

In summary, we have shown that in allylic radicals differences in electronegativity between the central atom and the terminal heavy atoms can greatly reduce the importance of allylic resonance. The same electronegativity differences might also be expected to reduce the importance of resonance in allylic systems containing even numbers of  $\pi$  electrons, for instance in neutral  $O(CH_2)_2$ . However, as will be discussed in our full paper, electron repulsion effects cause allylic resonance to remain important in  $O(CH_2)_2$  and related diradicals.

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**Registry No.**  $O(CH_2)_2$ , 56971-75-6;  $O(CH_2)_2^+$ , 74427-28-4.

### Practical Method for $\alpha$ -Alkenyl Ketone Synthesis Based on a Facile Reductive Rearrangement of Alkynyl Halohydrins

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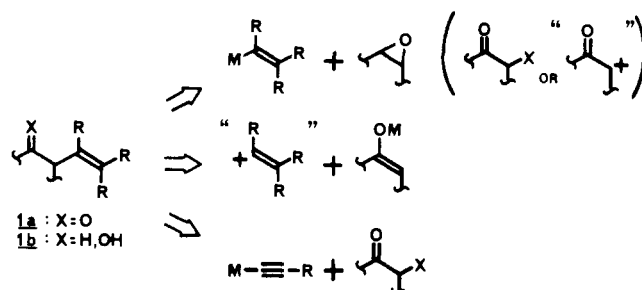
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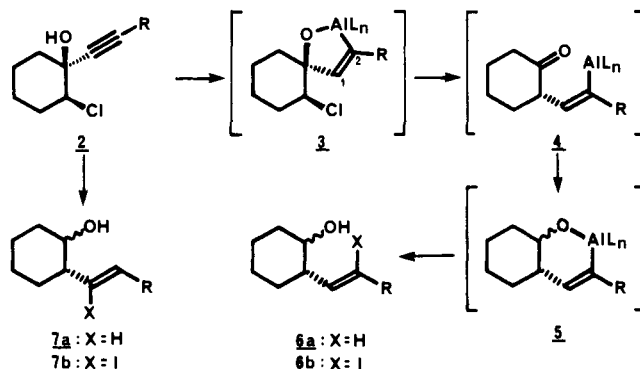
The importance of methodology for  $\alpha$ -alkenyl ketone (**1a**) and carbinol (**1b**) synthesis is amply documented in reports of their intermediacy in many synthetically significant transformations, particularly ring-expansion reactions,<sup>2</sup> and their occurrence in biologically active compounds such as the prostaglandins and cytotoxic terpenes.<sup>3</sup> Access to these systems has commonly involved reactions of metallo alkenes with electrophiles such as epoxides,<sup>4</sup>  $\alpha$ -halo ketones,<sup>5</sup> or the more recently introduced enolonium ion equivalents<sup>6</sup> (Scheme I). Vinyl cation equivalents, the polarity complement of the nucleophilic metallo alkene, have also found service in this area.<sup>7</sup> Herein, we describe an approach to  $\alpha$ -alkenyl ketones and carbinols from alkynes and halo ketones that involves a novel rearrangement and, in general, offers several advantages over existing methodology. This process affords a more cost-effective solution, which is based on readily available (frequently bulk) substrates and reagents, can be conducted on a large or small scale, and allows both for considerable variation in alkene substitution and for control of alkene geometry. The method additionally provides a practical route to hitherto difficult to prepare  $\alpha$ -alkadienyl ketones<sup>8</sup> and consequently a convenient route to large-ring compounds based on recently introduced macroexpansion methodology,<sup>9</sup> as evidenced below by its application in a strategically novel total synthesis of muscone (**12**).

Central to the success of this method is the finding that readily available alkynyl chlorohydrins under aluminum hydride reduction conditions<sup>10</sup> suffer an unusually facile rearrangement<sup>11</sup> to provide

Scheme I



Scheme II



alkenyl carbinols directly. Thus, treatment of *cis*-1-propynyl-2-chlorocyclohexanol (**2**, R = Me; Scheme II) with excess lithium aluminum hydride and sodium methoxide<sup>10d</sup> for 2 h at ambient temperature provided 2-*E*-propenylcyclohexanol (**6a**, R = Me)<sup>12</sup> as a 3:1 mixture of epimers in 97% yield as determined by GC analysis (72% yield after isolation). Of the possible mechanistic itineraries for this reaction it would appear that alkyne reduction precedes rearrangement, since the magnesium salt of **2** (R = Me) does not readily rearrange, even at 67 °C.<sup>13</sup> Equally important, exposure of the initial product expected from such an alkynyl migration, 2-propynylcyclohexanol, to the above noted conditions resulted only in carbonyl reduction, to provide 2-propynylcyclohexanol. For the alternative sequence, initial reduction would lead to an intermediate of the type **3**, whose formation can be inferred from the isolation (81% yield) of 2-(2-iodo-1-propenyl)cyclohexanol (**6b**, R = Me) when the reaction was quenched with iodine. However, attempts to detect **3** or its unrearranged derivatives in reactions run to partial conversion or under hydride-deficient conditions gave only starting material and rearranged reduced product, suggesting that the formation of **3** is rate determining. Even at temperatures as low as -20 °C, reduction rearrangement occurred. In contrast, the magnesium alkoxide of 1-vinyl-2-chlorocyclohexanol must be heated to temperatures in excess of 50 °C in order to induce its rearrangement.<sup>5</sup> It would appear, therefore, that this efficient and unusually facile process proceeds with initial hydroalumination. Subsequent propenyl migration is presumably facilitated by alanate stabilization of the electron-deficient center that develops at C2 during migration, involving initial  $\pi$ -electron participation (Scheme II).

In connection with the more synthetic features of this process, several points are noteworthy. First, the alkynyl halohydrins used in this method are readily prepared in high yield from either commercially available or readily prepared halocarbonyls and alkynes.<sup>11b</sup> As documented in extensive studies on nucleophilic

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(12) All new compounds gave satisfactory NMR, IR, and mass spectral and exact mass or combustion analyses.

(13) See also ref 11b.

Table I

ENTRY	CARBONYL	ALKYNYLIDE	HALOHYDRIN YIELD% (RATIO) <sup>a</sup>	ALKENYL CARBINOL YIELD% (RATIO) <sup>b</sup>
1		R-C≡C-M R=H M=MgBr	 83 (88:12) <sup>c</sup>	 80,92 <sup>d</sup> (1:2) <sup>e</sup> 85 (1:5.6) <sup>f</sup>
2		Me MgBr	94 (98:2)	72,97 <sup>d</sup> (1:3) <sup>e</sup> 75,89 <sup>d</sup> (3:1) <sup>f</sup> 85 (1:1) <sup>e,g,1</sup>
3		Li	94 (97:3)	90 (1:1) <sup>e</sup> 71 (1:1) <sup>e,g,1</sup>
4		Li	95 (97:3)	90 (1:1) <sup>e,k</sup> 76 (1:1) <sup>e,g</sup>
5		-MgBr	 78 <sup>h</sup>	 63, 89 <sup>d</sup> (1:4) <sup>e</sup>
6		-Li	 89 (96:4)	 93 (2:1) <sup>e</sup>
7		-Li	 86 <sup>h</sup>	 68 (1:1) <sup>e</sup>
8		-Li	 80	 46 <sup>e,g</sup>
9		-Li	 86	 76 (3:1) <sup>e</sup>

<sup>a</sup> Cis:trans as determined by GC. <sup>b</sup> Cis:trans for cyclic alcohols; undefined erythro:threo in acyclic alcohols as determined by GC. <sup>c</sup> Reaction conducted at ambient temperature instead of  $-78^{\circ}\text{C}$ . <sup>d</sup> Yield determined by GC. <sup>e</sup>  $\text{LiAlH}_4$ , NaOMe, THF, ambient temperature. <sup>f</sup>  $n\text{-BuLi}$ , DIBAL, THF, reflux. <sup>g</sup> Alkyne addition and reductive rearrangement carried out in a single operation. <sup>h</sup> Only one isomer observed. <sup>i</sup> 0.4 mole scale. <sup>j</sup> One mole scale. <sup>k</sup> Bromocyclohexanone gave nearly identical yields.

addition to  $\alpha$ -halocarbonyls<sup>14,15</sup> and in our present study, the halohydrin stereochemistry required for the rearrangement process is strongly favored, with ratios of  $>30:1$  found in most cases. Moreover, when compared with alkenyl carbanions, the alkynyl carbanions are less sterically encumbered and, as weaker bases, less likely to enter into yield-reducing, base-mediated side reactions. Second, several variations in substrate and nucleophile are possible. Cyclic  $\alpha$ -bromo or  $\alpha$ -chloro ketones and  $\alpha$ -chloro acid chlorides have been used successfully (Table I, entries 4 and 9). Conjugated and unconjugated alkynes are equally effective. The successful use of the former reagents is a particularly significant finding since it establishes a convenient route to dienes whose syntheses from 1-metallo alkadienes are complicated or precluded by the polymerization that attends metalation of 1-haloalkadienes.<sup>16</sup> While 1-metallo alkadienes can alternatively be prepared from the corresponding tin reagents,<sup>17</sup> a multistep sequence is required to produce homogeneous material. Third, only *E*-disubstituted alkenes are produced in this method, with no detectable contamination by the *Z* isomer. Furthermore, we have found that the

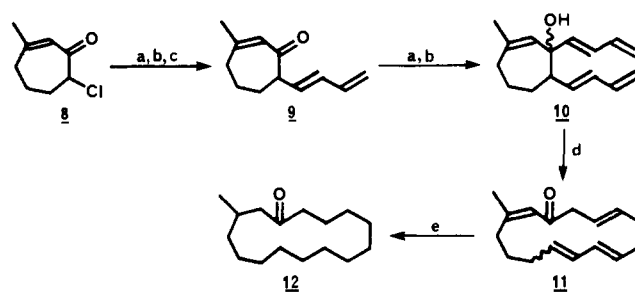
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Scheme III



<sup>a</sup> Lithium vinyl acetylide, THF,  $-78^{\circ}\text{C}$ . <sup>b</sup>  $\text{LiAlH}_4$ , NaOMe, THF, room temperature. <sup>c</sup>  $\text{CrO}_3 \cdot 2\text{Pyr}$ ,  $\text{CH}_2\text{Cl}_2$ . <sup>d</sup> KH, THF, 25 min, room temperature. <sup>e</sup>  $\text{H}_2$ , Pd/C.

reduction rearrangement can be effected by diisobutylaluminum hydride (DIBAL)<sup>10c</sup> as well as  $\text{LiAlH}_4$  (Table I, entries 1 and 2). Both reagents give essentially the same yields, although use of the former generally requires higher temperatures in order to achieve complete conversion. Importantly, in connection with the issue of product alkene geometry and substitution, the use of DIBAL in conjunction with an iodine quench<sup>10b,c</sup> provides 2-(1-iodo-1-propenyl)cyclohexanol (7b, R = Me), whereas as noted above, the regioisomeric iodide 6b (R = Me) is obtained in the case of  $\text{LiAlH}_4$ .<sup>10</sup> Therefore, through either further conversion of these iodides<sup>10c,18</sup> or their alane<sup>19</sup> or alanate<sup>20</sup> precursors, complete regio- and stereocontrol can be exercised in the preparation of  $\alpha$ -trisubstituted alkenyl carbonyls by this methodology. Finally, a particularly important attribute of this method is that it can be conducted easily on a mole scale (e.g., Table I, entry 2, 85% distilled). Moreover, we have found that the initial addition and the reduction rearrangement can be achieved in a single operation involving addition of the halo ketone to the metallo alkyne at low temperature followed by addition of  $\text{LiAlH}_4$  and subsequent warming to room temperature (Table I, entries 2-4 and 8).<sup>21</sup>

Integration of this methodology with our work in macroexplanation has led to a unique approach to the 15-membered ring carbocycle muscone<sup>23</sup> (Scheme III). Starting with chloro ketone 8,<sup>24</sup> addition of vinyl acetylide followed by in situ reductive rearrangement gave a mixture of trienyl alcohols (91%), which when subjected to Collins oxidation conditions,<sup>25</sup> cleanly produced ketone

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9 in 75% yield. Addition of a second equivalent of vinyl acetylide gave in 61% yield (95% based on unconsumed starting material) a 45:55 mixture of *trans* and *cis* alcohols, which were separately reduced (100%) to alcohols 10. When treated with KH in THF at room temperature,<sup>26</sup> both *trans*- and *cis*-10 gave a mixture of two *E/Z* isomers of the 15-membered tetraeneone 11 (61% and 40%, respectively). Catalytic hydrogenation of this mixture gave a 97% yield of muscone (12).

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### Observation of a Reversible Adsorbed Redox Couple Using Surface-Enhanced Raman Scattering: Pentaammine(pyridine)osmium(III)/(II) at Silver Electrodes

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We report surface-enhanced Raman scattering (SERS) for pentaamminepyridineosmium(III) and -(II) adsorbed on a silver electrode. This appears to be the first employment of SERS for following electron transfer with a simple adsorbed redox couple. We have been examining SERS of structurally simple adsorbates under electrochemically characterized conditions.<sup>1-3</sup> One objective is to relate SERS measurements to electrochemical phenomena; despite the recent proliferation of SERS studies,<sup>4</sup> few investigations of this type have been reported. Pentaammineosmium compounds<sup>5</sup> are particularly suitable for the present work since they are substitutionally inert in both III and II oxidation states and have formal potentials compatible with the potential range (ca. 0 to -1.0 V vs. the saturated calomel electrode, SCE) available at silver electrodes. Adsorbed redox couples having nitrogen heterocycle bridging groups constitute direct heterogeneous analogues of the much studied intramolecular redox systems in homogeneous solution.

Conventional conditions for the optimal appearance of SERS were employed,<sup>3,4a</sup> involving roughening the silver electrode by means of oxidation-reduction cycles using 0.1 M NaCl or NaBr supporting electrolytes, also containing 0.1-1.0 mM [Os(NH<sub>3</sub>)<sub>5</sub>py]Cl<sub>3</sub>·H<sub>2</sub>O<sup>5</sup> (py = pyridine) and 0.1 M HCl.<sup>6</sup> Raman excitation employed either 647- or 514-nm laser irradiation. All potentials quoted are vs. the SCE; other experimental details are given elsewhere.<sup>3,7</sup>

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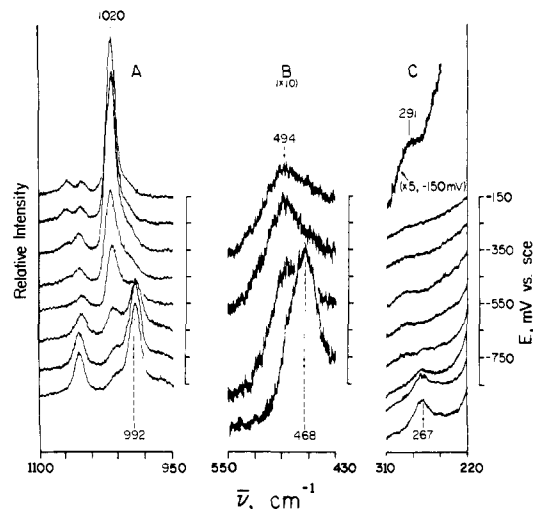
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**Figure 1.** Potential-dependent SERS of Os(NH<sub>3</sub>)<sub>5</sub>py III/II at roughened silver; 514.5-nm excitation, 100-mW incident power, scan speed 1 cm<sup>-1</sup> s<sup>-1</sup>, time constant 1 s, resolution 4 cm<sup>-1</sup>. Solution contained 0.1 mM Os(NH<sub>3</sub>)<sub>5</sub>py<sup>3+</sup> in 0.1 M NaBr and 0.1 M HCl (291-cm<sup>-1</sup> peak seen more clearly in  $\times 5$  top spectrum in C).

SERS spectra were recorded over the frequency range 140-3500 cm<sup>-1</sup> in 100-mV potential increments from -150 to -850 mV. A summary of some representative vibrational bands is given in Table I; typical spectra as a function of potential are shown in Figure 1.<sup>8</sup> Assignments are based on comparisons with spectra for structurally similar pyridine and ammine complexes<sup>9</sup> and from selective deuteration of the pyridine or ammonia ligands.<sup>3</sup> Aside from the appearance of the halide surface modes at 235 and 180 cm<sup>-1</sup> for chloride and bromide electrolytes, respectively, the spectral frequencies were essentially identical in both media. (This supports the assignment of the 291- and 267-cm<sup>-1</sup> vibrations to osmium-pyridine stretching rather than to surface-ligand modes.) At potentials positive of -500 mV, the SERS vibrational frequencies for adsorbed Os<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>py are closely similar to those seen for the bulk Raman and infrared spectra (Table I). However, notable spectral changes occurred as the potential was made more negative. In particular, the intensities of the Os-py stretching (291 cm<sup>-1</sup>), Os-NH<sub>3</sub> stretching (494 cm<sup>-1</sup>), and symmetric ring breathing (1020 cm<sup>-1</sup>) modes decreased sharply between -500 and -700 mV, being replaced by corresponding peaks having frequencies 20-30 cm<sup>-1</sup> lower. These changes could be entirely reversed by returning the potential to less negative values. In contrast, adsorbed pyridine shows little change ( $\leq 2$  cm<sup>-1</sup>) in SERS vibrational frequencies and only mild intensity changes over this potential region<sup>10</sup> (Table I).

These spectral changes are consistent with a one-electron reduction of the adsorbed Os(III) complex to the corresponding Os(II) species. Metal-ligand stretching modes commonly exhibit such a dependence upon oxidation state.<sup>9</sup> Of the various pyridine vibrations, the symmetric ring breathing mode is known to be sensitive to the coordinating environment, exhibiting decreasing frequencies as the electron density on the pyridine ring increases.<sup>11</sup> This latter effect is expected to be especially important for Os<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub>py on account of the high degree of  $\pi$ -bonding.<sup>5,12</sup>

(8) Essentially identical vibrational frequencies were obtained with supporting electrolytes containing 0.1 M chloride or bromide. However, the latter electrolyte was preferred for most measurements as it yielded markedly more intense SERS spectra at the more negative potentials ( $\sim -600$  mV) of particular interest here.<sup>3</sup>

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