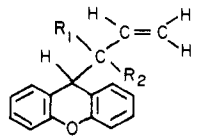
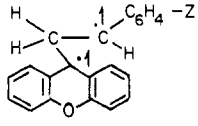


13; $R_1 = C_6H_5$, $R_2 = CH_3$

15; R_1 and $R_2 = CH_3$

methyl-1-butene at −5 °C gives 9-(1,1-dimethyl-2-propenyl)xanthene (**15**, 40%) and spiro[2-(2-propyl)cyclopropane-1,9′-xanthene] (**16**, 19%) along with **10** (4%). Thus reactions of photolytically generated **2** with the above olefins reveal that (1) insertion occurs on allylic C—H to give products without double-bond rearrangement and (2) C=C bonds undergo competitive addition to yield cyclopropanes. Insertion of **2** into allylic C—H bonds is thus highly specific and suggestive of a traditional singlet (**3**) process. If indeed allylic C—H insertion occurs via **3**, H abstraction, spin inversion, and recombination must be intimate (highly caged), possibly because of polar effects in dissimilar radical pairs, to occur without migration of C=C bonds. Formation of **10** from **2** and 3-methyl-1-butene indicates that 9-xanthyl radicals are formed at least in part in this system.

The stereochemistry and the relative reactivities of **2** with styrene derivatives have been studied under photochemical conditions in which thermal reactions of **1** and alteration of the initial olefins and the cyclopropanes formed are insignificant. Photolysis of sodium 9-xanthone tosylhydrazonate[6] at ~−25 °C converts *cis*-propenylbenzene stereoselectively (0.5–2 h) to **6** (75–80%) and **7** (20–25%), whereas *trans*-propenylbenzene yields **7** (100%) stereospecifically. The competitive reactivities of styrenes (H_2C=CHC_6H_4Z) with **2** as derived from irradiation of sodium 9-xanthone tosylhydrazonate at ~−25 °C follow: Z = 4-H, 0.64; 4-CH_3, 0.85; 4-Cl, 0.97; 4-OCH_3, 1.00; 4-Br, 1.68; and 3-Br, 2.23.[3,7] The relative reactivities do not give a linear free-energy correlation with σ or σ^+ values and reveal that **2** (and/or its excited precursors) does not behave as a dominent nucleophile or electrophile. The stereochemical results and the substituent kinetic effects are consistent, however, with addition of **4** to styrenes as in **17**. This



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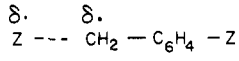

18

interpretation is also compatible with observations that both electronegative and electropositive substituents stabilize free-radical transition states of the benzyl type (**18**) in which polar effects are unimportant.[8] The stereochemical and reactivity data do not rule out, however, the possibility that additions to styrenes upon photolysis of **1** occur in part with **2** and/or excited **1**.

It is now clear that **1** and **2** do not exhibit the limited reactivities recently attributed them.[1] The present results thus allow **1** and **2** to take more usual positions among the legions of diazo compounds and carbenes that have been reported. We wish also to note that 14*H*-dibenzo[*a*,*j*]xanthylidene is an energetic carbene which behaves as a triplet in various environments and reacts with cumene to give 14-(1-methyl-1-phenylethyl)-14*H*-xanthene.[9] Xanthylidenes will have to be further modified to be isolable as stable carbenes.

Acknowledgment. We acknowledge support of this research by the National Cancer Institute (5-R01-CA11185) and the National Science Foundation (GP-22545).

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(2) 2-Methylpentane,[1b] hexane,[1b] cyclohexane,[1b] ethylene,[1a] 2-methyl-2-butene,[1d] 2,3-dimethyl-2-butene,[1d] 3,3-dimethyl-1-butene,[1a] and 2,3,3-trimethyl-1-butene[1a] are reported to be inert to **1** upon photolysis. The principal product reported from these experiments is conversion of **1** to 9-xanthone azine.
(3) (a) All new compounds presently reported are of proper analysis and mass, IR, and ^1H NMR spectra, respectively. (b) The relative reactivities were determined by reaction with various styrene pairs in which each styrene was in 10-equiv excess; the cyclopropanes formed were isolated quantitatively by column chromatography.
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Spin Trapping with α-Pyridyl 1-Oxide *N*-*tert*-Butyl Nitrones in Aqueous Solutions. A Unique Electron Spin Resonance Spectrum for the Hydroxyl Radical Adduct

Sir:

Much interest surrounds the possible intermediacy of hydroxyl radicals in reactions of chemical[1,2] and biological[3,4] interest. However direct methods for detecting hydroxyl radicals in solution are not satisfactory.[5] The method of spin trapping[6] using nitrone spin traps would seem to be a suitable indirect method for detecting hydroxyl radicals. However, early attempts in our laboratory to verify the assignments of the ESR spectra thought to be due to the hydroxy spin adducts of PBN (α-phenyl *N*-*tert*-butyl nitrone) and DMPO (5,5-dimethylpyrroline *N*-oxide) were unsuccessful.[7] These spectra were later published by Harbour, Chow, and Bolton.[8] In connection with a study of the spin trapping chemistry of water-soluble spin traps the pyridine *N*-oxide analogues of PBN have been synthesized.[9] We wish to report that these nitrones readily trap hydroxyl radicals and that the ESR spectrum obtained from the 4 isomer can be unequivocally assigned to the hydroxyl adduct. Available results indicate that this spin trap is unique in its suitability for the detection of hydroxyl radicals in solution at pH 6 and 7.

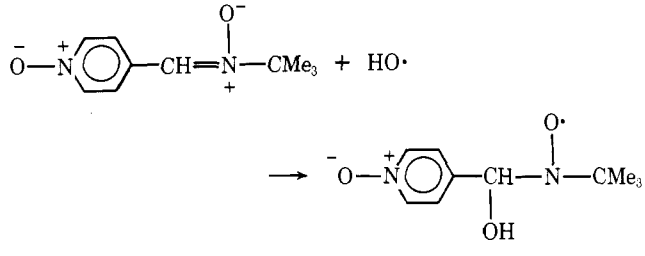

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Table I. Hyperfine Splitting Constants[a] of the Hydroxy Adduct of 4-POBN Produced from Various Sources[b]

		Hydroxy adduct			Second adduct	
pH	Buffer,[c] source	a_N	a_β^H	a_γ^H	a_N	a_β^H
	1% $H_2O_2 + h\nu$					
2	KCl + HCl	14.95	1.68	0.33	15.58	2.62
3	KHP + HCl	14.95	1.67	0.35	15.58	2.60
4	KHP + HCl	14.95	1.67	0.34	15.61	2.63
5	KHP + NaOH	15.00	1.68	0.34	15.59	2.62
6	K_2HPO_4 + NaOH	14.97	1.68	0.36	15.58	2.62
7	K_2HPO_4 + NaOH	15.00	1.70	0.34	*d*	*d*
8	K_2HPO_4 + NaOH	14.96	1.69	0.34	15.66	2.75
9	$Na_2B_4O_7$ + NaOH	14.96	1.70	0.33	15.65	2.69
10	$NaHCO_3$ + NaOH			*e*	*e*	*e*
	Average values[f]	14.97 ± 0.02	1.68 ± 0.01	0.34 ± 0.01		
2	2% $H_2O_2 + h\nu$	14.97	1.67	0.33		
g	30% $H_2O_2 + h\nu$	14.99	1.73	0.33		
2-6	0.05 M $Na_2S_2O_8$	14.97	1.68	0.36	14.16	1.56
7, 8	0.05 M $Na_2S_2O_8$			*h*	14.96	1.41
g	$FeCl_3$, ADP, H_2O_2	14.96	1.68	0.36		

[a] In gauss. [b] At room temperature. [c] Commercially available buffer solutions (Fisher); KHP = potassium acid phthalate; buffers at pH 2-6 contain formalin as inhibitor. [d] The appropriate peaks were too seriously overlapped to measure this value. [e] See text. [f] The deviations are the average of the deviations from the average value. [g] No buffer solution; 0.0001 M ADP, 4×10^{-7} M $FeCl_3$, 0.15 M POBN plus 1 drop of 30% H_2O_2 solution. [h] No hydroxy adduct.

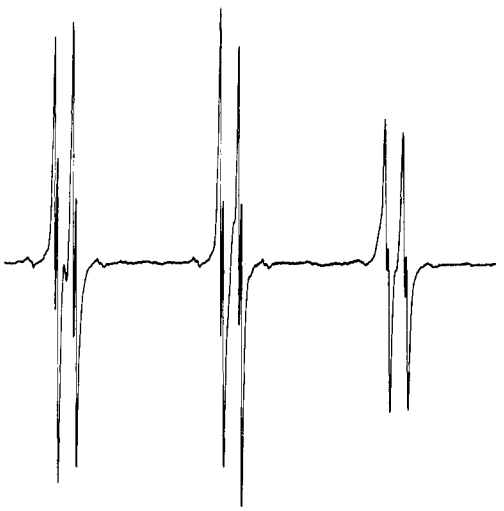


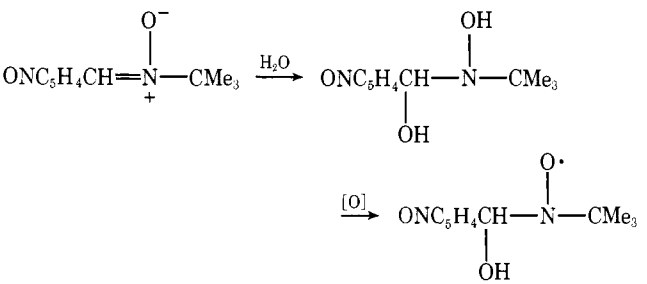
Figure 1. ESR spectrum of hydroxy adduct of 4-POBN in water at room temperature.

When an aqueous 1% H_2O_2 solution containing 0.05 M α-4-pyridyl 1-oxide *N-tert*-butyl nitrone (4-POBN) is irradiated with UV light in the cavity of an ESR spectrometer at room temperature, the spectrum shown in Figure 1 is obtained. The spectrum clearly shows hyperfine splitting from one nitroxide nitrogen, one β-type hydrogen and one γ-type hydrogen: a_N = 14.96, a_β^H = 1.68, a_γ^H = 0.34 G. The γ-hydrogen splitting is absent in D_2O which establishes that this γ hydrogen is attached to oxygen.[10] The line widths are unusually small for the hydroxy adduct spectrum (0.22 G). As a result a very low modulation amplitude setting must be used to resolve the γ-hydrogen doublet (0.08 G). The sharp line widths permit easy detection of the C-13 satellites ($a_{C\text{-}13}$ = 4.62 G).

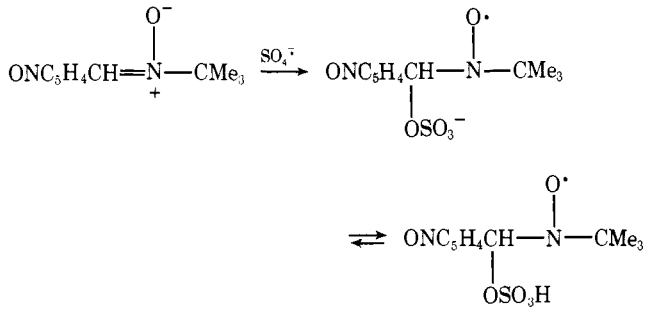
In Table I the hyperfine splitting constants (hfsc's) of the hydroxy adduct as a function of pH and H_2O_2 concentration are shown. The parameters are quite insensitive to pH within the pH range studied (pH 2-9). At pH 10 a weak broad spectrum is obtained which may contain lines due to the hydroxy adduct but the appropriate peaks are not detectable in the presence of a second spin adduct.

A second set of doublets is always seen to a greater or lesser extent depending on the pH of the solution, the nature of the buffer, and the total time of photolysis. The hfsc's for this nitroxide are also given in Table I. The second nitroxide probably has the same structure in all experiments at pH 2-10 and is thought to be the hydroperoxy adduct. We have no other support for this assignment at this time.

Although the structural assignment of the spectrum in Figure 1 has strong support, it is not necessary that the hydroxy adduct arises from trapping hydroxyl radicals. In water oxidation of the hydrolysis addition product could give the same nitroxide. This possibility was investigated by monitoring the UV absorption of the nitrone at 315 and 325 nm as a function of time at different pH's. A 0.0005 M 4-POBN solution at pH 6 or 7 showed no change in absorption for 32 h. However, at pH 2 the decay was rapid (half-life 13.8 min) and the ESR spectrum of the hydroxy adduct (and the hydroxy adduct alone) appeared spontaneously in the presence of H_2O_2 without photolysis. It thus appears that 4-POBN is stable enough for spin trapping at pH values of ~7, but more acidic solutions probably cannot be used (at least for the detection of hydroxyl radicals). A complete study of this problem as it applies to PBN, DMPO, and 4-POBN is underway.



The hydroxy adduct is also detected from sodium persulfate at pH 2-6 (see Table I). In the more acidic solutions persulfate probably oxidizes the hydrolysis addition product. At pH 6 sulfate radicals may be producing hydroxyl radicals but other mechanisms are also possible.[11] At pH 3-6 another adduct is detected: a_N = 14.16, a_β^H = 1.56 G. At pH 7 or 8 no hydroxy adduct is detected. Instead a triplet of doublets with a_N = 14.96, a_β^H = 1.41 G is seen. The two new nitroxides are believed to be the sulfate adducts, protonated at pH 3-6 and unprotonated at pH 7 and 8.[12]



Preliminary results with chelated Fe^{III} and H_2O_2 indicate the formation of hydroxyl radicals (see Table I).

Similar experiments were performed with 0.05 M 2- and 3-POBN and 0.05 M sodium persulfate for comparison with 4-POBN. The hydroxy adduct of 3-POBN gives a spectrum wherein the hfsc from the hydroxy proton is barely resolved: $a_N = 14.94$, $a_\beta^H = 1.60$, $a_\gamma^H = 0.26$ G at 0.08 G modulation amplitude (0.26-G line width). The spectrum obtained from 2-POBN consists only of a triplet of doublets: $a_N = 15.39$, $a_\beta^H = 2.25$ G (0.77-G line width). As such it cannot be assigned to the hydroxy spin adduct at this time.

Acknowledgment. This work was supported by the National Research Council of Canada. Grateful acknowledgment is hereby made.

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(10) Protons attached to oxygen or nitrogen but not to carbon are rapidly exchanged in D_2O in nitroxide spin adducts.
(11) Electron transfer to produce 4-$POBN^{+\cdot}$ could give the hydroxy adduct by reaction with water. The same could come from hydrolysis of the sulfate adduct.
(12) The fact that the hfsc's are substantially different in these two pH ranges suggests that the protonated adduct may be intramolecularly hydrogen bonded. One type of spin adduct which is intramolecularly hydrogen bonded has been previously detected (E. G. Janzen and I. G. Lopp, *J. Magn. Reson.*, **7**, 107 (1972)).

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Active Homogeneous Catalysts for the Water Gas Shift Reaction Derived from the Simple Mononuclear Carbonyls of Iron, Chromium, Molybdenum, and Tungsten

Sir:

A reaction of carbon monoxide of obvious importance in the use of coal as a clean energy source is the so-called water gas shift reaction

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad (1)$$

Recent papers have reported systems for the homogeneous catalysis of this reaction based on ruthenium[1] and rhodium[2] carbonyl derivatives. This paper describes the homogeneous catalysis of the water gas shift reaction using basic solutions of the mononuclear metal carbonyls $Fe(CO)_5$ and $M(CO)_6$(M = Cr, Mo, and W).

Some typical experiments using metal carbonyls as catalyst precursors for the water gas shift reaction are summarized in Table I. The indicated quantities of the metal carbonyl and base were added to the indicated solvent in a 700-mL stainless steel reaction vessel. After closing the reaction vessel, CO was added to the specified pressure. The reaction vessel was heated and held at the indicated constant temperature for one or more days. Gas samples were periodically withdrawn and analyzed by vapor phase chromatography on a 1/4 in. × 6 ft 5A molecular sieve column calibrated with known H_2/CO mixtures. To check for internal consistency occasional samples were analyzed for CO_2 on a silica column.

The results summarized in Table I indicate that a variety of mononuclear metal carbonyls in basic solutions have considerable activity for the catalysis of the water gas shift reaction. In these reactions the presence of the base appears to be essential since runs in the absence of added base produce little or no hydrogen (runs 5 and 14). The combination of $Mo(CO)_6$ with KBH_4 in methanol (run 13) shows comparable catalytic activity to $Mo(CO)_6$ with KOH in the same solvent (runs 7–9) but at much lower base/metal ratios.

In some cases with $Mo(CO)_6$, the reaction vessel contained dark solids suspended in a yellowish liquid at the end of the reaction. To exclude the possibility of this catalysis being heterogeneous, i.e., arising from these precipitated solids rather than the homogeneous supernatant liquid, the individual catalytic activities of both the precipitated solid and the supernatant solution remaining in the reaction vessel after conclusion of a reaction were checked. The precipitated solids were filtered off and added to a fresh solution of methanol and aqueous base (run 9a). The catalytic activity of the resulting suspension was relatively small. In contrast the supernatant solution when repressurized with CO exhibited essentially the same catalytic activity as before (run 7a). Thus the catalytically active species appears to be in the supernatant solution rather than in the precipitated solids indicating a homogeneous rather than heterogeneous mode of catalysis for this reaction.

Identification of the various metal carbonyl species present in the reaction solutions under catalytic conditions was attempted by recording their infrared spectra using a stainless steel high pressure infrared cell with Irtran I windows.[3,4] For example, $Fe(CO)_5$ (0.10 mL, 0.15 g, 0.76 mmol; measured ν(CO) in 1:20 water–1-butanol: 2020 (sh), 1996 (vs) cm^{-1}) was dissolved in a nitrogen-saturated solution of 0.12 g (3 mmol) of sodium hydroxide in 1.4 mL of water and 48 mL of 1-butanol. The infrared spectrum of the solution exhibited bands at 1915 (s, sh), 1885 (vs), and 1865 (sh) cm^{-1} indicating the expected[5,6] conversion of $Fe(CO)_5$ to $HFe(CO)_4^-$ by the base (reported[7] ν(CO) of $HFe(CO)_4^-$ in dimethylformamide: 2008 (w), 1914 (m), 1880 (s) cm^{-1}). This solution of $HFe(CO)_4^-$ was then pressurized with 330 atm of CO in the

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