

$J_{\text{HaH}\beta} = 6.5$ Hz) centered at δ 5.54. After 16 h, an ice cold NaHCO_3 workup gave 3.58 g (94%) of **2e** as a pale yellow solid, mp 40–42 °C. To demonstrate the utility of this method for the preparation of vinyl fluorides, the sulfoxide **3e**, obtained by MCPBA oxidation of **2e**, was heated at 160 °C for 40 min (N_2) to provide an 80% isolated yield of 1-fluoro-2-tetradecylethylene (**7**).^{6d}

In summary, we have described a new reaction of sulfoxides which provides a novel synthesis of α -fluoro thioethers (**2**) that can be used to prepare vinyl fluorides. The complete scope and mechanism of this new reaction are currently under study and will be described in a subsequent report.

Caution: Please note that DAST has been reported to be thermally unstable at elevated temperatures (see ref 12).

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Supplementary Material Available: General synthetic procedures as well as spectral data and physical properties for **2a–j**, **3a,b,e–l**, **4m,n**, and **7** (8 pages). Ordering information is given on any current masthead page.

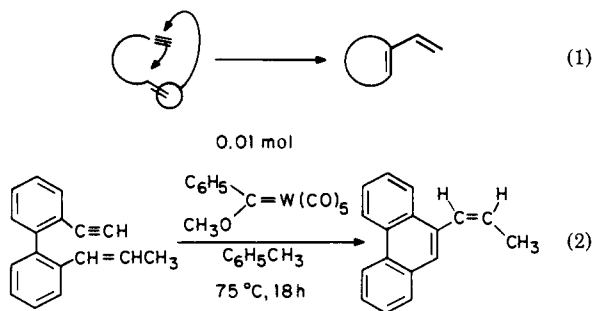
Metal-Catalyzed Rearrangement of Alkene-Alkynes and the Stereochemistry of Metallacyclobutene Ring Opening

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We are reporting a new molecular rearrangement, outlined in general form as eq 1 and illustrated by a specific example in eq 2, a hybrid of the metal-catalyzed acetylene polymerization¹ and



olefin metathesis² reactions. It demonstrates how metal-alkyl-carbenes are generated when metal derivatives (here stabilized carbene-tungsten carbonyls)³ combine with acetylenes and olefins,^{1d,4,5} and it shows that acetylenes insert into tungsten-carbenes that are not stabilized by heteroatoms, the essential postulate underlying the proposition that the acetylene polymerization is

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Scheme I

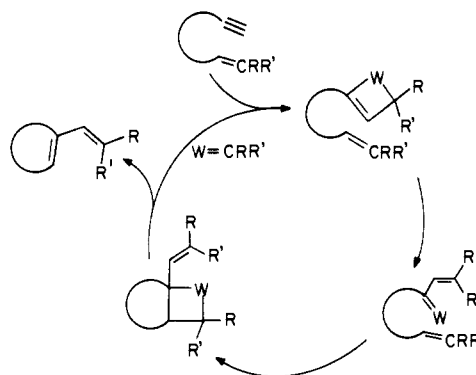


Table I. Yields and Stereochemistries of 9-Vinylphenanthrenes Obtained according to Eq 1 from Enynes **1**²¹ and Catalytic Amounts of Metal-Carbenes **2** in which R'' = C₆H₅^a

1		X in 2	yield, % ^b	product, % cis ^c
R	R'			
H	H	OCH ₃	31	
H	H	C ₆ H ₅	18	
CH ₃ (H) ^d	H(CH ₃)	OCH ₃	26	78
CH ₃ (H)	H(CH ₃)	C ₆ H ₅	19	95
CH ₃	CH ₃	OCH ₃	24	
CH ₃	CH ₃	C ₆ H ₅	24	

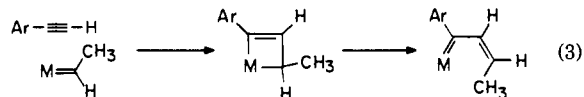
^aEnynes **1** (1 equiv) and *n*-nonane (0.5–1.0 equiv, internal standard for GLC analysis) were diluted to 0.10 M with toluene, added to metal-carbenes **2** (0.01 equiv), degassed, and sealed in a vacuum. When X was OCH₃, reactions were run for 18 h at 75 °C, and when C₆H₅, for 16 h at 50 °C. The products were identified by comparing GLC retention times (30 m × 0.316 mm capillary column coated with 0.25 μm Carbowax 20 M) and ¹H NMR spectra with those of authentic samples (see ref 22). ^bYields were determined by GLC. ^cStereochemistries were analyzed by ¹H NMR [CH₃ resonances in 9-(1-propenyl)phenanthrene (see ref 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)]. ^dInitially 56% cis.

Table II. Yields of 9-Vinylphenanthrenes **3** from Reactions of Molecules **1** with Stoichiometric Amounts of Metal-Carbenes **2** (Eq 4)^a

1		2		yield, % ^b
R	R'	R''	X	
H	H	C ₆ H ₅	OCH ₃	50
H	H	CH ₃	OCH ₃	42
H	H	C ₆ H ₅	C ₆ H ₅	51
CH ₃ (H) ^c	H(CH ₃)	C ₆ H ₅	OCH ₃	41
CH ₃ (H)	H(CH ₃)	CH ₃	OCH ₃	40
CH ₃ (H)	H(CH ₃)	C ₆ H ₅	C ₆ H ₅	40

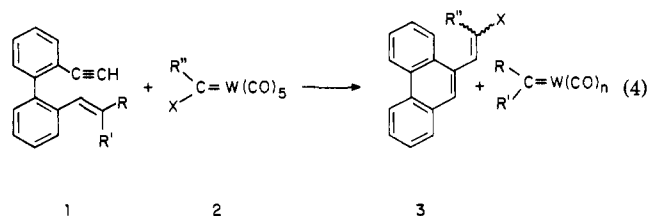
^aDegassed 0.05 M solutions of **1** (1 equiv) and metal-carbenes **2** (1 equiv) in toluene were heated in an evacuated ampule. When X was C₆H₅, reactions were run at 50 °C for 16 h, and when OCH₃, at 75 °C for 24 h, except that for the next-to-last entry the time was 18 h. Evaporation of solvent and chromatography on Florisil with pentane-methylene chloride gave **3** when R'' = X = C₆H₅ and the ketones (9-phenanthryl)-CH₂COR'' corresponding to enol ethers **3** when R'' = C₆H₅ or CH₃ and X = OCH₃ (see ref 30). Products were identified by comparing ¹H NMR spectra with those of authentic samples (see ref 32). ^bYields of isolated products. ^cInitially 56% cis.

an olefin metathesis.^{1b–d,4,5} It reveals that this insertion can be remarkably stereoselective in the sense indicated in eq 3.⁶



(6) Pentacarbonylchromium- and tungsten-carbenes carrying as stabilizers on the carbene carbon an alkoxy or two aryls insert into ynamines such as in eq 3⁷ (the stereochemistries of some of these insertions have been analyzed⁸) and react with carbon-substituted alkynes to give phenols, indenes, furans, and cyclobutenones.^{7,9} The only metal-monoalkylcarbene to have been added to an acetylene is a tantalum neopentylidene, but the stereochemistry of the single reported adduct is unknown.¹⁰

The rearrangement is presumed to follow the pathways in Scheme I after an initiation involving similar steps, summarized as eq 4.¹¹ Table I records the yields obtained (and where relevant



the stereochemistries) with various initiators **2** and molecules **1**,²¹

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(11) This formulation derives from previous studies showing that metal-carbenes induce acetylenes to polymerize,¹⁶ that acetylenes induce metal derivatives, including metal-carbenes, to metathesize olefins,⁴ that stabilized metal-carbenes add faster to acetylenes than to olefins,⁵ that the carbons of metal-carbenes bond preferentially to the less-substituted ends of acetylenes¹² (as also olefins¹³), and that olefinic metal-carbenes give cycloolefins.^{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 regioselectivity of the first of these steps would be peculiar for the substrate **1**, $R = R' = \text{CH}_3$.¹⁷

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(17) The translationally invariant structures of the polymers of 1-methylcyclobutene¹⁸ and *trans*-1-methylcyclooctene¹⁹ and the specific union of the less-substituted with the more-substituted moieties when 2-methyl-1-pentene metathesizes with 2-methyl-2-butene²⁰ 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.

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(21) Enynes **1** were prepared from $(\text{C}_6\text{H}_5)_3\text{PCHRR}^+\text{Br}^-/\text{NaNH}_2$ ²³ and monoacetals made from [1,1'-biphenyl]-2,2'-dicarboxaldehyde²⁴ and 0.8 equiv of ethylene glycol or 2,2-dimethyl-1,3-propanediol (*p*-TsOH, C_6H_6). Hydrolysis (5% aqueous HCl/THF) and then $\text{LiCl}_2\text{CPO}(\text{OEt})_2/n\text{-BuLi}$ ²⁵ (2.2 equiv) or $(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{Br}^+\text{Br}^-/t\text{-BuOK}$ ²⁶ (2 equiv) gave **1**.

(22) Authentic samples were prepared from phenanthrene-9-carboxaldehyde.^{23,27} The 9-(1-propenyl)phenanthrenes were 86% one isomer, presumably *cis*.²³ The olefin-olefin proton couplings (*cis*, $J = 11.2$ Hz, and *trans*, $J = 15.4$ Hz) support this assignment.²⁸

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which were chosen for study when two aliphatic enynes failed to rearrange, seemingly oligomerizing instead.²⁹ The presumption was that the restricted bond rotations in **1** would favor intramolecular cyclization. That eq 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 eq 4.³⁰

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.⁶ This stereochemistry should be embodied in the structures of acetylene polymers formed by metathesis reactions, but excepting polyacetylene itself,³⁸ whose formation may not involve the steps in eq 3,³⁹ the structures of these polymers have not been defined conclusively.⁴⁰ The high stereoselectivity recorded in Table I [95% at 50 °C when the initiator is pentacarbonyl(diphenylmethylene)tungsten] implies that when the cyclobutene in eq 3 opens, the methyl prefers to rotate toward the metal. Possibly one of its C-H bonds is attracted to the coordinatively unsaturated metal center.⁴⁵

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(29) The aliphatic enyne 6-octen-1-yne when combined with 0.01 or 1.0 equiv of $(\text{CO})_5\text{W}=\text{C}(\text{C}_6\text{H}_5)(\text{OCH}_3)$, or 7-nonen-1-yne when combined with 0.01 equiv under similar conditions and at even higher dilution (1.2×10^{-3} M), gives no vinylcyclohexene (GLC comparison) but >90% yield of oligomers including benzenoid trimers (δ 6.80). No high molecular weight polymers were recognized by gel-permeation chromatography.

(30) When $R'' = \text{C}_6\text{H}_5$, $X = \text{OCH}_3$, the crude reaction mixture (¹H NMR analysis, CDCl_3) contained the enol ethers (1.0:1.8 mixture of *E/Z* when $R = R' = \text{H}$ and 1.0:2.7 when $R, R' = \text{CH}_3, \text{H}$)³² and only traces of the ketone 9-phenanthryl- $\text{CH}_2\text{COC}_6\text{H}_5$ (δ 4.78).³¹ When $R'' = \text{CH}_3$, it contained the corresponding ketone [δ 2.14 (s, 3 H), 4.15 (s, 2 H), 7.6-8.8 (m, 9 H)] and no enol ether.³²

(31) The ¹H NMR spectrum (CDCl_3) of the *Z* isomer³² includes δ 3.58 (s, 3 H), 6.74 (s, 1 H), and 6.8-8.8 (m, 14 H). Resonances exhibited by the mixture at δ 3.99 (s, 3 H), 6.22 (s, 1 H), and 6.8-8.8 (m, 14 H) are assigned to the *E* isomer.

(32) Authentic samples of 9-vinylphenanthrenes **3** were prepared as follows: **3** ($R'' = \text{CH}_3$, $X = \text{OCH}_3$) from phenanthrene-9-carboxaldehyde and $(\text{C}_6\text{H}_5)_3\text{P}^+\text{CHCH}_3(\text{OCH}_3)\text{Cl}^-/t\text{-BuOK}$,³³ (*Z*)-**3** ($R'' = \text{C}_6\text{H}_5$, $X = \text{OCH}_3$) from 9-bromophenanthrene and *n*-BuLi, then styrene oxide,³⁴ oxidation with $\text{Pyr}/\text{HCl}/\text{CrO}_3$,³⁵ and stereospecific *O*-methylation using *t*-BuOK/HMPA/dimethyl sulfate;³⁶ **3** ($R'' = X = \text{C}_6\text{H}_5$) from phenanthrene-9-carboxaldehyde and $(\text{C}_6\text{H}_5)_3\text{PCH}(\text{C}_6\text{H}_5)_2^+\text{Br}^-/\text{NaNH}_2$. All were characterized satisfactorily by ¹H NMR.

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