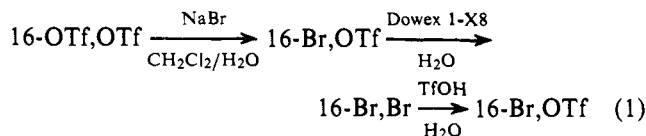
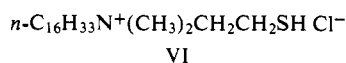


solutions of the surfactant halides precipitated the surfactant triflates. The cycle of reactions depicted in eq 1 has been carried out with high efficiency.<sup>24</sup>



In an important application, 16-SAcCl, prepared by ion exchange of 16-SAc,OTf (Scheme I), was deprotected with aqueous HCl; lyophilization then afforded thiocholine surfactant VI. The kinetic properties of this highly reactive micellar reagent are under intensive study.<sup>25</sup>



The water-insolubility of 16-OTf,OTf<sup>26</sup> precluded precise kinetic comparison with 16-OMsCl, but approximate relative reactivities were determined at 25 °C under two-phase, saturated aqueous NaBr/CH<sub>2</sub>Cl<sub>2</sub> conditions. Whereas 2.8 × 10<sup>-2</sup> M 16-OTf,OTf was completely converted to 16-Br,OTf in 300 s, both 2.4 × 10<sup>-2</sup> M 16-OMsCl and 10<sup>-2</sup> M cetyl triflate failed to react after 3600 s. Addition of 10<sup>-3</sup> M CTABr (as a phase transfer catalyst) to the cetyl triflate/NaBr system produced complete reaction after 750 s. Not only is 16-OTf seen to be considerably more reactive than 16-OMs,<sup>18</sup> but extrapolation of the cetyl triflate results strongly implies that 16-OTf is capable of *self-phase transfer catalysis*.<sup>27,28</sup>

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- Control experiments in micellar cetyltrimethylammonium (CTA) bromide showed that oxidative dimerization of thiophenoxide did not significantly compete with S<sub>N</sub>2 displacement under our experimental conditions. Additionally, 16-OMsCl was titrimetrically stable to aqueous NaOH at pH 9.0 or 10.0 over the duration of the 16-OMs/thiophenoxide reactions.
- The reaction product of 16-OMs and thiophenoxide was shown to be 16-SC<sub>6</sub>H<sub>5</sub> (IVa, Scheme I) by UV studies under kinetic conditions. We followed the disappearance of C<sub>6</sub>H<sub>5</sub>S<sup>-</sup> (273 nm) and the simultaneous formation of 16-SC<sub>6</sub>H<sub>5</sub> (260 nm). Authentic 16-SC<sub>6</sub>H<sub>5</sub><sup>7</sup> was prepared (as the CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> salt) by reacting 16-OMsCl with ethanolic NaSC<sub>6</sub>H<sub>5</sub> (25 °C, 1 h), followed by acidification (HCl), precipitation (ether), and removal of 16-SC<sub>6</sub>H<sub>5</sub>Cl (water).
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- The surfactant halides were characterized by NMR, IR, and elemental analysis. In particular, surfactant triflates (and NaOTf) show strong sulfonate and C-F stretching absorptions at ~1260, 1160, and 1035 cm<sup>-1</sup> (in Nujol).<sup>23</sup> These bands were absent in the IR spectra of the ion-exchanged, halide surfactants.
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- R. A. Moss, G. O. Bizzigotti, T. J. Lukas, and W. J. Sanders, submitted for publication. At pH 7.96, the cleavage of *p*-nitrophenyl acetate by 0.02 M micellar VI is characterized by  $k_{\psi} = 9.71 \text{ s}^{-1}$ , corresponding to a second-order rate constant of 485 L/mol s. Under comparable conditions, micellar VI is 34 600 times more reactive than CTACl as a micellar esterolytic reagent and is currently the most reactive self-contained functional micellar esterolysis reagent yet reported.
- 16-OTf,OTf could not be subjected to halide ion exchange without concomitant S<sub>N</sub>2 reaction.
- Related phenomena were encountered by King et al. in their study of betylates II.<sup>6</sup>
- The limited solubility of 16-OTf,OTf in water, coupled with its high reactivity, suggests that its self-phase transfer reactions may occur very near the aqueous/organic interface; cf. M. Makosza, *Pure Appl. Chem.*, **43**, 439 (1975).

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## Oxygenation of Cyclic Dienes to Endoperoxides

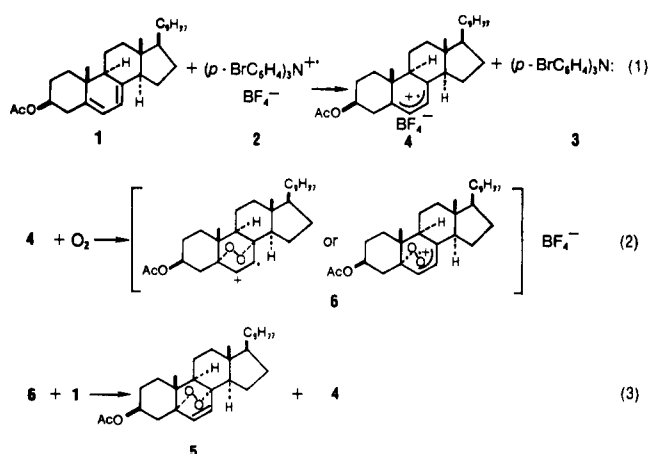
Sir:

Addition of ground-state triplet oxygen to conjugated dienes is spin forbidden. However, Barton and co-workers<sup>1,2</sup> reported that ammoniumyl radicals and certain Lewis acids are effective in catalyzing specific 1,4 addition of triplet oxygen to various 1,3-dienes. In their proposed mechanism, the novel concept<sup>1</sup> invoked is the function of the "catalyst" which, in the assembly with the diene and oxygen, overcomes the spin barrier impeding the cycloaddition. Our interest in specific oxygenation<sup>3</sup> of olefins led us to investigate this reaction in detail. We now report our findings that (1) the assembly of oxygen, diene, and "catalyst" is not central to the oxygenation; (2) the "catalyst" functions as a radical initiator; and (3) the "catalytic" oxygenation can best be described by a cation-radical chain mechanism.

We initiated our investigation using ergosteryl acetate (1) as the diene and tris(*p*-bromophenyl)ammoniumyl tetrafluoroborate (2) as the "catalyst", which were chosen on the basis of Barton's original work<sup>1</sup> and our intended magnetic resonance studies. Cation radical 2 dissolved in CH<sub>2</sub>Cl<sub>2</sub> at -70 °C and then frozen at -120 °C in the ESR cavity exhibited a broad singlet with  $\langle g \rangle = 2.009$ .<sup>4</sup> When 1 or more equiv of solid 1 were added to this solution with temperature maintained at -70 °C and then frozen in the ESR cavity as above, a broad unresolved signal with  $\langle g \rangle = 2.004$  resulted. A gradual shift of ESR signals, along with color changes from blue to red, was observed at intermediate stages of mixing. The resulting  $\langle g \rangle$

value indicates that perhaps a carbon center radical might have been generated. Electron transfer in this type of system is not uncommon.<sup>5</sup> However, existence of a "diene-ammoniumyl radical" complex cannot be ruled out since positive assignment would require hyperfine splitting in both sets of ESR signals. We, therefore, took advantage of NMR contact shifts, arising from spin delocalization in the paramagnetic species, for positive identification. According to Pearson and Walter,<sup>6</sup> the <sup>1</sup>H NMR of **2** is out of the normal 10-ppm range.<sup>7</sup> Indeed, no signals due to the aromatic protons were detected when **2** was dissolved in CD<sub>2</sub>Cl<sub>2</sub> and maintained at -65 °C with Me<sub>4</sub>Si as internal reference while negligible shift (<10 Hz) was detected for internal cyclohexane and CHDCl<sub>2</sub>. However, when 1 equiv of **1** was included in the solution, the signals (aromatic quartet centered at δ 7.19) due to tris(*p*-bromophenyl)amine (**3**) appeared. What is most revealing is that in the spectrum the diene protons on the B ring (quartet centered at δ 5.55) of **1** were missing while the olefinic protons on the side chain (multiplet centered at δ 5.26) of **1** remained. These results suggest that electron transfer had occurred from **1** to **2** and that the spin responsible for the contact shift in **2** was transferred to the diene moiety of **1**. Chemical shift data from <sup>13</sup>C NMR of the aromatic species formed in the mixture of **1** and **2** were found to be identical with those of amine **3** (δ 116.11 (C<sub>1</sub>), 125.70 (C<sub>2</sub>), 132.53 (C<sub>3</sub>), 146.06 (C<sub>4</sub>)), arguing against the formation of a charge-transfer complex or an ammonium salt (nitrogen addition on the diene) as being central to the oxygenation reaction. In addition, the signals of the carbons of the diene unit (originally<sup>8</sup> at δ 141.33 (C<sub>5</sub>), 120.28 (C<sub>6</sub>), 116.42 (C<sub>7</sub>), 138.50 (C<sub>8</sub>)) were not detected,<sup>9</sup> further confirming our contention that complete electron transfer had occurred with the formation of a four-center diene cation radical, **4**.

Although only "catalytic" quantities of **2** are required for the oxygenation, our results led us to question the "catalyst" function of **2** as suggested by Barton and co-workers.<sup>1,2</sup> Indeed the  $\langle g \rangle = 2.004$  ESR signal of a solution of 2:1 ratio of **1**:**2** in CH<sub>2</sub>Cl<sub>2</sub> under 1 atm of O<sub>2</sub>, kept at -70 °C, persisted. The  $\langle g \rangle = 2.009$  ESR signal of **2** was never regained. In this same experiment, roughly an equivalent quantity of **5** (based on **2**) was detected upon aqueous workup. We therefore proposed the mechanism shown in eq 1-3 for the oxygen-diene reaction as initiated by **2**.



According to this mechanism, the chain-propagating species are **4** and its oxygen adduct **6**.<sup>10,11</sup> We subjected this to a test. Electrolytic oxidation<sup>4b</sup> of **3** is known to generate **2**. Under our conditions, cyclic voltammetry indicated a reversible oxidation wave at 0.3 V.<sup>4b</sup> The blue solution obtained exhibited the same ESR signal as the material prepared by chemical oxidation<sup>1</sup> and also was capable of effecting the "catalytic" oxygenation. Likewise, **1** was electrolytically oxidized<sup>12,13</sup> and the ESR spectrum was identical with that obtained above by electron

transfer, eq 1. A constant current oxidation ( $i = 10 \mu A cm^{-2}$ ) of an equimolar solution of **1** and the amine **3**, at -78 °C, indicated that, of the two substrates, only **3** was first oxidized as judged by ESR. When this solution (with the current off) was slowly warmed to -70 °C, gradual ( $g$ ) value shift from 2.009 to 2.004 in the ESR spectrum occurred and electron transfer with the formation of **4** was again indicated. Apparently, anodic oxidation of **1** on Pt electrode has considerably higher overpotential than that of **3**.<sup>13</sup> The diene **1** was then electrolytically oxidized at -70 °C in the absence of **3** at a potential of 0.9 V vs. 0.1 N Ag<sup>+</sup>/Ag electrode. A total of 10.5 C were passed into the solution of **1** (2.23 mmol) in 75 mL of CH<sub>2</sub>Cl<sub>2</sub> with 0.17 M Bu<sub>4</sub>N<sup>+</sup>ClO<sub>4</sub><sup>-</sup> as supporting electrolyte under 1 atm of O<sub>2</sub>. After aqueous workup, the amount of endoperoxide **5** formed was determined by <sup>1</sup>H NMR to be 53% with the rest recovered as the diene **1**. This corresponds to a minimum chain length<sup>14</sup> of 10. These findings demonstrate that **2** is not necessary for the "catalytic" oxygenation except as an initiator and supports the cation-radical chain mechanism as proposed in eq 1-3. Preliminary results indicate that the mechanism (eq 1-3) valid for ammoniumyl radical initiated oxygenation is also representative for the Lewis acid "catalyzed" reactions.<sup>1,2</sup> These and other aspects of diene oxygenation are being investigated and are subjects of a future report.

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- For clarity, only two of the four structures for **8** are presented.
- According to this mechanism, the yield of product **5** is dictated by "the molar quantity of starting **1** minus that of **2**", since a molar equivalent of **1** (based on **2**) persists as **4** (or **8**). Therefore, the chain length or the product yield increases as the ratio of **1** to **2** increases. On the other hand, the yield of the product approaches zero as the ratio of **1** to **2** is  $\leq 1$ .
- Electrolysis conditions: CH<sub>2</sub>Cl<sub>2</sub> solution with 0.03 M substrate, 0.1 M Bu<sub>4</sub>N<sup>+</sup>ClO<sub>4</sub><sup>-</sup>, -78 °C, Pt anode vs. 0.1 N Ag<sup>+</sup>/Ag reference electrode.
- Cyclic voltammetry for **1** exhibited an irreversible oxidation wave at ~0.6 V. Irreversible potential waves do not represent true chemical potentials and, therefore, the  $E_{1/2}$  values obtained for **1** and **3** cannot be directly compared.
- A minimum average chain length of 15 was reported in ref 1.

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## Malonic Anhydride

Sir:

Malonic anhydride<sup>1</sup> is a classic unknown compound. Dehydration of malonic acid does not give the anhydride but leads