

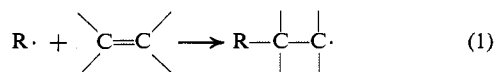
Detection and Identification of Short-Lived Free Radicals by Electron Spin Resonance Trapping Techniques (Spin Trapping). Photolysis of Organolead, -tin, and -mercury Compounds^{1,2}

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Abstract: A free-radical trapping technique is described which can be used to detect and identify reactive short-lived free radicals in reacting systems by obtaining the electron spin resonance spectrum of the radical addition product (a "spin adduct") of phenyl-*N-t*-butylnitrone (a "spin trap") (eq 6). The nitrogen and β -hydrogen hyperfine coupling constants of the spin adduct (an α -substituted benzyl-*t*-butylnitroxide) are a unique set of parameters for each reactive radical trapped. Verification for the structure of the spin adduct can be readily obtained for alkyl and aryl spin adducts by an addition reaction between the organolithium or Grignard compound of corresponding structure and phenyl-*t*-butylnitrone followed by oxygen oxidation. It has been shown that in the photolysis of organolead, -tin, and -mercury compounds the order of cleavage is phenyl > alkyl \gg acetate or halide. Phenyl or *n*-butyl carbon-tin bond cleavage occurs more readily than tin-tin bond cleavage. Stable radicals, *e.g.*, triphenylmethyl are not trapped. Very short-lived radicals, *e.g.*, acetoxy, are trapped without difficulty.

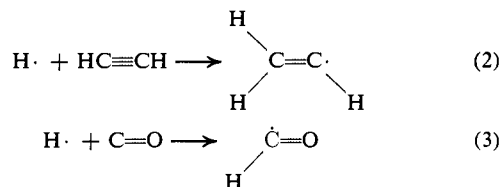
The addition of a free radical to an unsaturated bond is one of the most important reactions known in free-radical chemistry. Of particular relevance to this study are those free-radical additions which lead to a more "stable" (*i.e.*, longer lived) new radical (eq 1).



Compounds which react readily with reactive free radicals to produce stable radical addition products inhibit free-radical chain reactions and have received considerable attention in this regard.³ Quinones and di- and trinitro aromatic compounds are examples of such inhibitors.

The first application of electron spin resonance (esr) techniques to free-radical addition reactions was by Fraenkel, Hirshon, and Walling⁴ in a study of the free-radical-initiated polymerization of methyl methacrylate and by Bamford, Jenkins, Ingram, and Symons⁵ in the polymerization of acrylonitrile. More recently flow system techniques have been applied to this area by Fischer.⁶

The addition reaction of atoms or radicals to unsaturated bonds has been used to prepare free radicals of specific structure for esr study;^{7,8} *e.g.*, the addition of hydrogen atoms to acetylene or carbon monoxide produces vinyl⁹ or formyl¹⁰ radicals amenable for investigation (eq 2 and 3). Hydroxy,^{6,11} *t*-butoxy,¹² amino¹³



($\cdot\text{NH}_2$), and methyl¹¹ radical additions to olefins have been studied by esr. Hydroxy radical additions to benzene¹² (and other aromatic compounds¹²), oximes,¹⁴ and nitroalkane carbanions¹⁵ have also been observed. In all of these systems the radicals produced are relatively short lived and special techniques were employed to permit detection by esr (flow systems, high intensity radiation, and/or low temperatures). Development of such techniques has been of interest mainly for the purpose of obtaining spectra of new radicals for structural studies.

Since relatively few reactions which proceed by a free-radical mechanism can be studied directly by esr, because the concentration of radical intermediates is usually below the detection limit of commonly used spectrometers, a need exists for a technique whereby short-lived radicals can be detected and identified in reacting systems. Recently preliminary reports have appeared on esr studies of addition reactions which produce stable radicals. Thus the addition of a radical to either a nitro,^{16a} nitroso,^{16b} or nitrone¹⁷ function produces a nitroxide *e.g.*, eq 4. Mackor¹⁸ found the reaction of 2-nitroso-2-

(1) This work is being supported by AFOSR(SRC)-OAR U. S. Air Force Grant 1069-66.

(2) A preliminary report has appeared: E. G. Janzen and B. J. Blackburn, *J. Am. Chem. Soc.*, **90**, 5909 (1968).

(3) See, *e.g.*, C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, pp 75, 165-170.

(4) G. K. Fraenkel, J. M. Hirshon, and C. Walling, *J. Am. Chem. Soc.*, **76**, 3606 (1954).

(5) C. H. Bamford, A. D. Jenkins, D. J. E. Ingram, and M. C. R. Symons, *Nature*, **175**, 894 (1955).

(6) H. Fischer, *Z. Naturforsch.*, **19a**, 866 (1964).

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

(8) H. C. Heller, S. Schlick, and T. Cole, *J. Phys. Chem.*, **71**, 97 (1967).

(9) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **40**, 213 (1964).

(10) F. J. Adrain, E. L. Cochran, and V. A. Bowers, *ibid.*, **36**, 1661 (1962).

(11) For a review of this area see R. O. C. Norman and B. C. Gilbert, *Advan. Phys. Org. Chem.*, **5**, 53 (1967).

(12) J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, **90**, 7157 (1968).

(13) J. Dewing, G. F. Longster, J. Myatt, and P. F. Todd, *Chem. Commun.*, 391 (1965); C. Corvaja, H. Fischer, and G. Giacometti, *Z. Physik. Chem. (Frankfurt)*, **45**, 1 (1965).

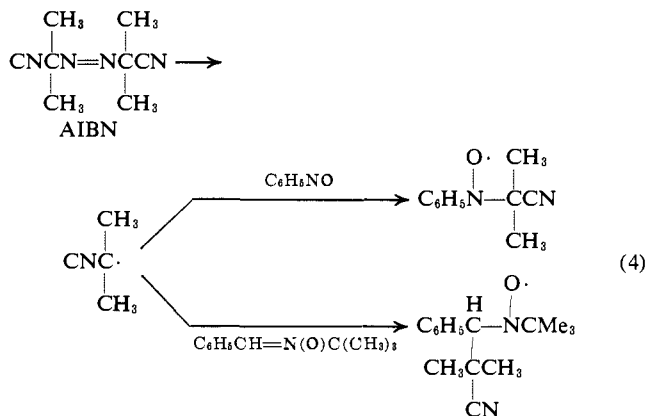
(14) J. Q. Adams, *J. Am. Chem. Soc.*, **89**, 6022 (1967).

(15) K. Eiben and R. W. Fessenden, *J. Phys. Chem.*, **72**, 3387 (1968).

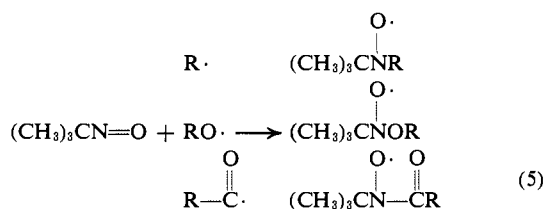
(16) (a) E. G. Janzen and J. L. Gerlock, *J. Am. Chem. Soc.*, **91**, 3108 (1969), and references therein; (b) A. K. Hoffmann, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *ibid.*, **86**, 639 (1964); see also B. A. Gingros and W. A. Waters, *J. Chem. Soc.*, 1920 (1954).

(17) M. Iwamura and N. Inamoto, *Bull. Chem. Soc. Japan*, **40**, 702, 703 (1967).

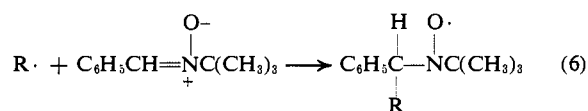
(18) A. Mackor "Photochemical Nitrosation of Hydrocarbons by Alkyl Nitrites," Thesis, University of Amsterdam, 1968, Bronder-Offset, Rotterdam (publishers); A. Mackor, Th. A. J. W. Wajer, Th. J. DeBoer, and J. D. W. van Voorst, *Tetrahedron Letters*, 2115 (1966); 385 (1967);



methylpropane (*t*-nitrosobutane) with alkyl, aralkyl, alkoxy, and acyl radicals produced the corresponding *t*-butylnitroxides (eq 5). The usefulness of *t*-nitroso-



butane for identification of radicals has also been recognized. Lagercrantz and Forshult¹⁹ trapped radiation-produced free radicals by dissolving previously irradiated solids in a solution of nitroso-*t*-butane and Chalfont, *et al.*,²⁰ detected a substituted *t*-butylnitroxide in *t*-butoxy-initiated styrene polymerization. In a preliminary paper^{2,21} we reported on a study of the feasibility of using phenyl-*t*-butylnitronone as a free-radical trap of general utility for the detection and identification of short-lived free radicals (eq 6). In this case identifica-



tion of the radical trapped is derived from the magnitude of the nitrogen and β -hydrogen hyperfine coupling constant (hfsc). This technique shows promise for the detection of free radicals in a variety of reactions and processes, *e.g.*, thermal decomposition, photolytic,^{16a} electrochemical, and biochemical reactions. Applications to radiation damage,¹⁹ polymerization,²⁰ and oxidation^{21b} reactions have already been made.

This paper describes the method and gives results on the radicals produced in the photolysis of certain organotin, -lead, and -mercury compounds.

Experimental Section

Method. A two-compartment sample holder previously described²² was used for all experiments. About 3 ml of benzene

A. Mackor, Th. A. J. W. Wajer, and Th. J. De Boer, *Tetrahedron Letters*, 2757 (1967); *Tetrahedron*, 24, 1623 (1968).

(19) C. Lagercrantz and S. Forshult, *Nature*, 218, 1247 (1968).

(20) G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Am. Chem. Soc.*, 90, 7141 (1968).

(21) (a) E. G. Janzen and B. J. Blackburn, Abstracts of Papers, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. ORGN-86; (b) E. G. Janzen, O. W. Maender, and B. Knaver, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. ORGN-73.

(22) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, 86, 1807 (1964); G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels,

containing approximately 0.06 *M* phenyl-*t*-butylnitronone was placed into one arm of the sample holder and covered with a rubber septum. Into the other arm was placed approximately 3 ml of benzene containing a varying amount of organometallic compound. Some of the materials tried were relatively insoluble in benzene and the saturated solution was used containing undissolved material. After outgassing with commercial "extra high purity" nitrogen for 15 min, the sample holder was inverted, and the solutions were thoroughly mixed and allowed to fill a flat quartz sample cell. The solutions remained colorless throughout. The cell was either a Varian product or one constructed in our laboratories of similar design. The first scan was obtained 5 min after mixing or sooner. In all cases a search was made for free radicals produced spontaneously by mixing the organometallic compound with the nitronone. Approximately 10 min was taken for this step. The sample cell was next irradiated for a short period of time, usually approximately 1 min (called "short irradiation" in description of results) and a careful search for free radicals made. Under these conditions the more unstable spin adducts could be detected. Finally the sample cell was irradiated continuously for at least 1 hr and the radicals produced were monitored.

Measurements were made on spectra obtained at scans of 100 G in 25 min at a chart speed of 1 in./min. Wherever possible and considered necessary three doublet spacings of two to four spectra were measured and averaged to give the β -H hfsc's reported. The spacings between the first and fifth peak, and the second and sixth peak were averaged and divided by two for two to four spectra to give the nitrogen hfsc reported. In some experiments both upfield and downfield scans were averaged. These measurements did not differ consistently but with a probable maximum error of 0.1 G for a given spacing. The averages of these measurements were very consistent for radicals obtained from different sources and at different concentrations. The averages were also reproducible in experiments performed over a period of months. The values given in Tables I and II show the kind of reproducibility observed for the same spin adducts obtained from various sources. For example for the phenyl spin adduct the average value for the nitrogen and β -H hfsc is 13.79 ± 0.033 and 2.11 ± 0.013 G, respectively, where the errors are average deviations. Maximum deviation was -0.08 G (for one experiment) but more commonly ± 0.06 G for the nitrogen hfsc and ± 0.03 G for the β -H hfsc. Reproducibility is good for spectra with sharp lines, for example, for the phenyl spin adduct (Figure 1). The values, for example, for the *n*-butyl spin adduct obtained from spectra with broader lines (Figure 2) show more scatter. Calibration of our scanning unit (Varian Fieldial purchased late 1963) has shown that the data were collected with an

Table I. Hyperfine Coupling Constants of *t*-Butyl α -Substituted Benzylnitroxides^a

R	Method	A_N	A_{β^H}
H	<i>b</i>	14.25	7.13
CH ₃	<i>b</i>	14.19	3.44
	<i>c</i>	14.15	3.41
	<i>d</i>	14.25	3.40
	<i>c</i>	13.93	3.21
CH ₂ CH ₂	<i>b</i>	14.04	3.04
	<i>c</i>	13.94	3.10
C ₆ H ₅ CH ₂	<i>d</i>	13.87	2.40
	<i>b</i>	13.73	2.06
	<i>c</i>	13.72	2.08
	<i>d</i>	13.73	2.07
	<i>e</i>	13.84	2.09
(C ₆ H ₅) ₃ C	<i>d</i>	13.86	2.00

^a In gauss in benzene at room temperature. ^b *p*-Nitroperbenzoic acid oxidation of the secondary amine of appropriate structure (see Experimental Section). ^c Addition of organolithium to PBN followed by oxygen oxidation. ^d Addition of organomagnesium bromide (iodide in the case of methyl) to PBN followed by oxygen oxidation. ^e Thermal decomposition of phenylazotriphenylmethane at room temperature in benzene.

A. J. Moye, S. Mak, and E. T. Strom, *Advances in Chemistry Series*, No. 51, American Chemical Society, Washington, D. C., 1965, p 167.

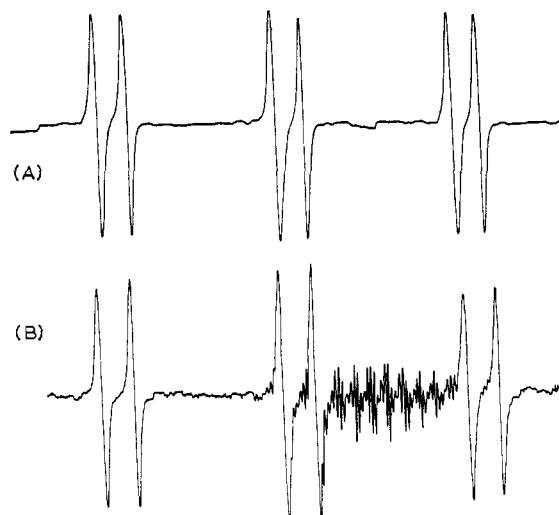


Figure 1. (A) The esr spectrum of benzhydryl-*t*-butylnitroxide obtained from the phenyllithium addition to phenyl-*t*-butylnitronone followed by oxygen oxidation. (B) The esr spectrum of benzhydryl-*t*-butylnitroxide obtained from phenyl radical addition to phenyl-*t*-butylnitronone using phenylazotriphenylmethane decomposition at room temperature as a source of phenyl radicals.

absolute error in field measurements of 4.4%. The data reported are not corrected by this calibration.

The same sample holder was used in the reactions of PBN with the organolithium and Grignard reagents. Approximately 3 ml of

Table II. Hyperfine Splitting Constants of Nitroxides Produced in the Photolysis of Organolead, -tin, and -mercury Compounds

$$\begin{array}{c} \text{O} \cdot \\ | \\ \text{C}_6\text{H}_5\text{CH}-\text{NC}(\text{CH}_3)_3 \\ | \\ \text{R} \end{array}$$

Source ^a	R	A_N^b	$A_{\beta^H}^b$
(C ₆ H ₅) ₄ Pb	C ₆ H ₅	13.79	2.09
<i>n</i> -Bu ₄ Pb	<i>n</i> -Bu	14.01	3.13
Et ₄ Pb	Et	13.89	3.20
(C ₆ H ₅) ₃ PbPb(C ₆ H ₅) ₃	C ₆ H ₅	13.81	2.13
(C ₆ H ₅) ₃ PbCl	C ₆ H ₅	13.78	2.09
(C ₆ H ₅) ₃ PbOAc	C ₆ H ₅	13.74	2.11
<i>n</i> -Bu ₃ PbOAc	<i>n</i> -Bu	13.94	3.10
Et ₃ PbOAc	Et	13.89	3.21
Me ₃ PbOAc	Me	14.22	3.45
(C ₆ H ₅) ₂ PbCl ₂	C ₆ H ₅	13.75	2.11
(C ₆ H ₅) ₂ Pb(OAc) ₂	C ₆ H ₅	13.85	2.11
<i>n</i> -Bu ₂ PbCl ₂	<i>n</i> -Bu	14.05	3.06
Et ₂ PbCl ₂	Et	13.93	3.24
C ₆ H ₅ Pb(OAc) ₃ ·H ₂ O	C ₆ H ₅	13.78	2.09
(C ₆ H ₅) ₄ Sn	C ₆ H ₅	13.73	2.08
(C ₆ H ₅) ₃ SnCl	C ₆ H ₅	13.81	2.14
(C ₆ H ₅ CH ₂) ₃ SnCl	C ₆ H ₅ CH ₂	13.90	2.31
<i>n</i> -Bu ₃ SnCl	<i>n</i> -Bu	14.15	3.13
(C ₆ H ₅ CH ₂) ₃ SnOAc	C ₆ H ₅ CH ₂	13.91	2.40
(C ₆ H ₅) ₃ SnCl ₂	C ₆ H ₅	13.83	2.11
(C ₆ H ₅) ₂ SnF ₂	C ₆ H ₅	13.83	2.12
<i>n</i> -BuSnCl ₃	<i>n</i> -Bu	13.94	3.09
<i>n</i> -Bu ₂ SnSn- <i>n</i> -Bu ₃	<i>n</i> -Bu	13.73	2.08
(C ₆ H ₅) ₃ SnSn(C ₆ H ₅) ₃	C ₆ H ₅	13.83	2.10
<i>n</i> -Bu ₂ SnH	H	14.22	7.11
(C ₆ H ₅) ₂ Hg	C ₆ H ₅	13.81	2.12
Et ₂ Hg	Et	14.00	3.19
(C ₆ H ₅ CH ₂) ₂ Hg	C ₆ H ₅ CH ₂	13.88	2.44
Me ₂ Hg	Me	14.20	3.45
MeHgI	Me	14.24	3.45
C ₆ H ₅ HgCl	C ₆ H ₅	13.80	2.09
C ₆ H ₅ HgOAc	C ₆ H ₅	13.71	2.11

^a Me = methyl; Et = ethyl; *n*-Bu = *n*-butyl; OAc = acetate.
^b In gauss in benzene at room temperature.

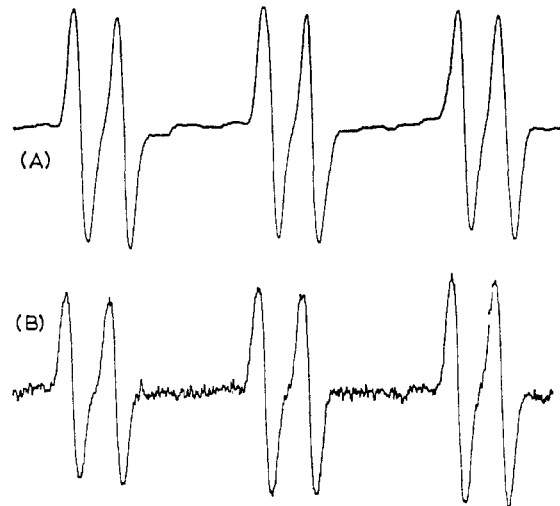


Figure 2. (A) The esr spectrum of the *n*-butyl spin adduct of phenyl-*t*-butylnitroxide (C₆H₅CH(C₆H₅)N(O·)C(CH₃)₃) produced by the *n*-butyllithium addition to phenyl-*t*-butylnitronone followed by oxygen oxidation. (B) The esr spectrum obtained upon photolysis of tetra-*n*-butyllead in the presence of phenyl-*t*-butylnitroxide in benzene.

0.06 *M* PBN in benzene solution was placed in one arm and 3 ml of benzene in the other. One or two drops of the organolithium or Grignard solution was added to the benzene solution after atmospheric air was flushed out of the cell with nitrogen. The solutions were mixed and oxygen was bubbled through the solution for 2 or 3 min. The solution was finally outgassed with nitrogen for 15 min and investigated. Usually the radical concentration was relatively high and a number of 50:1 dilutions were necessary to obtain good resolution.

The oxidation of the secondary amines to nitroxides were also performed in the same cell using *p*-nitroperbenzoic acid in benzene.²³

Chemicals. Methylithium, *n*-butyllithium, and phenyllithium were obtained from Alfa Inorganics, Inc. Ethyllithium was obtained from Foote Mineral Company.

Tetra-*n*-butyllead, tri-*n*-butyllead acetate, phenyllead triacetate monohydrate, and tetra-*n*-butyltin were obtained from Aldrich Chemical Co., Inc. Triphenyltin chloride, phenyl mercuric chloride, and phenylmercuric acetate were Eastman chemicals. Triphenyllead acetate, diphenyllead diacetate, and di-*n*-butyllead dichloride were received from Organisch Chem. Inst. TNO, Croesestraat, Utrecht, as free samples. Tri-*n*-butyltin chloride, di-*n*-butyltin dichloride, di-*n*-butyltin diacetate, and *n*-butyltin chloride were obtained as free samples from Carlisle Chemical Works, Inc., Reading, Ohio. Tribenzyltin chloride and mercuric acetate were obtained from Columbia and Baker Chemical Companies, respectively. Lead tetraacetate and hexaphenyldilead were available in our laboratories. Diphenyltin dichloride, hexaphenylditin, and hexaphenyldisilane were gifts from Dow Corning Corp. All the remaining organolead, -tin, and -mercury compounds were obtained from Alfa Inorganics, Inc. Benzoyl peroxide, *t*-butyl perbenzoate, and 40% peracetic acid in acetic acid were available from Dr. J. F. Garst and Dr. P. R. Story in these laboratories. *p*-Nitroperbenzoic acid was obtained from K + K Laboratories. Benzene was thiophene-free Mallinckrodt (analytical reagent grade) or Fischer (certified ACS grade) and was used without purification.

N-Benzylidene-*t*-butylamine was synthesized by the method of Emling, *et al.*²⁴ Benzaldehyde and *t*-butylamine were allowed to react in the presence of sodium hydroxide pellets at room temperature for 2 days. After work-up the dried product was distilled from potassium hydroxide pellets. The fraction boiling at 79.0–79.5° (9 mm) was collected.

2-*t*-Butyl-3-phenyloxazirane was prepared essentially by the method of Emmons.²⁵ Commercial 40% peracetic acid in peracetic

(23) G. Chapelet-Letourneaux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. France*, 3283 (1965); O. W. Maender and E. G. Janzen, *J. Org. Chem.*, in press.

(24) B. L. Emling, R. J. Horvath, A. J. Saraceno, E. F. Ellermeyer, L. Haile, and L. D. Hudac, *J. Org. Chem.*, 24, 657 (1959).

(25) W. D. Emmons, *J. Am. Chem. Soc.*, 79, 5739 (1957).

Table III. Summary of Spin Adducts Obtained from Photolysis of Organometallic Compounds^a

H·	CH ₃ ·	CH ₃ CH ₂ ·	CH ₃ (CH ₂) ₂ ·	C ₆ H ₅ ·	C ₆ H ₅ ·	C ₆ H ₅ CH ₂ ·	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}\cdot$	$\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}\cdot$
<i>n</i> -Bu ₃ SnH	Me ₃ PbOAc	Et ₃ Pb	<i>n</i> -Bu ₃ Pb	(C ₆ H ₅) ₄ Pb	(C ₆ H ₅) ₃ PbPb-	(C ₆ H ₅ CH ₂) ₃ SnCl	Et ₃ PbOAc	Hg(OBz) ₂
	Me ₄ Sn (weak)	Et ₃ PbOAc	<i>n</i> -Bu ₃ PbOAc	(C ₆ H ₅) ₃ PbCl	(C ₆ H ₅) ₃ PbOAc	(C ₆ H ₅ CH ₂) ₂ SnOAc	Me ₃ PbOAc	
	Me ₂ Hg	Et ₂ PbCl ₂	<i>n</i> -Bu ₂ PbCl ₂	(C ₆ H ₅) ₂ Pb(OAc) ₂	(C ₆ H ₅) ₂ PbCl ₂	(C ₆ H ₅ CH ₂) ₂ Hg	<i>n</i> -Bu ₂ Pb(OAc) ₂	C ₆ H ₅ Pb(OAc) ₃
	MeHgI	Et ₂ Hg	<i>n</i> -Bu ₂ Pb(OAc) ₂	C ₆ H ₅ Pb(OAc) ₃	(C ₆ H ₅) ₄ Sn		Hg(OAc) ₂	Pb(OAc) ₄
	MeHgCl		<i>n</i> -Bu ₄ Sn	(C ₆ H ₅) ₂ Sn- <i>n</i> -Bu ₂	(C ₆ H ₅) ₃ SnCl			
	Pb(OAc) ₄		<i>n</i> -Bu ₃ SnCl	(C ₆ H ₅) ₂ SnCl ₂	(C ₆ H ₅) ₂ SnF ₂			
	Hg(OAc) ₂		(C ₆ H ₅) ₂ Sn- <i>n</i> -Bu ₂	(C ₆ H ₅) ₂ Hg	C ₆ H ₅ HgCl			
			<i>n</i> -Bu ₂ Sn(OAc) ₂	C ₆ H ₅ HgOAc	(C ₆ H ₅) ₃ SnSn-			
			<i>n</i> -Bu ₃ SnSn-	Hg(OBz) ₂	(C ₆ H ₅) ₃			
			<i>n</i> -Bu ₃					

^a Me = methyl; Et = ethyl; *n*-Bu = *n*-butyl; OAc = acetate; OBz = benzoate.

acid previously stirred over anhydrous sodium acetate was added dropwise to a solution of *N*-benzylidene-*t*-butylamine in methylene chloride cooled in an ice bath. After work-up as described in ref 25, the oxazirane was sufficiently pure for conversion to the nitron.

Phenyl-*N*-*t*-butylnitron was prepared by refluxing 2-*t*-butyl-3-phenyloxazirane in dry acetonitrile for 3 days.²⁵

N-Benzyl-*t*-butylamine was prepared by the method of Bortnick, *et al.*,²⁶ which involves refluxing (2:1) *t*-butylamine and benzyl chloride for 12 hr in the presence of aqueous sodium hydroxide and a small amount of benzene, bp 96–97.5° (15 mm).

N-*t*-Butyl(α -methylbenzyl)amine was synthesized by the addition of methyl lithium (Alfa Chemical 2 *M* in diethyl ether) to *N*-benzylidene-*t*-butylamine.²⁴ The crude amine was used without purification after appropriate work-up.²⁴

N-*t*-Butyl(α -*n*-butyl)benzylamine was prepared by addition of *n*-butyllithium (Alfa Chemical, 22.9 wt % in hexane) to *N*-benzylidene-*t*-butylamine.²⁴ The crude amine was used without purification for the oxidation experiments. After purification and distillation (bp 53° (2 mm)) the nmr spectrum gave the following data: 0.97 (CH₃ and CH₂, 18), 3.68 (CH 1), and 7.20–7.31 ppm (aromatic, 5) in deuteriochloroform from tetramethylsilane.

N-Benzhydryl-*t*-butylamine was prepared by refluxing *t*-butylamine and benzhydryl chloride in the presence of silver sulfate for 6 weeks: mp 49.5–51.0°; nmr, 1.15 (CH₃, 9), 5.12 (CH, 1), and 7.22–7.65 ppm (aromatic, 10).

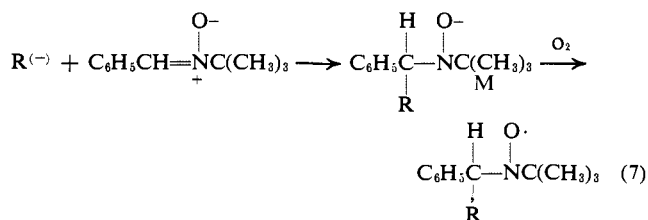
Results

In all work reported here phenyl-*t*-butylnitron was the radical trap used. For convenience phenyl-*t*-butylnitron is abbreviated PBN and is called a *spin trap*. The free-radical addition product is called a *spin adduct*. All experiments except where specified were carried out in benzene at room temperature.

Nitroxides of Known Structure. Although the *detection* of a spin adduct by esr appears (at this time) to provide proof of the presence of a short-lived reactive free radical in solution more information is required before *identification* of the structure of the free radical trapped can be made. The bulk and group electronegativity of the radical trapped determine the magnitude of the nitrogen and β -hydrogen coupling constants. However the magnitudes of these coupling constants are not necessarily known for a given spin adduct since relatively few nitroxides with these structures have been previously reported. Since solvent effects change the nitrogen coupling constant (increases to larger values in protic solvents) and in turn the β -H coupling, it is advantageous to have spectra of nitroxides of "known" structure available for comparison in the same solvent.

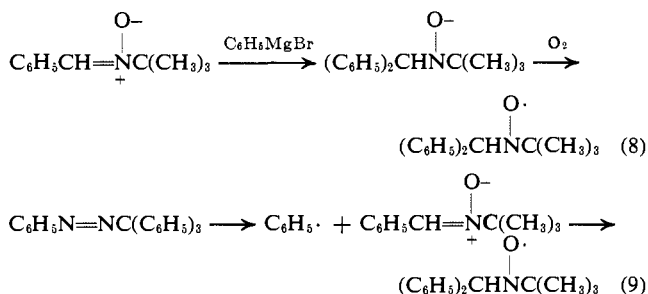
(26) N. Bortnick, L. S. Luskin, M. D. Hurwitz, W. E. Craig, L. J. Exner, and J. Mirza, *J. Am. Chem. Soc.*, **78**, 4039 (1956).

An obvious route is to synthesize the corresponding secondary amine and produce the nitroxide by oxidation (*e.g.*, with *p*-nitroperbenzoic acid).²³ For this purpose benzyl-, α -methylbenzyl-, α -(*n*-butyl)benzyl-, and benzhydryl-*t*-butylamine were synthesized (see Experimental Section) and oxidized to the corresponding nitroxides. The coupling constants obtained are recorded in Table I. A more rapid procedure for verifying the structure of a given nitroxide has been discovered. Either the Grignard or organometallic (lithium, sodium, etc.) compound is added directly to the nitron²⁷ and subsequently the hydroxylamine anion is air oxidized to the nitroxide (eq 7). This method



works extremely well for all primary carbanions. The final yield of nitroxide radical is obtained immediately and in very high yield. Extensive dilution of such solutions has been necessary for good resolution due to "concentration" broadening.

Benzhydryl-*t*-butylnitroxide (the phenyl spin adduct) was made by both phenyllithium and phenylmagnesium bromide addition to PBN (eq 8 and 9). As can be seen

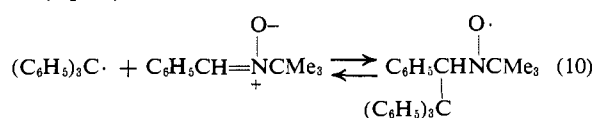


in Table I the values for the nitrogen and β -hydrogen hfsc are essentially the same as obtained when phenylazotriphenylmethane is allowed to decompose in the

(27) Certain Grignards are known to add to aldonitrones at the carbon atom: A. Angeli, L. Alessandri, and M. Aiazzi-Mancini, *Atti Accad. Nazl. Lincei*, **20**, 546 (1910); *Chem. Abstr.*, **5**, 3403 (1911); G. E. Utzinger and F. A. Regenass, *Helv. Chim. Acta*, **37**, 1892 (1954).

PBN-benzene solution.² Both methods also give the same quality of spectrum (Figure 1). The benzyl and methyl spin adducts were made by addition of benzyl or methyl Grignard to PBN and the methyl, ethyl, and *n*-butyl spin adducts were made by addition of the appropriate organolithium to PBN (Table I).

It was of interest to find the spectrum of triphenylmethyl radical in addition to the phenyl spin adduct in solution obtained from the thermal room temperature decomposition of phenylazotriphenylmethane (Figure 1). Apparently "stable" radicals are not trapped by PBN. In connection with this observation triphenylmethylmagnesium chloride was added to PBN and the resulting solution exposed to oxygen. A weak signal of three doublets (see Table I) was obtained which decayed with a half-life of approximately 20 min. However no trityl radical was detected. These experiments should be regarded as preliminary but do indicate the possibility of a reversible reaction, which in this case lies predominantly on the side of the triphenylmethyl radical (eq 10).



Organolead Compounds. R₄Pb. The photolysis of tetraethyllead in benzene containing PBN produced a nitroxide with the same hfsc's as obtained for the ethyl spin adduct synthesized by addition of ethyllithium to PBN (Table I). Similarly the photolysis of tetra-*n*-butyllead produced the *n*-butyl spin adduct (Figure 2). A small yield of the phenyl spin adduct was obtained in the photolysis of tetraphenyllead. The yield of phenyl spin adduct increased when the solution was irradiated continuously to approximately 50 times the amount obtained after a 1-min irradiation period. No other spin adducts or radicals were detected in any of the above experiments.

R₃PbPbR₃. No detectable signal was observed from a solution of hexaphenyldilead in benzene at room temperature. Upon irradiation a good yield of the phenyl spin adduct was obtained immediately. No other radicals were trapped. Under continuous irradiation the apparent yield of the phenyl spin adduct was at least ten times the yield obtained from tetraphenyllead (this result is approximate because a study of the yield as a function of the concentration of hexaphenyldilead has not been made at this time).

R₃PbX. The phenyl spin adduct was obtained in the photolysis of triphenyllead chloride or acetate. Similarly tri-*n*-butyllead acetate gave the *n*-butyl spin adduct upon irradiation. No other radicals were detected. After approximately 1-min irradiation triethyllead acetate gave mainly the ethyl spin adduct but in addition a small amount of the acetoxy spin adduct (~1:4) was detected. (The structure of the acetoxy spin adduct is verified in a future paragraph.) On continuous irradiation the acetoxy spin adduct was unstable. The ethyl spin adduct spectrum remained after continuous irradiation of triethyllead acetate. The photolysis of trimethyllead acetate gave mainly (~4:1) the acetoxy spin adduct (irradiation time, 2 min). In this case the acetoxy spin adduct spectrum vanished slowly upon continuous irradiation. The final spectrum was due to the methyl spin adduct.

R₂PbX₂. Diphenyllead diacetate and dichloride gave only the phenyl spin adduct upon short or continuous irradiation, although another spectrum appeared when the latter compound was allowed to stand in solution for some time after the light was turned off. With di-*n*-butyllead dichloride the spectrum of two nitroxides was obtained from a nonirradiated solution at room temperature. Analysis of the spectrum, after standing for approximately 3 hr, showed the presence of benzoyl-*t*-butylnitroxide, C₆H₅C(=O)N(O·)C(CH₃)₃, (this structural assignment is justified at the end of this paragraph) and a nitroxide almost identical with the acetoxy spin adduct. The former of these may have resulted from oxidation of PBN by a trace amount of lead oxide. The acetoxy "like" spin adduct may have resulted from the trapping of butyroxyl radical (CH₃CH₂CH₂C(=O)O·) from lead butyrate impurities. The spectrum of the butyroxyl spin adduct is not expected to differ greatly from that of the acetoxy spin adduct. During irradiation the *n*-butyl spin adduct was detected in addition to the presumed carboxy spin adduct. The spectrum due to the benzoyl-*t*-butylnitroxide disappeared during irradiation. Similar results were obtained with diethyllead dichloride. Although no significant concentration of radicals was produced on standing, two spin adducts were obtained after short irradiation. One spin adduct was due to the trapping of the ethyl radical. Upon continuous irradiation only the ethyl spin adduct was detected. Di-*n*-butyllead diacetate gave *n*-butyl and acetoxy spin adducts in the approximate ratio of 1:3, respectively, after a short irradiation period (1 min). Upon continuous irradiation the acetoxy spin adduct disappeared immediately and only the *n*-butyl spin adduct was observed.

Benzoyl-*t*-butylnitroxide. After mixing di-*n*-butyllead dichloride with PBN a spectrum of two nitroxides is obtained; one is due to a spin adduct which gives the usual set of three doublets. The other spectrum is simply a triplet with 7.67-G spacing (Figure 3). Only nitroxides with an α -keto function have such low nitrogen hfsc's: for example, C₆H₅N(O·)C(=O)C₆H₅, $A_N = 7.7$ G;^{18,28} C₆H₅N(O·)C(=O)CH₃, $A_N = 7.3$ G;^{18,28} (CH₃)₃CN(O·)C(=O)CH₃, $A_N = 8.0$ G.¹⁸ The triplet spectrum is assigned to benzoyl-*t*-butylnitroxide on this basis. The same spectrum is obtained in the reaction of PBN with chlorine, bromine, nitrous oxide, nitrosyl chloride, *t*-butyl nitrite, *m*-chloro- and *p*-nitroperbenzoic acids, and inorganic oxidizing agents such as potassium permanganate. The mechanism of production of this radical from these various reagents is under investigation.

RPbX₃. Phenyllead triacetate produced the phenyl spin adduct spontaneously at room temperature but no evidence for the acetoxy spin adduct was obtained. On continuous irradiation a small amount of the acetoxy spin adduct may have been resolved (~1:10).

PbX₄. Lead tetraacetate gave a nitroxide spectrum at room temperature in the absence of light which had a smaller nitrogen coupling than any spin adduct obtained to date ($A_N = 12.84$ and $A_\beta^H = 1.73$ G). It could not be ascribed to the methyl derivative. In no examples described above was evidence obtained for trapping of trivalent lead radicals. It thus seemed

(28) G. Chapelet-Letourneux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. France*, 3283 (1965); H. G. Aurich and F. Baer, *Tetrahedron Letters*, 43, 3879 (1965).



Figure 3. (A) The esr spectrum obtained from a solution of di-*n*-butyllead dichloride and phenyl-*t*-butyl nitron in benzene. (B) The esr spectrum of benzoyl-*t*-butyl nitroxide obtained from the addition of chlorine to phenyl-*t*-butyl nitron in benzene at room temperature.

highly unlikely that this spectrum was due to the lead triacetate spin adduct. The following experiments were performed to support the view that this spectrum was due to the acetoxy spin adduct. A tabulation of radical sources according to types of radicals detected is given in Table III.

Acetoxy Spin Adduct. The photolysis of mercuric acetate produced the spectra of two nitroxides after 12-min irradiation time (Figure 4). One of these was the methyl spin adduct. The other nitroxide has essentially the same nitrogen and β -hydrogen hfsc's as the spin adduct obtained from lead tetraacetate at room temperature in the absence of light. The photolysis of lead tetraacetate also produced the methyl spin adduct in addition to acetoxy spin adduct.

Further verification of the structural assignment of the acetoxy spin adduct was obtained upon addition of a small amount of 40% peracetic acid in acetic acid to PBN in benzene (Figure 4), in the reaction of silver acetate with bromine (Hunsdiecker reaction), and in the potassium permanganate oxidation²⁹ of acetic acid or acetaldehyde (see Table IV). Although the independent synthesis of the acetoxy spin adduct has not been accomplished, the structural assignment appears secure considering the large variety of systems, each with different chemistry, which produces the same nitroxide spectrum. The hfsc's of the acetoxy spin adducts vary from one system to another presumably because of solvent effects (Table IV). However a plot of the nitrogen *vs.* the β -H hfsc's should be linear for the same radical since the β -H coupling must vary directly with the spin density on nitrogen (assuming no solvent effect on the dihedral angle).³⁰ Figure 5 shows that this is the case.

(29) Unpublished results of O. W. Maender and B. Knauer.

(30) If $A_N = Q_N^N \rho_N + Q_O^N \rho_O = Q_N^N \rho_N + Q_O^N (1 - \rho_N)$. Then $A_N = [A_{\beta}^H (Q_N^N - Q_O^N) + Q_N^H Q_O^N] / (1/Q_N^H)$ where ρ_N and ρ_O the spin density on nitrogen and oxygen, and Q_N^N and Q_O^N the proportionality constants relating spin on nitrogen or oxygen with the nitrogen hfsc and Q_N^H the constant relating spin on nitrogen with the β -H hfsc (assuming a fixed dihedral angle as a function of solvent).

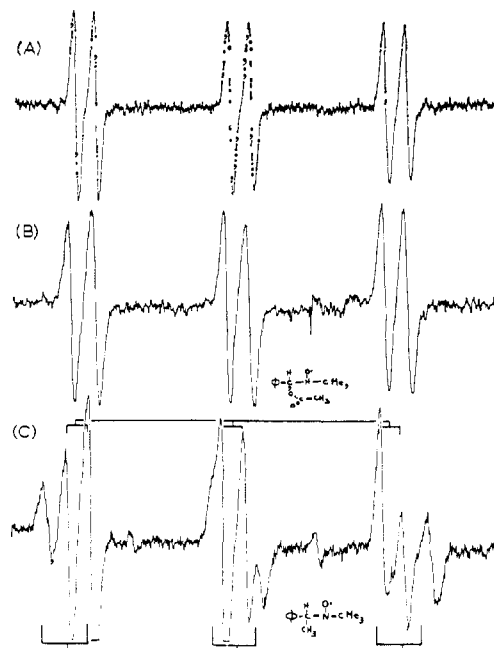


Figure 4. (A) The esr spectrum obtained from lead tetraacetate and phenyl-*t*-butyl nitron in benzene at room temperature believed to be due to the acetoxy spin adduct. (B) The esr spectrum of the acetoxy spin adduct obtained from a small amount of 40% peracetic acid in acetic acid added to phenyl-*t*-butyl nitron in benzene. (C) The esr spectrum obtained from photolysis of mercuric acetate in the presence of phenyl-*t*-butyl nitron in benzene. The spectrum is due to both the acetoxy and methyl spin adducts.

Organotin Compounds. R⁴Sn. Photolysis of tetramethyltin in benzene containing PBN gave a weak signal which increased slowly upon continued irradiation. The signal remained too weak to be well resolved. The final spectrum probably was due to two radicals.

Table IV. Hyperfine Splitting Constants of Acetoxy and Benzoyloxy Spin Adducts^a

Me ₃ PbOAc + <i>hν</i>	13.03	1.93
Pb(OAc) ₄ -trace HOAc	12.84	1.73
Hg(OAc) ₂ + <i>hν</i>	12.97	1.82
AgOAc + Br ₂	12.72	1.56
HOOAc-HOAc ^b	12.94	1.87
HOAc-KMnO ₄ ^{b,c}	12.92	1.78
AcH-KMnO ₄ ^{c,d}	13.10	2.05
Hg(OBz) ₂ + <i>hν</i>	12.71	1.40
BzOOBz	12.76	1.40
BzOO- <i>t</i> -Bu + <i>hν</i>	12.6	1.29
BzH + O ₂ ^{e,c}	12.85	1.48

^a In gauss in benzene at room temperature. ^b 1:4 acetic acid-benzene ratio. ^c Preliminary work of O. W. Maender and B. Knauer. ^d 1:4 acetaldehyde-benzene ratio; AcH = acetaldehyde. ^e BzH = benzaldehyde.

One set of lines was not inconsistent with that due to the methyl spin adduct. Tetra-*n*-butyltin gave the *n*-butyl spin adduct and another spin adduct of unknown structure although the signal was weak and resolution was incomplete. Irradiation of tetraphenyltin gave the phenyl spin adduct only. Diphenyldi-*n*-butyltin gave mainly the phenyl spin adduct during a short period of irradiation (1.5 min) although also some *n*-butyl spin adduct was produced. The spectrum of the latter nitroxide could only be recognized by overlapping this spectrum with spectra of authentic *n*-butyl spin

adducts. After extended irradiation (2 hr) another spectrum appeared with an unusually large β -H splitting. 1,1-Dimethyl-2,3,4,5-tetraphenylstannole gave a weak signal due to the methyl spin adduct.

R₃SnX. Photolysis of triphenyltin chloride gave a very clean spectrum due to the phenyl spin adduct. Similarly the photolysis of tribenzyltin chloride gave only the benzyl spin adduct either after a short period of irradiation (1.5 min) or during continuous irradiation. Photolysis of tri-*n*-butyltin chloride gave only *n*-butyl radicals and tribenzyltin acetate gave only benzyl radicals.

R₂SnX₂. Photolysis of diphenyltin dichloride gave only the phenyl spin adduct. Diphenyltin difluoride was very insoluble. Upon photolysis phenyl radicals were trapped. After a long period of irradiation (2 hr) additional lines could be detected not unlike the lines seen in the photolysis of hexaphenylditin and diphenyldi-*n*-butyltin except in this case a set of two doublets appeared in the region where before one outer line could be observed. Possibly the diphenylfluorotin spin adduct gave this spectrum. Di-*n*-butyltin dichloride photolysis gave a barely detectable signal. The β -H splitting could not be resolved. Photolysis of di-*n*-butyltin diacetate gave a weak signal due to the *n*-butyl spin adduct.

RSnX₃. The photolysis of methyltin trichloride did not give detectable amounts of a spin adduct. *n*-Butyltin trichloride gave a strong signal due to the *n*-butyl spin adduct. However the nitroxide produced was unusually unstable in the absence of light. Phenyltin trichloride did not give detectable amounts of radicals. A solid formed when the trichloride (a liquid) was mixed with PBN in benzene after degassing.

R₃SnSnR₃. After short irradiation hexa-*n*-butylditin gave the *n*-butyl spin adduct. During continuous irradiation the yield of *n*-butyl spin adduct increased and another nitroxide of unknown structure was detected. Possibly a trivalent tin radical was trapped, *e.g.*, tri-*n*-butyltin. Spin adducts of unknown structure were also detected in the irradiation of tetra-*n*-butyltin, diphenyldi-*n*-butyltin (as mentioned above), and tri-*n*-butyltin hydride (see below). The photolysis of hexaphenylditin produced the phenyl spin adduct and a second nitroxide of unknown structure. The spectrum did not match a spectrum obtained for the triphenyltin spin adduct (by addition of triphenyltinlithium to PBN followed by oxygen oxidation) and may be due to the pentaphenylditin spin adduct. Further experiments planned may verify these possibilities.

R₃SnH. Simply mixing tri-*n*-butyltin hydride with PBN in benzene produced benzyl-*t*-butylnitroxide, the hydrogen atom spin adduct. Photolysis greatly increased the hydrogen atom spin adduct signal and produced another nitroxide of unknown structure. Due to overlapping lines it was not possible to conclude that the second spectrum was *not* due to the *n*-butyl spin adduct.

Organomercury Compounds. R₂Hg. The photolysis of diphenylmercury gave only the phenyl spin adduct. Diethylmercury gave the ethyl spin adduct either after short irradiation or during continuous irradiation. Photolysis of dibenzylmercury gave the benzyl spin adduct during continuous irradiation. After an initial 1-5-min period of irradiation, the major part of the signal was probably due to the benzyl spin adduct

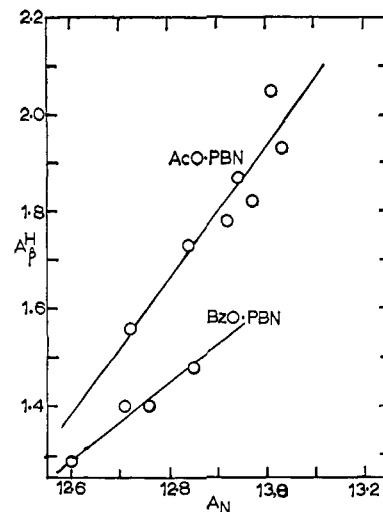


Figure 5. Plot of the nitrogen vs. β -H hyperfine coupling constants for the acetoxy and benzyloxy spin adducts in various solvents under various conditions of detection.

although at least one other nitroxide was detected. Both dibenzylmercury and dimethylmercury gave signals due to nitroxides in the absence of light. In the case of dimethylmercury at least three nitroxides were present: the methyl spin adduct, benzoyl-*t*-butylnitroxide, and a nitroxide of unknown structure. During continuous irradiation of dimethylmercury only the methyl spin adduct was observed.

RHgX. Methylmercuric iodide gave only the methyl spin adduct upon irradiation. Methylmercuric chloride gave a spectrum of at least three nitroxides upon initial irradiation very much like the initial spectrum obtained from dimethylmercury. The main set of peaks was due to the methyl spin adduct. Benzoyl-*t*-butylnitroxide and an unidentified radical were the other radicals present. The spectrum due to the methyl spin adduct and the unidentified species persisted during continuous irradiation. Phenyl radicals were trapped in the photolysis of phenylmercuric chloride and phenylmercuric acetate. In the latter case at very high gain, a small concentration of another nitroxide of unidentified structure was detected.

HgX₂. In the photolysis of mercuric acetate, acetoxy and methyl radicals were trapped as already discussed. The spectrum due to the acetoxy and methyl spin adducts persisted during continuous irradiation. Photolysis of mercuric benzoate gave a spectrum mainly due to a nitroxide with relatively small nitrogen and β -H hyperfine coupling ($A_N = 12.71$ and $A^H = 1.40$ G). By analogy to the values obtained for the acetoxy spin adduct this spectrum is believed to be due to the benzyloxy spin adduct, particularly since additional peaks in the spectrum could be assigned to the phenyl spin adduct (see Figure 6). The results of the following experiments support this structural assignment.

Benzyloxy Spin Adduct. Other sources of benzyloxy radicals were selected in order to compare the nitrogen and β -H hfsc for the nitroxides so obtained. Benzoyl peroxide gave a clean spectrum without irradiation (Figure 6). The coupling constants for the spin adduct were essentially the same as found in the photolysis of mercuric benzoate (see Table IV and Figure 5). *t*-Butyl perbenzoate upon photolysis gave benzoyl-*t*-

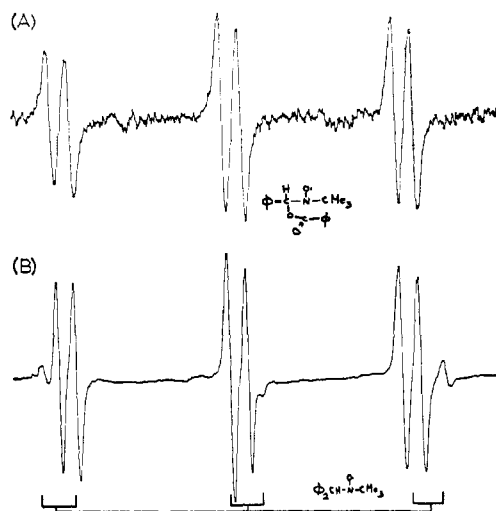


Figure 6. (A) The esr spectrum obtained from a dilute solution of benzoyl peroxide in benzene containing phenyl-*t*-butylnitron believed to be due to the benzoyloxy spin adduct. (B) The esr spectrum of the benzoyloxy spin adduct obtained from photolysis of mercuric benzoate in benzene containing phenyl-*t*-butylnitron. A small concentration of the phenyl spin adduct is also present.

butylnitroxide, the benzoyloxy spin adduct, and the *t*-butoxy spin adduct (verified by photolysis of di-*t*-butyl peroxide). Also in the oxygen oxidation of benzaldehyde in benzene the benzoyloxy spin adduct has been detected.²⁹

Discussion

The foregoing establishes that α -substituted benzyl-*t*-butylnitroxides are formed in the photolysis of a variety of organolead, tin, and mercury compounds in the presence of phenyl-*N-t*-butylnitron in benzene at room temperature. Although our initial objective was to use these organometallic compounds as sources of free radicals, the collected data now provide considerable information about the mode of photolytic decomposition of a variety of organolead, -tin, and -mercury compounds. The discussion of these results will assume that during irradiation the organometallic compounds are photolytically dissociated to produce free radicals and that the radicals are trapped by the spin trap to give the spin adduct. Other possible mechanisms of nitroxide formation will be considered later.

Organolead compounds are considered to be relatively unreactive organometallic compounds.³¹⁻³⁴ Most are stable in air at room temperature and up to 100°. However, it is well known that the photolysis³⁵ and pyrolysis³⁶ of tetraalkyllead compounds produce

(31) R. W. Leeper, L. Summers, and H. Gilman, *Chem. Rev.*, **54**, 101 (1954).

(32) G. E. Coates, "Organometallic Compounds," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1960.

(33) L. C. Willemsens, "Organolead Chemistry," International Lead Zinc Research Organization, Inc., New York, N. Y., 1965; L. C. Willemsens and G. J. M. van der Kirk, "Investigations in the Field of Organolead Chemistry," International Lead Zinc Research Organization, Inc., New York, N. Y., 1965.

(34) L. C. Willemsens and G. J. M. van der Kirk in "The Bond to Carbon," Vol. 1, Part II, A. G. MacDiarmid, Ed., Marcel Dekker, Inc., New York, N. Y., 1968.

(35) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. 1, 2nd ed, Reinhold Publishing Corp., New York, N. Y., 1954.

(36) (a) F. A. Paneth and W. Hofeditz, *Ber.*, **62B**, 1335 (1929); F. A. Paneth and W. Lautsch, *ibid.*, **64B**, 2702, 2708 (1931); F. A. Paneth and W. Lautsch, *J. Chem. Soc.*, 380 (1935); (b) J. H. Simons, W. McNamee, and C. D. Hurd, *J. Phys. Chem.*, **36**, 939 (1932); R. N. Meinert, *J. Am.*

alkyl radicals. The photolysis of tetramethyl-,³⁷ tetraethyl-,³⁸ and tetraphenyllead^{37a,c} have been studied in the gas phase or in solution. Alkyl or phenyl radicals are produced along with lead. In solutions open to air a white solid forms presumed to be an oxide of lead.^{37a} No evidence has been found for the transient existence of alkyllead radicals in the photolysis of organolead compounds. Apparently four alkyl radicals are produced very rapidly in a stepwise fashion.^{35,37-39} However, in the thermal decomposition of tetraethyllead the accumulation of hexaethyllead has been observed which suggests that triethyllead radicals may be intermediates in the reaction.^{34,38c}

Almost nothing is known about the thermal or photolytic pathways of decomposition for organolead chlorides or acetates. Some inferences about their stability can be drawn from melting point data. Triphenyllead chloride and bromide are stable in air and in daylight at room temperature³³ and melt at 206 and 166°, respectively,³¹ without apparent decomposition. Triethyllead chloride however decomposes at 120° without melting.^{31,32} Triphenyl-, trimethyl-, triethyl-, and tri-*n*-butyllead acetates melt without decomposition at 206, 194, 160, and 86°, respectively.^{31,33} Diaryl- and dialkyllead dihalides are relatively unstable. The latter reportedly decompose on standing and are light sensitive.³³ Diphenyl-, di-*n*-butyl-, and diethyllead dichlorides all decompose before melting³¹ at 285, 180, and 100° (steam distillation),⁴⁰ respectively. The diacetates by contrast are very stable compounds. Diphenyl- and di-*n*-butyllead diacetates melt without decomposition at 201 and 103°, respectively.^{31,33} Phenyllead triacetate is the only stable organolead compound known with three "anionic" groups. A melting point at 101° is reported³¹ although Willemsens³³ claims only the hydrate (mp 77-86°) can be obtained in crystalline form.

Intermediate lead radicals, of the type $R_3Pb\cdot$ are commonly postulated in photolytic, thermal, and chemical reactions of organolead compounds. However, no positive physical evidence for these intermediates has endured the test of time.⁴¹

Numerous attempts to detect trivalent lead by the use of esr in either thermolysis or photolysis of hexaryldileads have failed. In these methods the sensitivity was undoubtedly limited to approximately $>10^{-8}$ *M*. With the trapping technique described here, the

Chem. Soc., **55**, 979 (1933); G. L. Pratt and J. H. Purnell, *Trans. Faraday Soc.*, **60**, 519 (1964); (c) G. A. Razuvaev, N. S. Vyazankin, and N. N. Vyshinskii, *Zh. Obshch. Khim.*, **29**, 3662 (1959); **30**, 967, 4099 (1960); *Chem. Abstr.*, **54**, 17015, 23646 (1960); **55**, 24546 (1961); N. S. Vyazankin, G. A. Razuvaev, and Y. I. Dergunov, *Tr. po Khim. i Khim. Tekhnol.*, **4**, 652 (1962); *Chem. Abstr.*, **57**, 58543 (1963).

(37) (a) P. A. Leighton and R. A. Mortensen, *J. Am. Chem. Soc.*, **58**, 448 (1936); (b) J. G. Clouston and C. L. Cook, *Trans. Faraday Soc.*, **54**, 1001 (1958); (c) G. A. Razuvaev, G. G. Petukhov, and Yu. A. Kaplan, *Zh. Obshch. Khim.*, **33**, 2394 (1962); *J. Gen. Chem. USSR*, **33**, 2334 (1962); (d) M. F. Dull and J. H. Simons, *J. Am. Chem. Soc.*, **55**, 4328 (1933); M. M. Kotow, *ibid.*, **56**, 1118 (1934).

(38) N. Prileshapva and A. Terenin, *Trans. Faraday Soc.*, **31**, 1483 (1935); R. L. Milde and H. A. Beatty, *Advances in Chemistry Series*, No. 23, American Chemical Society, Washington, D. C., 1959, p 306.

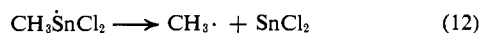
(39) N. J. Friswell and B. G. Gowenlock, *Advan. Free Radical Chem.*, **1**, 39 (1965).

(40) G. Calingaert, H. Shapiro, F. J. Dykstra, and L. Hess, *J. Am. Chem. Soc.*, **70**, 3902 (1948); R. Heap, B. C. Saunders, and G. J. Stacey, *J. Chem. Soc.*, 658 (1951), report diethyllead dichloride melts at 220° with decomposition.

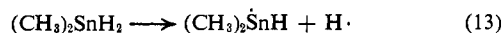
(41) (a) E. Müller, F. Günter, K. Scheffler, and H. Fettel, *Chem. Ber.*, **91**, 2888 (1958); (b) H. Gilman, W. H. Atwell, and F. K. Cartledge, *Advan. Organometal. Chem.*, **4**, 1 (1966).

sensitivity must be much better and still no evidence for trivalent lead intermediates has been obtained. However, one major drawback in the technique as used in this work is that radicals were detected during *in situ* irradiation. It is doubtful that the nitroxide radical arising from the trapping of lead radicals could survive photolysis. Two experiments still remain valid, the spontaneous formation of (1) acetoxy radical from lead tetraacetate and (2) phenyl radical from phenyllead triacetate at room temperature. Here lead triacetate could have been trapped but no indication of such a spin adduct was obtained. Possibly spin trapping at lower temperatures might provide evidence for such intermediates.

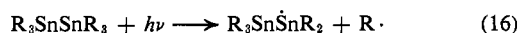
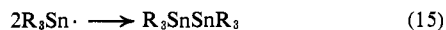
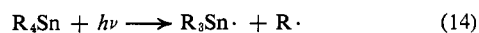
Organotin compounds particularly tetraalkyltin derivatives have high thermal stability.^{32,42} Most can be heated to 200° without decomposition. Thus, tetraoctyltin can be distilled without decomposition at 238°. Tetraaryl tin compounds decompose between 275 and 350°. The thermal decomposition of tetramethyltin,⁴³ tributyltin chloride,⁴⁴ and dimethyltin dichloride⁴⁵ has been studied at 440–493, 230, and 554–688°, respectively. In the latter study^{39,45} it was shown that a methyltin dichloride radical is produced which rapidly decomposes to methyl radicals and tin chloride (eq 11 and 12). In thermal decomposition and photol-



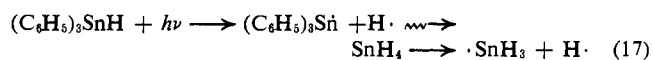
ysis of dimethyltin dihydride tin-hydrogen bond homolysis is suggested⁴⁶ (eq 13).



Photolysis of tetraalkyl-(methyl, ethyl, and *n*-propyl) tin compounds produces free radicals according to the scheme^{39,46} shown in eq 14–16. Unpublished work of



Luijten and van der Kerk⁴² on the uv irradiation of tetraalkyl tin compounds in air indicates decomposition to tri- and dialkyltin compounds. Decomposition is apparently retarded in the absence of air. The photolysis or high-energy irradiation of tin hydrides leads to tin-hydrogen bond cleavage. Thus esr spectra assigned to the tin radicals were obtained in the photolysis of triphenyltin and triisobutyltin hydrides⁴⁷ and the γ -ray irradiation of stannane^{48a} at low temperatures. Radiolysis of tetramethyltin gave a complex spectrum.^{48b}



(42) J. G. A. Luijten and G. J. M. van der Kerk in "The Bond to Carbon," Vol. 1, Part II, A. G. MacDiarmid, Ed., Marcel Dekker, Inc., New York, N. Y., 1968, p 91.

(43) C. E. Waring and W. S. Horton, *J. Am. Chem. Soc.*, **67**, 540 (1945).

(44) J. G. A. Luijten and G. J. M. van der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, Greenford, England, 1955; see ref 42, p 160.

(45) S. J. W. Price and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **54**, 1630 (1958).

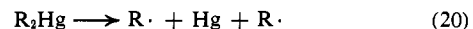
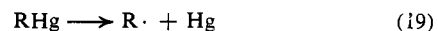
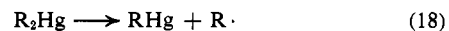
(46) H. C. Clark, S. G. Furnival, and J. T. Kwon, *Can. J. Chem.*, **41**, 2889 (1963); H. C. Clark and J. T. Kwon, *ibid.*, **42**, 1288 (1964).

(47) U. Schmidt, K. Kabitzke, K. Markau, and W. P. Neumann, *Chem. Ber.*, **98**, 3827 (1965).

(48) (a) R. L. Morehouse, J. J. Christiansen, and W. Gordy, *J. Chem. Phys.*, **45**, 1751 (1966); (b) W. Gordy and C. G. McCormick, *J. Am. Chem. Soc.*, **78**, 3243 (1956).

The production of tin radicals by homolytic cleavage of the tin-hydrogen bond in alkyltin hydrides has also been proposed in numerous reactions of tin hydrides with organic compounds particularly olefins.^{39,49,50}

Organomercury compounds are common and stable chemicals. The photolytic and thermal decompositions of these compounds are well-known radical reactions and have been studied extensively. The evidence for a one- or two-step radical mechanism has been reviewed by Friswell and Gowenlock³⁹ (eq 18–20).



In a number of cases the existence of monoalkylmercury radicals is postulated to explain the data. Radiolysis of diethylmercury provided the ethyl radical for esr studies.^{48b}

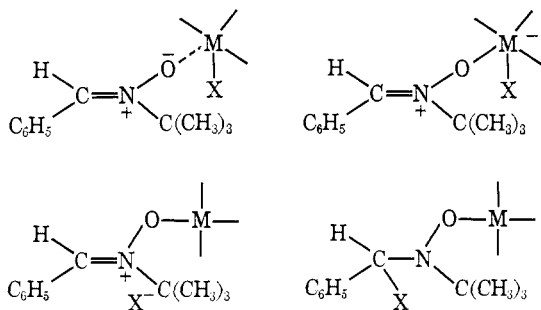
Thus it appears that in those cases where information is available, our spin trapping results on the photolysis (or room temperature decomposition) of organolead, -tin, or -mercury compounds are in agreement with literature data, *e.g.*, the detection of alkyl or phenyl spin adducts from tetraalkyl- or tetraphenyllead, -tin, or -mercury compounds. Of interest is the finding that in general photolysis cleaves on organic group (alkyl or phenyl) in preference to the halide or carboxylate group. This preference has been shown previously in only one analogous reaction, the thermal decomposition of dimethyltin dichloride. This generalization is also followed for dimeric tin compounds: the photolysis of hexaphenyl- and hexa-*n*-butylditin gave phenyl and *n*-butyl spin adducts, respectively, in agreement with previous work on the photolysis of hexaethyltin. The observation of additional spectra, admittedly due to nitroxides of unknown structure at this time (further work is in progress), in the photolysis of organotin and mercury compounds is also in general agreement with the previous conclusion that monoalkylmercury and particularly trialkyltin radicals are intermediates in the photolysis. The detection of a hydrogen atom spin adduct in the reaction at room temperature and photolysis of tri-*n*-butyltin hydride is of particular interest. However further work is necessary to eliminate the possibility of a hydrogen abstraction reaction by photoexcited PBN.

It is important to consider other possible mechanisms for formation of the spin adducts described. To this point radical production *via* photolysis of the organometallic compound has been assumed to occur independently of the spin trap. It is possible that an excited state of the nitron is involved and that photosensitization of the organometallic may have occurred. Preliminary experiments indicate the possible existence of a triplet excited state for PBN since spin adducts are detected upon irradiation of the nitron in hydrogen-donating solvents. Further experiments with filtered light are underway to investigate this possibility. Another question is the state of aggregation of the or-

(49) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964); R. H. Fish, H. G. Kuivila, and I. J. Tyminski, *J. Am. Chem. Soc.*, **89**, 5861 (1967); H. G. Kuivila and R. Sommer, *ibid.*, **89**, 5616 (1967).

(50) W. P. Neumann, *Angew. Chem.*, **76**, 849 (1964); W. P. Neumann and R. Sommer, *ibid.*, **76**, 52 (1964); *Ann.*, **675**, 10 (1964); W. P. Neumann and J. Pedain, *Tetrahedron Letters*, 2461 (1964); W. P. Neumann, H. J. Albert, and W. Kaiser, *ibid.*, 2041 (1967).

ganometallic compound. Since trimethyllead halides and dimethyllead dihalides have been shown to be monomeric in solution⁵¹ we assume that most of the organometallic compounds studied are monomeric also in the benzene solutions used. A more serious consideration is the possibility that the organometallic compound forms a complex or addition product with the nitrene. This could either tie up an appreciable frac-



(51) R. J. H. Clark, A. G. Davies, and R. J. Puddephatt, *J. Am. Chem. Soc.*, **90**, 6923 (1968).

tion of the substrate and/or the nitrene or in fact be the precursor to the spin adduct. The interaction could range from a weak attraction as in a complex to an actual bond formation as in an addition product of salt-like structure.

Perhaps the latter occurred in the reaction between phenyltin trichloride where a precipitate formed upon mixing and no spin adduct was detected in the photolysis. If complexes such as I photolyzed more readily than the uncomplexed molecules, trapping of the produced radical would be more efficient since it could take place as a cage reaction. The somewhat surprising successful trapping of acetoxy radicals in the thermal decomposition of lead tetraacetate, and in the photolysis of trimethyl- and triethyllead acetate and mercuric acetate might be rationalized in this way. However since the acetoxy spin adduct has been obtained from a number of other sources it appears that acetoxy radical can be trapped by PBN. Further investigations into this question are in progress.

Acknowledgment. We acknowledge the assistance of Susan Henson in some of the above experiments.

Organometallic Photochemistry. I. The Photolysis of Ethyllithium

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Abstract: The photolysis of ethyllithium with mercury resonance radiation apparently proceeds by two competing photolytic mechanisms: a lithium hydride elimination reaction which yields ethylene, and a homolytic process which yields lithium metal, ethane, and ethylene. The absence of butane and deuterated ethane (when the photolysis is carried out in C_6D_6 or C_6D_{12}) indicates that the homolytic process occurs *via* an intraaggregate disproportionation mechanism. Photolysis in the solid state yields ethane, ethylene, and butane as well as a polymeric material. Solution photolysis in the presence of a mercury pool yields only ethane (and no LiH).

The thermolysis of alkylolithium compounds has been the subject of several investigations¹⁻⁷ and is generally conceded to proceed *via* a concerted β elimination of lithium hydride, unless no β -hydrogens are available.⁷ The possibility of radical participation has been rejected by most workers,^{2,3} except possibly in the thermolysis of potassium and sodium alkyls.⁸ The photolysis of alkylolithium compounds has not been reported, and one purpose of the work reported here was to compare the mechanism of photolytic decomposition with that of the

corresponding thermal process. van Tamelen and co-workers⁹ have reported that phenyllithium photolyzes by an interesting intradimer process which yields principally biphenyl. A further purpose of this work was to examine the generality of this mechanism among aliphatic lithium compounds.

Absorption Spectrum of Ethyllithium. Notwithstanding a report to the contrary,^{10,11} the ultraviolet spectrum

(9) E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *J. Amer. Chem. Soc.*, **87**, 4964 (1965).

(10) T. L. Brown, *Advan. Organometal. Chem.*, **365** (1965).

(11) A referee has suggested that the absorption shown in Figure 1 is due to an allyllithium compound formed by α metalation of olefin impurities in the solvent, and that alkylolithiums show only end-type absorption.¹² In view of the high intensity of the absorption shown in Figure 1, however, the allyllithium so formed must have an extinction coefficient of a remarkable magnitude; we estimate *ca.* 10^5 l./mol cm). Moreover, we have observed no time dependency of the spectrum which would parallel the rather slow metalation process referred to above. Finally, Professor Oliver indicates in a private communication that he has found the same extinction coefficient for alkylolithium as we report in this work, a most fortuitous circumstance if one assumes that a metalated product is responsible for the absorption. (Note also the Beers law dependence of the absorption of butyllithium in benzene.¹³)

(12) R. Waack and M. A. Doran, *J. Amer. Chem. Soc.*, **85**, 1651 (1963).

(1) K. Ziegler and H. G. Gellert, *Ann. Chem.*, **567**, 179 (1950).

(2) D. Bryce-Smith, *J. Chem. Soc.*, 1712 (1955).

(3) R. H. Finnegan and H. W. Kutta, *J. Org. Chem.*, **30**, 4139 (1965).

(4) W. H. Glaze, J. Lin, and E. G. Felton, *ibid.*, **30**, 1258 (1965); **31**, 2643 (1966).

(5) W. H. Glaze and G. M. Adams, *J. Amer. Chem. Soc.*, **88**, 4653 (1966).

(6) R. L. Eppley and J. A. Dixon, *J. Organometal. Chem.*, **11**, 174 (1968).

(7) W. H. Glaze, T. L. Brewer, R. Hatch, and J. Nathan, "Decomposition of Organometallic Compounds to Refractory Ceramics, Metals, and Metal Alloys," K. S. Mazdhyasni, Ed., University of Dayton Press, Dayton, Ohio, 1968, pp 187-194.

(8) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **20**, 839 (1955); **21**, 93 (1956).