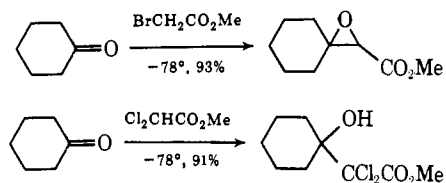dicyclohexylamide (1.2 equiv) (93% isolated yield).[6] Similarly, methyl dichloroacetate gave a hydroxy dichloro ester in 91% yield.

(6) Attempted isolation of the corresponding hydroxy bromide was unsuccessful.

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The 2,4,6-Tri-*tert*-butylphenyl Radical[1]

Sir:

Phenyl is known to be a σ radical from its electronic spectrum in the gas phase[2] and from its epr spectrum in matrices at low temperatures.[3,4] However, phenyl is so highly reactive that all attempts to detect it by spectroscopic methods in solution have, so far, been unsuccessful.[5]

In this laboratory, we have shown that free radicals of many different types can have their lifetimes increased substantially by attaching two (or more) *tert*-butyl groups close to the radical center.[6] We now wish to report the successful extension of this procedure to phenyl.

Photolysis, directly in the cavity of an epr spectrometer, of a solution of 2,4,6-tri-*tert*-butylbromobenzene, 1-Br, and hexamethylditin in cyclopropane yields a spectrum (Figure 1) we attribute to 2,4,6-tri-*tert*-butylphenyl, 1·, at ambient and lower temperatures.

$$\text{Me}_3\text{SnSnMe}_3 \xrightarrow{h\nu} 2\text{Me}_3\text{Sn}\cdot$$
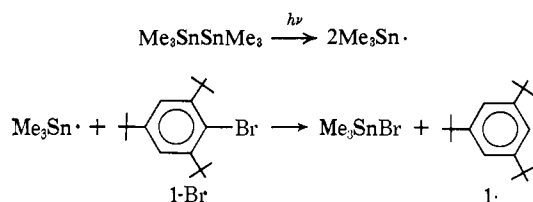
The stabilizing influence of the two ortho-*tert*-butyl groups is indicated by the absence of any epr spectrum when 3,5-di-*tert*-butylbromobenzene is treated in the same way as 1-Br. The spectrum of 1· can also be

(1) Issued as N.R.C.C. No. 13959.
(2) G. Porter and B. Ward, *Proc. Roy. Soc., Ser. A*, **287**, 457 (1965).
(3) J. E. Bennett, B. Mile, and A. Thomas, *Proc. Roy. Soc., Ser. A*, **293**, 246 (1966); J. E. Bennett, B. Mile, A. Thomas, and B. Ward, *Advan. Phys. Org. Chem.*, **8**, 1 (1970).
(4) P. H. Kasai, E. Hedaya, and E. B. Whipple, *J. Amer. Chem. Soc.*, **91**, 4364 (1969).
(5) However, the epr spectra of two phenyl radicals of the type $RC_6H_4\cdot$ (where $R = o$-C(O)N(CH$_3$)$_2$ and o-C(O)OCH$_3$), have been detected in solution under conditions of very rapid radical generation; see A. L. J. Beckwith, *Intra-Sci. Chem. Rep.*, **4**, 127 (1970).
(6) See, *e.g.*, J. L. Brokenshire, G. D. Mendenhall, and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 5278 (1971); G. D. Mendenhall and K. U. Ingold, *ibid.*, **95**, 2963, 3422 (1973); *Chem. Brit.*, in press; G. D. Mendenhall, D. Griller, D. Lindsay, T. T. Tidwell, and K. U. Ingold, *J. Amer. Chem. Soc.*, in press; D. Griller and K. U. Ingold, *ibid.*, **95**, 6459 (1973) and in press.
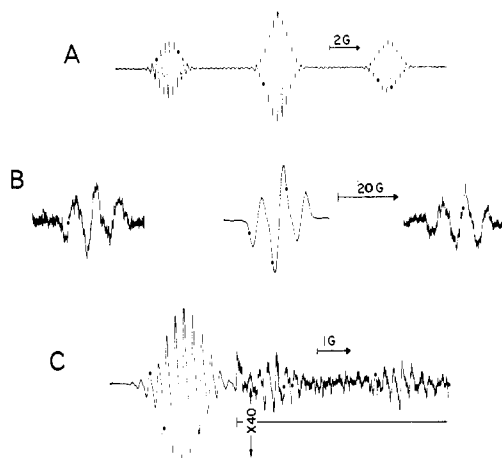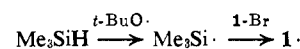
Figure 1. Epr spectrum of tri-*tert*-butylphenyl at $-40°$ in cyclopropane: A, main triplet; B, overmodulated spectrum showing $a^{13}\text{C}$ splitting; C, high field component of main triplet and ^{13}C splitting by ortho and meta carbons.

obtained by photolyzing cyclopropane solutions of 1-Br, trimethylsilane, and di-*tert*-butyl peroxide.

$$\text{Me}_3\text{SiH} \xrightarrow{t\text{-BuO}\cdot} \text{Me}_3\text{Si}\cdot \xrightarrow{1\text{-Br}} 1\cdot$$

No epr spectrum was obtained when 1-Br alone was photolyzed under the same conditions.

The spectrum of 1· consists principally of a 1:2:1 triplet (due to the meta protons) of multiplets (due to "through-space" coupling with the protons of the ortho-*tert*-butyl groups). The spectrum is sufficiently intense to detect coupling to ^{13}C in natural abundance at the α-position and at the ortho and meta positions. The epr parameters (Table I) are in good agreement

Table I. Epr Spectral Parameters for Phenyl Radicals (hyperfine splittings in Gauss)

	1· at $-40°$	Phenyl Exptl		Theoretical[c]
a^H(ortho)		18.1[a]	17.4[b]	18.7
a^H(meta)	7.31	6.4[a]	5.9[b]	6.1
a^H(para)		<3.0[a]	1.9[b]	3.9
a^H(o-t-Bu)	0.298			
$a^{13}C(\alpha)$	122.5	129[a]		151.3
$a^{13}C$(ortho)	6.16[d]			-4.8
$a^{13}C$(meta)	14.52[d]			10.7
$a^{13}C$(para)				-2.6
$a^{13}C$(CH$_3$ of o-t-Bu)	2.02[e]			
g	2.00238		2.00237[b]	

[a] From ref 3 and 4. Spectrum was obtained in an H$_2$O matrix at 77°K, slightly different splittings being obtained in other matrices. [b] From ref 5. Spectrum was obtained in an argon matrix at 4°K. [c] From ref 7. [d] Assigned on basis of theoretical phenyl spectrum. [e] From C$_6$H$_2$[C(CD$_3$)$_3$]$_3$.

with those found for phenyl in matrices and also with those calculated for phenyl.[7]

For best resolution, the spectrum of 1· is measured at low power levels ($\leqslant 0.2$ mW) and low modulation (0.1 G). On raising the power a second radical becomes visible (see Figure 2) whose spectral parameters (a^H(2 H) $= 21.70$ G, a^H(6 H) $= 1.02$ G, $g = 2.00248$ at 0°) are identical with those of 3,5-di-*tert*-butylneophyl, 2·,

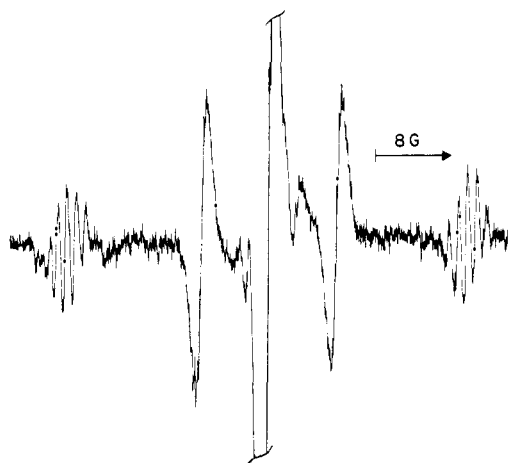(7) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968).
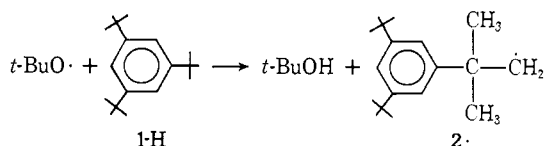
Figure 2. Epr spectrum of tri-*tert*-butylphenyl and di-*tert*-butyl-neophyl at −40°. Microwave power and modulation set to optimize the signal from di-*tert*-butylneophyl.

obtained by photolysis of **1**-H indi-*tert*- butyl peroxide under identical conditions.[8]

Under steady illumination, the concentration ratio [**2·**]/[**1·**] decreases with decreasing temperature. Furthermore, at any one temperature below 0° the concentration of **1·** is proportional to the first power of the light intensity, while the concentration of **2·** is proportional to the square root of the intensity. This implies that **1·** decays by a first-order process and **2·** by a second-order process. We presume that **1·** isomerizes to **2·**,[9] which then dimerizes at these temperatures.[11]

$$ 1\cdot \xrightarrow{k_{\text{isom}}} 2\cdot \xrightarrow{2\cdot} (2)_2 $$
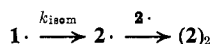
The rate constant for this isomerization was measured by the kinetic epr technique.[12] Over the temperature range −30 to −90°, k_{isom} was independent of the concentrations of **1**-Br, ditin, and cyclopropane and could be represented by

$$ \log\,(k_{\text{isom}}/\text{sec}^{-1}) = 5.3 - 4.5/\theta $$

where $\theta = 2.3RT$ kcal/mol. The preexponential factor for this isomerization is lower than is found for most intramolecular hydrogen abstractions,[13] possibly because this reaction involves a five- rather than the more usual six-membered transition state.

Photolysis in cyclopropane of the ditin and **1**-Br fully deuterated in the *tert*-butyl groups yielded a much more

(8) No signal was produced from the peroxide in the absence of **1**-H.
(9) Photolysis of **1**-Br in cyclohexane at room temperature yields **1**-H in over 65% yield.[10]
(10) I. T. McMaster, unpublished work.
(11) At higher temperatures **2·** would isomerize to the 2-methyl-2-(3′,5′-di-*tert*-butylbenzyl)ethyl radical, see *e.g.*, E. J. Hamilton, Jr., and H. Fischer, *Helv. Chim. Acta,* **56**, 795 (1973).
(12) See K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.,* **93**, 902 (1971), and subsequent papers in this series.
(13) See, *e.g.*, 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); *Can. J. Chem.,* **50**, 3738 (1972); *J. Phys. Chem.,* **77**, 2938 (1973); K. J. Mintz and D. J. LeRoy, *Can. J. Chem.,* **51**, 3534 (1973).

stable phenyl radical having the expected epr signal (*i.e.*, a triplet due to meta protons, with a^D(*o-tert*-butyl) = 0.047 G). The ^{13}C coupling to the six methyl groups of the ortho-*tert*-butyls was also resolved. There was only sufficient material for kinetic measurements at −30°. Decay was first order with $(k_{\text{isom}})_D = 0.38$ sec^{-1}, giving an isotope effect (primary plus secondary) for isomerization, $(k_H/k_D)^{-30°} \approx 50$.

A few unsuccessful experiments may also be worth reporting. Ditin and trimethylsilane reacted directly with **1**-Cl in the absence of light to yield epr signals that did not appear to be **1·**. These reactions were soon over and so the epr signals did not persist for long enough to be analyzed in detail. 2,4,6-Triphenylbromobenzene treated in the same way as **1**-Br gave no epr signal, possibly because of its low solubility in cyclopropane.

L. R. C. Barclay,[14] **D. Griller, K. U. Ingold***
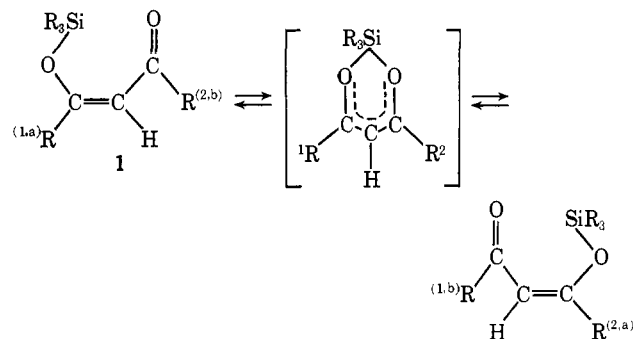*Division of Chemistry, National Research Council of Canada*
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Rearrangements of 1-Acetylacetonato-1-methyl-1-silacyclobutane *via* Internal Nucleophilic Displacement[1]

Sir:

Several acyclic silyl enol ethers[2-5] and related compounds[6,7] have been reported wherein the seqcis or *Z* isomers (**1**) undergo a facile 1,5-silyl group migration

between two oxygen centers exclusively with retention of configuration at silicon.[3-5] In accord with our originally proposed mechanism,[1] more recent results[5] indicate that these degenerate migrations are better viewed as internal nucleophilic displacement processes rather than as sigmatropic shifts. We now wish to

(1) This research was sponsored in part by the National Science Foundation Grant GP-29435.
(2) (a) J. J. Howe and T. J. Pinnavaia, *J. Amer. Chem. Soc.,* **91**, 5378 (1969); (b) T. J. Pinnavaia, W. T. Collins, and J. J. Howe, *ibid.,* **92**, 4544 (1970).
(3) I. K. Kusnezowa, K. Ruhlmann, and E. Grundemann, *J. Organometal. Chem.,* **47**, 53 (1973).
(4) J. A. Lindemulder, A. Schwartz, and T. J. Pinnavaia, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, INOR 20.
(5) H. J. Reich and D. A. Murcia, *J. Amer. Chem. Soc.,* **95**, 3418 (1973).
(6) Y. N. Kuo, F. Chen, and C. Ainsworth, *Chem. Commun.,* 137 (1971).
(7) (a) H. Shanan-Atidi and Y. Shvo, *Tetrahedron Lett.,* **7**, 603 (1971). (b) For a description of nomenclature see J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.,* **90**, 509 (1968).