## Synthesis and Electron Spin Resonance Chemistry of Nitronyl Labels for Spin Trapping. α-Phenyl *N*-[5-(5-Methyl-2,2-dialkyl-1,3-dioxanyl)] Nitrones and α-(*N*-Alkylpyridinium) *N*-(*tert*-Butyl) Nitrones

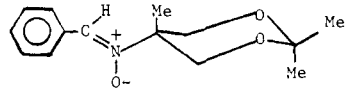
*Sir:*

The nitrone group appears to be a versatile spin trapping function for the study of free-radical reactions under a variety of conditions.[1-3] Typically the spin trap is added to the solution under investigation which is monitored by ESR spectroscopy. However, since the spin trapping technique is essentially a kinetic method, it is quite possible that the direct addition of a spin trap to a complex biphasic system containing regions of different viscosity and polarity may be unsatisfactory. The spin trap concentration may be too low in the immediate vicinity of the radical to be trapped to produce enough of the spin adduct for direct detection by ESR. It thus seems necessary to develop methods for connecting the nitronyl function to molecules of interest which, because of their structure, can introduce the trapping function into the neighborhood of the radical event.

The problem of synthesizing a nitrone with a polar head group and a nonpolar tail has been considered first. Thus a hydrocarbon chain conceivably could be attached either to the nitrogen or to the carbon of the nitronyl function through a connector, -Ⓒ-:

Because the phenyl group attached to the carbon atom of the nitronyl function imparts stability to the parent nitrone and because the tertiary alkyl group attached to the nitrogen atom of the nitroxide lends persistence to the spin adduct, the α-phenyl *N*-(*tert*-butyl) nitrone (PBN)[4] system was used in this study. The use of a 1,3-dioxane ring as a connector on nitrogen or the pyridinium function as a connector on carbon will be described here.

An aldehyde or ketone with the desired hydrocarbon group is converted to the 2-alkyl- or 2,2-dialkyl-5-nitro-1,3-dioxane[5,6] by acid-catalyzed condensation with 2-methyl-2-nitro-1,3-propanediol and the desired phenyl nitrone obtained by condensing benzaldehyde with the hydroxylamine produced from reduction of the nitrodioxane. The following nomencla-

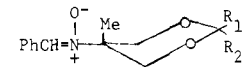


ture is proposed for these nitrones: for example from acetone, α-phenyl *N*-[5-(5-methyl-2,2-dimethyl-1,3-dioxanyl)] nitrone[7] or dimethyl PDN. It is understood that D stands for the 5-(5-methyl-1,3-dioxanyl) group.

The nitronyl dioxanes derived from acetone[8] and propanal[9] have been studied in some detail. The ESR spectra obtained from trapping a number of different radicals are typically triplets of doublets. The values for the hyperfine splitting constants (hfsc's) are quite similar to those obtained for PBN spin adducts (Table I). PDN spin adduct spectra are very persistent—signals are stable for hours and sometimes days.

Of immediate interest is the possibility of radical reactions with the dioxane ring. Of the radicals studied to date, only spectra from *tert*-butoxy radicals indicated reaction with the dioxanyl connector function. If the spectrometer gain is increased so that the normal spectrum obtained from dimethyl PDN is driven off scale a doublet of triplets is detected: $a_N$ = 14.58, $a_\beta^H$ = 16.90 G (in benzene); $a_N$ = 15.15, $a_\beta^H$ = 20.0 G (in $H_2O$). Because the β-H hfsc is relatively large ($a_\beta^H > a_N$), the nitroxide probably has a cyclic structure.[11] If hydrogen

**Table I.** Hyperfine Splitting Constants for PDN Spin Adducts[a]



| radical, source, solvent | $R_1$ = Me, $R_2$ = Me | | $R_1$ = Et, $R_2$ = H | |
|---|---|---|---|---|
| | $a_N$ | $a_\beta^H$ | $a_N$ | $a_\beta^H$ |
| $CH_3$·, $Me_3PbOAc$ ($h\nu$), $C_6H_6$ | 13.28 | 2.87 | 13.35 | 3.16 |
| $CH_3$·, $Me_3PbOAc$ ($h\nu$), $H_2O$ | 15.67 | 3.87 | 15.67 | 3.74 |
| $C_{11}H_{23}$·, lauroyl peroxide, $C_6H_6$ | 13.41 | 2.91 | 13.41 | 3.22 |
| $C_6H_5$·, PAT,[b] $C_6H_6$ | 14.06 | 2.83 | 13.96 | 3.09 |
| $Me_3CO$·, DBPO,[c] $C_6H_6$ | 13.72 | 2.63 | 13.87 | 2.32 |
| $CH_3\dot{C}$=O, MeCHO-DBPO, $C_6H_6$ | 13.35 | 3.03 | 13.35 | 3.25 |
| $CH_3\dot{C}$=O, MeCHO-DBPO, $H_2O$ | 15.35 | 3.74 | 15.22 | 4.52 |
| $Cl_3C$·, $CHCl_3$-DBPO, $CHCl_3$ | 13.67 | 2.52 | 13.61 | 2.52 |
| $CH_3\dot{C}HOH$, EtOH-DBPO, EtOH | 14.71 | 3.61 | 14.71 | 3.74 |
| $\cdot CO_2^-Na^+$, Na formate-DBPO, $H_2O$ (or COOH) | 15.09 | 4.32[d] | 15.09 | 4.32[e] |

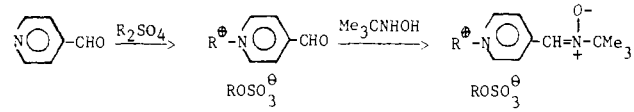
[a] In gauss at room temperature. [b] PAT = phenylazotriphenylmethane. [c] DBPO = di-*tert*-butyl peroxalate. [d] $a_\gamma^H$ = 0.45 (2 H). [e] $a_\gamma^H$ = 0.39 (2 H).

abstraction from the dioxane ring occurs, the most likely cyclic nitroxide would come from intramolecular trapping of the dimethylalkoxy group resulting from β cleavage of the radical produced from methylene hydrogen abstraction. Trapping of the initially formed radical is unlikely because a bicyclic four-membered ring nitroxide would be produced.

Ethyl PDN with *tert*-butoxy radicals in benzene gives a strong signal due to a carbon-centered radical ($a_N$ = 14.52, $a_\beta^H$ = 3.83 G) in addition to the normal *tert*-butoxy adduct: $a_N$ = 13.87, $a_\beta^H$ 2.32 G. To date no spectrum consistent with a large β-hydrogen hfsc has been detected. The second adduct is tentatively assigned to the product of intermolecular spin trapping.

It seems clear that the 2,2-dialkyldioxanes made from ketones are adequately stable to be used as connectors for the attachment of the phenyl nitronyl group to hydrocarbon chains of desired structure and functionality. The 2-alkyldioxanes made from aldehydes, however, cannot be used to search for oxyl radicals since the hydrogen in the 2 position appears to be of comparative reactivity with the nitronyl function.

2-, 3-, and 4-(*N*-methylpyridinium) *tert*-butyl nitrones (2-, 3- and 4-MePyBN's) can be synthesized by condensation of the *N*-alkylpyridinium carboxaldehyde with *tert*-butylhydroxylamine.[12] Aqueous solutions of these nitrones are stable for at least 3 days judging from their $^1H$ NMR spectra. Very



weak ESR spectra are obtained from the initially obtained nitrones when dissolved in water, but such impurities can be removed by recrystallization using mixtures of chloroform and anhydrous ether.

The spin trapping chemistry of hydroxyl radicals is of special interest because 4-pyridyl *N*-oxide *tert*-butyl nitrone (4-POBN) gives a unique ESR spectrum for the hydroxy adduct.[13,14] 3- and 4-MePyBN also gives ESR spectra consisting of triplets of doublets of doublets. The smallest doublet splitting is absent in $D_2O$ and is thus assigned to the hydroxy proton (Table II). The 2 isomer does not give hydroxy hydrogen splitting but the β hydrogen is substantially larger, indicating a sizable change in the time-averaged angle for the group attached to the nitroxyl function.

MePyBN spin adduct spectra appear to be much longer lived than those of PBN or POBN for equivalent radicals trapped. Such behavior is expected if the major decay route

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**Table II.** Hyperfine Splitting Constants for PyBN Spin Adducts[a]

| radical, source, solvent[b] | 2-MePyBN | | | 3-MePyBN | | | 4-MePyBN | | |
|---|---|---|---|---|---|---|---|---|---|
| | $a_N$ | $a_\beta^H$ | $a_\gamma^H$ | $a_N$ | $a_\beta^H$ | $a_\gamma^H$ | $a_N$ | $a_\beta^H$ | $a_\gamma^H$ |
| ·OH, $H_2O_2$ ($h\nu$), $H_2O$ | 14.95 | 3.90 | | 14.80 | 1.42 | 0.32 | 14.70 | 1.45 | 0.38 |
| ·OD, $D_2O_2$ ($h\nu$), $D_2O$ | 14.69 | 4.10 | | 14.78 | 1.38 | | 14.76 | 1.43 | |
| $\cdot SO_4^-$, $Na_2S_2O_8$, $H_2O$ | 13.82 | 3.41 | | 14.02 | 1.22 | 13.96 | 1.21 | | |
| ·H, $Na_2S_2O_8$, $H_2O$[c] | 15.42 | 6.22 (2 H) | | 15.40 | 6.21 (2 H) | | 15.51 | 6.24 (2 H) | |

[a] In gauss at room temperature; all are $MeOSO_3^-$ salts. [b] In pH 6 buffer ($K_2HPO_4$ + NaOH). [c] In pH 3 buffer ($NaHSO_4$ + $Na_2SO_4$) containing formalin or formaldehyde.

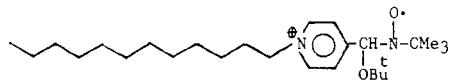
**Table III.** Hyperfine Splitting Constants for Dimethyl 4-MePyDN Spin Adducts[a]

| radical, source, solvent | $a_N$ | $a_\beta^H$ |
|---|---|---|
| $CH_3\cdot$, $Me_3PbOAc$ ($h\nu$), $H_2O$ | 14.84 | 2.39 |
| $CH_3\dot{C}{=}O$, MeCHO-DBPO, $H_2O$ | 14.06 | 2.58 |
| $\cdot CO_2^-$, Na formate-DBPO, $H_2O$ | 14.96 | 2.39 |
| ·OH, 1% $H_2O_2$ ($h\nu$), pH 6 | 14.77 | 2.39 |
| $C_6H_5\cdot$, PAT,[b] $C_6H_6$ | 14.32 | |

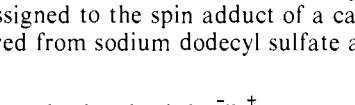
[a] In gauss at room temperature; $MeOSO_3^-$ salt. [b] Phenylazotriphenylmethane.

is disproportionation[15] since the rate constant should be smaller for radical-ion spin adducts with like charges. This feature is highly desirable for trapping low concentrations of radicals as might be produced in biological systems.

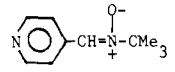
The first ionic nitrone with a long hydrocarbon chain has been synthesized.[16] 4-Lauryl PyBN (4-dodecyl PyBN) is a crystalline compound completely soluble in benzene but almost insoluble in water. The *tert*-butoxy adduct in benzene (from thermal decomposition of di-*tert*-butyl peroxalate, $a_N$ = 14, $a_\beta^H$ = 1.9 G) shows anisotropic broadening particularly in the third branch of the nitrogen triplet. However the first or second



set of doublets is still quite usable for spectrum identification. The spectrum is not unlike that obtained by Bakalik and Thomas[17] assigned to the spin adduct of a carbon-centered radical derived from sodium dodecyl sulfate and *tert*-nitrosobutane.

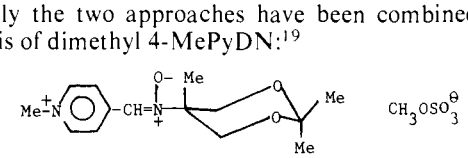


The 4-($\alpha$-pyridyl) *N*-(*tert*-butyl) nitrone has also been synthesized.[18] This spin trap has some desirable characteristics since it appears to be soluble both in polar ($H_2O$) as well as nonpolar (benzene) solvents. It also gives a unique ESR



spectrum for the hydroxy adduct: $a_N$ = 15.07, $a_\beta^H$ = 1.91, $a_\gamma^H$ = 0.23 G.

Finally the two approaches have been combined in the synthesis of dimethyl 4-MePyDN:[19]



Spin adduct spectra from a number of radical sources have been obtained. The parameters follow the same trends as shown by the PDN's (compare Table I with Table II).

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## References and Notes

(1) E. G. Janzen, Y. Y. Wang, and R. V. Shetty, *J. Am. Chem. Soc.*, **100**, 2923 (1978).
(2) P. Schmid and K. U. Ingold, *J. Am. Chem. Soc.*, **100**, 2493 (1978).
(3) For a recent review, see E. G. Janzen, C. A. Evans, and E. R. Davis, *ACS Symp. Ser.*, **No. 69**, 433 (1978).
(4) E. G. Janzen and B. J. Blackburn, *J. Am. Chem. Soc.*, **90**, 5909 (1968); **91**, 4481 (1969). E. G. Janzen, *Acc. Chem. Res.*, **4**, 31 (1971).
(5) The nitrodioxanes derived from acetone, 2- and 3-pentanone, acetaldehyde, propanal, and heptanal have been synthesized and characterized. Mixtures of isomers were obtained in some cases.
(6) Approximately 0.1 M ketone or aldehyde is refluxed in 150 mL of benzene with 0.1 M 2-methyl-2-nitro-1,3-propanediol (Aldrich) in the presence of *p*-toluenesulfonic acid for 8 h using a Dean-Stark trap to remove water. After benzene removal by rotoevaporation, the residue is dissolved in chloroform, washed with saturated $NaHCO_3$ (3 × 50 mL) and water (2 × 50 mL), and dried over $MgSO_4$. The nitrodioxane is obtained by removing chloroform by rotoevaporation. After purification by recrystallization or distillation, the nitrodioxane (0.43 M) is dissolved in 100 mL of THF containing 10 mL of $H_2O$ and 4 g (0.074 M) of $NH_4Cl$. To this mixture is added over a 20-min period 10 g of zinc with vigorous stirring, keeping the temperature below 40 °C. After 3.5 h the reaction mixture is filtered and the zinc salts washed with hot $H_2O$ (5 × 50 mL) and hot THF (4 × 50 mL). After the THF is removed under reduced pressure and filtering, the resulting aqueous solution is extracted with chloroform (6 × 50 mL). The extracts are reduced to 100 mL, treated with 4 mL of benzaldehyde, refluxed for 3 h, and dried over $MgSO_4$. The chloroform and excess benzaldehyde are removed under reduced pressure and the resulting material is recrystallized from ethyl acetate.
(7) This nomenclature follows that used for nitronyl alcohols: E. G. Janzen and R. C. Zawalski, *J. Org. Chem.*, **43**, 1900 (1978).
(8) The nitrodioxane derived from acetone was obtained as crystals after removal of chloroform. After recrystallization from 95% EtOH the following were obtained: yield 74%; mp 83 °C; white needles; $^1H$ NMR (in $CDCl_3$) $\delta$ 1.38 (s, 3 H, $CH_3$), 1.42 (s, 3 H, $CH_3$), 1.47 (s, 3 H, $CH_3$), 4.55 (H-4, H-6 equatorial, $J$ = 13 Hz), 3.80 (H-4, H-6 axial, $J$ = 13 Hz); $^{13}C$ NMR ($CDCl_3$) 20.31 (2-$^{13}C$, $CH_3$), 26.25 (1-$^{13}C$, $CH_3$), 65.08 (2-$^{13}C$, ring carbons), 82.96, 98.78 (1-$^{13}C$, quaternary C's); IR (KBr) 3050, 2950 (C-H), 1556 ($NO_2$), 1090 $cm^{-1}$ (COCOC). Calcd: C, 48.0; H, 7.42; N, 8.0. Found: C, 47.97; H, 7.39; N, 7.83. The nitrone (dimethyl PDN) was obtained in 40% yield, mp 76 °C, as white crystals: $^1H$ NMR ($CDCl_3$) $\delta$ 1.41 (s, 3 H, $CH_3$), 1.43 (s, 3 H, $CH_3$), 1.50 (s, 3 H, $CH_3$), 4.17 (AB q, $J_{AB}$ = 13 Hz), 7.81 (1 H, "vinyl"), 7.8 (m, 5 H, aromatic); $^{13}C$ NMR ($CDCl_3$) 20.04 (2-$^{13}C$, $CH_3$), 27.14 (1-$^{13}C$, $CH_3$), 65.79 (2-$^{13}C$, ring carbons), 68.22, 98.78 (1-$^{13}C$, quaternary C's), 128.35, 129.43, 130.15, 130.66, 133.37, 135.00 (aromatic ring carbons), 171.05 (1-$^{13}C$, "vinyl" carbon).
(9) The nitrodioxane derived from propanal was obtained as a brown oil. Two products were obtained after distillation under reduced pressure; total yield was 59%. Fraction 1: bp 33 °C (0.2 Torr); $^1H$ NMR ($CDCl_3$) $\delta$ 0.93 (t, 3 H, $CH_3$), 1.55 (m, 2 H, $CH_2$ in ethyl group), 1.78 (s, 3 H, $CH_3$), 4.0 (m, 4 H, $CH_2$ in ring), 4.34 (t, 1 H, CH); $^{13}C$ NMR ($CDCl_3$) 7.91 (1-$^{13}C$, $CH_3$), 19.23 (1-$^{13}C$, $CH_3$), 27.51 (1-$^{13}C$, $CH_2$ in ethyl group), 71.19 (2-$^{13}C$, $CH_2$ in ring), 83.50 (1-$^{13}C$ quaternary C), 103.28 (1-$^{13}C$ tertiary C); IR (film) 1550 ($NO_2$), 1350 (CH), 1125, 1180 $cm^{-1}$ (COCOC). C, H, N analysis was unsatisfactory. Fraction 2: bp 68 °C (0.05 Torr); $^1H$ NMR ($CDCl_3$) $\delta$ 0.88 (t, 3 H, $CH_3$), 1.32 (s, 3 H, $CH_3$), 1.58 (m, 2 H, $CH_2$ in ethyl group), 4.40 (t, 1 H, CH), 4.25 (AB q, $J_{AB}$ = 11 Hz);[10] $^{13}C$ NMR ($CDCl_3$) 8.09 (1-$^{13}C$, $CH_3$), 19.15 (1-$^{13}C$, $CH_3$), 27.59 (1-$^{13}C$, $CH_2$ in ethyl group), 71.36 (2-$^{13}C$, $CH_2$ in ring), 83.50 (1-$^{13}C$ quaternary C), 103.45 (1-$^{13}C$ tertiary C); IR essentially the same as in fraction 1. Calcd: C, 48; H, 7.42; N, 8.0. Found: C, 48.2; H, 7.24; N, 8.08. Fraction 2 was used to synthesize the nitrone (ethyl PDN): 21.4% yield; mp 87 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 0.92 (t, 3 H, $CH_3$), 1.35 (s, 3 H, $CH_3$), 1.67 (m, $CH_2$ in ethyl group), 4.17 (AB q, $J_{AB}$ = 13 Hz), 4.52 (t, 1 H, CH), 7.95 (s, 1 H, "vinyl"), 7.90 (m, 5 H, aromatic).
(10) Fraction 2 is assigned to the isomer with ethyl equatorial, nitro axial; see E. L. Eliel and R. M. Enanoza, *J. Am. Chem. Soc.*, **94**, 8075 (1972).
(11) E. G. Janzen and J. I.-P. Liu, *J. Magn. Reson.*, **9**, 510 (1973).
(12) 2-Methylpyridinium *tert*-butyl nitrone methyl sulfate: mp 127–128 °C from absolute EtOH–anhydrous ether; $^1H$ NMR ($CDCl_3$) $\delta$ 1.62 (s, 9 H, *tert*-butyl), 3.50, 4.41 (s, 3 H, $CH_3$'s), 7.65–8.00 (m, 1 H, aromatic), 8.14–8.52 (m, 1 H, aromatic), 8.29 (s, 1 H, vinyl), 8.90–9.21 (m, 2 H, aromatic). Calcd: C, 47.36; H, 6.62; N, 9.20. Found: C, 47.42; H, 6.30; N, 8.94. 3-Methylpyridinium *tert*-butyl nitrone methyl sulfate: mp 79–81 °C from $CHCl_3$–anhydrous ether; $^1H$ NMR ($CDCl_3$) $\delta$ 1.60 (s, 9 H, *tert*-butyl), 3.64, 4.58 (s, 3 H, $CH_3$'s), 7.92–8.25 (m, 1 H, aromatic), 8.40 (s, 1 H, "vinyl"), 9.08, 9.54 (d, 1 H each, aromatic), 10.10 (s, 1 H, aromatic). Analytical sample could not be obtained. 4-Methylpyridinium *tert*-butyl nitrone methyl sulfate: mp 127–128 °C from $CHCl_3$–anhydrous ether; $^1H$ NMR ($CDCl_3$) $\delta$ 1.60 (s, 9 H, *tert*-butyl), 3.65, 4.50 (s, 3 H, $CH_3$'s), 8.36 (s, 1 H, "vinyl"), 8.74–9.06 (m, 4 H, aromatic). Calcd: C, 47.36; H, 6.62; N, 9.20. Found: C, 47.25; H, 6.12; N, 9.22.

(13) E. G. Janzen, Y. Y. Wang, and R. V. Shetty, unpublished work.
(14) E. G. Janzen, D. E. Nutter, Jr., E. R. Davis, B. J. Blackburn, J. L. Poyer, and P. B. McCay, *Can. J. Chem.*, **56**, 2237 (1978).
(15) For discussion and recent references, see last paragraph of P. Schmid and K. U. Ingold, *J. Am. Chem. Soc.*, **100**, 2493 (1978).
(16) 4-Dodecylpyridinium *tert*-butyl nitrone dodecyl sulfate: mp 51–53 °C from benzene–petroleum ether; $^1$H NMR ($CDCl_3$) $\delta$ 0.90 (t, 6 H, $CH_3$'s), 1.23 (s, 40 H, $(CH_2)_{10}$'s), 1.61 (s, 9 H, *tert*-butyl), 4.00 (t, 2 H, $CH_2$), 4.73 (t, 2 H, $CH_2$), 8.43 (s, 1 H, "vinyl"), 8.80–9.00 (m, 4 H, aromatic). Calcd: C, 66.62; H, 10.52; N, 4.57. Found: C, 65.84; H, 10.23; N, 4.48.
(17) D. P. Bakalik and J. K. Thomas, *J. Phys. Chem.*, **81**, 1905 (1977).
(18) 4-Pyridyl *tert*-butyl nitrone: mp 99–101 °C from cyclohexane–petroleum ether; $^1$H NMR ($CDCl_3$) $\delta$ 1.58 (s, 9 H, *tert*-butyl), 7.70 (s, 1 H, "vinyl"), 8.10–8.30 (m, 2 H, aromatic), 8.73–8.90 (m, 2 H, aromatic). Calcd: C, 67.39; H, 7.92; N, 15.72. Found: C, 67.66; H, 7.38; N, 15.65.
(19) Dimethyl 4-methylpyridinium *tert*-butyl nitrone methyl sulfate: mp 150–151 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.46, 1.56, 1.60, 3.71, 4.51 (s, 3 H, $CH_3$'s), 4.23 (AB q, $CH_2$ in ring, $J_{AB}$ = 13 Hz), 8.41 (s, 1 H, "vinyl"), 8.83 (m, 4 H, aromatic); $^{13}$C NMR ($D_2O$) 20.67 (2-$^{13}$C, $CH_3$), 29.84 (1-$^{13}$C, $CH_3$), 50.42 (1-$^{13}$C, $CH_3$), 57.79 (1-$^{13}$C, $CH_3$), 67.05 (2-$^{13}$C, $CH_2$ in ring), 74.69, 102.47 ($^{13}$C, quaternary in dioxane ring), 128.53 (2-$^{13}$C, pyridine ring), 135.81 (1-$^{13}$C, "vinyl"), 146.06 (1-$^{13}$C, quaternary in pyridine ring), 147.86 (2-$^{13}$C, pyridine ring). Calcd: C, 47.8; H, 6.4; N, 7.4. Found: C, 46.6; H, 6.1; N, 7.2.

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## Gas-Phase Organometallic Chemistry. Mechanism and Energetics of Methane Formation Resulting from Protonation of $(CO)_5MnCH_3$

*Sir:*

Treatment of transition metal alkyl or hydrido complexes with acids in solution often leads to the evolution of alkanes or hydrogen.[1-3] Pentacarbonylmethylmanganese is one compound which shows this reactivity; it decomposes rapidly in acidic media with methane evolution.[1,2] Johnson and Pearson[2] suggest a reaction mechanism involving oxidative addition of the undissociated acid followed by reductive elimination of methane. In many such studies the mechanism of reductive elimination of alkanes remains controversial; in addition there is little quantitative data appropriate for describing the thermochemistry of these processes. This is due in part to the difficulties in characterizing reactive intermediates in solution. Many of the factors contributing to this situation can be eliminated by carrying out related studies in the gas phase, using the techniques of ion cyclotron resonance spectroscopy.[4] A recent gas phase study of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2)^+$, a carbene whose presence could only be inferred in solution, is a case in point.[5] We report here the gas phase reactions of $(CO)_5MnCH_3$ with proton donors, which provide interesting insights into both the mechanism and energetics of methane formation in this system.

Reaction of a variety of proton donors $BH^+$ with $(CO)_5MnCH_3$[6] yields two products, as indicated by eq 1 and 2.[7] At

$$(CO)_5MnCH_3 + BH^+ \begin{cases} \longrightarrow (CO)_5Mn^+ + CH_4 + B & (1) \\ \longrightarrow (CO)_5Mn(CH_3)H^+ + B & (2) \end{cases}$$

first glance the product of reaction 1 appears to involve loss of $CH_4$ from the conjugate acid formed in reaction 2. The usual situation in proton transfer reactions, generalized in eq 3, is for proton transfer from $B_1$ to $B_2$ to occur when $PA(B_2) \geq PA(B_1)$, where PA(B) is the proton affinity of B.[4] When the reaction is sufficiently exothermic, excess energy retained by $B_2H^+$ results in its decomposition. With this expected behavior, the present results are particularly surprising in that *the conjugate acid $(CO)_5Mn(CH_3)H^+$ is observed only with bases whose proton affinity is substantially below those which yield the product $(CO)_5Mn^+$ as an abundant ion.*

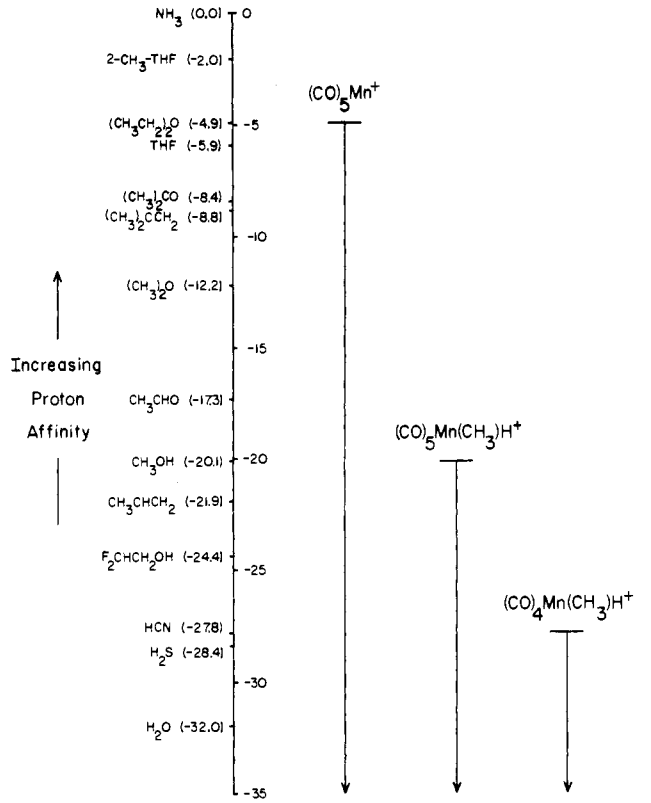


**Figure 1.** Range of proton donors for which the products $(CO)_5Mn^+$ (reaction 1), $(CO)_5Mn(CH_3)H^+$ (reaction 2), and $(CO)_4Mn(CH_3)H^+$ (reaction 4) are observed. The proton affinity (kilocalories/mole) of each base examined, $PA(B) - PA(NH_3)$, is given in parentheses.[8]

$$B_1H^+ + B_2 \rightleftharpoons B_2H^+ + B_1 \qquad (3)$$

The important features of the observed reactions, as illustrated in Figure 1, are as follows. Methane elimination takes place with proton donors for which $PA(B) \leq 203 \pm 3$ kcal/mol.[8] If it is assumed that, for $PA(B) > 203 \pm 3$ kcal/mol, reaction 1 is not observed because it is endothermic, the heat of formation of $(CO)_5Mn^+$ is calculated to be $8 \pm 4$ kcal/mol.[9,10] Onset of reaction 2 establishes a proton affinity of $(CO)_5MnCH_3$ as $188 \pm 3$ kcal/mol.[8] The homolytic metal hydride bond dissociation energy, $D[(CO)_5MnCH_3^+ - H]$, is calculated from this to be $67 \pm 3$ kcal/mol.[11] If the proton transfer reaction is sufficiently exothermic, internal excitation of the product of reaction 2 may be sufficient for dissociation to occur (eq 4), in which CO is lost in preference to $CH_4$.[12] Decomposition according to reaction 4 is observed with donors less basic than HCN. This result indicates $D[(CO)_4Mn(CH_3)(H)^+ - CO] \sim 7 \pm 2$ kcal/mol.[8]

$$[(CO)_5Mn(CH_3)H^+]^* \rightarrow (CO)_4Mn(CH_3)H^+ + CO \qquad (4)$$

These data are consistent with two available reactive sites on $(CO)_5MnCH_3$; reactions 1 and 2 are *not* competitive in the sense of having common or readily interconverted intermediates. We propose that protonation of the manganese-methyl bond leads to formation of methane with little or no activation barrier. Protonation at a second site, accessible with stronger proton donors, forms a kinetically stable protonated complex.[13] Solution data on protonation of similar species[1-3] lead us to believe the $(CO)_5Mn(CH_3)H^+$ ion is a hydridomethyl species with the proton on the metal center.[14] The manganese-hydride bond dissociation energy of $67 \pm 3$ kcal/mol is comparable with those of other first-row transition metal hydrides.[15-17] The elimination of methane from $[(CO)_5Mn(CH_3)H^+]$ is not competitive with loss of CO. The above data indicate an activation energy for reductive elimination in excess of $7 \pm 2$

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