20}D$ 1.4460), and ^1H nmr (CH_3 0.99, CH_2 2.00) were identical with literature[12] values.

Tri-*tert*-butylmethane, B_3CH, was prepared by Lee's method[13] except that the tri-*tert*-butylcarbinol, B_3COH, was isolated and purified prior to its conversion to tri-*tert*-butylcarbinyl *p*-nitrobenzoate.

Tri-*tert*-butylmethyl chloride, B_3CCl, was prepared by reacting the lithium salt of B_3COH with phosgene under argon at −25° using the same general procedure[10] as for B_2CHCl. B_3COH (4.2 g, 21 mmol) in 20 cm³ of ether was added to *tert*-butyllithium (27 mmol) in 20 cm³ of pentane under argon at −78°. After 3 hr, 4 cm³ of phosgene (∼56 mmol) was distilled into the B_3COLi solution. Reaction occurred on warming to −25° at which temperature lithium chloride was precipitated. The solution was warmed to room temperature and the organic phase washed with water and dried over anhydrous Na_2SO_4. After filtration and concentration to a yellow oil the infrared spectrum showed almost no carbonyl absorption, indicating the absence of chloroformate. However, photolysis of this oil in the presence of Me_6Sn_2 or of Me_3SiH and BOOB yielded a strong epr signal for the $B_3\dot{C}$ radical. It is clear that the chloroformate is formed but is thermally unstable at, or below, room temperature (*cf.* $B_2CHOC(O)Cl$[10]). Analysis of the oil by vpc indicated that it contained a lot of B_3COH and perhaps other compounds but that the chloride itself was unstable under the vpc conditions. For this reason, no attempt was made to purify the B_3CCl.

$$B_3COH \xrightarrow{BLi} B_3COLi \xrightarrow{COCl_2} [B_3COC(O)Cl] \longrightarrow B_3CCl + CO_2$$

Tris(trimethylsilyl)methane, $(Me_3Si)_3CH$, and **bis(trimethylsilyl)methane,** $(Me_3Si)_2CH_2$, were prepared by reaction of the Grignard of bromoform with trimethylchlorosilane following the procedure of Merker and Scott.[14] The boiling point, refractive index, and nmr spectra of both compounds were virtually identical with those reported in the literature.[14]

Tris(trimethylsilyl)methyl bromide, $(Me_3Si)_3CBr$, was prepared by reaction of $(Me_3Si)_3CH$ with *N*-bromosuccinimide following the procedure of Bock, *et al.*;[15] mp (sealed tube) 190° (lit.[15] 190°).

Product Studies. $B_2\dot{C}H$ from B_2CH_2 + BO·. The major products that could be formed in this reaction are those of bimolecular radical reactions involving $B_2\dot{C}H$ and the primary alkyl radical $BCH_2CMe_2\dot{C}H_2$, *i.e.*, **1**, **2**, and **3**, and the olefins that would be formed by β scission of $B_2\dot{C}H$ (*i.e.*, **4**) and $BCH_2CMe_2\dot{C}H_2$ (*i.e.*, isobutylene), together with *tert*-butyl alcohol.

$$BO\cdot + B_2CH_2 \longrightarrow BOH + BCH_2CMe_2\dot{C}H_2$$
$$BO\cdot + B_2CH_2 \longrightarrow BOH + B_2\dot{C}H$$

$$2BCH_2CMe_2\dot{C}H_2 \longrightarrow \underset{\mathbf{1}}{BCH_2CMe_2CH_2CH_2CMe_2CH_2B}$$

$$B_2\dot{C}H + BCH_2CMe_2\dot{C}H_2 \longrightarrow \underset{\mathbf{2}}{B_2CHCH_2CMe_2CH_2B}$$

$$2B_2\dot{C}H \longrightarrow \underset{\mathbf{3}}{B_2CHCHB_2}$$

$$B_2\dot{C}H \longrightarrow CH_3\cdot + \underset{\mathbf{4}}{B(H)C{=}CMe_2}$$

$$BCH_2CMe_2\dot{C}H_2 \longrightarrow B\dot{C}H_2 + Me_2C{=}CH_2$$

(7) D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6459 (1973), and unpublished results.

(8) Sceptic, "Getting reliable radical decay kinetics out of that mixture must be like trying to find a needle in a compost heap." Author, "It would be, if we did not use a magnet."

(9) For a recent example of a structural assignment problem with a carbon radical, see F. A. Neugebauer and W. R. Groh, *Tetrahedron Lett.*, 1005 (1973), and A. R. Bassindale, A. J. Bowles, A. Hudson, and R. A. Jackson, *ibid.*, 3185 (1973).

(10) M. S. Kharasch, Y. C. Liu, and W. Nudenberg, *J. Org. Chem.*, **19**, 1150 (1954).

(11) G. J. Abruscato and T. T. Tidwell, *J. Amer. Chem. Soc.*, **94**, 672 (1972).

(12) R. Ya. Levina and V. K. Daukshas, *Zh. Obshch. Khim.*, **30**, 3207 (1960); H. Friebolin, H. G. Schmid, S. Kabuss, and W. Faisst, *Org. Magn. Resonance*, **1**, 147 (1969).

(13) H. H. Lee, Thesis, University of Michigan, 1970.

(14) R. L. Merker and M. J. Scott, *J. Amer. Chem. Soc.*, **85**, 2243 (1963); *J. Organometal. Chem.*, **4**, 98 (1965).

(15) H. Bock, H. Seidl, and M. Fochler, *Chem. Ber.*, **101**, 2815 (1968).

Neat B_2CH_2 (0.5 g, 3.1 mmol) was reacted with BO· radicals produced by the thermal decomposition of di-*tert*-butyl hyponitrite, BONNOB (0.010 g, 5.8×10^{-2} mmol). The reactants were degassed and sealed under vacuum. They were held at room temperature for 8 days, at 30° for 3 days, and finally at 50° for 1 day to ensure complete destruction of the BONNOB. In the initial stages of this reaction the rate of BO· formation would be similar to that produced by photolysis of B_2CH_2 + BOOB mixtures in the epr cavity at full light intensity. The products were analyzed by vpc on an SE-30 column. In addition to unreacted B_2CH_2 there was BOH, BOOB, and two high molecular weight products that were formed in a ratio of 5:1, the more plentiful having a slightly shorter retention time (10 min *vs.* 14 min). The two compounds had no parent ions in their 70-eV mass spectra, but the remainder of their spectra were not inconsistent with that expected for any of the dimers **1**, **2**, and **3**. The olefin **4** was not detected in the reaction mixture and could not have been present in a yield exceeding 1% of the major high molecular weight product. It was shown that this olefin was stable to these experimental conditions, since in a separate reaction of BONNOB with B_2CH_2 containing 1% B(H)C=CMe₂ under otherwise identical conditions, very little olefin was consumed. The two high molecular weight compounds were again formed together with the two new products having somewhat shorter vpc retention times. These new products may come from the coupling of radicals derived from B_2CH_2 with the olefin or with radicals derived from the olefin.

In order to isolate larger quantities of the two high molecular weight compounds for structure determination, B_2CH_2 was reacted with BOOB (2:1 mol ratio) under argon at 110° for 166 hr (*ca.* 3 half-lives of BOOB). The compounds were formed in reasonable yield but in a ratio of 2:1 rather than 5:1. They were isolated by preparative vpc. The major compound is a liquid, bp 290–300° (cap), $n^{20}D$ 1.4490, with a molecular weight of 261 (vp osmometry), corresponding to one of the dimers **1**, **2**, or **3** (calcd mol wt = 254.50). The nmr spectra[16] indicates that it is the highly symmetric product produced by the coupling of two $BCH_2CMe_2\dot{C}H_2$ radicals, *i.e.*, **1**.

^{13}C nmr	**1**	^1H nmr
34.57 $(32.15)_3$	$C(CH_3)_3$	$(0.97\ s)_{3\times3}$
54.40	CH_2	$(1.22\ s)_2$
32.33 $(29.06)_2$	$C(CH_3)_2$	$(0.92\ s)_{3\times2}$
39.04	CH_2	$(1.18\ s)_2$

The minor compound is also a liquid (bp 289–292° (cap), $n^{20}D$ 1.4630) dimer (mol wt 261 by vp osmometry). Its nmr spectra indicate that it is produced by the coupling of a $BCH_2\dot{C}Me_2CH_2$ radical with a $B_2\dot{C}H$ radical, *i.e.*, **2**.

^{13}C nmr	**2**	^1H nmr
$[36.54\ (32.38)_3]_2$	$[C(CH_3)_3]_2$	$(0.97\ s)_{3\times3\times2}$
51.78	CH	1.16 m, $J = 3.5$
40.91	CH_2	$(1.39\ d)_2$
a $(30.99)_2$	$C(CH_3)_2$	$(0.94\ s)_{3\times2}$
59.36	CH_2	$(1.28\ s)_2$
35.45 $(32.39)_3$	$C(CH_3)_3$	$(0.97\ s)_{3\times3}$

[a] Probably not resolved from CH_3 groups at 32.38 and 32.39.

The primary alkyl radicals that combine to form **1** or trap $B_2\dot{C}H$ to give **2** may be formed by a direct reaction of BO· with B_2CH_2 or, possibly, from $B_2\dot{C}H$ by a 1–3 intramolecular hydrogen transfer.[17]

$$BO\cdot + B_2CH_2 \longrightarrow BOH + B_2\dot{C}H \dashrightarrow BCH_2CMe_2\dot{C}H_2$$

In order to determine the relative importance of these two processes, the hydrocarbon was chlorinated with *tert*-butyl hypochlorite, BOCl, the monochlorides were separated by preparative vpc, and the ratio of primary to secondary chloride was determined by nmr (B_2CHCl, 3.55; $BCH_2CMe_2CH_2Cl$, 3.28).

$$BO\cdot + B_2CH_2 \longrightarrow BOH + BCH_2CMe_2\dot{C}H_2 \xrightarrow{BOCl} BCH_2CMe_2CH_2Cl + BO\cdot$$

$$BO\cdot + B_2CH_2 \longrightarrow BOH + B_2\dot{C}H \xrightarrow{BOCl} B_2CHCl + BO\cdot$$

The rapidity of the reaction of alkyl radicals with BOCl[18] should prevent any significant rearrangement of the $B_2\dot{C}H$ radical.

Reaction of B_2CH_2 (4 ml) in CCl_4 (20 ml) containing $CHClCCl_2$ (1 ml)[19] with BOCl (2 ml) was carried out under argon for 4 hr at room temperature with photoinitiation by a tungsten filament lamp. The monochlorides were formed in *ca.* 50% yield and there was little polychlorination. The ratio of primary to secondary chlorides was *ca.* 10:1,[20] and this should be approximately equal to the rates of formation of the primary and secondary alkyl radicals in the BONNOB experiment. It seems not unreasonable to assume that the rate constants for the formation of **1** ($BCH_2CMe_2\dot{C}H_2$ coupling) and **2** (the cross-coupling reaction) will be similar (diffusion controlled), in which case the relative yields of **1** and **2** will be about 5:1 as is observed. That is, the dimeric products detected in the BONNOB experiments do *not* answer the question as to the mode of the slow first-order decay of $B_2\dot{C}H$ that is monitored by the epr since they can be wholly accounted for by fast-coupling and cross-coupling reactions. It would appear that the "residual" amount of $B_2\dot{C}H$ that decays slowly (because it is not trapped by the primary alkyl radical) is relatively small, at least in the BONNOB experiment where the radicals are being formed continuously. Our failure to detect the olefin **4** does not, therefore, necessarily exclude a slow β scission of "residual" $B_2\dot{C}H$ in the discontinuous epr experiments. Decay of "residual" $B_2\dot{C}H$ by a 1,3-intramolecular hydrogen transfer is also consistent with these product studies.

$B_2\dot{C}H$ from B_2CHCl + Na. In an attempt to generate $B_2\dot{C}H$ uncontaminated by the primary alkyl radical, neat B_2CHCl (0.30 g, 1.8 mmol) was stirred with finely divided sodium (0.10 g, 4.4 mmol) under argon for 6 days at room temperature and then 1 day at 50°. The pasty reaction mixture was diluted with cyclopentane, the excess sodium was destroyed with water, and the organic layer was washed with water and then dried over Na_2SO_4. Analysis by vpc indicated that all the chloride had reacted. No **4** was detected (though a small amount was produced at higher temperatures[4]) nor were compounds **1** or **2** formed, but B_2CH_2 was formed in 5–10% yield. The only other product (or products) was thermally unstable at the vpc temperatures (200–240°) used to analyze for **1** and **2**. However, vpc analyses on a short (3 ft) silicone–rubber column at 150° showed a single peak with a retention time of 31.5 min. (Under the same conditions **1** took 16.5 min and **2** 24 min). Mass spectrometry indicated that this peak was due to a hydrocarbon that did not give a parent ion. Removal of the volatiles by mechanical pumping gave 0.12 g of crystals in a yellow oil. Chromatography on a short silica column with hexane as elutant, followed by recrystallization from MeOH, yielded 0.045 g of white crystals, mp 168–172°, with considerable softening and fusion of the crystals at temperatures well below the melting point. The molecular weight (vp osmometry) of this compound was 257 which suggests that it is the remaining dimer **3** (calcd mol wt = 254.50). The ^1H and ^{13}C nmr spectra of this compound show resonances from two types of methyl groups, one type of methine group and two types of quaternary carbon atoms in the ratio 3:3:1:1:1. In $CDCl_3$ at room temperature the chemical shifts are: CH_3, 1.13 s; CH_3, 1.23 s; *CH*, 2.30 s; CH_3, 35.64; CH_3, 36.05; C_{quat}, 37.01; C_{quat}, 39.61; *CH*, 58.37. While various conformations of **3** *could* produce equivalent methine groups and nonequivalent *tert*-butyl groups, molecular models suggest that in the least hindered, staggered conformation **3a** the *tert*-butyl groups cannot rotate because their methyl groups are interlocked, **3b**. The methyl groups themselves should, however, be able to rotate freely. In such a rigid conformation one methyl group of each *tert*-butyl lies approximately

(16) We are indebted to Dr. I. C. P. Smith for help in interpretation of the ^{13}C spectra. The chemical shifts for both ^1H and ^{13}C are given in parts per million downfield from TMS.

(17) The occurrence or otherwise of 1–3 H shifts is still a matter in dispute; see, *e.g.*, R. Kh. Freidlina, *Advan. Free-Radical Chem.*, **1**, 211 (1965); J. W. Wilt, "Free Radicals," Vol. I, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, Chapter 8.

(18) K. U. Ingold in "Free Radicals," Vol. I, J. K. Kochi, Ed., Wiley, New York, N. Y., 1972, Chapter 2.

(19) To "mop-up" chlorine atoms, *cf.* C. Walling and J. A. McGuiness, *J. Amer. Chem. Soc.*, **91**, 2053 (1969); A. A. Zavitsas and J. D. Blank, *ibid.*, **94**, 4603 (1972).

(20) For comparison, this ratio is 4.5:1 and 1:1 for photochlorination by chlorine in CCl_4 and in 4 *M* benzene in CCl_4, respectively: G. A. Russell and P. G. Haffley, *J. Org. Chem.*, **31**, 1869 (1966). The predominant attack on the primary hydrogens by BO· (which is normally more selective than Cl) is probably due to steric factors.

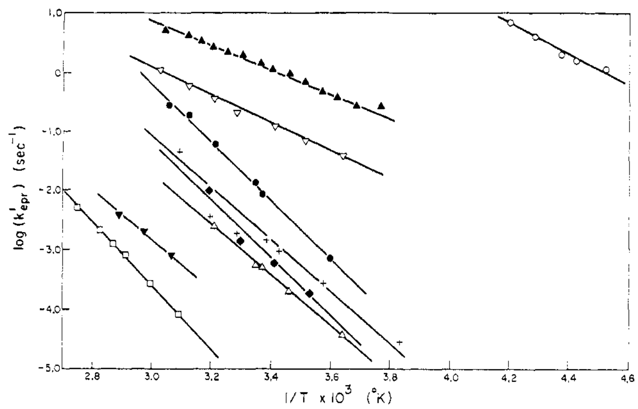
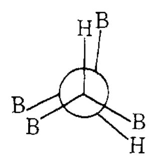
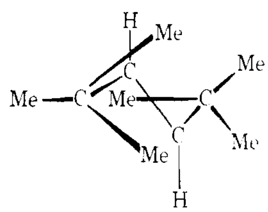


Figure 1. Arrhenius plots for the first-order decay of di-*tert*-butylmethyl and related radicals: (□) $(Me_3Si)_3\dot{C}$; (▼) $B_2\dot{C}CH_2C_6H_5$; (△) Me_6-cyclohexyl; (◆) $B_3\dot{C}$; + Me_5-cyclohexyl; (●) $B_2\dot{C}H$; (▽) $B_2\dot{C}CH_2P(O)(OEt)_2$; (▲) $B_2\dot{C}CH_2SiBu_3{}^n$; (○) $B_2\dot{C}CH_2SCF_3$.



3a



3b
side view of 3
showing only two B groups

in the plane defined by the four quaternary carbon atoms while the other two methyl groups make an angle of 60° with this plane, nursing between themselves the "coplanar" methyl group of the next *tert*-butyl. In this way two types of quaternary carbon are produced, one having the "coplanar" methyl pointing in approximately the same direction as the central C–C bond and the other with the "coplanar" methyl pointing approximately perpendicular to this bond (see **3b**). This model produces four types of methyl groups in a 2:1:2:1 ratio but, to account for the nmr spectra, these must fortuitously be magnetically equivalent in triads (3:3). The barrier to rotation of the *tert*-butyl groups must be fairly high since the ^{1}H nmr spectrum at 120° in $CHCl_2CHCl_2$ is the same as the room-temperature spectrum.

We suggest that *if* this compound is indeed **3** that it is formed *via* the sequence

$$B_2CHCl + Na \longrightarrow B_2\dot{C}H + Cl^-Na^+$$

$$B_2\dot{C}H + Na \longrightarrow B_2CH^-Na^+$$

$$B_2CH^-Na^+ + B_2CHCl \longrightarrow B_2CHCHB_2 + Cl^-Na^+$$

rather than by the coupling of $B_2\dot{C}H$ radicals. All the steps in this scheme are likely to be extremely fast.[21] The low thermal stability of **3** is not entirely unexpected.[22]

$(Me_3Si)_3\dot{C}$. Determined attempts were made to isolate this radical since it was the most stable carbon-centered radical discovered[23] in this work[4] but without success. None of the following procedures yielded sufficient concentration of radicals to justify further work along the same lines: reaction of $(Me_3Si)_3CBr$ with (i) sodium, (ii) potassium, (iii) sodium–potassium alloy, (iv) zinc, (v) magnesium, (vi) mercury, and (vii) hexamethylditin. There was no reaction between $(Me_3Si)_3CBr$ and (i) cuprous bromide, (ii) silver, and (iii) the solvated electron, e_{aq}^-, nor did $(Me_3Si)_3CH$ react with silver oxide. Photolysis of $[(Me_3Si)_3C]_2Hg$ in hexane yielded the desired radicals, but they were of short lifetime. Attempts to carboxylate $(Me_3Si)_3CMgBr$ (with the object of preparing the acyl peroxide) were also unsuccessful. We are indebted to Dr. Din Lal for these studies.

(21) *Cf.* J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971).
(22) *Cf.* H. D. Beckhaus and C. Rüchardt, *Tetrahedron Lett.*, 1971 (1973).
(23) A. R. Bassindale, A. J. Bowles, M. A. Cook, C. Eaborn, A. Hudson, R. A. Jackson, and A. E. Jukes, *Chem. Commun.*, 559 (1970).

Results

Di-*tert*-butylmethyl radicals, $B_2\dot{C}H$, generated at concentrations in the range 10^{-5} to 10^{-6} *M* by methods A, B, C, and E had somewhat different half-lives ($\tau_{1/2}$).

Method A (B_2CH_2 + BOOB, *ca.* 1:1 by volume) gave long-lived radicals. Decays followed "clean" first-order kinetics (after the first 0.1–1.0 sec required to destroy the $B_2CH_2CMe_2\dot{C}H_2$ radical). The half-life at room temperature was unaffected by the initial $B_2\dot{C}H$ concentration (from *ca.* 2×10^{-5} to 5×10^{-7} *M*) and was not significantly altered (<5%) by dilution of a 1:1 v/v B_2CH_2:BOOB mixture with 5 parts of benzene or $CFCl_3$. The half-life was also independent of the B_2CH_2:BOOB ratio in the absence of solvent (from 1:5 to 5:1 v/v). In the temperature range 5–55° the decay can be represented by [24]

$$B_2\dot{C}H \xrightarrow{k^1_{epr}} \text{products}$$

with k^1_{epr} (sec^{-1}) = $(10^{14.9\pm1.5})(10^{-22.9\pm2.0/\theta})$, $\tau_{1/2}{}^{25°}$ = 58 sec, where θ = 2.3*RT* kcal/mol (see Figure 1 and Table I).

Method B ($B_2CHCl + Me_6Sn_2$, *ca.* 2:1 by volume) gave slightly curved first-order decay plots suggesting that there may have been some small contribution to decay from a kinetically second-order process. At initial $B_2\dot{C}H$ concentrations of 1×10^{-6} and 6×10^{-6} *M* $\tau_{1/2}{}^{25°}$ values were 2.2 and 1.8 sec, respectively. Since it seemed likely that the decay process involved hydrogen abstraction from the hexamethylditin, these decay kinetics were not examined further.

Method C ($B_2CHCl + Me_3SiH$ + BOOB, *ca.* 1:1:1 by volume) also gave somewhat curved first-order decay plots. At initial $B_2\dot{C}H$ concentrations of 1.5×10^{-6} and 1×10^{-5} *M*, $\tau_{1/2}{}^{25°}$ values were 0.85 and 0.35 sec, respectively. Presumably, the $B_2\dot{C}H$ radical attacks the silane (at the Si–H bond) even more readily than it attacks Me_6Sn_2. These decay kinetics were not further examined.

Method E ($B_2CHC(O)OOB$) gave reasonably good first-order decay kinetics. However, at a constant light intensity dilution with benzene gave both higher concentrations of radicals and increasing half-lives (see Table II). It seems very probable that this perester, like so many other peroxidic compounds, undergoes a radical-induced decomposition[25] and so does not provide a useful source of $B_2\dot{C}H$ for kinetic studies.

2,2,4,6,6-Pentamethylcyclohexyl radical, Me_5 cyclohexyl, is a cyclic analog of $B_2\dot{C}H$. The radicals were generated only by method A and concentrations in the range 10^{-5} to 10^{-6} *M* were readily obtained. The radicals were fairly long-lived as expected and decayed with first-order kinetics (with perhaps a small second-order component) at rates comparable to those found for $B_2\dot{C}H$ (see Figure 1).

2,2,4,4,6,6-Hexamethylcyclohexyl radical, Me_6 cyclohexyl, was "cleanly" prepared by method A. (This is not quite the case for pentamethylcyclohexyl, presumably because the BO· attacks the parent hydrocarbon

(24) This Arrhenius equation has been revised from that originally given[4] as a result of further work.
(25) For leading references, see C. Walling, "Free Radicals in Solutions," Wiley, New York, N. Y., 1957; A. G. Davies, "Organic Peroxides," Butterworths, London, 1961; D. Swern, "Organic Peroxides," Wiley, New York, N. Y., 1970, 1971; T. Koenig in "Free Radicals," Vol. 1, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973.

Table I. Kinetic Parameters for the Decay of Di-*tert*-butylmethyl and Related Radicals

Radical	Method of formation	$\tau_{1/2}^{25°}$, sec	log A^1_{epr}, sec^{-1}	E^1_{epr}, kcal/mol	$(k^2_{epr})^{-60°}$, M^{-1} sec^{-1}
$B_2\dot{C}H$	A	58	14.9 ± 1.5	22.9 ± 2.0	
Me_5 cyclohexyl	A	280	12.2 ± 2.3	20.2 ± 3.0	
Me_6 cyclohexyl	A	990	11.0 ± 1.5	19.3 ± 2.0	
$B_3\dot{C}$	A[a]	530	13.5 ± 4.0	22.3 ± 5.0	
$(Me_3Si)_3\dot{C}$	A	190,000	12.3 ± 1.5	24.1 ± 2.0	
$(Me_3Si)_2\dot{C}H$	A				$10^{8.6}$ [h]
$B_2\dot{C}Cl$	A				$10^{5.0}$
$B_2\dot{C}CH_2CCl_3$	D + A	6			19
$B_2\dot{C}CH_2Si$-n-Bu_3	D + A	0.3	(6.9 ± 1.5)[b]	(9.2 ± 2.0)[b]	43
$B_2\dot{C}CH_2P(O)(OEt)_2$	D[c]	3.5	(7.2 ± 1.5)[b]	(10.8 ± 2.0)[b]	32
$B_2\dot{C}CH_2SCF_3$	D[d]	0.0014[e]	10.5 ± 3.0	10.6 ± 4.0	
$B_2\dot{C}CH_2OCF_3$	D[f]	8			140
$B_2\dot{C}CH_2C_6H_5$	D[g]	8,700[e]	8.3 ± 3.0	16.9 ± 4.0	

[a] See text. [b] Arrhenius parameters obtained from the best line through the experimental points. However, it is likely that the decays may have some second-order component at the lower temperatures and that the points should be fitted by a curve, not a straight line. [c] $P(O)(OEt)_2$ by photolysis of BOOB + $(EtO)_2POP(OEt)_2$. [d] CF_3S by photolysis of CF_3SSCF_3. [e] Extrapolated. [f] CF_3O by photolysis of CF_3OOCF_3. [g] By photolysis of BOOB and triphenylborane. [h] At 25°.

Table II. Decay of $B_2\dot{C}H$ Generated from $B_2CHC(O)OOB$ in Benzene at 25°

$[B_2CHC(O)OOB]$, M	$[B_2\dot{C}H] \times 10^6$, M	$\tau_{1/2}^{25°}$, sec
3.3 (neat)	2	0.28
0.8	4	1.0
0.3	6	1.9
0.07	6	2.6
0.007	2	3.0

at a number of positions.) Decay occurs with clean first-order kinetics and a good Arrhenius plot is obtained.

At temperatures below 20° this radical is fairly stable and it was observed that, with the light off, if the sample was cooled to −40° the signal height decreased markedly, but the original signal was reobtained (without photolysis) by rewarming to 20°. This is *not* due to reversible dimerization of the radical since the radical concentration, determined by double integration, was essentially the same at the two temperatures (Table III). That is, the lines broaden on cooling so that the hyperfine resolution tends to be lost and the peak height due to the radical decreases without any actual loss of radicals.

Table III. Effect of Temperature on the Hexamethylcyclohexyl Radical

Temp, °C	Epr signal height[a,b]	Double integral[b]
+20	40	41
−40	14	39
+20	40	40

[a] Peak to peak on first derivative. [b] Arbitrary units.

Tri-*tert*-butylmethyl radical, $B_3C\cdot$, was generated by a modified method A in which the epr tube was immersed in boiling water for 30 sec and then dried rapidly and transferred to the epr cavity. Decays appeared to follow reasonably clean first-order kinetics and gave a reasonably good Arrhenius plot. However, the $B_3C\cdot$ concentrations were much smaller than were those of the previously discussed radicals and for this reason the errors in the Arrhenius equation are considerably greater than might be indicated by the deviation of the experimental points from the line.

Generation of $B_3C\cdot$ by method B (impure $B_3CCl:Me_6Sn_2$:benzene; 1:1:3 by volume) yielded the radical in much higher concentration and it was even longer lived, $\tau_{1/2}^{25°} \sim 21$ min, $\tau_{1/2}^{80°} \sim 2$ min. However, at 80° $B_3\dot{C}$ was present in the sample even in the absence of light, presumably because the B_3CCl is thermally unstable as is also indicated by our inability to vpc this compound. Measured half-lives of photochemically generated $B_3\dot{C}$ at *ca.* 80° are not easily related to true decay rate constants and for this reason Arrhenius parameters for decay are not quoted.

Generation of $B_3\dot{C}$ by method C yielded a very much shorter lived radical with $\tau_{1/2}^{25°} = 0.25$ sec.

Tris(trimethylsilyl)methyl radical, $(Me_3Si)_3\dot{C}$, generated by method A decayed with clean first-order kinetics and gave an excellent Arrhenius plot.[4] When generated by method B or C[23] the lifetime is very much shorter. All attempts to isolate the radical were unsuccessful (see Experimental Section).

Bis(trimethylsilyl)methyl radical, $(Me_3Si)_2\dot{C}H$, decays rapidly with *second*-order kinetics when generated by method A.[4]

$$2(Me_3Si)_2\dot{C}H \xrightarrow{k^2_{epr}} \text{products}$$

The rate constant for decay, k^2_{epr}, is $10^{8.6}$ M^{-1} sec^{-1} at 25°, which is close to the diffusion-controlled limit.[6]

Di-*tert*-butylchloromethyl radical, $B_2\dot{C}Cl$, generated by method A decayed rapidly and with *second*-order kinetics. In the temperature range −85 to +32° decay can be represented by

$$k^2_{epr}(M^{-1}\ \text{sec}^{-1}) = (10^{10\pm2})(10^{-5.2\pm3/\theta})$$

1,1-Di-*tert*-butyl-2-substituted ethyl radicals, $B_2\dot{C}CH_2R$, contain β hydrogens and are therefore, in principle, able to disproportionate, unlike the radicals discussed above.

$$2B_2\dot{C}CH_2R \longrightarrow B_2CHCH_2R + B_2C{=}CHR$$

The remarkable steric influence of the di-*tert*-butylmethyl moiety greatly retards this reaction. For the majority of these radicals at the concentrations normally employed (*ca.* 10^{-4} M) bimolecular decay, presumably the above disproportionation, does not dominate the kinetics until the temperature has been reduced to −50° or even lower. At ambient temperatures decays appear to follow first-order kinetics, though with $R = P(O)(OEt)_2$ there may be curvature in the Arrhenius plot (see Figure 1), which suggests a significant contribution from the second-order process at the lower temperatures.

When method A was used to generate R from RH (and in certain other cases), the possibility that a chain reaction might influence the decay kinetics was examined by varying the concentrations of the reagents.

$$B_2\dot{C}CH_2R + RH \longrightarrow B_2CHCH_2R + R\cdot$$

$$R\cdot + B_2C{=}CH_2 \longrightarrow B_2\dot{C}CH_2R$$

In no case was the first-order decay rate constant affected by the reagent concentration (see Table IV for some typical data).

Table IV. Effect of Reagent Concentration (% v/v) on k^1_{epr} at 25° for Decay of Two $B_2\dot{C}CH_2R$ Radicals

n-Bu_3SiH [RH]	$B_2C{=}CH_2$	BOOB	k^1_{epr}, sec^{-1}
3	3	94	0.89
21	26	53	0.92
31	38	31	0.94
36	27	37	0.96
42	16	42	0.95
47	6	47	0.95
86	3	11	0.83
$(EtO)_2POP(OEt)_2$ [$RP(OEt)_2$]			
22	11	67	0.17
53	7	40	0.16
80	3	17	0.15
87	2	11	0.15

All the $B_2\dot{C}CH_2R$ radicals examined, apart from $B_2\dot{C}CH_2C_6H_5$, had shorter lifetimes than the $B_2\dot{C}H$ radicals generated by method A. For the majority, the first-order decay rate constant was measured at 25° and the second-order rate constant at −50°. These data are included in Table I.

Discussion

The most interesting feature of the present work is the great lifetime of virtually all $B_2\dot{C}X$ radicals. Of course, many of the radicals studied could not disproportionate. Their first-order decay kinetics imply that these radicals do not dimerize at any significant rate at the concentrations at which they are generated, and $B_2\dot{C}H$ did not dimerize even at −130°.[4] However, the *tentative* identification of B_2CHCHB_2 (**3**) in the B_2CHCl + Na reaction implies that some $B_2\dot{C}X$ dimers can, perhaps, be formed but not, it would appear, at all readily by radical–radical reactions. Thus, at 25° the bimolecular rate constant for any dimerization of $B_2\dot{C}H$ must be less than 10^3 M^{-1} sec^{-1}.

The similarities in the values of $\tau_{1/2}^{25°}$, A^1_{epr}, and E^1_{epr} found for $B_2\dot{C}H$, Me_5- and Me_6-cyclohexyl, and $B_3\dot{C}$ radicals (see Table I and Figure 1) suggest that the mechanism of the first-order decay of all four of these radicals is similar. There are three conceivable reactions. Firstly, a pseudo-first-order process in which the radical abstracts hydrogen from a molecule of reactant to produce a much more reactive radical, *e.g.*

$$B_2\dot{C}H + B_2CH_2 \xrightarrow{\text{slow}} B_2CH_2 + BCH_2CMe_2\dot{C}H_2$$

$$B_2\dot{C}H + BCH_2CMe_2\dot{C}H_2 \xrightarrow{\text{fast}} \mathbf{2}$$

This possibility can, we believe, be ruled out by the fact that k^1_{epr} does not appear to depend on the B_2CH_2 (or BOOB) concentration. Furthermore, the A^1_{epr} values do not seem to be consistent with this mechanism. That is, under typical experimental conditions in method A the hydrocarbon concentration would be *ca.* 1 *M*. The preexponential factor for the slow (rate-controlling) reaction of the long-lived radical with its parent hydrocarbon, *e.g.*, $B_2\dot{C}H$ with BCH_2, would therefore be in the range 10^{11}–10^{15} M^{-1} sec^{-1}. Such a value is far too large for a hydrogen atom abstraction.[26]

The other two potential reactions are true unimolecular processes: an intramolecular 1,3 hydrogen transfer,[17] *e.g.*

$$B_2\dot{C}H \xrightarrow{\text{slow}} BCH_2CMe_2\dot{C}H_2$$

and a β scission with elimination of a methyl radical, *e.g.*

$$B_2\dot{C}H \xrightarrow{\text{slow}} B(H)C{=}CMe_2 + Me\cdot$$

The latter reaction might be expected to have a preexponential factor of 10^{13}–10^{16} sec^{-1} and the former a factor of 10^{10}–10^{12} sec^{-1}.[27,28] However, the inaccuracies in our *A* factors and the difficulty of estimating *A* factors for reactions involving such sterically hindered radicals prevents a choice between the two reactions based only on kinetic grounds. For either process the observed rate constants for decay will be twice as great as the rate constants for the unimolecular reaction, since the active radical that is formed will, presumably, trap a second $B_2\dot{C}H$ radical.

We are inclined to favor the methyl elimination on several grounds. First, there is the facile β scission of the primary alkyl radical, $B_2CHCMe_2\dot{C}H_2$ ($\rightarrow B_2\dot{C}H + Me_2C{=}CH_2$). Presumably, this β scission is promoted by the relief of steric hindrance in the radical. In the $B_2\dot{C}H$ radical and other like radicals a methyl elimination would also decrease crowding. In contrast, an intramolecular hydrogen transfer in $B_2\dot{C}H$ would change the hybridization of the central carbon from sp^2 to sp^3 which would increase steric hindrance and might therefore be expected to be slow.

A methyl elimination is also somewhat favored by the greater stability of $(Me_3Si)_3\dot{C}$ compared with $B_3\dot{C}$, it being well known that carbon–silicon double bonds are not easily formed.[31]

Although the above arguments favor methyl elimination as the first-order decay process, this could not be

(26) Typical *A* factors for H atom abstractions are in the range 10^8–10^9 M^{-1} sec^{-1}.[27]

(27) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

(28) Although much lower preexponential factors have been reported for some 1,4- and 1,5-intramolecular hydrogen transfers,[29] it is possible that these low values are in error.[30]

(29) L. Endrenyi and D. J. LeRoy, *J. Phys. Chem.*, **70**, 4081 (1966); K. W. Watkins and L. A. Ostreko, *ibid.*, **73**, 2080 (1969); K. W. Watkins, *J. Amer. Chem. Soc.*, **93**, 6355 (1971); K. J. Mintz and D. J. LeRoy, *Can. J. Chem.*, **51**, 3534 (1973).

(30) K. W. Watkins, *Can. J. Chem.*, **50**, 3738 (1972).

(31) For recent information on this point, see P. Boudjouk, J. R. Roberts, C. M. Golino, and L. H. Sommer, *J. Amer. Chem. Soc.*, **94**, 7926 (1972); P. Boudjouk and L. H. Sommer, *Chem. Commun.*, 54 (1973); D. N. Roark and L. H. Sommer, *ibid.*, 167 (1973); T. J. Barton and C. L. McIntosh, *ibid.*, 861 (1972).

confirmed by product studies (see Experimental Section). That is, the expected olefin, B(H)C=CMe$_2$, was not detected when B_2CH_2 was reacted with thermally generated BO· or when B_2CHCl was reacted with sodium. The absence of olefin provides some support for the slow first-order decay occurring by an intermolecular 1,3 hydrogen transfer. However, as was pointed out (see Experimental Section) the absence of olefin under conditions where the radicals are being generated continuously does *not* rule out its formation during the slow decay of "residual" $B_2\dot{C}H$ (and other radicals) that is epr monitored. Until $B_2\dot{C}H$ radicals can be "cleanly" generated in unreactive media and their products analyzed, the question as to their mode of slow decay must remain unanswered.

The preexponential factors for the first-order decay of several of the $B_2\dot{C}CH_2R$ radicals are impossibly low for true unimolecular reactions. We believe this is due to the incursion of second-order decay processes. That is, at sufficiently low temperatures the $B_2\dot{C}CH_2R$ radicals decay by a bimolecular reaction that is presumed to be a disproportionation. Some contribution from this process increases the apparent value of k^1_{epr} to an increasing extent as the temperature is lowered and as a consequence the Arrhenius plots are probably curves rather than straight lines and hence the apparent value of A^1_{epr} is reduced.

The first-order decay rates for $B_2\dot{C}CH_2R$ radicals increase along the series R = $C_6H_5 \ll OCF_3 \leq CCl_3 <$ P(O)(OEt)$_2$ < Si-*n*-Bu$_3 \ll SCF_3$. The reversible addition of thiyl radicals to olefins has been firmly established in many studies,[32] which suggests that the rapid decay of $B_2\dot{C}CH_2SCF_3$ is due to the facile elimination of $CF_3S\cdot$

$$B_2\dot{C}CH_2SCF_3 \longrightarrow B_2C{=}CH_2 + CF_3S\cdot$$

An analogous β scission may be responsible for the first-order decay of most of the other $B_2\dot{C}CH_2R$ radicals. However, we would not expect the C_6H_5 radical to be eliminated, and in keeping with this the $B_2\dot{C}CH_2C_6H_5$ radical is remarkably stable. It probably decays in a manner analogous to $B_2\dot{C}H$, $B_3\dot{C}$, etc., but it is not clear why it should be more stable than these radicals.

The rapid bimolecular decay of $(Me_3Si)_2\dot{C}H$ and of $B_2\dot{C}Cl$ appears to be anomalous, although it is likely that the former radical is not particularly hindered.[33] The peculiar behavior of $B_2\dot{C}Cl$ is perhaps a consequence of the strong dipole present in this radical, which by dipole–dipole interaction holds pairs of radicals in close proximity to one another for sufficient time for them to react.

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(32) For leading references, see C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957; W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

(33) For example, $(Me_3Si)_4C$ can be prepared readily,[34] but B_4C has yet to be prepared.

(34) See, *e.g.*, H. Gilman and C. L. Smith, *J. Amer. Chem. Soc.*, **86**, 1454 (1964); R. L. Merker and M. J. Scott, *J. Organometal. Chem.*, **4**, 98 (1965); G. Kobrich and R. v. Nagel, *Tetrahedron Lett.*, 4693 (1970).

An Electron Spin Resonance Investigation of the 1-Aziridylcarbinyl and Related Free Radicals[1]

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Abstract: The 1-aziridylcarbinyl radical (**2**) could conceivably prefer a bisected conformation (**2a**) in which radical stabilization is derived by interaction with the three-membered ring as in the cyclopropylcarbinyl radical or a perpendicular alignment (**2b**) in which interaction with the nitrogen lone pair is maximized. The 1-aziridylcarbinyl radical has been generated from *N*-methylaziridine by abstraction of hydrogen by photochemically generated *tert*-butoxyl radicals at −136°. The observed hyperfine couplings, a^N = 10.68 G and $a_\alpha{}^H$ = 17.07 G, are consistent with a perpendicular conformation (**2b**) in contrast to the cyclopropylcarbinyl radical. INDO calculations support this conclusion predicting **2b** to be more stable than **2a**. At higher temperatures **2** undergoes ring opening to produce **4** in a manner analogous to the cyclopropylcarbinyl radical. Attempts to produce the (1-aziridyl)-1-ethyl radical (**7**) always gave spectra of the corresponding ring-opened radical **8**. An out-of-phase line-width effect in the β-proton splittings was noted for **4** and **8** indicating a significant difference in conformation between these radicals and the related allylcarbinyl radical. It is suggested that a 1,3 interaction between the unpaired electron and the lone pair of electrons on the nitrogen atom may be preferred over interaction with the double bond. Efforts to produce the cyclopropylamino radical (**3**) yielded the ring-opened radical **11** in solution and the imino species **12** in an adamantane matrix. INDO calculations suggest that the bisected conformation **3a** is more stable than the perpendicular alignment **3b**.

Cyclopropylcarbinyl radicals have been the subject of investigation for a number of years in order to determine whether these radicals are nonclassical in nature in analogy to the purported nonclassical cyclopropylcarbinyl cation. Product analyses in systems generating cyclopropylcarbinyl and allylcarbinyl radicals indicated that both exist as classical radicals with the cyclopropylcarbinyl radical as an unstable inter-

(1) (a) Nitrogen-Centered Free Radicals. Part VII. For part VI see W. C. Danen, C. T. West, and T. T. Kensler, *J. Amer. Chem. Soc.*, **95**, 5716 (1973). (b) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.