The manganic acetate reaction differs from the lead tetraacetate reaction in two fundamental respects: (1) no methyl acetate adducts to $\beta$-methylstyrene are produced even at relatively high olefin concentrations, while with lead tetraacetate, under comparable reaction conditions, these adducts constituted the major isolated product; (2) only traces of $CO_2$ (0.03 mol/mol of $Mn^{3+}$ consumed) and methane (0.004 mol/mol of $Mn^{3+}$ consumed) are formed during the decomposition of manganic acetate in the presence of olefin. These differences indicate that free methyl or acetoxyl radicals are not the primary products of the thermolysis of manganic acetate in acetic acid.

We therefore propose a mechanism to account for the formation of $\gamma$-lactones similar to the one suggested for the lactone component of the lead tetraacetate reaction except that the necessary $\cdot CH_2COOH$ radicals are produced directly by thermolysis of the manganic complex.[6] The high yield of the lactones would indicate that the $\cdot CH_2COOH$ radical adds to the olefin faster than it is oxidized by Mn(III).

An expected minor side product of this reaction is the allylic acetate produced by the abstraction of an allylic hydrogen atom by the $\cdot CH_2COOH$ radical. However, the high yields of $\gamma$-lactones produced relative to the allylic acetates, ~30:1 for $\beta$-methylstyrene and ~50:1 for octene-1, clearly demonstrate the great selectivity of the $\cdot CH_2COOH$ radical toward addition to the olefin over allylic hydrogen abstraction.

The relative rate of addition of the carboxymethyl radical to various olefins was determined by applying a competitive technique and measuring the relative ratio of the lactones produced (Table II). In general the reactivity of various olefins toward the addition of the carboxymethyl radical is governed by the stability of the resulting radical intermediate. The relative rate constants of addition to *trans* and *cis* olefins are comparable to those reported for the methyl radical at 65°.[7]

**Table II.** Relative Reactivity of Various Olefins toward Carboxymethyl Radical Addition at 130°

| | | | |
|---|---|---|---|
| $\alpha$-Methylstyrene | 27 | Cyclooctene | 0.78 |
| 1,1-Diphenylethylene | 19 | *cis*-Stilbene | 0.36 |
| Styrene | 12 | *cis*-Octene-4 | 0.21 |
| 2-Methylheptene-1 | 2.4 | *trans*-Octene-4 | 0.20 |
| *trans*-$\beta$-Methylstyrene | 2.1 | Styrene | 1.00[b] |
| *trans*-Stilbene | 1.3 | *m*-Bromostyrene | 1.01 |
| *cis*-$\beta$-Methylstyrene | 1.0 | *p*-Bromostyrene | 1.04 |
| Octene-1 | 1.0[a] | *p*-Methylstyrene | 1.26 |

[a] Octene-1 arbitrarily chosen as standard. [b] Styrene arbitrarily chosen as standard.

Acids other then acetic acid can be used in this reaction, thereby leading to lactones with substituents in the $\alpha$ position. Thus, when manganic acetate was decomposed in a solution of styrene in propionic acid containing potassium propionate, the lactone with a methyl substituent in the $\alpha$ position was isolated in 50% yield.[10] By analogy, manganic propionate is initially formed, which then decomposes to give the $CH_3\dot{C}HCOOH$ radical.

**Acknowledgment.** We thank G. E. Stead and R. J. Cier for their skillful laboratory assistance.

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(5) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **90**, 2706 (1968).

(6) Recent experiments in our laboratory show that ceric acetate behaves in an analogous manner.

(7) In the additions of $\cdot CH_3$ to $\beta$-methylstyrene and stilbene $k_{trans}/k_{cis} = 2.3^8$ and $3.6^9$, respectively, which are comparable to the values of 2.1 and 3.6 obtained from Table II.

(8) F. Carrock and M. Szwarc, *J. Am. Chem. Soc.*, **81**, 4138 (1959).

(9) M. Gazith and M. Szwarc, *ibid.*, **79**, 3339 (1957).

(10) The compound analyzed for $C_{11}H_{12}O_2$ and exhibited a lactone carbonyl at 5.58 $\mu$. The nmr spectrum contained a methyl doublet at $\tau$ 9.2 ($J$ = 6 cps) which was spin decoupled by irradiating at $\tau$ 7.75.

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*Received June 28, 1968*

## Metalation Reactions. III.[1] Nuclear Magnetic Resonance Study of the Metalation of 4,5-Methylene- and 4,5-Iminophenanthrenes[2]

*Sir:*

In connection with a study of the electron spin resonance of dianion radicals formed by the reduction of stable hydrocarbon carbanions[1] the mechanism of metalation of weak carbon acids became of interest.[1b] Weak carbon acids react with alkali metals to produce the corresponding carbanion, the more acidic (*e.g.*, cyclopentadiene or indene) evolve hydrogen whereas others do not[1,3] (*e.g.*, fluorene or benzofluorenes).

The reduction of fluorene first produces a short-lived green color which at room temperature rapidly changes to the pale yellow color of fluorenide carbanion.[1,3] At lower temperatures the green color is stable and is due to the radical anion of fluorene.[4] The stability of the radical depends on the nature of the cation (Li > Na > K).[4] With 4,5-methylenephenanthrene the radical anion can be obtained at room temperature with sodium but not with potassium.[1b] The radical is stable if no unreacted hydrocarbon is present in solution. This observation in addition to the apparent correlation between the p$K_0$ of the carbon acid and the stability of the radical anion[1b] supports a proton-transfer mechanism (originally suggested by Eisch[3] in the metalation of fluorene) for the decomposition of the initially formed radical anion.

In this report we present nmr evidence for the formation of two anions in the reaction of potassium with both 4,5-methylene- and 4,5-iminophenanthrenes: the phenanthrenyl anion (I) and 9,10-dihydrophenanthrenyl anion (II). The carbanions and nitranions will be designated Ia, IIa, Ib, and IIb, respectively.

The reactions of 4,5-methylene- and 4,5-iminophenanthrenes with potassium metal were followed by

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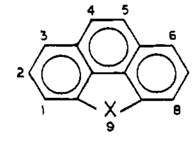
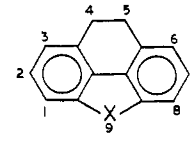
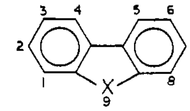
(1) (a) E. G. Janzen and J. G. Pacifici, *J. Am. Chem. Soc.*, **87**, 5504 (1965); (b) E. G. Janzen and J. L. Gerlock, *J. Organometal Chem.* (Amsterdam), **8**, 354 (1967), should be considered parts I and II of this series.

(2) This research was supported by the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(3) J. J. Eisch and W. C. Kaska, *Chem. Ind.* (London), 470 (1961); *J. Org. Chem.*, **27**, 3745 (1962), and references cited therein.

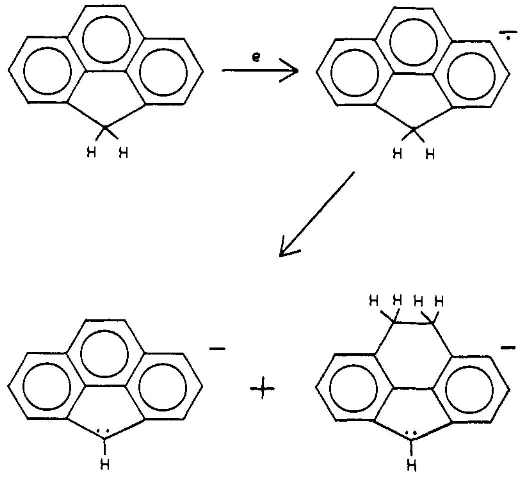
(4) (a) R. L. Kugel, W. G. Hodgson, and H. R. Allcock, *Chem. Ind.* (London), 1949 (1962); (b) K. A. Bilevich, N. N. Bubnov, V. V. Bukhtiyarov, and O. Y. Okhlobseptin, *Dokl. Akad. Nauk SSSR*, **174**, 594 (1967); *Proc. Acad. Sci. USSR*, **174**, 473 (1967). We have repeated this work and find the reported analyses of the fluorene radical anion spectrum in error. The values $a^{H}{}_{1,3,6,8}$ = 0.83, 1.14, $a^{H}{}_{2,7}$ = 4.82, $a_{4,5}$ = 3.99, and $a^{H}{}_{9}$ = 3.64 gauss reproduce the spectrum obtained with lithium in tetrahydrofuran and are in agreement with coupling constants obtained from spectra of 9-methyl-, 9-phenyl-, and 9,9-dimethylfluorene radical anions (to be published).

**Table I.** Nmr Parameters of Anions

| Compd | $\nu_{1,8}$[a] | $\nu_{2,7}$ | $\nu_{3,6}$ | $\nu_{4,5}$ | $\nu_{9}$ | $J_{1,2}$[b] | $J_{1,3}$ | $J_{1,4}$ | $J_{2,3}$ | $J_{2,4}$ | $J_{3,4}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| <br>I | 7.405 (a)[c] | 7.351 | 7.003 | 7.534 | 6.051 | 7.81 | 0.32 | | 7.34 | | |
| | 7.759 (b) | 7.664 | 7.362 | 7.851 | | 7.64 | 0.32 | | 7.50 | | |
| <br>II | 6.996 (a) | 6.752 | 6.181 | 3.115 | 5.593 | 7.97 | 0.47 | | 6.71 | | |
| | 7.340 (b) | 7.105 | 6.601 | 3.228 | | 8.05 | 0.37 | | 7.01 | | |
|  | 7.272 (a)[d] | 6.808 | 6.442 | 7.865 | 5.893 | 8.11 | 0.92 | 0.86 | 6.69 | 1.16 | 7.81 |
| | 7.596 (b) | 7.152 | 6.755 | 7.947 | | 8.09 | 1.08 | 0.74 | 6.86 | 1.37 | 7.63 |

[a] In parts per million downfield from TMS. [b] In hertz. [c] a, X = CH; b, X = N. [d] The chemical shifts for fluorenyllithium (7.20, 6.72, 6.30, 7.78 Hz) and for fluorenylsodium (7.33, 6.82, 6.64, 7.92 Hz) have been previously reported (ref 8a and 8b, respectively).

an nmr *in situ* technique.[5] For 4,5-methylenephenanthrene, the peak due to the methylene protons decreases in intensity with successive reduction until no longer detectable. Concurrently, new signals appear whose intensities increase with further reduction. At the point of complete conversion of the hydrocarbon to the carbanion, the spectrum consisted of four singlets at 3.115, 5.593, 6.051, and 7.719 ppm, and two complex three-spin patterns. Since the starting hydrocarbon possesses an axis of symmetry, observation of two three-spin patterns present the three following possibilities: (a) the carbanion is nonplanar, (b) bonds are broken in the reduction, or (c) two (or more) species are formed. Integration shows the three-spin patterns to be present in a ratio of 12:6. Furthermore the singlets integrate for four, one, two, and four protons, respectively. The singlets at 5.593 and 6.051 ppm appear very close to the singlet observed at 5.80 ppm for the C-9 proton of fluorenyllithium.[6a] These peaks are thus assigned to the C-9 proton of Ia and IIa (Table I; note change in numbering used). The chemical shift and integration data eliminate possibilities a and b and are only consistent with two species which are assigned structures Ia and IIa.



Ia IIa

The sequence of visible spectra obtained during reduction is also consistent with the above data. A broad absorption with a maximum at 500–510 mμ and a shoulder at 460 mμ in addition to a sharp peak at 365 mμ develops during reduction of 4,5-methylenephenanthrene. For lithium and cesium 4,5-methylenephenanthrenyl anions only one absorption (at 505 mμ) is reported in cyclohexylamine.[7] The visible spectrum of IIa is expected to be similar to that of fluorenyl anion which has an intense peak at 365 mμ and a broad three-peak absorption between 440 and 500 mμ with the maximum at 470 mμ.[1b] The spectrum obtained during reduction can be well accounted for by overlapping the spectra of 4,5-methylenephenanthrenyl and fluorenyl anions.

The reaction with sodium in THF first produces the 4,5-methylenephenanthrenide anion radical.[1b] On further reduction, the anion radical decomposes to produce Ia (which has the same nmr spectrum as that with potassium) and a new species which has peaks at 2.967 and 3.684 ppm plus peaks due to aromatic protons. On standing, these peaks decrease in intensity with simultaneous decrease in intensity of peaks attributed to Ia and increase in intensity of peaks due to IIa. The structure of this new species is assigned to IIIa. Apparently IIIa is more acidic than 4,5-methylenephenanthrene, and equilibrium is reached within a period of

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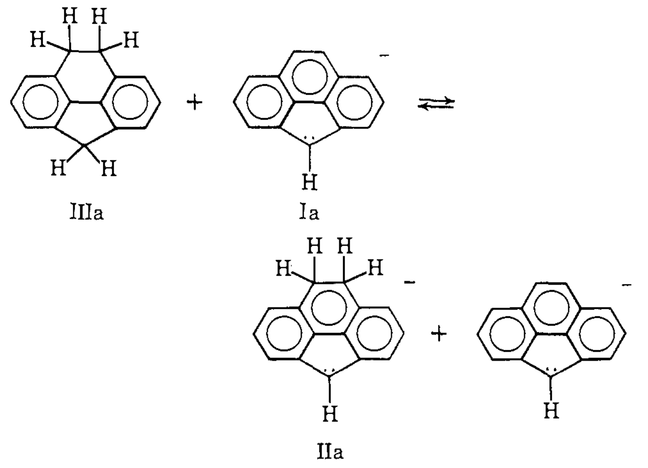
(5) Samples were prepared under high vacuum in usual nmr tubes designed with an "onion-dome" bulb containing the alkali metal mirror. The solvent was tetrahydrofuran-$d_8$ (THF) containing 3% tetramethylsilane (TMS). Spectra were obtained with a Varian Associates HA-100 spectrometer. Final parameters were calculated with the computer program LAOCN3 (a more efficient version of the LAOCOON II program described by S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964)). Line positions used in the calculations were the average of four spectra. The probe temperature was 29°.

(6) (a) J. A. Dixon, P. A. Gwinner, and D. C. Lini, *J. Am. Chem. Soc.*, **87**, 1379 (1965); (b) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

(7) A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *J. Am. Chem. Soc.*, **87**, 384 (1965).



minutes. That the rate of proton transfer is slower with sodium than with potassium is consistent with other studies.[8]

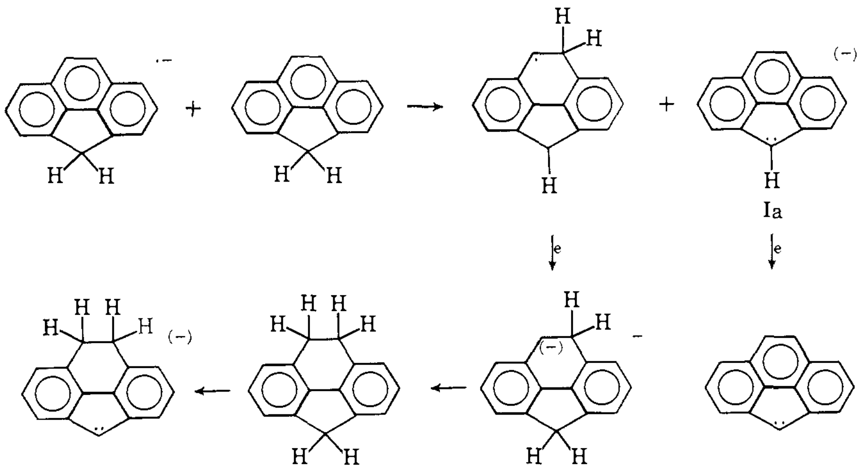
The reduction of 4,5-iminophenanthrene similarly produces two singlets at 3.228 and 7.851 ppm and two complex three-spin patterns which integrate for four, four, twelve, and six protons, respectively. Absence of the two singlets at 5.593 and 6.051 ppm in this spectrum confirms the assignment of these peaks to the C-9 proton in Ia and IIa.

On further reduction, the signals from Ia and Ib disappear and those of IIa and IIb are slightly broadened. Therefore, Ia and Ib are reduced to the respective dianion radicals whereas IIa and IIb are not further reduced under these conditions. A proton-transfer mechanism accounts for the observed results. Such a mechanism is in agreement with recent studies of the electrolytic reduction of 4,5-methylenephenanthrene in the presence of proton donors.[9] This mechanism does not account for the observed 2:1 ratio for I and II. No completely satisfactory answer is obvious. The best explanation at this time is that the reduction of IIIa competes with the reduction of 4,5-methylenephenanthrene.[10] Subsequent protonation and reduction steps probably compete favorably with reactions of the other components in the system, thus producing eventually hexahydro- or octahydrophenanthrene derivatives. Since for every molecule of hexahydro-4,5-methylenephenanthrene produced six of Ia are generated (or eight of Ia for every octahydro-4,5-methylenephenanthrene), only a small amount of IIIa need be reduced to give a high ratio of Ia to IIa. Presumably the relatively small

$$19RH \longrightarrow 12R^- + 6RH_2^- + RH_7$$

$$25RH \longrightarrow 16R^- + 8RH_2^- + RH_9$$

amount of $RH_7$ or $RH_9$ produced is not detectable by nmr. The obvious criticism of this explanation is the fortuitous 2:1 ratio. Further attempts to understand this mechanistic inconsistancy are in progress.



Fluorene and carbazole give spectra attributable to the carbanion and nitranion only. In these compounds the initially reduced materials are probably further reduced more readily than are the starting materials, giving eventually tetra- or hexahydrofluorene anions[3] at concentrations too low to detect.

Nmr parameters for the carbanions are given in Table I. All protons are more shielded in the anions than in the parent compounds with the exception of the C-9 proton of Ia and IIa. The downfield shift of these protons on forming the carbanions is consistent with a change from $sp^3$ to $sp^2$ hydridization for the C-9 carbon. The protons of the reduced carbanion IIa and nitranion IIb appear to higher field than those of Ia and Ib. The difference between the ring-proton chemical shifts in the anions and those in the parent hydrocarbon is larger for 4,5-methylenephenanthrene than for 4,5 iminophenanthrene, suggesting that more of the excess charge resides on nitrogen than on carbon in the anions.

The reactions of 4,5-iminophenanthrene with sodium and cesium give similar reduction results. A small, but real, dependence of the chemical shifts on the metal ion exists. The chemical shifts of the ring protons in the anions appear to lower field in the order Cs < K < Na. Similar results have been reported for fluorene.[6] Further studies are under way to determine the dependence of reduction upon the nature of the solvent

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(8) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **89**, 2764 (1967); M. I. Terekhova, E. S. Petrov, and A. I. Shatenshtein, *Org. Reactivity*, **4**, 638 (1967).

(9) J. Janata, J. Gendell, R. G. Lawton, and H. B. Mark, Jr., *J. Am. Chem. Soc.*, **90**, 5226 (1968); J. Janata and H. B. Mark, Jr., *J. Phys. Chem.*, **72**, 3616 (1968). We thank Dr. Mark for making preprints of these papers available to us.

(10) The half-wave reduction potential of biphenyl is quite similar to that of phenanthrene (2.075 *vs.* 1.935 V *vs.* Hg in 2-methoxyethanol: A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley & Sons, Inc., New York, N. Y., 1961, p 178.

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

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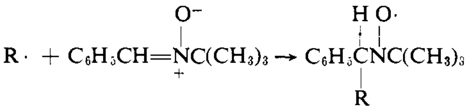
*Received May 23, 1968*

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

*Sir:*

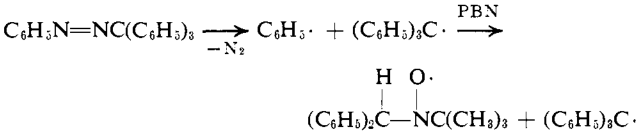
Numerous electron spin resonance (esr) studies of short-lived free radicals produced by *in situ* irradiation or rapid mixing techniques have been reported. These methods depend on rapid radical-producing reactions and frequently large volumes of materials are required. In addition, the optimum conditions 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 $\beta$-hydrogen ($\beta$-H) and nitrogen hyperfine coupling (hfc). The $\beta$-H hfc depends on the dihedral angle which in turn depends on the bulk of R. The magnitude of the $\beta$-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 $\beta$-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.



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

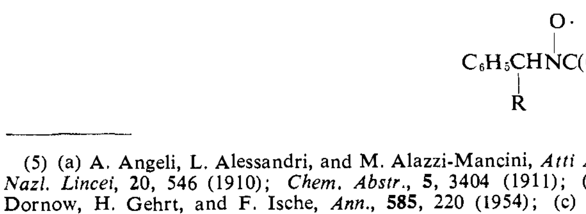
Thus phenylazotriphenylmethane (PAT) decomposes at room temperature in benzene containing PBN to give a strong esr signal consisting of three doublets, $a_N = 13.84$, $a_\beta{}^H = 2.09$ gauss, and a complex set of lines due to the triphenylmethyl radical. Since the same three doublets are obtained 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).



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

Similarly, the trifluoromethyl radical can be trapped in the photolysis of trifluoroiodomethane or trifluoronitrosomethane. A $\gamma$-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).



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

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[1] A. Mackor, Th. A. J. W. Wajer, and Th. J. De Boer, *Tetrahedron*, 1623 (1967); A. Mackor, Th. A. J. W. Wajer, Th. J. De Boer, and J. D. W. van Voorst, *Tetrahedron Letters*, 385, 2115 (1966); C. Lagercrantz and S. Forshult, *Nature*, **218**, 1247 (1968).

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

[3] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 37, 1326 (1962); D. H. Geske, *Progr. Phys. Org. Chem.*, 4, 129 (1967).

[4] E. T. Strom, A. L. Bluhm, and J. Weinstein, *J. Org. Chem.*, 32, 3853 (1967), and references therein. The electronegativity of $\beta$ substituents in $\mathrm{RCH_2C_6H_4N(O\cdot)OH}$ has a relatively small effect on the $\beta$-H coupling but quite a sizable effect on the nitrogen hfc: unpublished work of J. L. Gerlock in our laboratory.

[5] (a) A. Angeli, L. Alessandri, and M. Alazzi-Mancini, *Atti Accad. Nazl. Lincei*, 20, 546 (1910); *Chem. Abstr.*, **5**, 3404 (1911); (b) A. Dornow, H. Gehrt, and F. Ische, *Ann.*, **585**, 220 (1954); (c) G. E. Utzinger and F. A. Regenass, *Helv. Chim. Acta*, 37, 1892 (1954).