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### Novel Electrochemical Reactions of Compounds Containing Strong Metal-Metal Bonds. Oxidation of Rhenium(II) Dimers, $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ , by Both EECC and ECEC Pathways

Sir:

The use of electrochemistry to probe the chemical properties of metal systems is well established.<sup>1</sup> However, while much interest has centered on the structural and chemical properties of rhenium dimers,<sup>2,3</sup> little use has been made, with the exception of studies involving the octachlorodirhenate(III) anion,<sup>4-6</sup> of electrochemical techniques for the study of these and other metal halides containing strong metal-metal bonds.

As previously reported,<sup>2,7</sup> the reduction of the octahalodirhenate(III) anions by monodentate tertiary phosphines affords complexes of the type  $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ , where X = Cl or Br. Subsequently, Cotton and Pedersen<sup>8</sup> investigated the properties of  $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$  and  $[\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4]^+$  using electrochemical and electron paramagnetic resonance experiments. While they found that the rhenium(II) dimer can be oxidized to the 1+ and 2+ ions



and that the 1+ ion was reasonably stable, electrochemical studies on this system were not pursued further. As a consequence of our interest in the chemical and redox properties of metal phosphine complexes which contain metal-metal bonds of multiple bond orders,<sup>7,9</sup> we have investigated the electrochemical properties of the complete series of rhenium(II) dimers of the type  $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ , where X = Cl, Br, or I and R = Et, Pr<sup>n</sup> or Bu<sup>n</sup>,<sup>10</sup> in order to explore the consequences of oxidizing species which possess two electrons over and above those of a fully occupied  $\sigma^2\pi^4\delta^2$  configuration.<sup>2</sup> This study has led to the discovery of a novel form of electrochemical behavior for this series of transition metal complexes.

The electrochemical properties of this series of complexes are summarized in Table I. In Figure 1A is shown a cyclic voltammogram<sup>12</sup> of  $\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4$  (this compound will be used as a representative example of all the  $\text{Re}_2\text{X}_4(\text{PR}_3)_4$  compounds studied) which demonstrates that the dimer has two electrochemical reversible,<sup>13</sup> one-electron (by coulometry) oxidations.

However, upon electrolysis at 0.0 V ( $n = 0.98$ ),<sup>14</sup> in addition to the major product,  $[\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4]^+$ , two new waves ( $E_{1/2} = +0.31$  and  $-0.88$  V) appear in the resultant cyclic voltammogram (Figure 1B). The origin of these new waves was found to be  $\text{Re}_2\text{Cl}_5(\text{PPr}_3)_3$ , since a cyclic voltammogram of an analytically pure sample of  $\text{Re}_2\text{Cl}_5(\text{PPr}_3)_3$  shows two waves at  $e_{1/2} = +0.31$  and  $-0.88$  V. Further oxidation at +1.0 V (i.e., past the second wave of  $\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4$  ( $n = 0.95$ )) produces  $[\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4]^{2+}$ ,  $[\text{Re}_2\text{Cl}_5(\text{PPr}_3)_3]^+$ , and another wave at

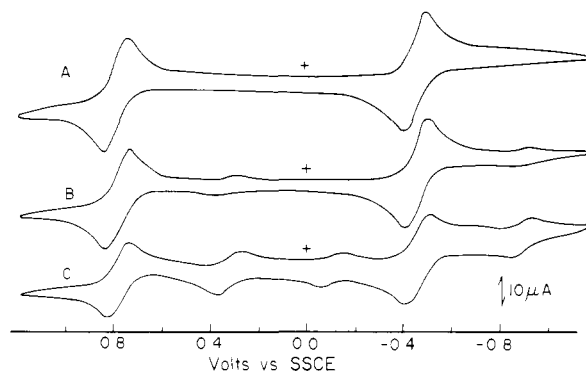


Figure 1. Cyclic voltammograms in 0.2 M TBAH-dichloromethane of A,  $\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4$ ; B, solution A following oxidation at 0.0 V; C, solution A following oxidation at +1.0 V (scan rate 200 mV/s at a Pt-bead electrode vs. the saturated sodium chloride calomel electrode at  $22 \pm 2$  °C).

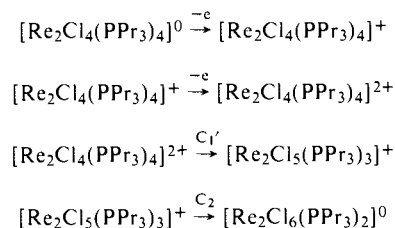
Table I.  $E_{1/2}$  Values for Rhenium Dimers,  $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ ,<sup>a</sup> in Dichloromethane<sup>b</sup>

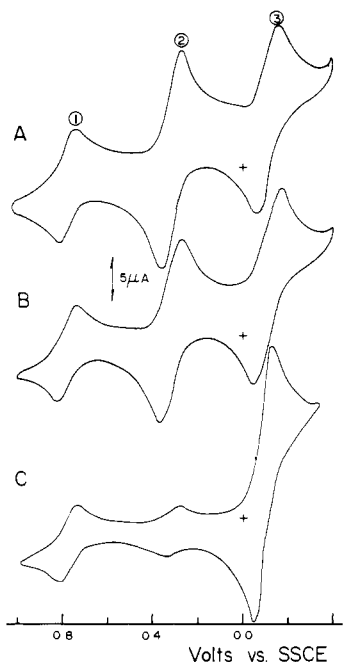
Complex	$E_{1/2}(\text{ox})(1)^c$	$E_{1/2}(\text{ox})(2)^c$
$\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$	-0.42	0.80
$\text{Re}_2\text{Br}_4(\text{PEt}_3)_4$	-0.31	0.825
$\text{Re}_2\text{I}_4(\text{PEt}_3)_4$	-0.27	0.77
$\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4$	-0.44	0.79
$\text{Re}_2\text{Br}_4(\text{PPr}_3)_4$	-0.38	0.84
$\text{Re}_2\text{I}_4(\text{PPr}_3)_4$	-0.22	0.85
$\text{Re}_2\text{Cl}_4(\text{PBu}_3)_4$	-0.44	0.82
$\text{Re}_2\text{Br}_4(\text{PBu}_3)_4$	-0.40	0.82
$\text{Re}_2\text{I}_4(\text{PBu}_3)_4$	-0.25	0.825

<sup>a</sup> X = Cl, Br, I; R = C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, C<sub>4</sub>H<sub>9</sub>. <sup>b</sup> With 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. <sup>c</sup> Volts vs. the saturated sodium chloride calomel electrode (SSCE) with a Pt-bead working electrode.

$E_{1/2} = -0.11$  V in the resultant cyclic voltammogram (Figure 1C). This new wave at  $E_{1/2} = -0.11$  V was found to be associated with  $\text{Re}_2\text{Cl}_6(\text{PPr}_3)_2$ ; a pure sample of  $\text{Re}_2\text{Cl}_6(\text{PPr}_3)_2$  was found to have a wave at  $-0.11$  V in its cyclic voltammogram.  $\text{Re}_2\text{Cl}_6(\text{PPr}_3)_2$  can also be electrochemically generated by oxidation of  $\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4$  at +0.5 V. These two pathways for the electrochemical production of  $\text{Re}_2\text{Cl}_6(\text{PPr}_3)_2$  from  $\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4$  are summarized in Schemes I and II and are representative of EECC and ECEC processes,<sup>15</sup> respectively. The difference between these two schemes is the potential used for the oxidation. If the oxidation is carried out at 1.0 V, then the initial product will be  $[\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4]^{2+}$  which will then, by a series of chemical reactions ( $C_1'$  and  $C_2$ ), produce  $\text{Re}_2\text{Cl}_6(\text{PPr}_3)_2$ . If the oxidation potential is 0.5 V, then the first product will be  $[\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4]^+$  which will, by a chemical step ( $C_1$ ), be converted to  $\text{Re}_2\text{Cl}_5(\text{PPr}_3)_3$ . Since 0.5 V is anodic of the  $E_{1/2}$  for  $\text{Re}_2\text{Cl}_5(\text{PPr}_3)_3$ , then this complex will in turn be oxidized and the resultant  $[\text{Re}_2\text{Cl}_5(\text{PPr}_3)_3]^+$  will, by a chemical step ( $C_2$ ), form  $\text{Re}_2\text{Cl}_6(\text{PPr}_3)_2$ . Therefore, the choice of pathway which produces  $\text{Re}_2\text{Cl}_6(\text{PPr}_3)_2$  from  $\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4$  is governed by the electrochemical potential used for the oxidation.

#### Scheme I. EECC Process





**Figure 2.** Cyclic voltammograms in 0.2 M TBAH-dichloromethane following exhaustive electrolysis of  $\text{Re}_2\text{Cl}_4(\text{PPR}_3)_4$  at +1.0 V: A, 15 min after complete electrolysis; B, 30 min; C, 120 min (scan rate 200 mV/s at a Pt-bead electrode vs. the saturated sodium chloride calomel electrode at  $22 \pm 2^\circ\text{C}$ ); 1,  $\text{Re}_2\text{Cl}_4(\text{PPR}_3)_4$ ; 2,  $\text{Re}_2\text{Cl}_5(\text{PPR}_3)_3$ ; 3,  $\text{Re}_2\text{Cl}_6(\text{PPR}_3)_2$ .

#### Scheme II. ECEC Process

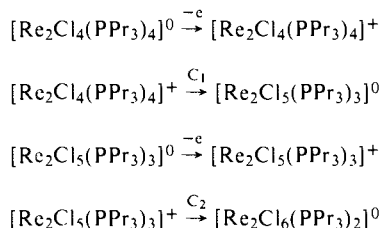


Figure 2 shows a series of cyclic voltammograms, at different times, of a solution of  $\text{Re}_2\text{Cl}_4(\text{PPR}_3)_4$  after oxidation at +1.0 V. (For the sake of clarity and because oxygen was allowed into the solution, only the anodic half of the cyclic voltammogram is pictured.) These cyclic voltammograms indicate that, once  $[\text{Re}_2\text{Cl}_5(\text{PPR}_3)_3]^+$  ( $E_{1/2} = +0.31$  V) is formed, it is fairly quickly converted to  $\text{Re}_2\text{Cl}_6(\text{PPR}_3)_2$  ( $E_{1/2} = -0.11$  V), while the rate of conversion of  $[\text{Re}_2\text{Cl}_4(\text{PPR}_3)_4]^{2+}$  to  $[\text{Re}_2\text{Cl}_5(\text{PPR}_3)_3]^+$  is somewhat slower (i.e.,  $k_{C_1'} < k_{C_2}$ ). Because of the experimental conditions involved in these oxidations, the use of peak currents as a measure of change in concentration is not very reliable. While the individual cyclic voltammograms in Figure 2 can be taken as a measure of the relative concentration of reaction products, they should not be used to determine the reaction stoichiometry. However, coulometry can be used to determine, at least semiquantitatively, the yields of  $\text{Re}_2\text{Cl}_6(\text{PPR}_3)_2$  from the oxidation of  $\text{Re}_2\text{Cl}_4(\text{PPR}_3)_4$ .<sup>16</sup>

Following Scheme II electrochemically is difficult because conversion of a  $10^{-3}$  M solution of  $[\text{Re}_2\text{Cl}_4(\text{PPR}_3)_4]^+$  to  $\text{Re}_2\text{Cl}_5(\text{PPR}_3)_3$  (reaction  $C_1$ ) takes  $\sim 24$  h. Despite the fact that reaction  $C_1$  is slow, the very low value for the first oxidation of  $\text{Re}_2\text{X}_4(\text{PR}_3)_4$  ( $-0.44$  to  $-0.25$  V) makes them susceptible to aerial oxidation, thereby requiring freshly made samples for electrochemical determinations.<sup>17</sup>

The mechanisms of reactions  $C_1$ ,  $C_1'$  and  $C_2$  do not involve a disproportionation step since the amounts of  $\text{Re}_2\text{Cl}_5(\text{PPR}_3)_3$  and  $\text{Re}_2\text{Cl}_6(\text{PPR}_3)_2$  formed (estimated from coulometric determinations) from the oxidation of  $\text{Re}_2\text{Cl}_4(\text{PPR}_3)_4$  do not

conform to any obvious reaction stoichiometry. Also, we have no electrochemical evidence for the formation of any other rhenium halide-phosphine complexes (e.g.,  $\text{ReX}_3(\text{PR}_3)_3$  and  $\text{ReX}_4(\text{PR}_3)_2$ )<sup>18,19</sup> as a result of such a disproportionation reaction. We believe that the mechanism for the oxidation of  $\text{Re}_2\text{Cl}_4(\text{PPR}_3)_4$  involves the break-up of some of the dimer units, a process which is the rate-determining step in these coupled reactions. This releases chloride ions which are then incorporated in the oxidized dimer  $[\text{Re}_2\text{Cl}_4(\text{PPR}_3)_4]^+$  to form  $\text{Re}_2\text{Cl}_5(\text{PPR}_3)_3$  and finally  $\text{Re}_2\text{Cl}_6(\text{PPR}_3)_2$ .<sup>20</sup> Strong support for this contention is the observation that addition of an external source of chloride ions<sup>22</sup> to a dichloromethane solution of  $[\text{Re}_2\text{Cl}_4(\text{PPR}_3)_4]^+$  leads to the almost instantaneous formation of  $\text{Re}_2\text{Cl}_5(\text{PPR}_3)_3$ . Similarly, oxidation of  $\text{Re}_2\text{Cl}_5(\text{PPR}_3)_3$  to  $[\text{Re}_2\text{Cl}_5(\text{PPR}_3)_3]^+$  (at +0.5 V) in the presence of added  $\text{Cl}^-$  affords  $\text{Re}_2\text{Cl}_6(\text{PPR}_3)_2$ . Since we find that the electrochemical behavior of  $\text{Re}_2\text{Cl}_4(\text{PPR}_3)_4$  in acetonitrile is identical with that observed in dichloromethane, this rules out the involvement of the solvent in the reaction mechanisms.

Electrode processes with coupled homogeneous chemical reactions are a central theme in electroanalytical chemistry. While these processes are well known for organic systems,<sup>23</sup> relatively few studies have been reported involving metal systems.<sup>24,25</sup> The discovery that the electrochemical oxidation of  $\text{Re}_2\text{X}_4(\text{PR}_3)_4$  proceeds by both EEC and ECEC coupled reaction series is quite remarkable and of considerable general interest because, to our knowledge, not only are there no previous reports of ECEC and EEC reaction series<sup>15</sup> involving metal systems, but the occurrence of both reaction pathways within the same system is unprecedented. Our results point to the existence of extensive series of coupled reactions in the electrochemistry of metal complexes containing strong metal-metal bonds (triple or quadruple)<sup>26</sup> where oxidation (or reduction) processes involving metal based orbitals can occur without disruption of the metal-metal bonds.

Further elucidation of the kinetics and mechanisms of the electrochemical oxidation of  $\text{Re}_2\text{X}_4(\text{PR}_3)_4$  is being currently pursued in our laboratory.

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#### References and Notes

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- (10) The preparations of the chloride and bromide derivatives have been described previously.<sup>7</sup> Our recent isolation<sup>11</sup> of the octaiododirhenate(III) salt  $(\text{Bu}_4\text{N})_2\text{Re}_2\text{I}_8$  has permitted us a direct synthetic route to  $\text{Re}_2\text{I}_4(\text{PR}_3)_4$ .
- (11) H. D. Glicksman and R. A. Walton, unpublished work.
- (12) All cyclic voltammetry and coulometry experiments were carried out in  $\text{CH}_2\text{Cl}_2$  with 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. All potentials are referenced to the saturated sodium chloride calomel electrode (SSCE) and are uncorrected for junction potentials. Either a platinum bead (for cyclic voltammetry) or a platinum gauze (for coulometry) electrode was used as the working electrode.
- (13)  $\Delta E_p \approx 60$  mV and  $i_{p,a}/i_{p,c} \approx 1$ ; see R. W. Murray and C. N. Reilly,

"Electroanalytical Principles", Interscience, New York, N.Y., 1963.

- (14) Values of  $n$ , where  $n$  is the total number of electrons transferred in exhaustive electrolysis at constant potential, were calculated after measuring the total area under current vs. time curves for the complete reaction. Reactions were judged to be complete when the current had fallen to 1% of its initial value.
- (15) E means an electrochemical reaction, either an oxidation or a reduction, while C means a chemical reaction. Thus an EC reaction would be an electrode process followed by a chemical reaction.
- (16) Yields of  $\text{Re}_2\text{Cl}_6(\text{PPr}_3)_2$  are in the range of 60–70%.
- (17) A benzene solution of  $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$  when exposed to  $\text{O}_2$  produces  $\text{Re}_2\text{Cl}_6(\text{PEt}_3)_3$  together with small quantities of  $\text{ReO}_4^-$  and phosphine oxide; see C. A. Hertzler, M.S. Thesis, Purdue University, 1977.
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- (20) When a solid sample of  $\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4$  is exposed to the air, the major oxidation product is  $\text{Re}_2\text{Cl}_6(\text{PPr}_3)_3$  together with a small amount of perchlorate. The presence of the latter species was confirmed by infrared spectroscopy ( $\nu_{\text{Re-O}}$  at  $900\text{ cm}^{-1}$ ) and ESCA measurements.  $\text{Re } 4f_{5/2,7/2}$  binding energies at 47.9 and 45.9 eV are typical of the  $\text{ReO}_4^-$  anion.<sup>21</sup>
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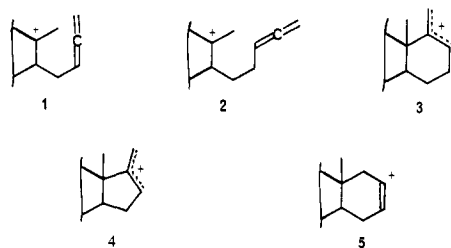
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### Cationic Cyclization of Allenes. Preferential Cyclization via Vinyl Cations

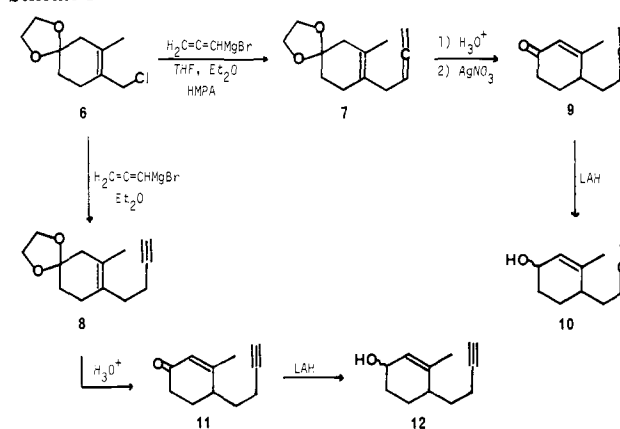
Sir:

An area of continuing interest in the development of cationic olefin cyclizations as a method for generating carbocyclic ring systems involves study of variations in the  $\pi$  moiety participating in these cyclizations.<sup>1</sup> We report herein the results of cyclization studies involving  $\gamma$ -allenyl cation systems (**1**) which differ markedly from results reported previously<sup>3</sup> with  $\delta$ -allenyl cation systems (**2**).

Cyclizations involving  $\delta$ -allenyl cations (or their equivalent) have been shown to result in attack on the central carbon of the allene to form products resulting from an allylic cation (**2**  $\rightarrow$  **3**). Since the formation of five-membered rings in a similar fashion would be useful synthetically, we decided to examine some  $\gamma$ -allenyl cation systems to determine if reaction would lead to the allylic system **4** or the vinyl system **5**.<sup>5,7</sup>



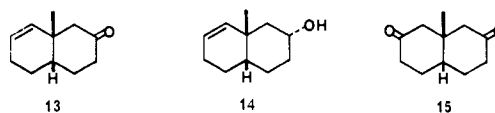
Scheme I



gave pure ketone **9**. Reduction then gave alcohol **10**. Hydrolysis and reduction of acetylene **8** led to the related acetylenic compounds **11** and **12**.

Treatment of alcohol **10** with anhydrous formic acid gave, after hydrolysis, a single (NMR, GC, TLC) product in 70% yield. The product was shown to be the *cis*-octalone **13** by comparison (IR, NMR) with an authentic sample prepared by oxidation of alcohol **14**.<sup>14</sup> No evidence was obtained for an allylic alcohol product. The same ketone **13** was obtained (70% yield) from cyclization of acetylenic alcohol **12**.<sup>15</sup> Alcohol **10** did not undergo cyclization with trifluoroacetic acid under conditions used by Johnson and Hall.<sup>3a</sup>

Preferential formation of a six-membered ring was also observed in the cyclization of ketone **9**. Treatment of **9** with either acetic anhydride in acetic acid with perchloric acid catalysis (66% yield)<sup>16</sup> or with trifluoroacetic anhydride in trifluoroacetic acid (74% yield)<sup>17</sup> gave, after hydrolysis, the crystalline (mp 115–116 °C) *cis* diketone **15**. This material was identical (melting point, IR, NMR) with material prepared by cyclization of 4-(3-butenyl)-3-methyl-2-cyclohexenone<sup>12,14</sup> with TFAA/TFA, followed by hydrolysis and Jones oxidation. Diketone **15** was also obtained in a 90% yield by TFAA/TFA cyclization of acetylenic ketone **11**.



Thus these cyclizations of  $\gamma$ -allenyl systems gave only products derived from cationic attack on the terminus of the allene. No evidence for five-membered ring products was obtained. This divergence from previous results with  $\delta$ -allenyl cation systems<sup>3</sup> where attack only on the central carbon of the allene was observed demonstrates that additional studies are necessary to define the factors controlling the course of cationic cyclizations involving an allene as the  $\pi$  moiety. One potentially important difference between the  $\gamma$ - and  $\delta$ -allenyl systems can be discerned by examination of molecular models. A  $\delta$ -allenyl cation **2** readily interacts with the C-2,C-3  $\pi$  bond of the allene (**2**  $\rightarrow$  **16**). The orbital overlap in **16** is exactly analogous to the overlap found in cyclization of  $\delta$ -alkenyl systems to form six-membered rings. It has been demonstrated that, although electrophilic attack on an unsubstituted allene takes place preferentially at the terminal carbon, substitution with alkyl groups leads to increased attack at the central carbon.<sup>6,18</sup> Thus the reaction of **2** through **16** to give **3** may be a result of alkyl substitution at C-3 of the allene. However, examination of a model of cation **1** shows that overlap with the C-2,C-3  $\pi$  bond of the allene is much less favorable. In fact the orthogonal C-1,C-2  $\pi$  bond appears to overlap very favorably (**1**  $\rightarrow$  **17**). Thus, a fundamental difference exists between **16** and **17**. In

We chose allylic alcohol **10** as a substrate for our cyclization studies because of its ready availability and its expected ease of cyclization. The cyclization of the corresponding allenyl ketone **9** was also investigated. The substrates for cyclization were prepared as shown in Scheme I.<sup>8</sup> Reaction of propargylmagnesium bromide<sup>9</sup> with the allylic halide **6**<sup>10</sup> in ether gave the acetylene **8** in good yield.<sup>11</sup> However, reaction in THF with added HMPA gave the allene **11** containing only ~20% acetylene.<sup>13</sup> Hydrolysis of the mixture and removal of acetylenic material by precipitation with silver nitrate in methanol