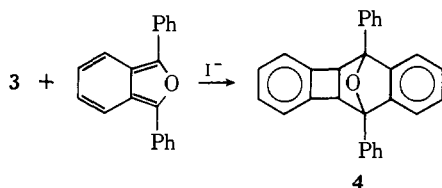


able exotherm at room temperature. Decomposition in solution ( $\text{MeNO}_2$ ,  $\text{Me}_2\text{CO}$ ,  $\text{PhNO}_2$ ,  $\text{SO}_2$ , THF) is very rapid as evidenced by bubbling and darkening of the mixture. Unfortunately, due to its instability or insolubility in appropriate solvents, we have not been able to recrystallize **3** to remove paramagnetic impurities which have thus far thwarted our efforts to obtain an nmr spectrum of **3**. The carbonyl stretching frequencies of **3** (2070 and  $2035\text{ cm}^{-1}$ ) are typical of cationic olefin complexes of  $\eta^5$ -cyclopentadienyldicarbonyliron. The overall infrared spectrum of **3** is very similar to that of the related styrene complex,  $(\text{PhCH}=\text{CH}_2)\text{Fp}^+\text{PF}_6^-$ .

The identity of **3** was established by the characterization of a series of trans 1,2-disubstituted benzocyclobutenyl complexes formed by the addition of a variety of nucleophiles to **3**.<sup>5,6</sup> Thus, **3** is reduced to the known benzocyclobutenyl complex (**1a**) by lithium borohydride in tetrahydrofuran in 20% yield.<sup>3</sup> Treatment of **3** with a mixture of methanol and sodium bicarbonate gives an 83% yield of the trans methoxy adduct (**1c**): ir (KBr) 1995,  $1940\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ), nmr ( $\text{CS}_2$ )  $\tau$  6.61 (s, 3,  $\text{CH}_3$ ), 6.00 (d, 1,  $J_{1,2} = 1.5\text{ Hz}$ ,  $\text{H}^1$ ), 5.59 (d, 1,  $\text{H}^2$ ), 5.23 (s, 5, Cp), 2.96 (m, 4, Ar). Although **3** is initially sparingly soluble in methylene chloride, it rapidly dissolves in the presence of triphenylphosphine to form, in 82% yield, the trans phosphonium salt (**1d**): ir (hexachlorobutadiene) 2000,  $1937\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ), nmr ( $\text{CD}_3\text{NO}_2$ )  $\tau$  5.51 (m, 1,  $J_{1,2} = 1\text{ Hz}$ ,  $J_{\text{P,H}^1} = 12\text{ Hz}$ ,  $\text{H}^1$ ), 5.03 (m, 1,  $J_{\text{P,H}^2} = 5\text{ Hz}$ ,  $\text{H}^2$ ), 4.95 (s, 5, Cp), 2.74 (m, 19, Ar). Analogously, **3** is readily alkylated by a cold methylene chloride solution of  $\eta^1$ -3-propenyl- $\eta^5$ -cyclopentadienyldicarbonyliron to yield 63% of the cationic binuclear complex (**1e**). The neutral trans alkylated complex **1f** is generated in 30% yield by subsequent treatment of **1e** with sodium iodide in acetone: (**1f**) ir (neat) 1995,  $1930\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ), nmr ( $\text{CS}_2$ )  $\tau$  7.60 (m, 2,  $\text{CH}_2$ -), 6.91 (m, 1,  $J_{1,2} = 1.8\text{ Hz}$ ,  $\text{H}^2$ ), 6.29 (d, 1,  $\text{H}^1$ ), 5.33 (s, 5, Cp), 5.00 (m, 2,  $=\text{CH}_2$ ), 4.07 (m, 1,  $-\text{CH}=\text{}$ ), 3.02 (m, 4, Ar). Treatment of **3** with a methylene chloride solution of tetra-*n*-butylammonium iodide in the presence of 1,3-diphenylisobenzofuran gives the known Diels-Alder adduct (**4**)<sup>7</sup> of benzocyclobutadiene in 25% yield and thereby demonstrates the lability of the cyclobutadienoid ligand. At present, we have no evidence to suggest that **3** decomposes by rearrangement to **2**.



All of the aforementioned reactions are typical of cationic olefin complexes of  $\eta^5$ -cyclopentadienyldicarbonyliron<sup>8-11</sup> and thus strongly support structure **3a**

(5) Trans 1,2-disubstituted benzocyclobutenes are readily characterized by a small coupling ( $J_{\text{HH}^2} \sim 2\text{ Hz}$ ) between the four-membered ring protons: I. L. Klundt, *Chem. Rev.*, **70**, 471 (1970).

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possessing a dihapto benzocyclobutadiene ligand. However, in view of the propensity of cyclobutadienoid hydrocarbons to act as tetrahapto ligands<sup>12</sup> and the ability of cationic cyclobutadiene complexes to add nucleophiles to the four-membered ring,<sup>13</sup> an alternative structure, **3b**, possessing a tetrahapto four-membered ring and a trihapto five-membered ring cannot be excluded as a possibility. We are now attempting to obtain single crystals suitable for an X-ray structure determination to resolve this problem.

**Acknowledgment.** We gratefully acknowledge the generous support of the Graduate School of Boston University and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(12) P. M. Maitlis and K. W. Eberius in "Nonbenzoid Aromatic Compounds," J. P. Snyder, Ed., Academic Press, New York, N. Y., pp 360-426.

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### Nuclear Magnetic Resonance Spectroscopy Using Flowing Liquids. CIDNP Study of the Oxidation of Isopropyl Alcohol Using Titanous Ion with Hydrogen Peroxide

Sir:

Previously<sup>1</sup> we have reported the use of a flow system to detect the proton nuclear magnetic resonance (nmr) spectrum of a short-lived intermediate formed during the reaction between methoxide ion and 3,5-dinitrobenzene. In the present paper we wish to report the application of this technique to the study of reactions between radicals generated by the oxidation of isopropyl alcohol in  $\text{H}_2\text{O}$  using  $\text{TiCl}_3$  plus  $\text{H}_2\text{O}_2$ . In this study we observed enhanced absorption and emission nmr lines indicating non-Boltzmann nuclear spin polarization. The interpretation of this phenomenon is based on a model in which non-Boltzmann nuclear spin polarization occurs as a result of reaction *via* a radical pair.<sup>2</sup> Details of the theory used to calculate the nuclear spin polarization based on this model have been given previously<sup>3</sup> and are not repeated here.

In essence, the experiment consists of mixing an aqueous solution of 0.01 *M*  $\text{TiCl}_3$  plus 0.1 *M*  $\text{H}_2\text{SO}_4$  with a solution of 0.1 *M*  $\text{H}_2\text{O}_2$  plus 0.3 *M* isopropyl alcohol. A probe is used which includes two reservoirs which permit the nuclei of the two solutions to come to thermal equilibrium in the magnetic field before they are mixed in a high-pressure mixing chamber and passed through the measuring coils. At suitable flow rates, the absolute signal-noise ratio is appreciably better than that of a stationary sample. In this approach, the flow rates are limited by the capacities of the reservoirs, but these can be maximized by using a probe design in which transmitter and receiver coupling is minimized by time sharing. That the flow system is necessary to obtain good

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Figure 1. Proton nmr spectra obtained at 100 MHz by mixing a solution containing 0.01 *M*  $\text{TiCl}_3$  plus 0.1 *M*  $\text{H}_2\text{SO}_4$  with a solution containing 0.3 *M* isopropyl alcohol plus 0.1 *M*  $\text{H}_2\text{O}_2$ . The field increases from left to right: A, mixed outside the probe without the flow system; B, flowing liquid at 40 ml/min; C, flowing liquid at 55 ml/min; D, same as Figure 1B except solvent is changed to  $\text{D}_2\text{O}$ .

enough spectra to investigate this reaction can be seen by comparing Figure 1A (recorded using conventional technique) with Figures 1B and 1C when the flow system was used. Figure 1A was obtained without using the flow system by mixing the  $\text{TiCl}_3$  solution with the alcohol solution outside of the probe. The time between mixing and starting the recorder was about 5 sec.

As the delay between mixing and recording increases, the intensity of the emission line decreases. Figures 1B and 1C were obtained using the flow system at flow rates of 40 and 55 ml/min, respectively. For these spectra, the mixing chamber mentioned above was employed to mix the flowing liquids, and the nmr receiver coil was positioned a short distance from the exit of the chamber. As can be seen, the signal to noise ratio is greatly improved by the flow system, and the line widths are reduced, also. In addition, while the doublet at higher field gives no indication of nuclear spin polarization in Figure 1A, the polarization is indicated clearly in Figures 1B and 1C. The resonance lines in these figures are assigned as follows: low field emission line, methyl hydrogen of acetone; high field doublet, methyl hydrogen of isopropyl alcohol. The methine hydrogen resonance of isopropyl alcohol is not shown in these figures since it is partly masked by the very intense  $\text{H}_2\text{O}$  lock signal. However, when  $\text{D}_2\text{O}$  is used as the solvent and HDO is the lock signal, the methine resonance is clearly resolved as illustrated in Figure 1D. Finally, the presence of paramagnetic  $\text{TiCl}_3$  might be expected to shorten  $T_1$  for the nuclei of the products and prevent the observation of nuclear spin polarization. The fact that polarization is observed indicates that this effect is not significant, perhaps because  $\text{TiCl}_3$  reacts too rapidly with  $\text{H}_2\text{O}_2$  to affect the products.

The spectra given in Figures 1B and 1C also illustrate the advantages of the flow technique in measuring the non-Boltzmann nuclear spin polarization derived from this chemical system. At the slower flow rate (Figure 1B), the doublet of isopropyl alcohol appears as one strong absorption line and a very weak line. However, at the faster flow rate (Figure 1C), this doublet appears as one absorption and one emission line. This faster flow rate appears to give the limiting spectrum since the relative intensities of the lines do not change at flow rates faster than 55 ml/min although some additional line broadening occurs.

The analysis of the nuclear spin polarization was done using electron spin resonance (esr) information and the radical pair model. For this chemical system, four radicals have been detected by esr.<sup>4</sup> These radicals along with their *g* factors and hyperfine coupling constants are as follows:  $(\text{CH}_3)_2\dot{\text{C}}(\text{OH})$ ,<sup>5</sup> 2.0032, 19.7 G ( $\alpha$ );  $\dot{\text{C}}\text{H}_2\text{CH}(\text{OH})\text{CH}_3$ ,<sup>4</sup> 2.0022,<sup>5</sup> 22.4 ( $\alpha$ ), 23.8 ( $\beta$ ), 0.78 G ( $\gamma$ ); two forms of  $\dot{\text{O}}\text{H}$  or  $\dot{\text{O}}_2\text{H}$  complexed with  $\text{Ti}(\text{IV})$ ,<sup>4</sup> 2.0132 and 2.0118. From the analysis, it is possible to account for the polarization of isopropyl alcohol by disproportionation reactions *via* three radical pairs formed from free radicals:  $[(\text{CH}_3)_2\dot{\text{C}}(\text{OH}) (\text{HO})\dot{\text{C}}(\text{CH}_3)_2]^{\text{F}}$ ,  $[\text{CH}_3\text{CH}(\text{OH})\dot{\text{C}}\text{H}_2 \dot{\text{C}}\text{H}_2\text{CH}(\text{OH})\text{CH}_3]^{\text{F}}$ , and  $[\text{CH}_3\text{CH}(\text{OH})\dot{\text{C}}\text{H}_2 (\text{HO})\dot{\text{C}}(\text{CH}_3)_2]^{\text{F}}$ . The polarization calculated for each of these radical pairs agrees with the observed pattern of low field absorption, high field emission for the doublet for methyl resonance of the alcohol. However, while the first two give zero net polarization, the last radical pair gives a positive net polarization. Comparison of the spectrum in Figure 1B with one obtained under the same conditions with  $\text{TiCl}_3$  absent indicates some positive net polarization. However, the observed

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(6) Measured in our laboratory using a Bruker BE-414 esr spectrometer and experimental conditions similar to those given in ref 4.

A:E ratio is lower than the calculated ratio, indicating contributions from the other two radical pairs. The relative contributions made to the polarization by the three radical pairs cannot, however, be determined by this method.

A study of the photochemistry of acetone<sup>7</sup> indicates that the disproportionation of  $[(\text{CH}_3)_2\dot{\text{C}}(\text{OH})(\text{OH})\dot{\text{C}}(\text{CH}_3)_2]^{\text{F}}$  to give the alcohol plus the enol of acetone  $\text{CH}_2\text{C}(\text{OH})\text{CH}_3$  is responsible for at least part of the observed polarization of alcohol. It seems reasonable to expect that this path occurs in the present case, also. Unfortunately, the generation of  $[(\text{CH}_3)_2\dot{\text{C}}(\text{OD})(\text{OD})\dot{\text{C}}(\text{CH}_3)_2]^{\text{F}}$  by using  $\text{D}_2\text{O}$  in place of  $\text{H}_2\text{O}$  is not a good test of this path since  $[(\text{CH}_3)_2\dot{\text{C}}(\text{OD})\dot{\text{C}}\text{H}_2\text{CH}(\text{OD})\text{CH}_3]^{\text{F}}$  and  $[\text{CH}_3\text{CH}(\text{OD})\dot{\text{C}}\text{H}_2\dot{\text{C}}\text{H}_2\text{CH}(\text{OD})\text{CH}_3]^{\text{F}}$  can contribute to the alcohol polarization, also. Thus although alcohol polarization is observed when  $\text{D}_2\text{O}$  is the solvent (Figure 1D), we can conclude only that enol formation may be occurring, and this may be *via* any or all of these radical pairs.

None of the above mentioned radical pairs can account for the negative polarization observed for acetone since they either give no net polarization or, in the case of  $[(\text{CH}_3)_2\dot{\text{C}}(\text{OH})\dot{\text{C}}\text{H}_2\text{CH}(\text{OH})\text{CH}_3]^{\text{F}}$ , net positive polarization for acetone. Consequently, we attribute the negative polarization to the formation of acetone *via* the radical pairs  $[(\text{CH}_3)_2\dot{\text{C}}(\text{OH})\text{R}_1]^{\text{F}}$  and  $[(\text{CH}_3)_2\dot{\text{C}}(\text{OH})\text{R}_2]^{\text{F}}$  whereas  $[\text{CH}_3\text{CH}(\text{OH})\dot{\text{C}}\text{H}_2\text{R}_1]^{\text{F}}$  and  $[\text{CH}_3\text{CH}(\text{OH})\dot{\text{C}}\text{H}_2\text{R}_2]^{\text{F}}$  give positive polarization.  $\text{R}_1$  and  $\text{R}_2$  indicate forms of  $\dot{\text{O}}\text{H}$  or  $\dot{\text{O}}_2\text{H}$  complexed with  $\text{Ti}(\text{IV})$ . For the last two radical pairs, acetone must result from a disproportionation to give the enol  $\text{CH}_2\text{C}(\text{OH})\text{CH}_3$  which presumably under the aqueous acid conditions might convert to acetone at a rate which is competitive with the spin-lattice relaxation rates of the protons.

The fact that the nmr technique provides evidence for radical reactions not detected by esr<sup>4</sup> (and *vice versa*) indicates the complementary fashion in which these techniques may be employed in studying reaction mechanisms of radicals generated by  $\text{TiCl}_3$  plus  $\text{H}_2\text{O}_2$ . The reactions proposed in this paper could perhaps account for the deviation from first order found for the decay rates of the organic radicals measured in the esr study.

**Acknowledgments.** This work has been supported in part by the National Research Council of Canada (M. C. and C. A. F.) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (M. C.).

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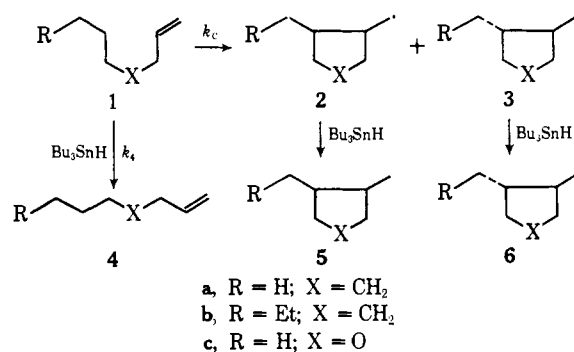
### Preferential Cis Cyclization of 6-Hepten-2-yl and Related Radicals. An Example of Orbital Symmetry Control

Sir:

Previous work has afforded conflicting evidence concerning the stereochemical course of intramolecular

addition in suitably substituted alkenyl radicals. Although earlier studies<sup>1</sup> indicated that 6-hepten-2-yl radical, **1a**, gives predominately the cis isomer of the cyclic product, the most recent report<sup>2</sup> suggests that **1a** undergoes exclusive trans cyclization. We now present evidence that the cis mode of cyclization is favored in 6-hepten-2-yl radical, **1a**, and two related species,<sup>3</sup> **1b** and **1c**, and we offer an explanation for this "perplexing"<sup>4</sup> phenomenon.

Treatment of 6-chlorohept-1-ene with tributylstannane in pentane<sup>5,6</sup> at 65° gave 1-heptene (**4a**), *cis*- and *trans*-1,2-dimethylcyclopentane (**5a** and **6a**), and a trace of



methylcyclohexane, each of which was unequivocally identified by comparison with authentic compounds.<sup>7</sup> The relative yields of cyclized and straight-chain products, determined by gas chromatography,<sup>8</sup> were related in the expected way to the initial concentration of stannane,<sup>2,6,9</sup> but the *cis*:*trans* ratio remained constant within the limit of experimental error. Similar results were obtained when the radicals **1b** and **1c**, were generated from the appropriate chloro compounds by treatment with tributylstannane.

Steady-state treatment of the dependence of the yields of cyclized products from each radical on initial stannane concentration enabled  $k_c/k_4$  to be calculated,<sup>2,9</sup> where  $k_c$  represents the rate constant for total cyclization. The rate constant for hydrogen atom transfer from stannane,  $k_4$ , is expected<sup>6</sup> to have a value of  $\sim 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ . The results (Table I) show that the two radicals, **1a** and **1b**, have similar values of  $k_c$ , but the oxygen-containing radical **1c** cyclizes much more rapidly. Replacement of a methylene group by an oxygen atom in an equivalent position in *o*-3-butenyl-phenyl radical has been shown previously to cause a similar rate enhancement.<sup>10</sup>

The data clearly show that for each of the radicals

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- (8) Gas chromatography was carried out on an Apiezon L 100 m  $\times$  0.508 mm capillary column at 65° with nitrogen carrier gas (0.5 ml  $\text{min}^{-1}$ ).
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