a ketene,[23,24] possibly one involving metal coordination (F).[24] In regard to mechanism, it is important to note that NMR studies[12] of **6a**, **6b**, and **6c** indicate that *C and ‡C rigorously retain their respective identities in the homologation process (eq 3). Further mechanistic studies of actinide dihaptoacyl reactivity, including this new mode of CO activation and coupling, are in progress.

Acknowledgments. We thank the National Science Foundation (T.J.M., CHE76-84494 A01) and the University of Nebraska Computing Center (V.W.D.) for generous support of this work.

Supplementary Material Available: Spectral and analytical data for **2a**,**b**, **5a**,**b**, and **6a–c** (2 pages). Ordering information is given on any current masthead page.

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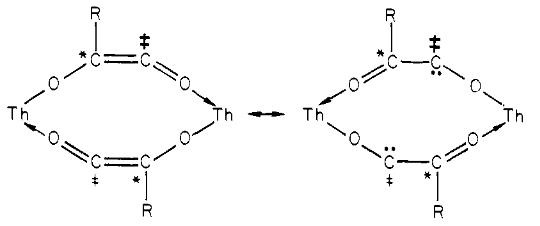
(23) (a) Reference 21c, p 14–16. (b) Rautenstrauch, V.; Joyeux, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 85–86. (c) Wilson, T. B.; Kistiakowsky, G. B. *J. Am. Chem. Soc.* **1958**, *80*, 2934, 2939.

(24) (a) Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Weidenhammer, K. *J. Am. Chem. Soc.* **1979**, *101*, 3133–3135. (b) Herrmann, W. A.; Plank, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 525–526. (c) Redhouse, A. D.; Herrmann, W. A. *Ibid.* **1976**, *15*, 615–616. (d) Hermann, W. A. *Ibid.* **1974**, *13*, 335–336. (e) Schorpp, K.; Beck, W. *Z. Naturforsch., B.: Anorg. Chem., Org. Chem.* **1973**, *28*, 738–740. (f) Hoberg, H.; Korff, J. *J. Organomet. Chem.* **1978**, *152*, 255–264. (g) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1978**, *100*, 1921–1922, and references therein. (h) Formation of **6** via a bimetallic ketene complex such as shown below is also conceivable; however, ‡C–‡C fusion must be accompanied by a change in the oxygen atoms coordinated to each thorium atom.



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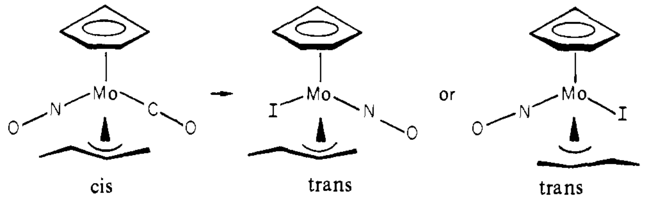
Received March 18, 1980

Retention of Configuration in Displacement of Carbonyl Ligands from Allyl(cyclopentadienyl)carbonylnitrosylmolybdenum Cations

Sir:

The observation that the electronic difference between NO and CO directs the stereoselective attack of nucleophiles on the allyl moiety in $(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_3H_5)(NO)(CO)$ cations[1-3] suggested a more thorough investigation of the chirality, stability, and properties of the $(\eta^5\text{-}C_5H_5)Mo(NO)(X)$ fragment, where X = CO, I, $C_6H_5SO_3$, and CH_3CN. For synthetic purposes, particularly of asymmetric compounds, a method of directing the attack to the opposite terminus of the allyl or reversing the allyl coordination is desirable. Thus, we have explored carbonyl displacement reactions as a potential method of reversing the $(\eta^5\text{-}C_5H_5)Mo(NO)(X)$ configuration relative to a substituted allyl moiety.

We found that attack of halides on these cations resulted in displacement of the carbonyl rather than production of a coordinated allyl halide, as might have been anticipated on the basis of the chemistry found in the attack of softer nucleophiles, such as enamines. Examination of carbonyl displacement in the crotyl homologue, $(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_4H_7)(NO)(CO)$, indicated a stereospecific inversion of stereochemistry at either the molybdenum center of the allyl center;[4] however, the crystal structures of these racemic mixtures provided no means of distinguishing which center inverted.



Since the methyl group of the crotyl ligand might have had a directing effect on the stereochemical outcome of the reaction, the complex with deuterium cis to NO was prepared, $(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_3H_4D)(NO)(CO)$,[5] and treated with iodide (eq 1).

$$
\begin{aligned}
&cis\text{-}(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_3H_4D)(NO)(CO)^+ \xrightarrow{I^-} \\
&\quad cis\text{-}(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_3H_4D)(NO)(I)\ (65\%) + \\
&\quad (35\%)\,trans\text{-}(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_3H_4D)(NO)(I) \quad (1)
\end{aligned}
$$

Analysis of the deuterium distribution suggested an ~90% retention of configuration of a given terminus relative to NO.[6] Furthermore, if one assumed the allyl moiety to retain its configuration, then the crotyl experiments suggested complete inversion of configuration at the molybdenum center whereas the allyl-*d* experiments suggested retention.

We have now prepared and resolved the neomenthylcyclopentadienyl complexes which allow us to establish unequivocally the stereochemistry of carbonyl displacement. Treatment of $(allyl)Mo(CO)_2(CH_3CN)_2Cl$[7] with the lithium salt of (+)-neomenthylcyclopentadiene[8] in THF produces the (neomenthyl-

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(1) J. W. Faller and A. M. Rosan, *Ann. N.Y. Acad. Sci.*, **295**, 186 (1977).

(2) R. D. Adams, D. F Chodosh, J. W. Faller, and A. M. Rosan, *J. Am. Chem Soc.*, **101**, 2570 (1979).

(3) J. W. Faller, D. Katahira, and D. F. Chodosh, *J. Organomet. Chem.*, in press.

(4) J. W. Faller, D. Katahira, D. F. Chodosh, and Y. Shvo, *J. Organomet. Chem.*, submitted for publication.

(5) Treatment of the allyl cation with $NaBD_3CN$ stereoselectively produces $cis\text{-}(\eta^5\text{-}C_5H_5)Mo(\eta^2\text{-}C_2H_3CH_2D)(NO)(CO)$. A 8:1 deuterium isotope effect, in addition to a 2:1 statistical preference for removal of H to D, produces $cis\text{-}[(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_3H_4D)(NO)(CO)]PF_6$ in high yield.[3] The product contains predominantly the exo isomer (80%) with a *cis*-D to *trans*-D ratio of 85:15 by NMR.

(6) The iodide exists in solution as a rapidly equilibrating mixture of endo and exo isomers, the mechanism of which (π–σ–π) does not scramble the deuterium. The *endo-cis*-D/*endo-trans*-D ratio is 64:36. Consideration of the mode of isomer interconversion and the deuterium distribution in the cation implies that 100% retention would yield 71% *cis*-D iodide.[4]

(7) R. G. Hayter, *J. Organomet. Chem.*, **13**, P1 (1968).

(8) E. Cesarotti, H. B. Kagan, R. Goddard, and C. Krueger, *J. Organomet. Chem.*, **162**, 297 (1978). The rotation was $[\alpha]^{25}_D$ +42.0° (*c* 0.0353, $CHCl_3$) [lit. $[\alpha]^{25}_D$ +33.0° (*c* 3.10, $CHCl_3$)].

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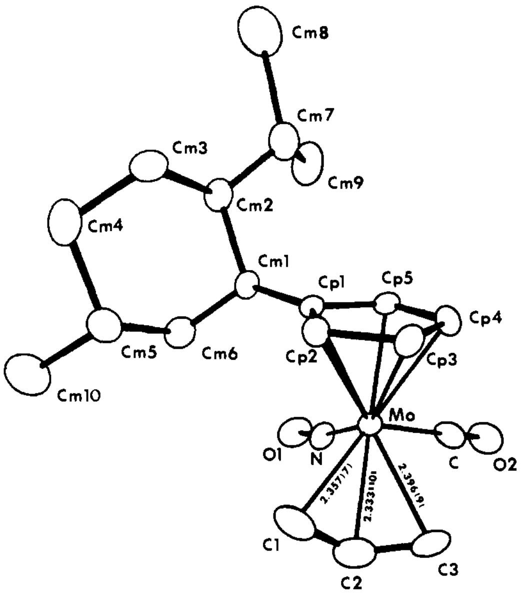

Figure 1. An ORTEP view of the (+)-[(η^5-NMCp)Mo(η^3-C_3H_5)-(NO)(CO)] cation, which has the *R* configuration at the metal and an *endo*-allyl.

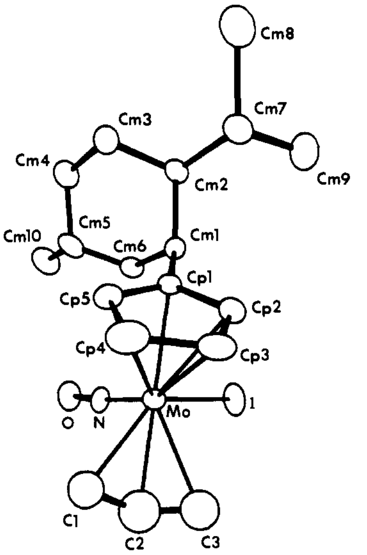

Figure 2. An ORTEP view of (−)-(η^5-NMCp)Mo(η^3-C_3H_5)(NO)(I), which has an *S* configuration at the metal and an *endo*-allyl.

cyclopentadienyl)dicarbonyl complex (+)-(NMCp)Mo(η^3-C_3H_5)$(CO)_2$.[9] Treatment of this complex with $NOPF_6$ produces a diastereomeric mixture of 59% (+)- and 41% (−)-[(NMCp)-Mo(η^3-C_3H_5)(NO)(CO)]PF_6[10] from which the pure (+) isomer is readily separated in two crystallizations.[11] Treatment of the pure (+) isomer with NaI in acetone stereospecifically produces the (−) isomer of the iodide, $[\alpha]^{25}{}_{D}$ −133° (*c* 0.443, acetone) (eq 2).

$$(+)\text{-}[(\text{NMCp})\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{NO})(\text{CO})]\text{PF}_6 + \text{NaI} \rightarrow (-)\text{-}(\text{NMCp})\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{NO})(\text{I}) + \text{NaPF}_6 \quad (2)$$

Since the signs of rotation are not reliable indicators of relative configuration, we have determined the crystal structures of the optically active cation and the iodide product, the absolute configurations of which are shown in Figures 1 and 2.[12] Both structures show a rotation of the allyl toward the Mo–X direction, a distortion toward a σ–π-type allyl structure with a shorter bond cis to NO, and an *endo*-allyl group.[13,14] These structures show no particularly unusual structural features relative to other structures of the (η^5-C_5H_5)Mo(η^3-C_3H_5)(NO)(X) type.[3,4,16] The configuration at the metal center is established by reference to the absolute configuration of the chiral centers of the neomenthyl group.[17,18] It is also interesting to note that the cyclopentadienyl ring occupies an axial position in the cyclohexyl ring of the neomenthyl group in both structures. Regardless, it is evident from the structures that *carbonyl displacement occurs with retention of configuration at molybdenum.*

Kinetic studies indicate that the reaction is first order with respect to both complex and iodide, suggesting a stereospecific bimolecular nucleophilic reaction.[19] We believe that this attack occurs either on the carbonyl or directly on the metal, and the

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(9) This complex showed carbonyl bands at 1962.7, 1953.9, 1894.3, and 1878.3 cm^{-1} (cyclohexane), the four bands arising from the presence of endo and exo isomers. Crystallization from hexane afforded yellow needles; mp 59–60 °C, $[\alpha]^{25}{}_{D}$ +44.5° (*c* 0.0113, hexane). Anal. Calcd. for $C_{20}H_{28}O_2Mo$: C, 60.6; H, 7.07. Found: C, 61.0; H, 7.47.

(10) The fractions of the two isomers are readily detectable by NMR in acetone. The (+) isomer shows *endo*-allyl resonances at 5.83 (c), 5.08, 4.34 (s), 3.82, 3.25 (a) and the (+)-*exo*-allyl at 5.40 (c), 5.17, 4.88 (s), 3.61, 3.42 (a). The (−) isomer shows *exo*-allyl at 5.37 (c), 5.08, 4.87 (s), 3.67, 3.37 (a). The crude product, $[\alpha]^{25}{}_{D}$ +60° (acetone), was obtained by adding an equimolar quantity of nitrosonium hexafluorophosphate to a suspension of the dicarbonyl in acetonitrile at 0 °C and after 15 min pouring the mixture into cold ether.

(11) The pure (+) cation can be resolved by two crystallizations from acetone/ether mixtures at 0 °C. This crystallization must be carried out rapidly to prevent endo–exo isomerism. The (+) cation shows carbonyl and nitrosyl bands at 2091 and 1723 cm^{-1} in methylene chloride and melts with decomposition at 187–190 °C. The rotation immediately after dissolving the sample in acetone is $[\alpha]^{25}{}_{D}$ +117°; however, the ion begins interconversion to the exo isomer with a half life of 25 min at 25 °C and 52 min at 20 °C, such that the rotation keeps increasing until endo–exo equilibrium is reached. The rotation of the equilibrium mixture is $[\alpha]^{25}{}_{D}$ +170° (*c* 0.0236, acetone).

(12) (+)-[(NMCP)Mo(η^3-C_3H_5)(NO)(CO)]PF_6 crystallizes in the space group $P2_1$, No. 4: a = 7.400 (7), b = 14.807 (6), c = 10.528 (1) Å, Z = 2, V = 1143.1 (7) Å^3. The final values of the residuals R_1 and R_2 (p = 0.03) were 0.038 and 0.039, respectively. Although CO and NO often disorder if they can be interchanged by a rotation of the molecule, this type of disorder cannot occur here because a single enantiomer was present. The identity of the X in the M–XO bonds was determined by isotropic refinement of both atoms as carbons. The atom eventually assigned to N had a thermal parameter of 2.2, Mo–X length of 1.785 Å whereas C had B = 5.1 and M–X = 2.100 Å. (−)-[(NMCP)Mo(η^3-C_3H_5)(NO)(I)] crystallizes in the space group $P2_12_12_1$, No. 19: a = 7.221 (1), b = 12.686 (7), c = 21.603 (7) Å, Z = 4, V = 1979 (2) Å^3; R_1 = 0.038, R_2 = 0.044. Due to a small disorder in the allyl group (presumably some exo isomer), the allyl carbons were refined isotropically and no allyl hydrogen atoms were included in the least-squares cycles. The structures were solved by heavy-atom methods by using the Enraf-Nonius SDP library. With monochromated Mo Kα radiation, 1789 and 1807 unique reflections with $F_o^2 < 3\sigma(F_o^2)$ for the carbonyl and iodide, respectively, were collected with an Enraf-Nonius CAD-4 automated diffractometer.

(13) Selected bond lengths (Å) for the cation: C1–C2 = 1.365 (13), C2–C3 = 1.323 (11), Mo–C = 2.096 (8), C–O = 1.109 (8), Mo–N = 1.777 (5), N–O = 1.219 (7). Bond lengths for the iodide: C1–C2[5] = 1.393 (13), C2–C3[15] = 1.209 (14), Mo–I = 2.814 (1), Mo–N = 1.773 (5), N–O = 1.194 (6), Mo–C1 = 2.343 (8),[15] and Mo–C2 = 2.27 (1),[15] Mo–C3 = 2.42 (1).[15]

(14) Selected bond angles (deg) for the cation and iodide, respectively: C1–C2–C3 = 124.1 (9), 138 (1);[13] Mo–N–O = 168.6 (5), 174.7 (4). Others are Mo–C–O = 177.9 (7), N–Mo–C = 88.3 (3), and N–Mo–I = 89.7 (2).

(15) Because of the disorder, statistics may underestimate the error in the dimensions of the allyl moiety.

(16) T. J. Greenhough, P. Legzdins, D. T. Martin, and J. Trotter, *Inorg. Chem.*, **18**, 3268 (1979).

(17) The absolute configurations of the three chiral centers in the neomenthyl group are known.[18] The configuration at the metal can be determined by reference to them. Although potentially unreliable, inversion of coordinates and refinement increased R_2 to 0.040 in the cation and 0.048 in the iodide, suggesting the configurations presented were correct. Friedl pair intensities were measured for selected reflections having high anomalous dispersion corrections in the iodide. The Bijvoet differences were consistent with the *S* configuration for the iodide (see supplementary material). This independently confirms the neomenthyl configuration as well as that of the metal center.

(18) W. Klyne and J. Buckingham, "Atlas of Stereochemistry–Absolute Configurations of Organic Molecules", Vol. I, 2nd ed., Oxford University Press, London, 1978, p 78.

(19) A discussion of the possible intermediates, kinetics, and thermodynamics of isomer interconversion is presented in manuscripts which have been submitted[4] or are in preparation.

intermediate which is formed allows rearrangement of the allyl group. Apparently, the predominance of the *trans*-crotyl isomer is a result of preferential formation and collapse of certain σ-crotyl isomers.[19]

These systems are among the few chiral organometallic compounds for which the absolute configuration at the metal has been determined.[20-23] Since these complexes are quite stable to racemization, they provide a ready route to asymmetric synthesis by using previously developed chemistry.[24,1] Stereospecificity in replacement of the X group in the (NMCp)Mo(η^3-C_3H_5)(NO)(X) systems appears to be general. The specific rotations of the iodide complexes recovered from the cycles shown in eq 3 were identical within experimental error to that of the starting iodide.

$$(+)\text{-}[(\mathrm{NMCp})\mathrm{Mo}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{NO})(\mathrm{O_3SC_6H_5})] \xrightleftharpoons[\mathrm{C_6H_5SO_3Ag}]{\mathrm{NaI}} (-)\text{-}[(\mathrm{NMCp})\mathrm{Mo}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{NO})(\mathrm{I})] \xrightleftharpoons[\mathrm{NaI}]{\mathrm{AgPF_6/CH_3CN}} (-)\text{-}[(\mathrm{NMCp})\mathrm{Mo}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{NO})(\mathrm{CH_3CN})]\mathrm{PF_6} \quad (3)$$

Acknowledgments. We thank Professor Richard D. Adams for helpful discussions. This research was supported by a grant from the National Science Foundation (CHE79-11201).

Supplementary Material Available: A listing of structure factor tables (34 pages). Ordering information is given on any current masthead page.

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(20) H. Brunner, *Acc. Chem. Res.*, **12**, 250 (1979).

(21) C. -K. Chou, D. L. Miles, R. Bau, and T. C. Flood, *J. Am. Chem. Soc.*, **100**, 7271, 7278 (1978).

(22) P. Reich-Rohrwig and A. Wojcicki, *Inorg. Chem.*, **13**, 2457 (1974).

(23) The sequencing rules used here for the assignment of *R* and *S* stereochemical designations are those of K. Stanley and M. C. Baird, *J. Am. Chem. Soc.*, **97**, 6598 (1975).

(24) On sabbatical leave from Tel-Aviv University.

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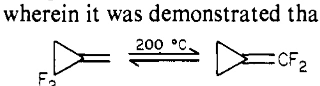
Received December 3, 1979

Synthesis and Thermal Isomerization of 2,2,3,3-Tetrafluoromethylenecyclopropane

Sir:

In an earlier communication, we reported a kinetic and thermodynamic investigation of the difluoromethylenecyclopropane system **1** ⇌ **2**, wherein it was demonstrated that the *gem*-difluoro

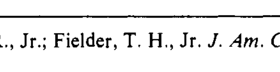


1 2

log A = 13.2 $E_a = 38.3 \pm 0.4$ kcal/mol

substituents of **1** modestly enhance its rate of rearrangement relative to the parent hydrocarbon.[1] Furthermore, the equilibrium thermodynamics ($\Delta H° = -1.9$ kcal/mol) indicated that cyclopropyl *gem*-difluoro substituents are more destabilizing than vinylic *gem*-difluoro substituents on a methylenecyclopropane.

We now report the synthesis of the two tetrafluoromethylenecyclopropane isomers **3** and **4** and the remarkable effect of the second pair of fluorine substituents on their thermal interconversion.



3 4

Scheme I

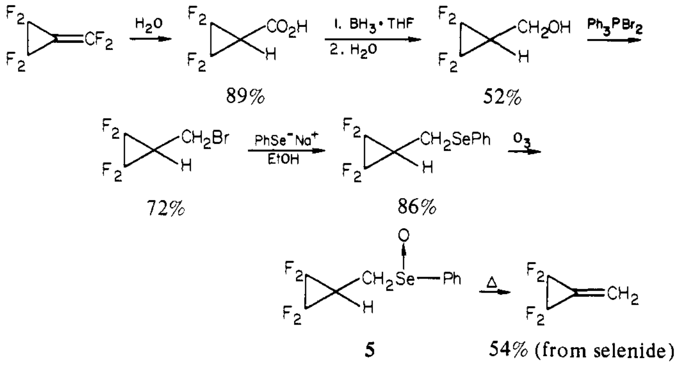
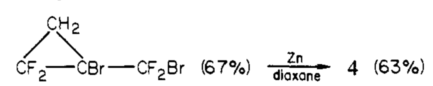


Table I. Rate Constants for 3 → 4

temp, °C	150.50	151.75	153.33	155.25	156.75	159.25
10^5k, s^{-1}	234	254	284	350	383	469

1-(Difluoromethylene)-2,2-difluorocyclopropane (**4**) was synthesized relatively easily from 2,3-dibromo-3,3-difluoropropene[2] by the two-step sequence shown below.[3] Unfortunately, **4** did



not isomerize to **3** when heated to temperatures as high as 350 °C. At temperatures above 360 °C, **4** extruded :CF_2 to form 1,1-difluoroallene. It is concluded from these results that **3** must be *significantly* more destabilized than we had anticipated.

A direct synthesis of 2,2,3,3-tetrafluoromethylenecyclopropane, therefore, was required. After several unsuccessful approaches, **3** was prepared from perfluoromethylenecyclopropane[4] (Scheme I).[5,6]

It was found that **3** rearranged to **4** cleanly, with good first-order kinetics in the gas phase at 150 °C. Rates were obtained at six temperatures,[8] and an Arrhenius plot of these data gave a good straight line with the frequency factor and energy of activation being calculated by the least-squares method: log $A = 12.6 \pm 0.5$, $E_a = 29.6 \pm 1$ kcal/mol.

The relative rate of rearrangement of **3** vs. **1** at 150 °C is calculated to be 7850—a remarkable indication of the *nonadditivity* of the two CF_2 group effects on the stability of the methylenecyclopropane system. (At 150 °C, the relative rate of rearrangement of **1** vs. methylenecyclopropane itself is calculated to be only 4.4.) The seemingly small effect, if any, of fluorine substituents on radical stability[9-11] suggests that this is truly a

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(1) Dolbier, W. R., Jr.; Fielder, T. H., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 5577.

(2) Blomquist, A. T.; Longone, D. T. *J. Am. Chem. Soc.* **1957**, *79*, 4981.

(3) Satisfactory analytical data were obtained for all new compounds. The structure of **4** was unambiguously established by its physical and spectral properties: bp 18–19 °C; IR (gas) 1810 cm^{-1} (C═CF_2); NMR (neat) δ 1.72 (t of t, J = 6.5, 1.8 Hz); ϕ 71.5 (d of p, 1, J = 32.5, 6.5 Hz), 85.3 (d of p, 1, J = 32.5, 6.5 Hz), 131.3 (complex m, 2).

(4) (a) Smart, B. E. *J. Am. Chem. Soc.* **1974**, *96*, 927. (b) Smart, B. E. U.S. Patent 3 816 553, 1974.

(5) Spectral properties of **3**: IR (gas) 1740 cm^{-1} (C═CH_2); NMR ($CDCl_3$) δ 6.5 (s); ϕ 141.33 (complex m). Mass spectroscopy gave (M^+) 126.00951 [standard deviation = 0.00078 (6.2 ppm)]. Calculated (M^+) 126.00926 [deviation = 0.00025 (2.0 ppm)].

(6) Although most alkyl selenoxides eliminate under very mild conditions and generally cannot be isolated, selenoxide **5** was isolated as a white crystalline compound, and it needed to be heated to temperatures >100 °C before elimination was observed.[7]

(7) Cyclopropyl selenoxides recently have been used to synthesize alkylidenecyclopropanes, with a similar high temperature being required for their elimination: Halazy, S.; Krief, A. *Tetrahedron Lett.* **1979**, 4233.

(8) The relatively small range of temperatures used in this study was dictated by the melting point of the eutectic mixture used in our salt-bath thermostat (150 °C).

(9) O'Neal, H. E.; Benson, S. W. *J. Phys. Chem.* **1968**, *72*, 1866.

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