$J_{H\alpha H\beta}$ = 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).

Acknowledgment. We thank Prof. Robert E. Ireland and Prof. Victor J. Hruby for helpful discussions.

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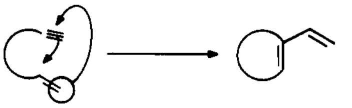
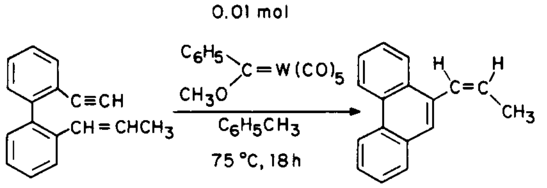
We are reporting a new molecular rearrangement, outlined in general form as eq 1 and illustrated by a specific example in eq 2, a hybrid of the metal-catalyzed acetylene polymerization[1] and

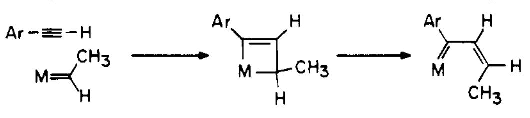


(1)



(2)

olefin metathesis[2] reactions. It demonstrates how metal-alkylcarbenes 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 an olefin metathesis.[1b–d,4,5] It reveals that this insertion can be remarkably stereoselective in the sense indicated in eq 3.[6]



(3)

Scheme I

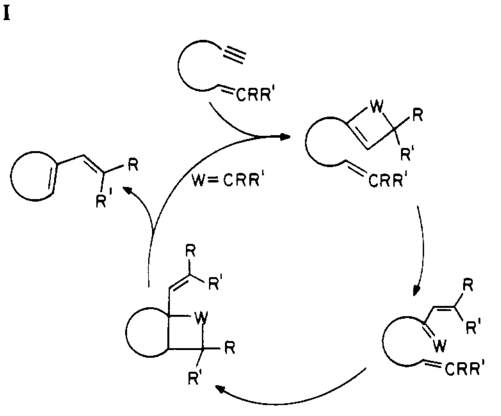


Table I. Yields and Stereochemistries of 9-Vinylphenanthrenes Obtained according to Eq **1** from Enynes **1**[21] and Catalytic Amounts of Metal–Carbenes **2** in which R″ = C_6H_5[a]

1				
R	R′	X in **2**	yield, %[b]	product, % cis[c]
H	H	OCH_3	31	
H	H	C_6H_5	18	
CH_3(H)[d]	H(CH_3)	OCH_3	26	78
CH_3(H)	H(CH_3)	C_6H_5	19	95
CH_3	CH_3	OCH_3	24	
CH_3	CH_3	C_6H_5	24	

[a] 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 OCH_3, reactions were run for 18 h at 75 °C, and when C_6H_5, 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). [b] Yields were determined by GLC. [c] Stereochemistries were analyzed by ^1H NMR [CH_3 resonances in 9-(1-propenyl)phenanthrene (see ref 22) in $CDCl_3$: cis δ 1.83 (dd, 7.0 and 1.8 Hz); trans δ 2.04 (dd, 6.6 and 1.7 Hz)]. [d] Initially 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**		
R	R′	R″	X	yield, %[b]
H	H	C_6H_5	OCH_3	50
H	H	CH_3	OCH_3	42
H	H	C_6H_5	C_6H_5	51
CH_3(H)[c]	H(CH_3)	C_6H_5	OCH_3	41
CH_3(H)	H(CH_3)	CH_3	OCH_3	40
CH_3(H)	H(CH_3)	C_6H_5	C_6H_5	40

[a] Degassed 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 C_6H_5, reactions were run at 50 °C for 16 h, and when OCH_3, 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 = C_6H_5 and the ketones (9-phenanthryl)-CH_2COR'' corresponding to enol ethers **3** when R″ = C_6H_5 or CH_3 and X = OCH_3 (see ref 30). Products were identified by comparing ^1H NMR spectra with those of authentic samples (see ref 32). [b] Yields of isolated products. [c] Initially 56% cis.

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(6) Pentacarbonylchromium- and tungsten-carbenes carrying as stabilizers on the carbene carbon an alkoxyl or two aryls insert into ynamines much as in eq 3[7] (the stereochemistries of some of these insertions have been analyzed[8]) 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]

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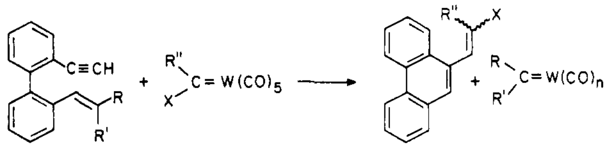
The rearrangement is presumed to follow the pathways in Scheme I after an initiation involving similar steps, summarized as eq 4.[11] Table I records the yields obtained (and where relevant the stereochemistries) with various initiators **2** and molecules **1**,[21] which were chosen for study when 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]



(4)

1 2 3

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]

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.

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(21) Enynes **1** were prepared from $(C_6H_5)_3PCHRR'^+Br^-/NaNH_2$[23] and monoacetals made from [1,1'-biphenyl]-2,2'-dicarboxaldehyde[24] 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 $LiCl_2CPO(OEt)_2/n$-BuLi[25] (2.2 equiv) or $((C_6H_5)_3PCH_2Br)^+Br^-/t$-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, presumbably 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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(30) When R'' = C_6H_5, X = 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' = H and 1.0:2.7 when R, R' = CH_3, H)[32] and only traces of the ketone 9-phenanthryl-$CH_2COC_6H_5$ (δ 4.78).[31] When R'' = 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 isomer[32] 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'' = CH_3, X = OCH_3) from phenanthrene-9-carboxaldehyde and $(C_6H_5)_3P^+CHCH_3(OCH_3)Cl^-/t$-BuOK;[33] ($Z$)-**3** (R'' = C_6H_5, X = OCH_3) from 9-bromophenanthrene and n-BuLi, then styrene oxide,[34] oxidization with $Pyr/HCl/CrO_3$,[35] and stereospecific O-methylation using t-BuOK/HMPA/dimethyl sulfate;[36] **3** (R'' = X = C_6H_5) from phenanthrene-9-carboxaldehyde and $(C_6H_5)_3PCH(C_6H_5)_2{}^+Br^-$[37]$/NaNH_2$. All were characterized satisfactorily by ^1H NMR.

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