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Correlation of Radical Structure with EPR Spin Adduct Parameters: Utility of the ^{1}H, ^{13}C, and ^{14}N Hyperfine Splitting Constants of Aminoxyl Adducts of PBN-*nitronyl*-^{13}C for Three-Parameter Scatter Plots

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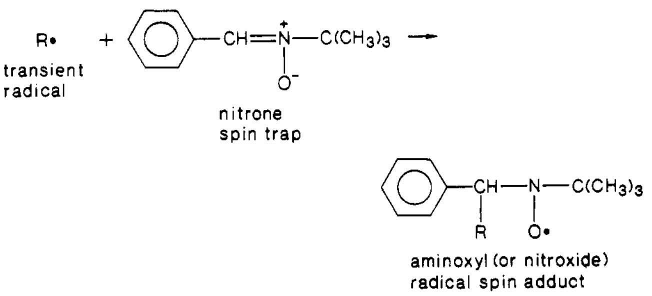
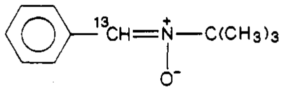
The novel ^{13}C-labeled compound α-phenyl-*N*-*tert*-butyl [^{13}C]nitrone (PBN-*nitronyl*-^{13}C) is introduced as an improved spin trap for the electron paramagnetic resonance (EPR) spectral identification of transient radicals. A series of approximately 30 nonpolar as well as polar radical adducts of PBN-*nitronyl*-^{13}C have been prepared in organic and aqueous solutions. We have found that the α-^{13}C hyperfine splitting (HFS) provides a better indication of the radical center than the N HFS and also is less sensitive to solvent polarity effects. For instance, the α-^{13}C HFS's for halogen-centered radicals are smaller than 1 G; oxygen-, nitrogen-, and sulfur-centered radicals are between 3 and 5 G; carbon-, silicon-, and germanium-centered radicals (except NC$^{\bullet}$) are between 5 and 6 G, while phosphorus-centered radicals are larger than 6 G in typical organic solvents such as toluene or benzene. Both the N and α-^{13}C HFS exhibit useful trends with respect to the dipolar nature of the radical addend; however, neither correlate in a simple linear manner with standard substituent constants such as Taft's σ_I scale. Some speculation on the origin of the EPR HFS trends or lack thereof is also included. The β-H HFS does not exhibit any consistent trends with respect to either the dipolar or steric nature of the added radical. The utility of three spectral parameters, namely, the ^{14}N, β-H, and α-^{13}C HFS's, to provide signatures for radical adduct structures has also been explored.

Detection of transient free radicals in solution at ambient temperatures by EPR is often hampered by low steady-state radical concentrations or by adverse electronic relaxation behavior. A successful means to overcome these difficulties is the spin-trapping technique[1-3] whereby nitrones such as α-phenyl-*N*-*tert*-butyl nitrone (PBN),[4] or 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO),[5] or *C*-nitroso compounds (such as 2-methyl-2-nitrosopropane (MNP)[2] yield persistent radical addition products (spin adducts) that ideally permit facile identification of the added radical.



In contrast to *C*-nitroso compounds, nitrone spin traps produce stable radical adducts with a wide range of carbon- as well as heteroatom-centered (e.g., S, N, O, halogen) radicals including the biologically relevant hydroxyl and superoxide/hydroperoxyl radicals. Determination of the structure of these radical adducts of nitrones, however, may sometimes be difficult because hyperfine splittings (HFS's) from the radical addend are usually not detectable.[6-8] Thus, it is necessary in general to rely on HFS's originating from the spin trap moiety (i.e. the N and β-H HFS's) to act as spectral fingerprints[9,10] for the added radical.

The spin trap PBN-*nitronyl*-^{13}C (I) was synthesized with the anticipation that the α-^{13}C HFS's from the resulting adducts might provide valuable additional information about the structure of the added radical. Although the β-H HFS is a very useful marker in the identification of PBN spin adducts, its magnitude is not likely to vary in an easily predictable (i.e. systematic) manner. This is because the β-H HFS exhibits a dihedral dependence (with respect to the aminoxyl p_{π} orbital, see IV)[1,11] and is thus susceptible to radical addend conformational changes that might arise from steric effects or intramolecular interactions between the radical addend and the aminoxyl function (e.g. intramolecular H bonding).[12] The β-H HFS is also prone to solvent polarity effects.[13,14]



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[6] Additional hyperfine splitting may be seen if the β-nucleus of the radical addend possesses nuclear spin in high natural abundance, e.g. PBN-NHNH$_2$: Noda, A.; Noda, H.; Ohno, K.; Sendo, T.; Misaka, A.; Kanazawa, Y.; Isobe, R.-I.; Hirata, M. *Biochem. Biophys. Res. Commun.* **1985**, *133*, 1086–1091.

[7] Additional HFS may also be observed if the β-nucleus of the radical addend possesses spin from isotopic substitution, e.g. PBN-^{17}OC(CH$_3$)$_3$: Howard, J. A.; Tait, J. C. *Can. J. Chem.* **1978**, *56*, 1776–178.

[8] Use of a perdeuterated spin trap e.g. PBN-d_{14} and/or endor (electron nuclear double resonance) techniques can bring to light long-range HFS's hidden in the EPR linewidth: Janzen, E. G.; Oehler, U. M.; Haire, D. L.; Kotake, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6858–6863.

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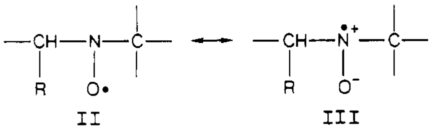
The N and α-^{13}C HFS's may not be as sensitive to these kinds of conformational considerations; therefore, these HFS's might be expected to better reflect the nature (i.e. polar vs nonpolar) of the added radical. Even though it has been recognized for years that the magnitude of the N HFS was often suggestive of the type of radical trapped by PBN (e.g. oxyl adducts generally exhibit lower N HFS's than their alkyl counterparts)[1-3] a systematic attempt to correlate these effects with a standard chemical substituent constant (e.g. σ_I[15,16]) has yet to appear.[17,18] We decided to explore the variation of the N and α-^{13}C HFS's with substituent in the hopes that the latter might prove to be more sensitive to the radical addend structure because the radical addend is directly bonded to the ^{13}C nucleus.

The simplified trend of expected behavior is as follows: spin adducts with electron-donating radical addends (i.e. −ve σ_I's) should favor the resonance form (III) and therefore should exhibit larger N HFS's along with larger α-^{13}C HFS's (since spin is assumed to originate at the ^{13}C nucleus by a spin polarization transfer mechanism from the aminoxyl nitrogen). The converse should also be true (i.e. smaller N and α-^{13}C HFS's) for spin adducts with progressively stronger electron-withdrawing groups (i.e. increasingly more +ve σ_I's) because the importance of the polar resonance form (III) should diminish as a result of unfavorable dipolar interactions.



II III

Experimental Section

The EPR spectra were recorded in the X-band mode on either a Varian E-104 spectrometer or a Bruker ER 200D spectrometer. The latter is interfaced to an Aspect 2000 (ER 140) data system. Hyperfine splittings of PBN-*nitronyl*-^{13}*C* radical adduct spectra with degenerate lines, as well as those comprising spin adduct mixtures were routinely extracted via computer simulation techniques.[19] In situ photolyses were conducted with an Oriel Model 6137 75-W low-pressure xenon lamp.

Radical adduct generation in benzene was accomplished by thermolysis at room temperature or photolysis of the appropriate precursors. Generally, approximately 1–2-mL solutions containing ~50 mM nitrone and ~10 mM radical precursor (or anion) were used. Examples of thermal radical sources include: 2-methyl-2-propyl from azo-*tert*-butane (*tert*-butyldiazene), 2-cyano-2-propyl from 1,1′-azobis(isobutyronitrile) (AIBN), phenyl from (phenylazo)triphenylmethane (PAT), 2-cyano-2-propyloxyl from AIBN plus traces of oxygen, *tert*-butyloxyl from di-*tert*-butylperoxalate (DBPO),[5] benzoyloxyl from benzoyl peroxide, fluorine atom from silver difluoride, and ethylthiyl from ethylthionitrite.[20] Radicals from the various photolyses include: triphenylgermanyl from hexaphenyldigermane, trichloromethyl from bromotrichloromethane, trifluoromethyl from iodotrifluoromethane, *tert*-butyloxyl from di-*tert*-butyl peroxide, 2-methyl-1-propyloxyl from 2-methyl-1-propylnitrite, chlorine atom from hexachloroethane and hydroxyl from hydrogen peroxide, cyanyl from (trimethylsilyl)cyanide.

A number of carbon radical adducts were made by alkyl and aryl Grignard additions to the nitrone in toluene, followed by quenching with water to form the hydroxylamine. Oxidation to the aminoxyl was possible with the addition of lead dioxide or by purging the solution with O_2.[4] The hydrogen atom adduct was likewise prepared by hydride addition (from sodium borohydride). The carbazol-*N*-yl adduct was prepared by oxidation of the amine with potassium superoxide in benzene, and the azidyl radical was prepared by photolysis of a mixture of tetra-*n*-butylammonium azide and tetrabromomethane in benzene.

The remaining radicals were generated mainly by H-abstraction reactions. Symbols for the radical abstractors are designated as follows: thermolysis of DBPO to *tert*-butyloxyl (A_1), or sodium persulfate to sulfate anion radicals (A_2); photolysis of di-tert-butylperoxide to *tert*-butyloxyl (A_3), or hydrogen peroxide to hydroxyl (A_4); photoexcitation of benzophenone to its triplet (A_5).

Triethylsilyl radicals were generated from triethylsilane (A_1), hydroxylalkyls from alcohols (A_5), propanoyl and benzoyl from aldehydes (A_1), *tert*-butylperoxyl from *tert*-butyl hydroperoxide (A_1), dicyclohexylphosphinyl from dicyclohexylphosphine (A_1), diethylphosphityl from diethylphosphite (A_1), carbon dioxide anion radical from sodium formate (A_2), aminoformyl from formamide (A_2), aminyl from ammonia (A_2), hypophosphityl radical anion from sodium hypophosphite (A_2) and azidyl by oxidation of sodium azide with sodium persulfate (A_2). Please note that further details on conditions for these experiments can be found in references listed in the tables.

Spectral *g* values were determined either by comparison with Fremy's salt (sodium aminoxyldisulfonate) in saturated sodium bicarbonate in a capillary taped to the EPR cell ($g = 2.005\,50$)[21] or with a small solid sample of 1,1-diphenyl-2-picrylhydrazyl (DPPH) ($g = 2.0037$).[22] The EPR spectrometer calibration was also determined by the use of Fremy's salt whose N HFS is known to be 13.091 G.[21] HFS's are reproducible to within 0.05 G. The title spin trap, α-phenyl-*N*-*tert*-butyl [^{13}C]nitrone (PBN-*nitronyl*-^{13}*C*), was synthesized from benzaldehyde-*carbonyl*-^{13}*C* (from MSD isotopes) and 2-methyl-2-nitropropane by a recently published procedure.[23] 5,5-Dimethyl-1-pyrrolidine *N*-oxide (DMPO) was obtained as commercial grade from Aldrich or Sigma and was purified by distillation under reduced pressure prior to use.

Results and Discussion

A wide range of the PBN-*nitronyl*-^{13}*C* radical adducts were prepared in order to provide a good selection of σ_I values for comparison purposes[24] (i.e. with a range of radical addend polarities). Since the various HFS's can be quite sensitive to solvent polarity,[13] the collection of EPR spectral data was restricted to one organic solvent (benzene, Tables I and III) and water (Tables II and IV).

Radical Adducts of PBN-*nitronyl*-^{13}*C*. EPR spectra of a nonpolar radical adduct (e.g. CH_3 with σ_I −0.01) as well as that of a very polar example (e.g. Cl, σ_I 0.47) both exhibit readily resolvable α-^{13}C HFS's (Figures 1 and 2). It is notable that the N and α-^{13}C HFS's are both significantly smaller for the Cl atom adduct. This is expected because in the chlorine adduct the polar resonance structure of the aminoxyl should be disfavored. An advantage of the use of the α-^{13}C HFS is that its range of values is approximately twice that of comparable N HFS's (compare CH_3 vs F) and therefore is potentially more diagnostic.

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(24) For a recent compilation of EPR parameters of radical spin adducts of nitrones and *C*-nitroso compounds, see: Buettner, G. R. *Free Rad. Biol. Med.* **1987**, *3*, 259–303.

Table I. EPR Hyperfine Splittings for Radical Adducts of PBN-*nitronyl*-^{13}C in Benzene[a]

radical addend	σ_I[b]	a_N	a_β^H	a_α^{13C}	a^{other}	g value	ref.
$Si(C_2H_5)_3$[c]	−0.11	14.67	6.00	5.14	β-^{29}Si, ~13.0	2.0062	30
$Ge(C_6H_5)_3$		14.66	6.27	5.40			
CH_3	−0.01	14.85	3.53	5.29		2.0062	8
$C(CH_3)_3$	−0.01	14.66	2.32	5.49			
H	0.00	14.87	7.41	5.38			4
$C(CH_3)_2CN$		14.28	3.29	5.78			31
$CH(CH_3)_2$	0.01	14.67	2.59	5.30			32
$CH_2CH{=}CH_2$	0.02	14.64	3.27	5.38			33
$CH_2C_6H_5$	0.03	14.45	2.54	5.68			32
$CHOHCH_3$[d]	0.04	15.1	4.7	5.4			12
	0.04	15.1	5.4	5.8			12
CH_2OH	0.11	14.88	6.51	5.74			12
$CH{=}CH_2$	0.11	14.85	2.68	5.31			
C_6H_5	0.12	14.37	2.18	5.53		2.0061	34
$C(O)C_2H_5$[e]	0.28	14.27	3.14	5.90			
$C(O)C_6H_5$[e]	0.28	14.30	4.54	5.79			13
CCl_3	0.36	14.01	1.77	5.82			35
CF_3	0.40	13.97	1.85	5.92	γ-3F, 1.54		4
$NC_{12}H_8$		14.65	4.64	4.64	β-N, 4.40		36
N_3	0.43	13.95	1.92	3.47	β-N, 1.78		
OCH_3	0.27	13.59	1.84	4.55			12
$OCH_2CH(CH_3)_2$[f]	0.27	13.72	1.97	4.56			
$OC(CH_3)_2CN$[g]		13.93	2.16	4.70			26
$OC(CH_3)_3$[h]	0.27	14.28	2.03	4.91		2.0061	37
$OOC(CH_3)_3$		13.25	1.15	4.65			37
$OC(O)C_6H_5$	0.43	13.29	1.48	3.17			38
$P(c\text{-}C_6H_{11})_2$		14.39	3.35	6.33	β-P, 12.11		
$P(O)(OC_2H_5)_2$	0.32	14.65	3.06	6.16	β-P, 24.33	2.0063	39
SCH_2CH_3[i]	0.30	13.80	2.00	4.90			20
Cl[j]	0.47	12.25	0.70	0.70	β-^{35}Cl, 6.15	2.0064	40
	0.47	12.25	0.70	0.70	β-^{37}Cl, 5.12	2.0064	40
F[k–m]	0.54	~12.4	~0.8	~0.8	β-F, ~46.21		
CN	0.56	14.84	1.76	3.40			40

[a] All the EPR data are from this work unless otherwise noted. The spectra were recorded at room temperature. The hyperfine splittings (HFS's) are given in Gauss (G). References are to recent papers where the radical spin adducts were detected in benzene or solvents of very similar solvent polarity (eg. according to $E_{T(30)}$ scale, ref 14) such as toluene. [b] Please note: σ_I values (in contrast to Hammett's σ scale) are appropriate when the substituent is bonded to a tetrahedral center (i.e. where inductive (through-bond) and field (through-space) effects are dominant and delocalization minimal). Positive σ_I values indicate electron-withdrawing groups (EWG's) whereas negative σ_I's define electron-donating groups (EDG's) (with respect to H as the internal standard, $\sigma_I = 0$), see ref 15 and 16. [c] σ_I value actually for $Si(CH_3)_3$, see ref 15. [d] A mixture of two diastereomeric spin adducts are resolvable in this solvent. [e] σ_I value actually for $C(O)CH_3$, see ref 16. [f] σ_I value actually for $O(CH_2)_2CH_3$, see ref 15. [g] This radical addend is assigned as $OC(CH_3)_2CN$, which presumably is formed from the decomposition of the peroxyl radical obtained from the reaction of $^\bullet C(CH_3)_2CN$ with O_2. [h] σ_I value for $OCH(CH_3)_2$, see ref 15. [i] σ_I value for SCH_3, see ref 15. [j] The HFS's for a common oxidation product of PBN-*nitronyl*-^{13}C, benzoyl [*carbonyl*-^{13}C]*tert*-butylaminoxyl in benzene are: $a^N = 7.98$, $a_\alpha^{13C(carbonyl)} = 4.76$ G (for comparison with the ^{12}C analogue, see ref 41). [k] Estimated HFS's (from a very weak spectrum obtained in benzene). [l] PBN-*nitronyl*-^{13}C-Cl in acetonitrile exhibited the following HFS's: $a^N = 12.65$, $a_\alpha^{13C} = 1.00$, and $a_\beta^F = 46.21$ G. [m] The difluoro adduct of PBN-*nitronyl-C* (i.e. 1,1-difluorophenylmethyl [1-^{13}C]*tert*-butylaminoxyl) was also detected and exhibited the following HFS's in benzene: $a^N = 12.55$, $a_\alpha^{13C} = 3.94$, and $a_\beta^{2F} = 21.35$ G (for comparison with the ^{12}C derivative, see ref 42.

Table II. EPR Hyperfine Splittings for Radical Adducts of PBN-*nitronyl*-^{13}C in Water[a]

radical addend	σ_I[b]	a^N	a_β^H	a_α^{13C}	a^{other}	g value	ref
CH_3	−0.01	16.49	3.61	6.05		2.0059	
$C(CH_3)_3$	−0.01	16.25	3.12	6.04			
H	0.00	16.61	10.79	6.44		2.0054	43
$CHOHCH_3$	0.04	15.58	3.63	6.23			12
CH_2OH	0.11	15.99	3.80	6.09		2.0058	12
C_6H_5	0.12	16.02	4.26	6.07		2.0057	13
CO_2^-	0.19	15.80	4.63	6.65		2.0058	44
$C(O)NH_2$[c,d]	0.28	15.73	3.27	5.86	β-^{13}C, 10.53	2.0058	
NH_2[c]	0.17	16.06	3.54	5.32	β-N, 0.82	2.0059	
N_3	0.43	15.25	2.35	4.37	β-N, 2.00		45
OH	0.24	15.46	2.70	4.36		2.0057	46
$OC(CH_3)_3$[e]	0.27	15.69	4.11	5.65		2.0059	
PHO_2^-		15.90	1.99	6.40	β-P, 16.15 γ-H (on P), 3.17	2.0058	
SO_3^-[f]	0.15	15.02	1.95	6.92			

[a] All the EPR data are from this work unless otherwise noted. The spectra were recorded at room temperature. The hyperfine splittings are given in Gauss. References are to recent papers where the spin adducts were detected in aqueous solutions. [b] For the σ_I values, see ref 15. [c] These HFS's correspond to the dideuterio analogue(s). [d] This adduct is also produced from NaCN and $Na_2S_2O_8$ in water, Rehorek, D., University of Leipsig, DDR (unpublished results). [e] σ_I value for $OCH(CH_3)_2$, see ref 15. [f] See the paper by Motten, A. G.; Levy, L. A.; London, R. E., submitted for publication in *J. Magn. Reson.*

A plot of the N HFS vs σ_I for the same substituents is shown in Figure 3. A line with slightly negative slope through the carbon-type radical adducts (i.e. from C-, H-, Si-, and P-centered radicals) may be envisaged. Radical addends from the more polar heteroatom-centered radicals (i.e. from S-, N-, O-, Cl- and F-centered radicals and atoms)

Table III. EPR Hyperfine Splittings for Radical Adducts of DMPO in Benzene[a]

radical addend	σ_I[b]	a^N	a_β^H	a^{other}	*g* value	ref
CH_3	−0.01	14.25	20.64		2.0059	5
$C(CH_3)_3$	−0.01	14.23	20.88			
H	0.00	14.30	18.80		2.0061	5
CH_2OH	0.11	14.71	21.66		2.0057	12
C_6H_5	0.12	13.78	19.21		2.0062	47
$C(O)C_6H_5$[c]	0.28	14.18	14.18			5
CCl_3	0.36	13.17	15.28			
CF_3[c]	0.40	13.22	15.54			5
$OC(CH_3)_3$[d]	0.27	13.19	8.16	γ-H, 1.97	2.0061	13, 48
$OC(O)C_6H_5$[c]	0.43	12.24	9.63			5
$P(O)(OC_2H_5)_2$[c]	0.32	13.2	16.9	β-P, 45.0		49
SCH_2CH_2OH[c]	0.30	13.8	14.2	γ-2H, 0.7	2.0061	20

[a] All the EPR data are from this work unless otherwise noted. The spectra were recorded at room temperature. The hyperfine splittings are given in Gauss. References are to recent papers where the spin adducts were detected in benzene or organic solutions of similar solvent polarity based on $E_{T(30)}$, e.g. toluene, (see ref 14). [b] For the σ_I values, see ref 15. [c] EPR parameters are literature values, see: individual references at the right. [d] σ_I value for $OCH(CH_3)_2$, see ref 15.

Table IV. EPR Hyperfine Splittings for Radical Adducts of DMPO in Water[a]

radical addend	σ_I[b]	a^N	a_β^H	a^{other}	*g* value	ref
CH_3	−0.01	16.35	23.71		2.0054	50
H	0.00	16.55	22.61		2.0055	51
CH_2OH	0.11	15.92	22.56			12
C_6H_5	0.12	15.63	23.12		2.0058	52
CO_2^-[c]	0.19	15.8	19.1			53
NH_2[c]	0.17	15.9	19.3	β-N, 1.60		54
N_3[c]	0.43	14.8	14.2	β-N, 3.1		45
OH	0.24	15.01	15.01		2.0060	46
$OC(CH_3)_3$[d]	0.27	14.8	16.0			13
SO_3^-[c]	0.15	14.7	16.0		2.0056	55

[a] All the EPR data are from this work unless otherwise noted. The spectra were recorded at room temperature. The hyperfine splittings are given in Gauss. References are to recent papers where the spin adduct was detected in aqueous solutions. [b] For the σ_I values, see ref 15. [c] EPR parameters are literature values, see: individual references at the right. [d] σ_I value for $OCH(CH_3)_2$, see ref 15.

produce N HFS's that are much smaller than predicted from the values of σ_I. These polar adducts, indicated by darkened squares, may lie on a curve that falls away from the line through the carbon-like adducts. Qualitatively both these observations are consistent with destabilization of the polar resonance form of the aminoxyl function as the radical addend becomes more polar. Because the cyanyl adduct contains a very polar radical addend (σ_I = 0.56), the observed N HFS of 14.84 G is apparently anomalously large. This N HFS is within the range of values expected for the family of carbon-centered type radical adducts.

A plot of the α-^{13}C HFS vs σ_I (Figure 4) could also perhaps be best accommodated with two traces: a straight line and a curve! The α-^{13}C HFS's for increasingly polar addends are expected to decrease as the radical addend becomes more polar, and this is observed for the strongly electronegative heteroatom-centered adducts (i.e. from S, N, O, Cl, and F radicals and atoms). The trend with the carbon-type adducts (i.e. from C-, H-, P-, and Si-centered radicals), however, may be a line with a slightly positive slope. This trend for the carbon-type adducts obviously cannot be accounted for by the simple picture of dipolar stabilization of the aminoxyl resonance structures (II or III). The cyanyl adduct seems to be a special borderline case. Here, features of a carbon-centered type adduct are reflected in the N HFS (i.e. 14.85 G) whereas the α-^{13}C HFS (i.e. 3.40 G) is suggestive of the electronegative heteroatom series.

An interpretation of this latter anomaly as well as the lack of linearity in ^{13}C (as well as N) HFS vs σ_I plots may arise from the complex interrelationship between the effect of spin-density distribution on planar vs nonplanar aminoxyl nitrogen and α-carbon atoms upon introduction of radical addends of different electronegativity. Steric effects for the same type of bond (e.g. carbon) do not play an important role; the α-^{13}C HFS for the methyl and *tert*-butyl adducts are very similar (5.3 vs 5.5 G, respectively).

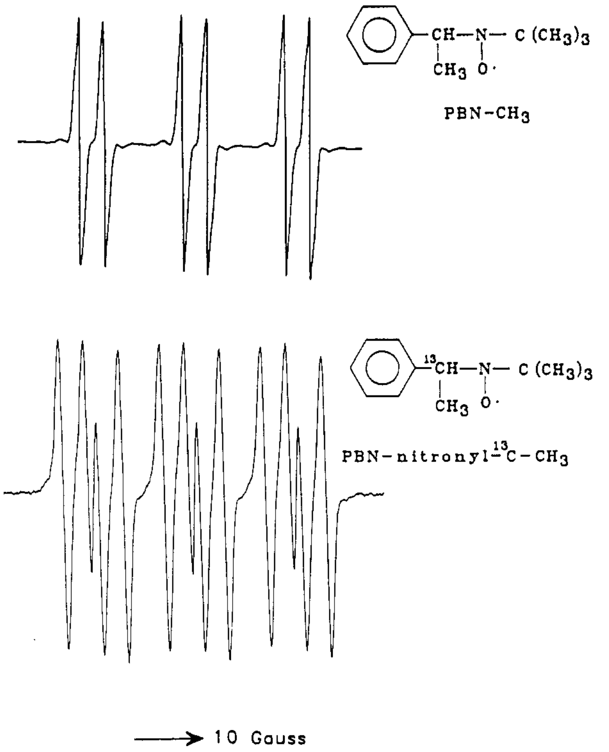


Figure 1. (A, top) EPR spectrum of the methyl radical adduct of PBN in benzene. (B, bottom) EPR spectrum of the methyl radical adduct of PBN-nitronyl-^{13}C in benzene.

A plot of the β-H HFS vs σ_I should show the influence of both the effect of polarity of the radical addend as well

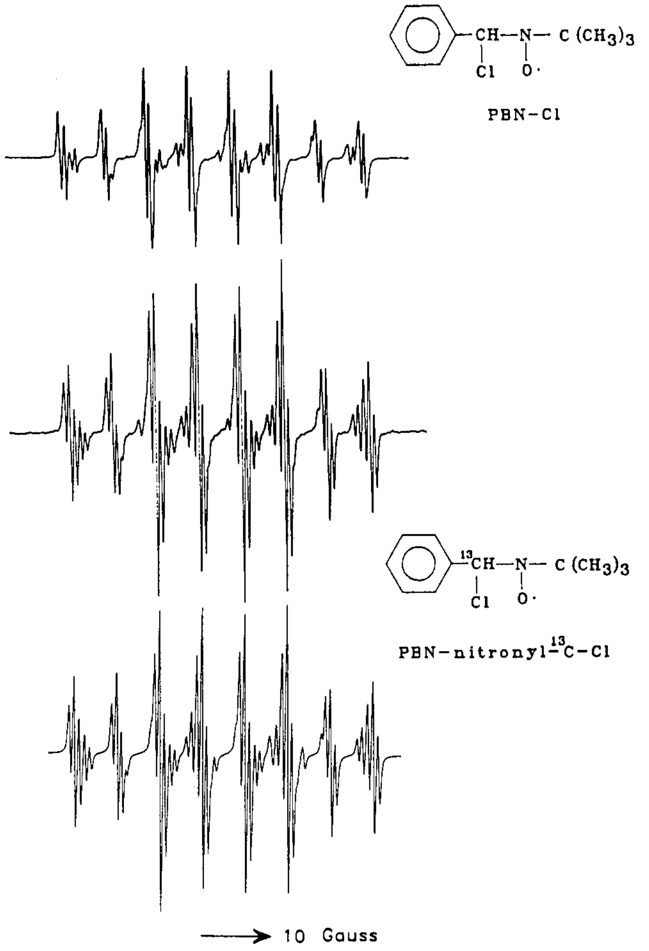
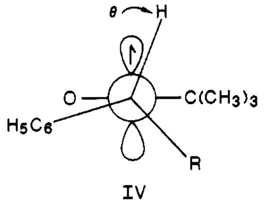


Figure 2. (A, top) EPR spectrum of the chlorine atom adduct of PBN in benzene. (B, middle) EPR spectrum of the chlorine atom adduct of PBN-*nitronyl*-^{13}C in benzene. (C, bottom) Computer simulation of PBN-*nitronyl*-^{13}C-Cl (i.e. a 3 to 1 mixture of ^{35}Cl and ^{37}Cl adducts): $a^{\mathrm{N}} = 12.25$, $a_\beta{}^{\mathrm{H}} = 0.7$, $a_\alpha{}^{^{13}\mathrm{C}} = 0.7$, $a_\beta{}^{^{35}\mathrm{Cl}} = 6.15$ G (spin = 1.5), and $a^{\mathrm{N}} = 12.25$, $a_\beta{}^{\mathrm{H}} = 0.7$, $a_\alpha{}^{^{13}\mathrm{C}} = 0.7$, $a_\beta{}^{^{37}\mathrm{Cl}} = 5.12$ G (spin = 1.5). A 1 to 3 ratio of benzoyl [*carbonyl*-^{13}C]-*tert*-butylaminoxyl (vs PBN-*nitronyl*-^{13}C-^{35}Cl) was also included in the simulation: $a^{\mathrm{N}} = a_\alpha{}^{^{13}\mathrm{C}} = 4.76$, $\Delta g = -1.09$ G. The linewidth was 0.4 G and the lineshape was 0.7 Lorentzian (and 0.3 Gaussian) for all three components.

as the steric requirements of the total system in achieving an equilibrium conformation at room temperature. The β-H HFS is expected to exhibit a dependence upon the dihedral angle (θ) (IV).[1,11] Scatter is expected and certainly found (Figure 5). A plot of β-H vs N HFS has similar attributes and has previously been used to suggest the best choice of spin trap for separating patterns of lines in mixtures of spin adducts (scatter plots[5]).



IV

Since the spin adducts of PBN-*nitronyl*-^{13}C provide for the first time a series of aminoxyls with three sets of parameters it is of interest to present a three-dimensional scatter plot showing these data (Figure 6). Thus, it is possible to evaluate the uniqueness of a given set of parameters to assist in the assignment of spectra.

Carbon- vs Oxygen-Centered Radical Addends. One potentially useful feature of the α-^{13}C HFS (at least in

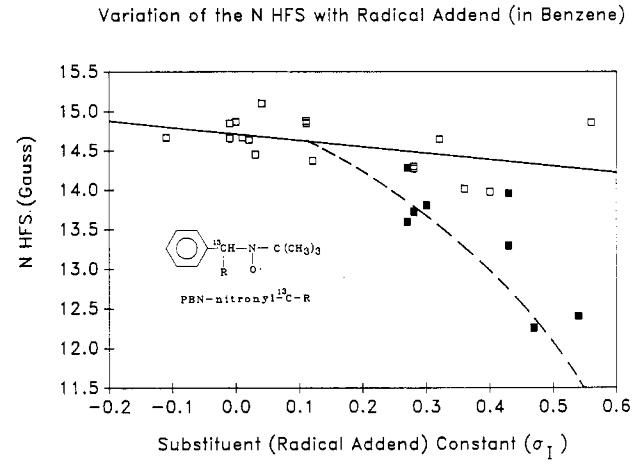


Figure 3. Variation of the N HFS of the radical adducts of PBN-*nitronyl*-^{13}C in benzene with the substituent constant (σ_I). Lightened squares refer to the carbon-like C-, H-, Si-, and P-centered radical adducts whereas the darkened squares correspond to the very polar S, N, O, Cl, and F heteroatom centered radical and atom adducts. R value for line = 0.5, slope = −0.9.

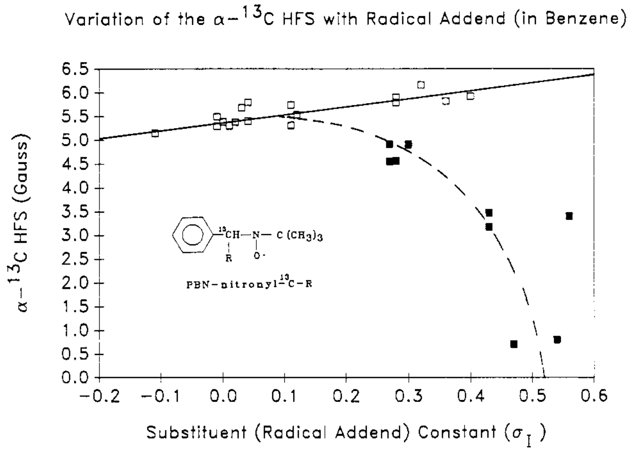


Figure 4. Variation of the α-^{13}C HFS of radical adducts of PBN-*nitronyl*-^{13}C in benzene with the substituent constant (σ_I). Lightened squares refer to the carbon-like C-, H-, Si-, and P-centered radical adducts whereas the darkened squares correspond to the very polar S, N, O, Cl, and F heteroatom (and cyanyl) radical and atom adducts. *R* value for line = 0.82, slope = +1.5.

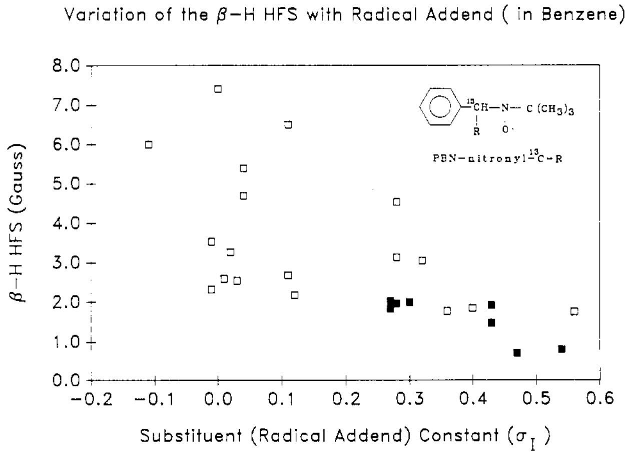


Figure 5. Variation of the β-H HFS's of radical adducts of PBN-*nitronyl*-^{13}C in benzene with the substituent constant (σ_I). Lightened squares refer to the carbon-like C-, H-, Si-, and P-centered radical adducts whereas the darkened squares correspond to the very polar S, N, O, Cl, and F heteroatom centered radical and atom adducts.

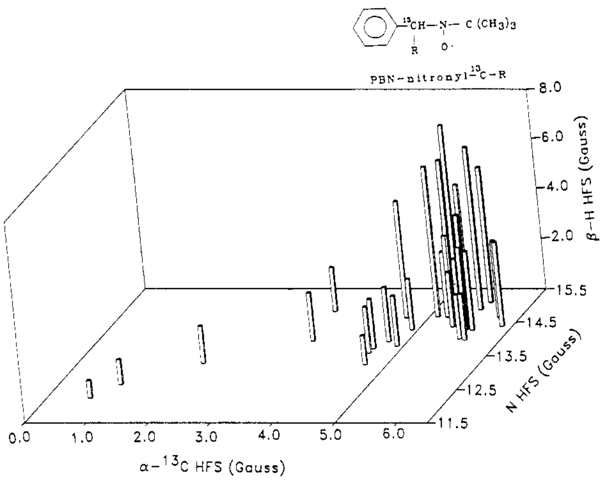
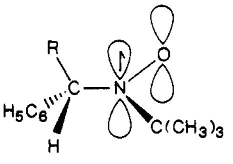


Figure 6. Three dimensional EPR "spectralscape" generated from the β-H, α-^{13}C, and N HFS's of the radical adducts of PBN-*nitronyl*-^{13}*C* in benzene. The carbon-like C-, H-, Si-, and P-centered adducts exhibit α-^{13}C HFS's above the line at 5.0 G. In contrast, the very polar S, N, O, Cl, F heteroatom (and cyanyl) radical and atom adducts exhibit α-^{13}C HFS's below this value.

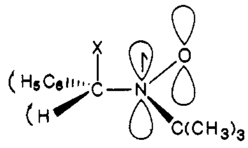
benzene solution) is that carbon-centered radical adducts generally exhibit HFS's significantly greater than 5 G (i.e. 5.3–5.9) whereas oxygen-centered adducts display values below 5 G (i.e. 3.2–4.9). In contrast, the ranges of N HFS's for C- and O-centered radical adducts overlap (e.g. 14.0–14.8 vs 13.3–14.2 G, respectively). Since differences in *g* values for carbon- vs oxygen-centered adducts are very small, it is difficult to differentiate them in this way.[25] It is noteworthy that *g* values, however, do change significantly with solvent polarity and that the change is in an opposite direction to that of the change in α-^{13}C and N HFS's: namely, the *g* value decreases with increasing solvent polarity (e.g. PBN-CH_3 in benzene, $g = 2.0062$; in water, $g = 2.0059$; (Tables I and II).

We decided to utilize PBN-*nitronyl*-^{13}*C* to clarify a spectral assignment in the literature. Ohto et al.[26] reported EPR parameters for the 2-cyanopropyl adduct of PBN that appeared very similar to those of a typical oxyl adduct (i.e. $a^N = 13.87$, $a_\beta{}^H = 2.09$ G). We repeated this experiment and found an α-^{13}C HFS at 4.70 G (Table I), which strongly points to an oxyl adduct. In all likelihood the 2-cyano-2-propyl radical (from 1,1′-azobis(isobutyronitrile) (AIBN)) reacts with traces of oxygen in solution to give the 2-cyano-2-propyloxyl radical, which is trapped by PBN. We have found that the intensity of the EPR signal associated with the α-^{13}C HFS of 4.70 G is strongly dependent upon the dissolved oxygen concentration. Furthermore, we have obtained definitive GC/MS structural evidence for the intermediacy of the 2-cyano-2-propyloxyl radical adduct. Details of these observations will be included in another manuscript that is in preparation.

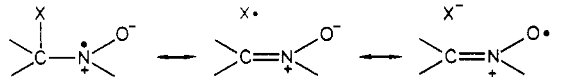
Specific Radical Addend–Aminoxyl Interactions. The very electronegative halogen addends (e.g. Cl and F) are expected to exhibit smaller α-^{13}C HFS's, but the observed values (~1 G) are considerably lower than those predicted by σ_I. One explanation for this phenomenon may be that the hybridization at the α-carbon atom could be substantially altered by bonding to the strongly electron withdrawing halogen atoms VI. This change should cause a decrease in the β-H HFS, and this is found. The resonance hybrid shown below, wherein spin is transmitted to the α-carbon by a delocalization mechanism (VI(c)) could conceivably contribute some spin of opposite sign (to that from the usual spin polarization mechanism) and thereby reduce the net magnitude of the α-^{13}C HFS. If the α-^{13}C HFS in the difluoro adduct also obtains some spin in this way the net α-^{13}C HFS may actually be opposite in sign to that of the other adducts (i.e. −3.94 G, Table I). We attempted to obtain the sign of α-^{13}C HFS's for some of these adducts by triple resonance but found that the ^{13}C endor lines did not saturate as easily as the corresponding ^{1}H lines.[8]



V

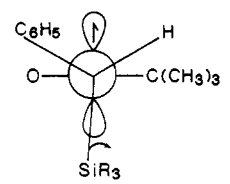


VI

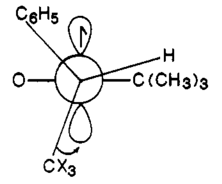


VI(a) VI(b) VI(c)

The electropositive silicon-centered addend (SiR_3) with the most negative σ_I value (Table I) should exhibit the largest α-^{13}C HFS. However, the observed value 5.14 G is even lower than that of its carbon-based equivalent group, *tert*-butyl, which is 5.49 G. The large β-^{29}Si HFS (13.0 G) along with the β-H HFS of 6.0 G suggests that the PBN-SiR_3 radical adduct adopts the conformation shown below (VII). In this conformation withdrawal of electron density from the aminoxyl function by the SiR_3 group (i.e. via p_π–d_π interactions) may account for the lowering of the α-^{13}C HFS.



VII



VIII

VII = SiR , R = alkyl, dihedral angle = 3° (estimated based on β-H HFS); VIII = CX_3, X = halogen, dihedral angle = 15° (estimated based on β-H HFS)

The strongly electronegative halogenated carbon-centered addends (e.g. CCl_3 and CF_3) on the other hand display α-^{13}C HFS's which are much higher than expected. The large radical addend β-^{13}C HFS due to the CX_3 moiety (e.g. ~10 G for CCl_3)[27] and the relatively small β-H HFS suggest that this group also eclipses the aminoxyl p_π orbital (VIII); however, an explanation for the larger α-^{13}C HFS in this situation is not obvious.

Radical Adduct Substituent Constants (the $\sigma_{RA\cdot}$ Scale). The lack of a good linear correlation between the N or the α-^{13}C HFS (of PBN-*nitronyl*-^{13}*C* adducts) and (σ_I) (Figures 3 and 4) may be due to a multitude of reasons. Specific radical addend–aminoxyl group interactions or related intermolecular effects, or perhaps even deficiencies in σ_I[28] may all contribute. For the polar heteroatom-cen-

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[25] Spectral mixtures of various radical spin adducts may occasionally be distinguished by very small differences in *g* value, e.g. PBN-alkyl vs PBN-alkyloxyl: Janzen, E. G.; Towner, R. A.; Haire, D. L. *Free Rad. Res. Commun.* **1987**, *3*, 357–364.

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[28] For some critical discussion on substituent constants including σ_I values (e.g. incomplete separation of field and resonance contributions, effects of solvent, charged groups, etc.), see: Reynolds, W. F.; Topson, R. D. *J. Org. Chem.* **1984**, *49*, 1989–1992 and the four following papers in that issue.

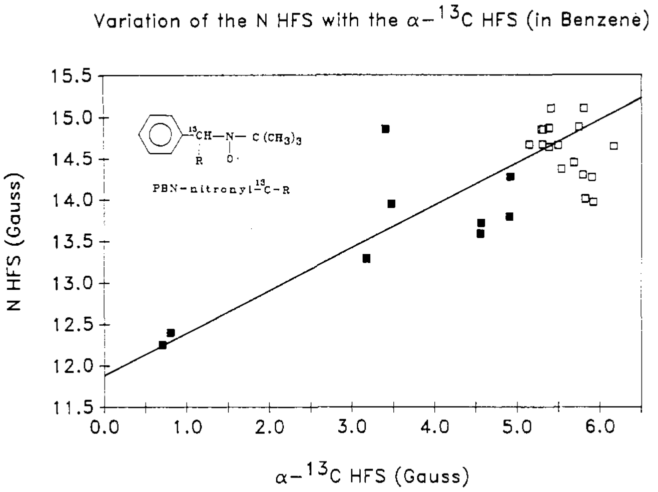

Figure 7. Variation of the N HFS of radical adducts of PBN-*nitronyl*-^{13}C in benzene with the corresponding α-^{13}C HFS. Lightened squares refer to the carbon-like C-, H-, Si-, and P-centered radical adducts whereas the darkened squares correspond to the very polar S, N, O, Cl, F heteroatom (and cyanyl) radical and atom adducts. R value for line = 0.8, slope = +0.41.

tered radical adducts the general trend of decrease in N and α-^{13}C HFS with increase in σ_I also holds for aqueous solutions (Table II), although even more scatter is observed (possibly due to specific H bonding with the radical addend or aminoxyl groups). In an attempt to circumvent these difficulties we decided to test the N or α-^{13}C HFS of radical adducts as possible alternative scales for substituent constants. In contrast to the $\sigma_{\alpha\bullet}$ substituent scale recently devised by the Arnold group,[29] which is based upon spin delocalization effects (in α-substituted benzyl radicals), the generation of a $\sigma_{RA\bullet}$ ("radical adduct") scale would be essentially based on spin polarization effects (in α-substituted aminoxyl radicals).

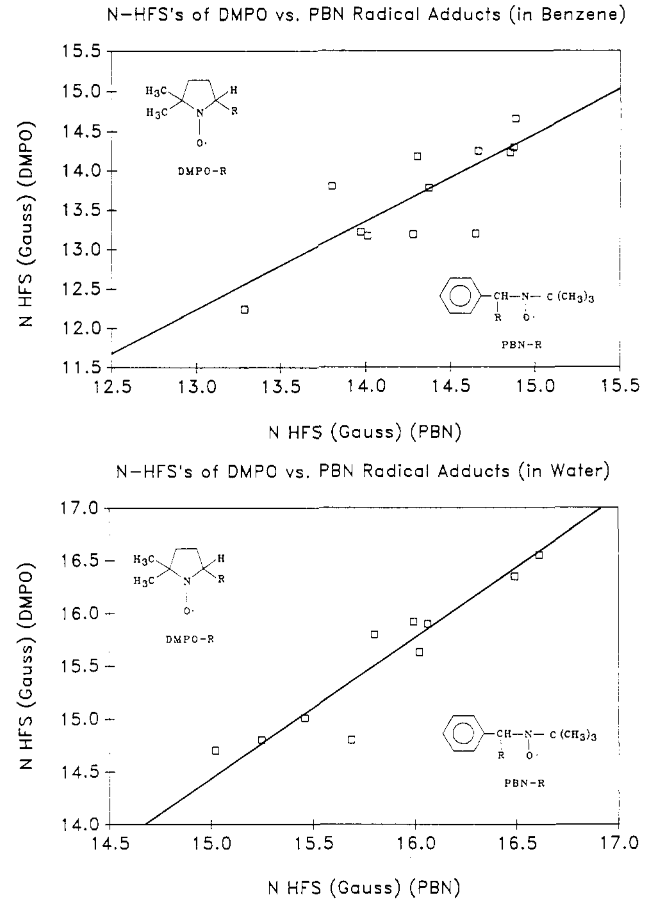

Figure 8. (A, top) Plot of the N HFS of radical adducts of DMPO vs the corresponding N HFS of PBN in benzene. R value for line = 0.8, slope = +1.11. (B, bottom) Plot of the N HFS of radical adducts of DMPO vs the corresponding N HFS of PBN adducts in water. R value for line = 0.94, slope = +1.25.

A plot of the N HFS vs the α-^{13}C HFS (as the substituent constant) of PBN-*nitronyl*-^{13}C radical adducts exhibits some linear character although there is still significant scatter (Figure 7). This result suggested that some of the apparent idiosyncrasies of the aminoxyl–radical added substituent effects might be factored out in plots of aminoxyl EPR parameters against each other for different spin adducts. In Figure 7 one readily observes the superiority of the α-^{13}C HFS (vs the N HFS) for elucidation of the radical center. For all the very polar heteroatom-centered radical adducts (i.e. from S, N, O, Cl, and F radicals and atoms), the α-^{13}C HFS's clearly fall below 5 G whereas for the carbon-type adducts (i.e. from C, H,

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P, and Si radicals) the values are clustered above 5 G. The only anomalous carbon-centered radical adduct is the very polar cyanyl species with its α-^{13}C HFS value of 3.40 G, which is consistent with the pseudohalide nature of this substituent.

It is also possible to plot the N HFS's of α-substituted aminoxyls from various radical adducts for two different spin traps, DMPO and PBN. These plots in benzene and water are shown in Figure 8. Despite the considerable differences in the parent structures of these radical adducts, both the benzene and water plots exhibited significant linear character. These results suggest that the N HFS's of radical adducts of PBN or DMPO may themselves serve as viable substituent scales ($\sigma_{RA\bullet}$) for the determination of the substructures of other α-substituted aminoxyls. Spectral correlations of this type between the radical adducts[24] of PBN and DMPO analogues or *C*-nitroso compounds may also prove to be useful.

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Regioselective and Stereoselective Oxirane Ring-Openings of 2,3-Anhydropentopyranosides with Some Methyl Group Donating Organometallic Reagents

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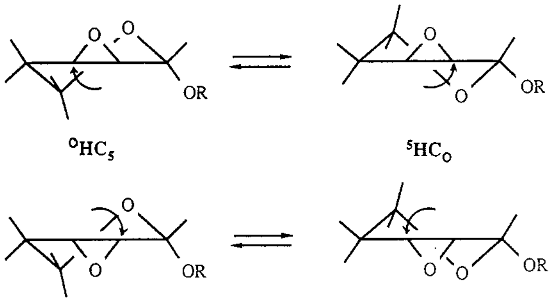
By the proper choice of methyl group transferring organometallic reagents (Me_4AlLi, $Me_4AlLi/MeLi$ (1:1), Me_2CuLi, Me_3Al, Me_2Mg) it is possible to selectively introduce a methyl group into the 2- or 3-position via epoxide ring-opening of four easily available benzyl 2,3-anhydro-4-*O*-(*tert*-butyldimethylsilyl)pentopyranosides (**2**, **6**, **8**, **12**). The resulting 2-deoxy-2-*C*-methyl- and 3-deoxy-3-*C*-methylglycosides (**14**–**21**) were obtained in 84–35% yield and may be useful as chiral starting materials in organic synthesis.

In connection with work on the total synthesis of natural products, we required access to suitably protected 2-deoxy-2-*C*-methylpentopyranosides. As far as we know, no efficient method for the preparation of these potentially valuable chiral synthons[1] has hitherto been described. It has been reported that catalytic hydrogenation of 2-*C*-methylenepentoses gave moderate yields of 2-deoxy-2-*C*-methyl sugars.[2,3] However, the stereoselectivity was low and the diastereomers were not easily separated. A more convenient approach would be to introduce the methyl group via a regio- and stereoselective oxirane ring-opening.

The nucleophilic opening of conformationally rigid 2,3-anhydrohexopyranosides, notably the 4,6-di-*O*-benzylidene and 1,6-anhydro sugars, predominantly yields the trans-diaxial products, in accordance with the Fürst–Plattner rule.[4,5] Among the carbon nucleophiles, organocuprates, dialkylmagnesiums, and functionalized alkynylalanes have proven effective.[6] Organolithiums as well as Grignard reagents, with the exception of allylmagnesium halides,[7] lead to considerable amounts of various reduction and elimination products, as well as to halohydrins.[8]

Scheme I[a]



[a] Curved arrows indicate the preferential site of attack by a nucleophile according to the Fürst–Plattner rule.

Due to the ease of interconversion between the two half-chair forms of 2,3-anhydropentopyranosides (Scheme I), the regiochemistry of their opening is likely to be more sensitive to steric and coordinative properties of the reagent, as compared to the hexoses, and lack of selectivity is often found.[4,9] In the few cases reported of carbon nucleophiles, i.e., with various organolithiums,[10] cyanide,[11]

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