and cation in these and other systems and will be described in the future.

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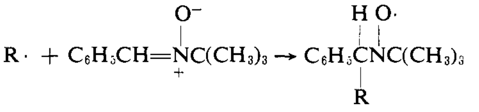
Received May 23, 1968

Detection and Identification of Short-Lived Free Radicals by an Electron Spin Resonance Trapping Technique

Sir:

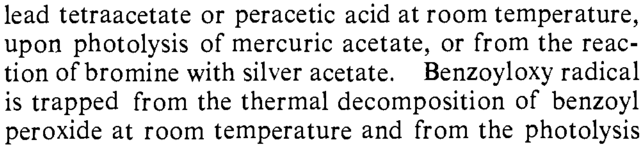
Numerous electron spin resonance (esr) studies of short-lived free radicals produced by *in situ* irradiation or rapid mixing techniques have been reported. These methods depend on rapid radical-producing reactions and frequently large volumes of materials are required. In addition, the optimum conditions for radical detection are frequently not similar to the conditions prevailing in reacting systems where the same radicals are presumed to be reaction intermediates. A need exists for readily applicable methods of detecting and identifying low concentrations of free radicals (below the esr detection threshold) in reacting systems. A trapping technique designed for this purpose is described in this report.

The approach is to use an efficient radical trap such that the radical-trap adduct is reasonably stable and detectable by esr. If the hyperfine spectrum of the radical adduct has a characteristic feature which is sensitive to the detailed structure of the attached groups this information can be used to identify the radical trapped. 2-Methyl-2-nitrosopropane,[1] diphenyl nitrone,[2] and phenyl *t*-butyl nitrone[2] have been shown to trap free radicals to give stable nitroxides. We have investigated the feasibility of using phenyl *t*-butyl nitrone (PBN) as a radical trap for the identification of reactive short-lived free radicals. The information necessary to define the structure of the radical trapped lies in the magnitude of the β-hydrogen (β-H) and nitrogen hyperfine coupling (hfc). The β-H hfc depends on the dihedral angle which in turn depends on the bulk of R. The magnitude of the β-H hfc decreases with increase in bulk of attached groups.[3] The nitrogen hfc on the other hand is sensitive to the electronegativity of R, inductive electron withdrawal producing a smaller nitrogen hfc.[4] The β-H and nitrogen hfc's under given temperature and solvent conditions are a unique set of parameters which define the nature of the particular radical trapped once these values have been established from known experiments. This approach has been successfully used to define the structure of the radical trapped in the case of phenyl, benzyl, methyl, trifluoromethyl, ethyl, *n*-butyl, acetoxy, and benzoyloxy radicals produced in benzene at room temperature either thermally or photolytically.



$$R\cdot + C_6H_5CH{=}\overset{O^-}{\underset{+}{N}}C(CH_3)_3 \rightarrow C_6H_5\underset{R}{\overset{H}{C}}\overset{O\cdot}{N}C(CH_3)_3$$

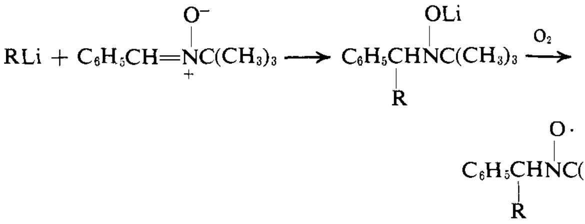
Thus phenylazotriphenylmethane (PAT) decomposes at room temperature in benzene containing PBN to give a strong esr signal consisting of three doublets, $a_N = 13.84$, $a_\beta{}^H = 2.09$ gauss, and a complex set of lines due to the triphenylmethyl radical. Since the same three doublets are obtained from the photolysis of iodobenzene, tetraphenyllead, triphenyllead acetate, triphenyllead chloride, phenylmercuric acetate, phenylmercuric chloride, and a number of other phenyl-substituted organometallic compounds, the observed spectrum is assigned to benzhydryl *t*-butyl nitroxide, the phenyl radical adduct of PBN (note triphenylmethyl does not add to PBN).



$$C_6H_5N{=}NC(C_6H_5)_3 \xrightarrow[-N_2]{} C_6H_5\cdot + (C_6H_5)_3C\cdot \xrightarrow{PBN} (C_6H_5)_2\overset{H}{C}-\overset{O\cdot}{N}C(CH_3)_3 + (C_6H_5)_3C\cdot$$

Similarly, the trifluoromethyl radical can be trapped in the photolysis of trifluoroiodomethane or trifluoronitrosomethane. A γ-F hfc coupling of 1.54 gauss establishes the structure of this nitroxide (Table I). The acetoxy radical is produced spontaneously from lead tetraacetate or peracetic acid at room temperature, upon photolysis of mercuric acetate, or from the reaction of bromine with silver acetate. Benzoyloxy radical is trapped from the thermal decomposition of benzoyl peroxide at room temperature and from the photolysis of mercuric benzoate. Note the smaller nitrogen hfc for these two nitroxides (Table I).

The following radicals are obtained in the photolysis of the following compounds: benzyl radicals from dibenzylmercury, tribenzyltin acetate, and tribenzyltin chloride; *n*-butyl radicals from tetra-*n*-butyllead, di-*n*-butyllead diacetate, tri-*n*-butyllead acetate, di-*n*-butyllead dichloride, and *n*-butyltin trichloride; ethyl radicals from diethylmercury, diethyllead dichloride, and triethyllead acetate; methyl radicals from dimethylmercury and trimethyllead acetate. The structure of certain nitroxide radicals was verified by synthesis of the appropriate secondary amine followed by *p*-nitroperbenzoic acid oxidation to the nitroxide. Further verification was obtained by addition of organolithium or Grignard compounds to PBN (Grignard reagents are known to add to aldonitrones in a 1,3 fashion)[5] followed by oxygen oxidation to the nitroxide (see Table I).



$$RLi + C_6H_5CH{=}\overset{O^-}{\underset{+}{N}}C(CH_3)_3 \longrightarrow C_6H_5\underset{R}{CH}\overset{OLi}{N}C(CH_3)_3 \xrightarrow{O_2} C_6H_5\underset{R}{CH}\overset{O\cdot}{N}C(CH_3)_3$$

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Table I

Radical source[a]	Radical trapped	Hyperfine coupling of nitroxide[b] A_N	$A_\beta{}^H$
Phenylazotriphenylmethane	$C_6H_5\cdot$	13.84	2.09
		13.72[c]	2.08[c]
		13.73[d]	2.06[d]
Dibenzylmercury	$C_6H_5CH_2\cdot$	13.88	2.44
Trifluoromethyl iodide	$CF_3\cdot$	13.30	1.54[e]
Dimethylmercury	$CH_3\cdot$	14.20	3.45
		14.15[c]	3.41[c]
		14.19[d]	3.44[d]
Diethylmercury	$C_2H_5\cdot$	14.00	3.19
		13.93[c]	3.21[c]
Di-*n*-butyllead diacetate	$C_4H_9\cdot$	13.95	3.10
		13.94[c]	3.10[c]
		14.04[d]	3.04[d]
Lead tetraacetate	$CH_3COO\cdot$	12.84	1.73
Benzoyl peroxide	$C_6H_5COO\cdot$	12.76	1.40

[a] See text for other sources. [b] A Varian 4502 epr spectrometer was used. Coupling constants were calculated using the Fieldial calibrations with an error of 0.05 gauss maximum deviation from the average of three or more determinations. A low-pressure mercury lamp and quartz cell were used. [c] Nitroxide produced by addition of the appropriate organolithium to PBN followed by reaction with oxygen. [d] Nitroxide produced by *p*-nitroperbenzoic acid oxidation of the appropriate secondary amine. [e] $A_\gamma{}^F$ = 1.54 gauss.

In all experiments the concentration of PBN was approximately 0.03 *M* in benzene. In a 0.003 *M* PAT solution the nitroxide concentration was approximately 5.6×10^{-5} *M* after 40 min at room temperature. This accounts for approximately 80% of the phenyl radicals produced.[6] Phenyl radicals produced from PAT are also trapped in other solvents such as toluene, xylene, nitrobenzene, benzonitrile, acetonitrile, aqueous acetonitrile, dimethyl sulfoxide, methylene chloride, carbon tetrachloride, and dioxane. However, in solvents reactive toward phenyl radicals, *e.g.*, dioxane or carbon tetrachloride,[7] the triphenylmethyl radical spectrum is diminished and other radicals (presumably derived from solvent) are trapped by PBN in addition to phenyl. This indicates that PBN competes favorably with triphenylmethyl for reactive radicals (at least at concentrations where $[PBN] \cong 10^2\text{–}10^3[(C_6H_5)_3C\cdot]$).

This method provides a means of readily obtaining answers for a number of interesting questions in free-radical chemistry, two of which are illustrated. (1) It can be concluded from the results of photolyses of a large number of phenyl- and alkylorganometallic acetates and chlorides (Pb, Sn, Hg) that bond cleavage preferentially follows the sequence $C_6H_5 > n\text{-Bu} > CH_3COO > Cl$ if approximately equal trapping efficiency of PBN is assumed. (2) Since at this time we have no reason not to expect the adduct of $Pb(OAc)_3$[8] and the nitrone to be stable, we can conclude that the lifetime of lead triacetate radical is shorter than the lifetime of the acetoxy radical. In fact, no evidence for the presence of other trivalent lead radicals has been obtained. However, in the photolysis of organotin compounds sometimes more than one type of radical was trapped. The identification of the structures of these radicals is being attempted.

Acknowledgment. This work was supported by AFOSR(SRC)-OAR U. S. Air Force Grant 1069-66.

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Received July 29, 1968

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Tricyclopropylaluminum Dimer

Sir:

Several recent studies have shown that electron-deficient, three-centered bridge bonds in group III organometallic compounds are stabilized by the presence of π orbitals on the hydrocarbon moiety. It has been suggested[1] that in trivinylgallium dimer the bridge bonds are stabilized due to an interaction between the nonbonding molecular orbital of the three-centered bridging system with the π orbitals of the vinyl group. Evidence for this type of interaction has also been obtained from the crystal structure of triphenylaluminum[2] and from the nmr studies on dimethyl(phenylethynyl)aluminum and dimethyl(*p*-tolyl)aluminum.[3] These studies have further demonstrated that this enhanced stability slows the exchange rate between the bridge and terminal positions in the dimeric species; but even then, at room temperature exchange is rapid on the nmr time scale for all but the phenylethynyl derivative.

We now wish to report that tricyclopropylaluminum dimer appears to have the most stable hydrocarbon bridges so far reported in group III derivatives. This implies that the cyclopropylaluminum system possesses unique bonding characteristics wherein additional π-type interactions explain the unusual stability of the compound.

Tricyclopropylaluminum was prepared by the exchange reaction

$$3Hg(C_3H_5)_2 + Al_2(CH_3)_6 \rightleftharpoons Al_2(C_3H_5)_6 + 3Hg(CH_3)_2$$

It was driven to completion by heating with excess dicyclopropylmercury[4] and removal of the more volatile products *in vacuo*. The remaining white solid was zone refined to give the product, mp 58–61°, in 70% yield. Hydrolysis of a 0.224-g sample gave 4.23 mmoles of cyclopropane and 1.37 mg-atoms of Al (calculated 4.5 mmoles of cyclopropane and 1.5 mg-atoms of Al). The molecular weight determined cryoscopically in cyclohexane was 310 ± 15 (calcd for $Al_2(C_3H_5)_6$, 300).

In Figure 1 the 100-MHz nmr spectrum of tricyclopropylaluminum at room temperature is shown. The spectrum may be interpreted as representing two kinds of cyclopropyl groups in an integrated ratio of 2:1 which correspond to the cyclopropyl groups in the terminal and bridging positions, respectively. The assignments of the regions labeled B_1, B_2, B_3, and T_1, T_2, T_3 are based on the magnitudes of the various coupling constants (Table I) and a comparison of these values with those obtained from the analyses of the nmr spectra of other cyclopropylmetal compounds.[5] One observes from

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