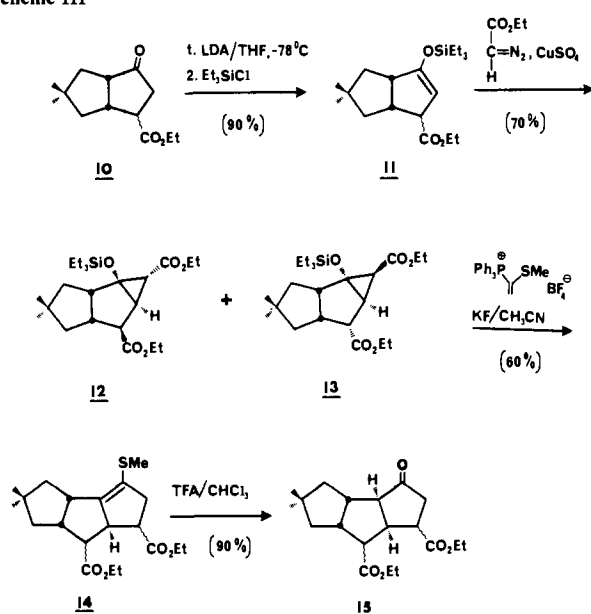


Scheme III



amount of 18-crown-6 in refluxing acetonitrile, high yields of bicyclo[3.3.0]octenes **9** were obtained. The bicyclooctenyl sulfides produced from the reaction with **8** could be easily hydrolyzed to the corresponding bicyclooctanones **10** with trifluoroacetic acid in chloroform.<sup>13</sup>

The stereochemistry at the ring juncture in **9b** was fixed by the cyclopropanation reaction, and in **10b**, the more stable *cis* fusion is required. While the stereochemistry of the carboxy group in **9** and **10** is mixed ( $\beta/\alpha = 2/1$ ),<sup>14</sup> the less thermodynamically stable  $\alpha$ -isomer could be epimerized to the  $\beta$ -isomer. Alternatively, the carbon atom bearing the ester group could be further transformed into a carbonyl group.<sup>15</sup>

The conditions for the disilylation-trapping step are quite well-defined experimentally. The 18-crown-6 ether is needed to help solubilize the potassium fluoride. The use of more acidic desilylation agents, such as *n*-Bu<sub>4</sub>F, was deleterious to the reaction of **6b**, since the intermediate  $\gamma$ -oxo ester enolate was either protonated or equilibration of ester-ketone enolates occurred.

The potential of this strategy for the construction of functionalized tricyclo[6.3.0.0<sup>2,6</sup>]undecanes ("linear triquinanes"<sup>16</sup>) prompted us to carry out a reiterative [3 + 2] annulation as outlined in Scheme III.

Thus, the addition of carboethoxycarbene to the kinetic silyl enol ethers **11** of bicyclooctanones **10a** (2:1 mixture of  $\beta$ - and  $\alpha$ -carboxy isomers, respectively) afforded the expected tricyclic diesters **12** and **13** (ca. 2:1 ratio, respectively) in 70% yield from **10a**. It should be mentioned that the observed stereoselectivity for this reaction is the one expected on steric grounds and agrees with the reported antisiselectivity of carboethoxycarbene.<sup>17</sup> Treatment of the (silyloxy)cyclopropane esters **12** and **13** with the thio-substituted vinylphosphonium salt **8** under the conditions described for the [3 + 2] annulation provided the tricyclic vinyl sulfides **14** (mixture of all four possible isomers). Subsequent hydrolysis gave the corresponding tricyclo[6.3.0.0<sup>2,6</sup>]undecanones **15** in good overall yield. It should be noted that the *cis,anti* ring

fusion of the final products **15** is secured from that of the starting tricyclic (silyloxy)cyclopropane esters **12** and **13**.

In summary, the present strategy provides a mild and expedient route for the construction of functionalized bicyclo[3.3.0]octanes and tricyclo[6.3.0.0<sup>2,6</sup>]undecanes in high yield. Work is under way to elaborate the resulting intermediates into suitable precursors for the synthesis of naturally occurring compounds and to extend the present methodology to other ring systems.

**Acknowledgment.** We acknowledge NSF for partial support of a Bruker WM-360 FT NMR spectrometer. E.L. thanks the American Chemical Society for a grant to assist his participation at the 188th National Meeting of the American Chemical Society, Philadelphia, PA, Aug 26-31, 1984.

**Supplementary Material Available:** Characterization data on all new compounds (10 pages). Ordering information is given on any current masthead page.

## (Diethylamino)sulfur Trifluoride in Organic Synthesis.

### 2. The Transformation of Sulfoxides to $\alpha$ -Fluoro Thioethers<sup>1</sup>

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New methods for the introduction of fluorine into organic molecules are of increasing importance, especially for the design of novel enzyme-activated irreversible inhibitors.<sup>2</sup> Several  $\beta$ -fluorophenethylamines,<sup>1</sup>  $\beta$ -fluoroamino acids,<sup>3</sup> 3-fluoroallylamines,<sup>4</sup> and amino acids<sup>5</sup> (vinyl fluorides) have proven to be specific irreversible inhibitors of selected enzymes. A convenient synthetic route to vinyl fluorides<sup>6</sup> would make molecules containing this functionality more attractive as synthetic targets.

This activity has prompted us to explore new routes to fluoro compounds utilizing (diethylamino)sulfur trifluoride (DAST).<sup>1</sup> We wish to report a novel synthetic transformation that provides the previously unreported  $\alpha$ -fluoro thioethers **2**, which are convenient precursors to vinyl fluorides via the thermolysis of the corresponding fluoro sulfoxides (**3**).<sup>6d</sup> This transformation offers a superior alternative to the Wittig reaction<sup>6a</sup> for the synthesis of terminal vinyl fluorides.

We reasoned that DAST should react with sulfoxides as does acetic anhydride in the Pummerer rearrangement<sup>7</sup> and found that the proposed transformation was readily accomplished. For example, when methyl phenyl sulfoxide was treated with DAST in chloroform at room temperature for 24 h and then at 50 °C for several hours (until complete by <sup>1</sup>H NMR), an 85% yield of fluoromethyl phenyl sulfide (**2a**) resulted.<sup>8</sup> Sulfide **2a** was readily

(1) For part I, see: LeTourneau, M. E.; McCarthy, J. R. *Tetrahedron Lett.* **1984**, 25, 5227.

(2) (a) Seiler, N.; Jung, M. J.; Koch-Weser, J. "Enzyme-Activated Irreversible Inhibitors"; Elsevier/North-Holland Biomedical Press: Amsterdam, 1978. (b) Rando, R. R. *Pharmacol. Rev.* **1984**, 36, 111.

(3) Kollonitsch, J. In "Biomedical Aspects of Fluorine Chemistry"; Filler, R., Kobayashi, Y., Eds; Elsevier Biomedical Press: Amsterdam, 1982; p 93.

(4) McDonald, I. A.; Lacoste, J. M.; Bey, P.; Wagner, J.; Zreika, M.; Palfreyman, M. G. *J. Am. Chem. Soc.* **1984**, 106, 3354.

(5) Bey, P.; Fozard, J.; Lacoste, J. M.; McDonald, I. A.; Zreika, M.; Palfreyman, M. G. *J. Med. Chem.* **1984**, 27, 9.

(6) For synthetic methods to vinyl fluorides, see ref 4 and 5 as well as, for an example of the Wittig reaction: (a) Burton, D. J.; Greenlimb, P. E. *J. Org. Chem.* **1975**, 40, 2797. This method requires extremely dry solvents to obtain satisfactory and reproducible yields. (b) Schlosser, M. *Tetrahedron* **1978**, 34, 3. (c) Hayashi, S.; Nakai, T.; Ishikawa, N.; Burton, D. J.; Nae, D. G.; Kesling, H. S. *Chem. Lett.* **1979**, 983. (d) Reutrakul, V.; Rukachaisirkul, V. *Tetrahedron Lett.* **1983**, 24, 725.

(7) For reviews of the Pummerer rearrangement, see: (a) Russell, G. A.; Mikol, J. G. *Mech. Mol. Migr.* **1968**, 1, 157. (b) Durst, T. *Adv. Org. Chem.* **1969**, 6, 356.

(11) Schweizer, E. E.; Bach, R. D. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. 5, p 1145.

(12) Prepared by a modification of the procedure given in ref 7c.

(13) Grayson, J. I.; Warren, S. J. *Chem. Soc., Perkin Trans. 1* **1977**, 2263.

(14) These results indicate that there is scrambling in the configuration of the carbanionic center during the reaction and that the observed ratio must, therefore, reflect the relative stabilities of the  $\alpha$ - and  $\beta$ -carboxy isomers.

(15) Trost, B. M.; Tamaru, Y. *J. Am. Chem. Soc.* **1975**, 97, 3528.

(16) For a recent review on polyquinane chemistry, see: Paquette, L. *Top. Curr. Chem.* **1984**, 119.

(17) (a) Moss, R. A. *Sel. Org. Transform.* **1970**, 1, 35 ff. (b) Closs, G. L. "Structures of Carbenes and the Stereochemistry of Carbene Additions"; Eliel, E. L., Allinger, N. L., Eds.; Interscience: New York, 1968; Vol. 3, pp 193 ff.

Table I. Formation of  $\alpha$ -Fluoro Thioethers (**2**) and Conversion to the Corresponding Sulfoxide (**3**) or Sulfone (**4**)
$$\text{RCH}_2\text{S(=O)R}' \xrightarrow{\text{DAST}} \text{RCHF}\text{SR}' \xrightarrow{\text{MCPBA}} \text{RCHF}\text{S(=O)}_n\text{R}'$$

$\underset{1}{\text{RCH}_2\text{S(=O)R}'}$ 
 $\xrightarrow{\text{DAST}}$ 
 $\underset{2}{\text{RCHF}\text{SR}'}$ 
 $\xrightarrow{\text{MCPBA}}$ 
 $\underset{3, n=1}{\text{RCHF}\text{S(=O)}_n\text{R}'}$   
 $\underset{4, n=2}{\text{RCHF}\text{S(=O)}_n\text{R}'}$

cpd	time, <sup>a</sup> h	temp, <sup>b</sup> °C	substituents		cat.	% yield <sup>c</sup>		
			R	R'		2	3	4
a	30	RT-50	H	C <sub>6</sub> H <sub>5</sub>	none	85	80	
b	8	RT	H	4-MeOC <sub>6</sub> H <sub>4</sub>	none	95	89	
c	96	50	F	C <sub>6</sub> H <sub>5</sub>	none	23		
d	96	50	F	4-MeOC <sub>6</sub> H <sub>4</sub>	none	68		
e	16	RT	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	none	8		
e	16	RT	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	ZnI <sub>2</sub>	94	82	
f	72	RT	PhthNCH <sub>2</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	ZnI <sub>2</sub>	91	90	
g	16	RT	EtO <sub>2</sub> CCH <sub>2</sub> CH <sub>2</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	ZnI <sub>2</sub>	79	73	
h	16	RT	NCCH <sub>2</sub> CH <sub>2</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	ZnI <sub>2</sub>	89	66	
i	16	RT	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	ZnI <sub>2</sub>	100	69	
j	18	RT	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	none	85	83	
k	18	RT	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	ZnI <sub>2</sub>		86	
l	63	RT	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	ZnI <sub>2</sub>		44	
m	16	RT	H	CH <sub>3</sub>	none			83
n	16	RT	H	CH <sub>3</sub> CH <sub>2</sub>	none			69

<sup>a</sup>Reactions were followed to completion by NMR. <sup>b</sup>RT = room temperature. <sup>c</sup>If no yield of **2** is given, yield of **3** or **4** was overall yield from **1**.

oxidized to sulfoxide **3a** with 1 equiv of 3-chloroperbenzoic acid (MCPBA) at -20 °C. Reagent **3a** was originally prepared by Wemple and More<sup>9</sup> (and later used by Reutrakul and Rukachaisirikul<sup>6d</sup>) by treating chloromethyl phenyl sulfoxide with rigorously dried potassium fluoride and 18-crown-6 in acetonitrile at reflux for 4-5 days. Seebach and co-workers have recently prepared <sup>13</sup>C-labeled **3a** for NMR studies using this method.<sup>10</sup> It is important to note that the method we report here provides a more convenient and shorter route to the useful reagent **3a**.

A number of examples of this novel reaction have been carried out (Table I). The reaction proceeded in good to excellent yield for a variety of primary alkyl aryl sulfoxides and methyl alkyl sulfoxides. The transformation was compatible with a number of functional groups including nitriles, esters, amides, and ethers.<sup>11</sup>

In some cases, a slow rate of reaction was observed, even at 50 °C. Due to the instability of DAST above 80 °C,<sup>12</sup> methods other than increased reaction temperature were studied to facilitate the reaction. The introduction of a 4-methoxy group on the benzene ring of **1a**, i.e., **1b**, dramatically increased the rate of the reaction. 4-Methoxyphenyl methyl sulfoxide (**1b**) reacted with DAST at room temperature in a few hours to provide a 95% yield of fluoromethyl sulfide **2b**. In other cases it was found that a Lewis acid such as ZnI<sub>2</sub> catalyzed the reaction. Magnus<sup>13</sup> has noted a similar catalytic effect for ZnI<sub>2</sub> in the conversion of methyl alkoxymethyl sulfoxides to aliphatic cyanomethyl ethers with trimethylsilyl cyanide. Treatment of 4-methoxyphenyl hexadecyl sulfoxide (**1e**) with DAST for 16 h at room temperature provided only 8% (by <sup>1</sup>H NMR) of the desired product **2e**, whereas the addition of a catalytic amount of ZnI<sub>2</sub> under identical conditions gave a 94% isolated yield of  $\alpha$ -fluoromethyl sulfide **2e**. In the case of benzyl phenyl sulfoxide (**11**), the presence of ZnI<sub>2</sub> provided the desired product, which was isolated as the sulfoxide (**31**) in a 44% overall yield, whereas without ZnI<sub>2</sub> only 7% of the  $\alpha$ -fluoro sulfide was obtained.

(8) All new compounds are fully supported by <sup>1</sup>H NMR, mass spectrometry, elemental analysis, and/or high-resolution mass spectrometry.

(9) More, K. M.; Wemple, J. *Synthesis* 1977, 791.

(10) Najera, C.; Yus, M.; Hassig, R.; Seebach, D. *Helv. Chim. Acta* 1984, 67, 1100.

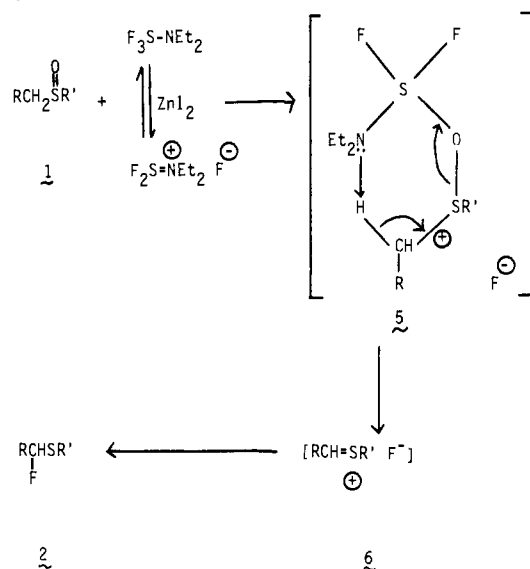
(11) For additional examples of functional groups compatible with DAST, see: (a) Boulton, K.; Cross, B. E. *J. Chem. Soc., Perkin Trans. 1* 1981, 1293. (b) Blackburn, G. M.; Kent, D. E. *J. Chem. Soc., Chem. Commun.* 1981, 511.

(12) (a) Middleton, W. J. *Chem. Eng. News* 1979, 57(21), 43. (b) Cochran, J. *Ibid.* 1979, 57(12), 4.

(13) Schwindeman, J. A.; Magnus, P. D. *Tetrahedron Lett.* 1981, 22, 4925.

(14) Prepared in two steps by treating 1-hexadecyl bromide with the sodium salt of 4-methoxybenzenethiol in methanol at room temperature providing 1-hexadecyl 4-methoxyphenyl sulfide in 98% yield, mp 57-58 °C,<sup>8</sup> by aqueous workup. The sulfoxide **1e**, mp 65-66 °C (hexane),<sup>8</sup> was isolated in 80% by treatment of the sulfide with 1 equiv of MCPBA at 0 °C in CH<sub>2</sub>Cl<sub>2</sub>.

Scheme I



The mechanism of this fluorine insertion reaction has not yet been studied in detail. However, some observations have led us to surmise a mechanism similar to that of the Pummerer rearrangement.<sup>7</sup> The increase in the rate of the reaction for 4-methoxyphenyl alkyl sulfoxides over the phenyl analogues indicates that the slow step in the reaction is the first step as in the Pummerer rearrangement (see Scheme I). The formation of a sulfonium cation (**5**) from the first intermediate (**4**) can be rationalized by a six-membered transition state in which nitrogen acts as a base. This transition state explains the regioselective formation of fluoromethyl ethyl sulfide (**2n**) from methyl ethyl sulfoxide (**1n**) as a result of steric factors. Similar regioselectivity has also been observed in the Pummerer rearrangement of **1n** with acetic anhydride.<sup>15</sup> The catalytic effect of ZnI<sub>2</sub> can be rationalized by the formation of a reactive sulfiminium cation from DAST.

The following procedure for the preparation of **2e** is illustrative: To a stirred solution of 1-hexadecyl 4-methoxyphenyl sulfoxide<sup>14</sup> (**1e**, 3.80 g, 0.01 mol) and ZnI<sub>2</sub> (0.096 g, 0.0003 mol) in CHCl<sub>3</sub> (20 mL) was added DAST (3.22 g, 0.02 mol) under N<sub>2</sub>, and the dark mixture was stirred at room temperature. The progress of the reaction was monitored by the appearance in the <sup>1</sup>H NMR of the CHF product signal (doublet of triplets, *J*<sub>HF</sub> = 54.6 Hz,

(15) Parham, W. E.; Edwards, L. D. *J. Org. Chem.* 1968, 33, 4150.

(16) Rico, I.; Wakselman, C. *Tetrahedron* 1981, 37, 4209.

$J_{\text{HaH}\beta} = 6.5$  Hz) centered at  $\delta$  5.54. After 16 h, an ice cold  $\text{NaHCO}_3$  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 ( $\text{N}_2$ ) to provide an 80% isolated yield of 1-fluoro-2-tetradecylethylene (**7**).<sup>6d</sup>

In summary, we have described a new reaction of sulfoxides which provides a novel synthesis of  $\alpha$ -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.

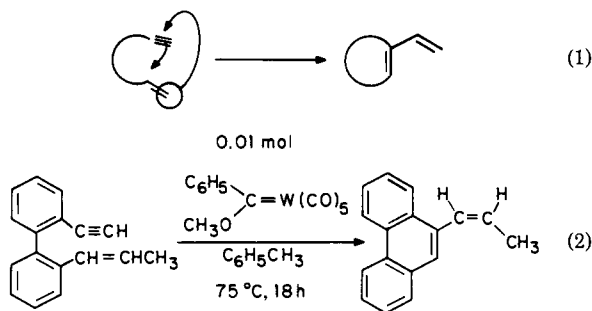
### Metal-Catalyzed Rearrangement of Alkene-Alkynes and the Stereochemistry of Metallacyclobutene Ring Opening

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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<sup>1</sup> and



olefin metathesis<sup>2</sup> reactions. It demonstrates how metal-alkyl-carbenes are generated when metal derivatives (here stabilized carbene-tungsten carbonyls)<sup>3</sup> combine with acetylenes and olefins,<sup>1d,4,5</sup> 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

(1) (a) Simionescu, C. I.; Percec, V. *Prog. Polym. Sci.* **1982**, *8*, 133. (b) Masuda, T.; Higashimura, T. *Acc. Chem. Res.* **1984**, *17*, 51. (c) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422. (d) Katz, T. J.; Lee, S. J.; Shippey, M. A. *J. Mol. Catal.* **1980**, 219. (e) Chausser, M. G.; Rodionov, Yu. M.; Misin, V. M.; Cherkashin, M. I. *Russ. Chem. Rev. (Engl. Transl.)* **1976**, *45*, 348.

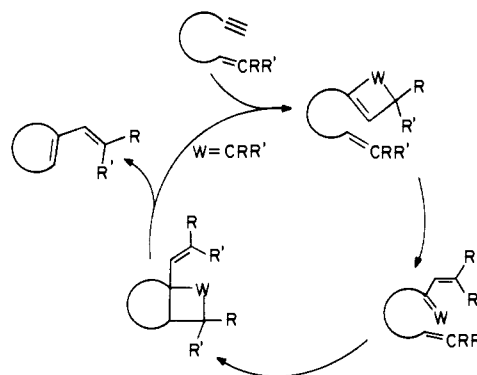
(2) (a) Grubbs, R. H. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 8, p 499. (b) Ivin, K. J. "Olefin Metathesis"; Academic Press: London, 1983.

(3) Fischer, H. In "The Chemistry of the Metal-Carbon Bond"; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; Vol. 1, pp 181–231.

(4) (a) Katz, T. J.; Lee, S. J.; Nair, M.; Savage, E. B. *J. Am. Chem. Soc.* **1980**, *102*, 7940. (b) Katz, T. J.; Han, C.-C. *Organometallics* **1982**, *1*, 1093.

(5) (a) Katz, T. J.; Savage, E. B.; Lee, S. J.; Nair, M. *J. Am. Chem. Soc.* **1980**, *102*, 7942. (b) Han, C.-C.; Katz, T. J., submitted for publication in *J. Am. Chem. Soc.*

### Scheme I



**Table I.** Yields and Stereochemistries of 9-Vinylphenanthrenes Obtained according to Eq 1 from Enynes **1**<sup>21</sup> and Catalytic Amounts of Metal-Carbenes **2** in which R'' = C<sub>6</sub>H<sub>5</sub><sup>a</sup>

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

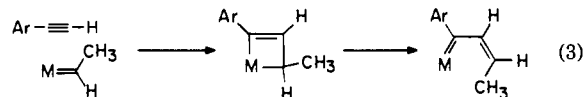
<sup>a</sup>Enynes **1** (1 equiv) and *n*-nonane (0.5–1.0 equiv, internal standard for GLC analysis) were diluted to 0.10 M with toluene, added to metal-carbenes **2** (0.01 equiv), degassed, and sealed in a vacuum. When X was OCH<sub>3</sub>, reactions were run for 18 h at 75 °C, and when C<sub>6</sub>H<sub>5</sub>, 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 <sup>1</sup>H NMR spectra with those of authentic samples (see ref 22). <sup>b</sup>Yields were determined by GLC. <sup>c</sup>Stereochemistries were analyzed by <sup>1</sup>H NMR [CH<sub>3</sub> resonances in 9-(1-propenyl)phenanthrene (see ref 22) in CDCl<sub>3</sub>: cis  $\delta$  1.83 (dd, 7.0 and 1.8 Hz); trans  $\delta$  2.04 (dd, 6.6 and 1.7 Hz)]. <sup>d</sup>Initially 56% cis.

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

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

<sup>a</sup>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<sub>6</sub>H<sub>5</sub>, reactions were run at 50 °C for 16 h, and when OCH<sub>3</sub>, 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<sub>6</sub>H<sub>5</sub> and the ketones (9-phenanthryl)-CH<sub>2</sub>COR'' corresponding to enol ethers **3** when R'' = C<sub>6</sub>H<sub>5</sub> or CH<sub>3</sub> and X = OCH<sub>3</sub> (see ref 30). Products were identified by comparing <sup>1</sup>H NMR spectra with those of authentic samples (see ref 32). <sup>b</sup>Yields of isolated products. <sup>c</sup>Initially 56% cis.

an olefin metathesis.<sup>1b–d,4,5</sup> It reveals that this insertion can be remarkably stereoselective in the sense indicated in eq 3.<sup>6</sup>



(6) Pentacarbonylchromium- and tungsten-carbenes carrying as stabilizers on the carbene carbon an alkoxy or two aryls insert into ynamines such as in eq 3<sup>7</sup> (the stereochemistries of some of these insertions have been analyzed<sup>8</sup>) and react with carbon-substituted alkynes to give phenols, indenes, furans, and cyclobutenones.<sup>7,9</sup> 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.<sup>10</sup>