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A Metal-Catalyzed Rearrangement of Alkene-Alkynes
and the Stereochemistry of Metallacyclobutene Ring Opening

by

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A Metal-Catalyzed Rearrangement of Alkene-Alkynes
and the Stereochemistry of Metallacyclobutene Ring Opening

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Abstract. A new molecular rearrangement is described that demonstrates how alkyl-metal-carbenes are generated when metal derivatives (here stabilized carbene-tungsten carbonyls) combine with acetylenes and olefins and shows that tungsten-carbenes not stabilized by heteroatoms insert into acetylenes. It reveals that this insertion can be remarkably stereo-selective.

With catalytic amounts of carbene-tungsten carbonyls, biphenyls substituted at the 2 and 2' positions by vinyl and acetylene groups yield isomeric 9-vinylphenanthrenes. With stoichiometric amounts, they yield 9-vinylphenanthrenes whose structures contain the carbene moiety of the metal-carbene.
We are reporting a new molecular rearrangement, outlined in general form as equation 1 and illustrated by a specific example in equation 2, a hybrid of the metal-catalyzed acetylene polymerization\(^1\) and olefin metathesis\(^2\) reactions. It demonstrates how alkyl-metal-carbenes are generated when metal derivatives (here stabilized carbene-tungsten carbonyls)\(^3\) combine with acetylenes and olefins,\(^{1d,4,5}\) and it shows that tungsten-carbenes not stabilized by heteroatoms insert into acetylenes, the essential postulate underlying the proposition that the acetylene polymerization is an olefin metathesis.\(^{1b-d,4,5}\) It reveals that this insertion can be remarkably stereoselective in the sense indicated in equation 3.\(^6\)
The rearrangement is presumed to follow the pathways in Scheme I after an initiation involving similar steps, summarized as equation 4.\textsuperscript{11} Table I records the yields obtained (and where relevant the stereochemistries) with various molecules \textsuperscript{1,21,29} and initiators 2. That equation 4 does accurately depict the initiation, and consequently that Scheme I probably does indicate how the reaction works, is demonstrated by the experiments summarized in

Table II, which show that examples of molecules 1 combine with stoichiometric amounts of metal-carbenes 2 to give the products 3 of equation 4.

\begin{equation}
\text{Scheme I}
\end{equation}
The experiments define for the first time what the stereochemistry is of the pericyclic transformation of a metallacyclobutene to a metallabutadiene when there are no stabilizing heteroatoms. This stereochemistry should be embodied in the structures of acetylene polymers formed by metathesis reactions, but except for that of polyacetylene itself, the structures of these polymers have not been positively defined. The high stereoselectivity recorded in Table I [95% at 50 °C when the initiator is pentacarbonyl(diphenylmethylene)tungsten] implies that when the cyclobutene in equation 3 opens, the methyl prefers to rotate toward the metal. Possibly its C-H is attracted to the coordinatively unsaturated center.

Acknowledgment. We are grateful to the National Science Foundation (grant CHE 81-08998) and the U.S. Navy, Office of Naval Research, for supporting this work.
References and Notes


(6) Pentacarbonylchromium- and tungsten-carbenes carrying as stabilizers on the carbene carbon an alkoxyl or two aryls insert into vnamines much as in equation 3 (the stereochemistry of some of these insertions have been analyzed) and react with carbon-substituted alkynes to give phenols, indenes, furans, and cyclobutenones. The only metal-monoalkylcarbene to have been added to an acetylene is a tantalum neopentyldiene, but the stereochemistry of the single reported adduct is unknown.


(11) This formulation derives from previous studies showing that metal-carbenes induce acetylenes to polymerize,\textsuperscript{1c} that acetylenes induce metal derivatives, including metal-carbenes, to metathesize olefins,\textsuperscript{4} that stabilized metal-carbenes add faster to acetylenes than to olefins,\textsuperscript{5} that the carbons of metal-carbenes bond preferentially to the less substituted ends of acetylenes\textsuperscript{12} (as also olefins\textsuperscript{13}), and that olefinic metal-carbenes give cycloolefins.\textsuperscript{14,15} An alternative is possible, in which after the initiation external metal carbenes attack the olefin and internal metal carbenes attack the acetylene, but the regiospecificity of the first of these steps would be peculiar for the substrate \( \text{I, } R = R' = \text{CH}_3 \).\textsuperscript{17}


(15) Related metal-carbenes that are stabilized by heteroatoms chelate to pendant olefins and yield cyclopropanes.\textsuperscript{16}

(17) The translationally invariant structures of the polymers of 1-methylcyclobutene\(^{18}\) and trans-1-methyl-cyclooctene\(^{19}\) and the specific union of the less-substituted with the more-substituted moieties when 2-methyl-1-pentene metathesizes with 2-methyl-2-butene\(^{20}\) imply that the carbon end of a metal-carbene (disubstituted, not monosubstituted as in the alternative considered here) bonds preferentially to the less-substituted end of a trisubstituted double bond.


(21) Enynes \(\text{I}^\text{I}\) were prepared from \((\text{C}_6\text{H}_5)_3\text{PCHR}^+\text{Br}^-/\text{NaNH}_2\)\(^{23}\) and monoacetals made from \([1,1'-	ext{biphenyl}]-2,2'-	ext{dicarboxaldehyde}\)\(^{24}\) and 0.8 equiv ethylene glycol or 2,2-dimethyl-1,3-propanediol (p-TsOH, \(\text{C}_6\text{H}_6\)). Hydrolysis (5% aq HCl/THF) and then LiCl\(_2\)CPO(OEt)\(_2\)/\(\text{t-BuLi}\)\(^{25}\) (2.2 equiv) or \(((\text{C}_6\text{H}_5)_3\text{PCH}_2\text{Br})^+\text{Br}^-/\text{t-BuOK}\)\(^{26}\) (2 equiv) gave \(\text{I}^\text{I}\).
(22) Authentic samples were prepared from phenanthrene-9-carboxaldehyde.\textsuperscript{23,27} The 9-(1-propenyl)phenanthrenes were 86\% one isomer, presumably cis.\textsuperscript{23} The olefin-olefin proton couplings (cis, $J = 11.2$ Hz, and trans, $J = 15.4$ Hz) support this assignment.\textsuperscript{28}


(29) The aliphatic enynes 7-nonen-1-yne and 6-octen-1-yne when combined with 0.01 equiv (CO)$_5$W=C(C$_6$H$_5$)(OCH$_3$) under similar conditions and at even higher dilution (1.2 x $10^{-3}$ M) gave no vinyl cyclohexene (GLC comparison), but > 90\% yield of oligomers including benzenoid trimers ($\delta$ 6.80). No high molecular weight polymers were recognized by gel-permeation chromatography.

(30) When $R'' = $ C$_6$H$_5$, the crude reaction mixture ($^1$H NMR analysis) contained the enol ethers (1.0 : 1.8 mixture of $E$ : $Z$)$^{32}$ and only traces of the ketone 9-phenanthryl-CH$_2$COC$_6$H$_5$ ($\delta$ 4.78).\textsuperscript{31} When $R'' = $ CH$_3$ it contained the corresponding ketone [$\delta$ 2.14 (s, 2 H), 4.15 (s, 2 H), 4.15 (s, 2 H), 7.6 - 8.8 (m, 9 H)] and no enol ether.\textsuperscript{32}
The $^1$H NMR spectrum (CDCl$_3$) of the $Z$-isomer$^{32}$ includes $\delta$ 3.58 (s, 3 H), 6.74 (s, 1 H), 6.8 - 8.8 (m, 14 H). Resonances exhibited by the mixture at 3.99 (s, 3 H), 6.22 (s, 1 H), 6.8 - 8.8 (m, 14 H) are assigned to the E-isomer.

Authentic samples of 9-vinylphenanthrenes $^3$ were prepared as follows: $^3$ (R$^\prime'' = CH_3$, X = OCH$_3$) from phenanthrene-9-carboxaldehyde and (C$_6$H$_5$)$_3$P$^+CHCH_3(OCH_3)Cl^-$/t-BuOK$^{33}$; $^3$Z-3 (R$'' = C_6H_5$, X = OCH$_3$) from 9-bromophenanthrene and n-BuLi, then styrene oxide$^{34}$, oxidization with Pyr.HCl.CrO$_3$, and stereospecific O-methylation using t-BuOK/HMPA/dimethyl sulfate; $^3$ 3 (R$'' = X = C_6H_5$) from phenanthrene-9-carboxaldehyde and (C$_6$H$_5$)$_3$PCH(C$_6$H$_5$)$_2$Br$^{37}$/NaNH$_2$. All were characterized satisfactorily by $^1$H NMR.


IR$^{41}$ and $^1$H NMR$^{41a,42}$ spectra have been used to assign stereochemistries to poly(phenylacetylene)s and $^{13}$C NMR spectra to
poly(t-butylacetylene)s, but the basis for the assignments is not rigorous.


Table I. Yields and Stereochemistries of 9-Vinylphenanthrenes Obtained According to Equation 1 from Enynes 121 and Catalytic Amounts of Metal-Carbenes 2 in which R'' = C6H5.

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>X</th>
<th>yield (%)</th>
<th>product % cis</th>
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<tr>
<td>H</td>
<td>H</td>
<td>OCH3</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>C6H5</td>
<td>18</td>
<td></td>
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<tr>
<td>CH3(H)</td>
<td>H(CH3)</td>
<td>OCH3</td>
<td>26</td>
<td>78</td>
</tr>
<tr>
<td>CH3(H)</td>
<td>H(CH3)</td>
<td>C6H5</td>
<td>19</td>
<td>95</td>
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<tr>
<td>CH3</td>
<td>CH3</td>
<td>OCH3</td>
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<td></td>
</tr>
<tr>
<td>CH3</td>
<td>CH3</td>
<td>C6H5</td>
<td>24</td>
<td></td>
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</table>

Enynes 1 (1 equiv) and n-nonane (0.5 - 1.0 equiv, internal standard for GLC analysis) were diluted to 0.10 M with toluene, added to metal-carbenes 2 (0.01 equiv), degassed, and sealed in a vacuum. When X was OCH3, reactions were run for 18 h at 75 °C, and when C6H5, for 16 h at 50 °C. The products were identified by comparing GLC retention times (30 m x 0.316 mm capillary column coated with 0.25 µm Carbowax 20 M) and 1H NMR spectra with those of authentic samples (see note 22). Yields were determined by GLC. Stereochemistries were analyzed by 1H NMR [CH3 resonances in 9-(1-propenyl)phenanthrene (see note 22) in CDCl3: cis, δ 1.83 (dd, 7.0 and 1.8 Hz); trans, δ 2.04 (dd, 6.6 and 1.7 Hz)]. Initially 56 % cis.
Table II. Yields of 9-Vinylphenanthrenes 2 from Reactions of Molecules 1 with Stoichiometric Amounts of Metal-Carbenes 2 (Equation 4). a

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>R''</th>
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<tr>
<td>H</td>
<td>H</td>
<td>C₆H₅</td>
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<tr>
<td>H</td>
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<td>OCH₃</td>
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<tr>
<td>H</td>
<td>H</td>
<td>C₆H₅</td>
<td>C₆H₅</td>
<td>51</td>
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<tr>
<td>CH₃(H)</td>
<td>H(CH₃)</td>
<td>C₆H₅</td>
<td>OCH₃</td>
<td>41</td>
</tr>
<tr>
<td>CH₃(H)</td>
<td>H(CH₃)</td>
<td>CH₃</td>
<td>OCH₃</td>
<td>40</td>
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<tr>
<td>CH₃(H)</td>
<td>H(CH₃)</td>
<td>C₆H₅</td>
<td>C₆H₅</td>
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aDegassed 0.05 M solutions of 1 (1 equiv) and metal-carbenes 2 (1 equiv) in toluene were heated in an evacuated ampoule. When X was C₆H₅, reactions were run at 50 °C for 16 h, and when OCH₃, at 75 °C for 24 h, except that for the next-to-last entry the time was 18 h. Evaporation of solvent and chromatography on Florisil with pentane-methylene chloride gave 2 when R'' = X = C₆H₅, and the ketones 9-phenanthryl-CH₂COR'' corresponding to enol ethers 2 when R'' = C₆H₅ or CH₃ and X = OCH₃ (see note 30). Products were identified by comparing ¹H NMR spectra with those of authentic samples (see note 32). bYields of isolated products.

cInitially 56 % cis.
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