(**8**),[11] which was isolated as orange-yellow crystals from the re-

$$\mathrm{RhHL_3} \xrightarrow[-\mathrm{L}]{\mathrm{CO}} \underset{\mathbf{6}}{trans\text{-}\mathrm{RhH(CO)L_2}} \xrightarrow[-\mathrm{H_2},-\mathrm{L}]{\mathrm{CO}}$$

$$\underset{\mathbf{8}}{[\mathrm{Rh(CO)_3L}]_2} \xrightarrow[\text{under } \mathrm{N_2}]{\mathrm{L},-\mathrm{CO}} \underset{\mathbf{7}}{\mathrm{Rh_2(CO)_3L_3}}$$

action of $RhHL_3$ and CO. **8** is extremely unstable in the absence of CO. Thus, when the CO atmosphere of the flask containing the *n*-hexane solution of **8** was replaced with dinitrogen, **7** was obtained in a low yield (18%). The yield (from **8**) was much improved by adding free L [P(*i*-Pr)$_3$] to the reaction. It was confirmed that **8** and **7** are also formed from the reaction of CO with **6** separately prepared.[12]

It is of interest to note that the carbonylrhodium(0) compound **7** reacts with water, producing H_2. Thus, a red solution of **7** in pyridine containing 1 mol of free P(*i*-Pr)$_3$ turned pale yellow immediately on addition of water at room temperature with H_2 evolution (50% based on **7**). From the solution was isolated **4b** (68%) by adding $NaBPh_4$. The capability of rhodium carbonyl compounds to undergo facile oxidative addition of water is remarkable in view of the presence of electron-withdrawing CO ligands. The formation of the Rh(I) compound **4a** is also interesting, since **4a** reacts with CO to give CO_2 and **6**, thus suggesting the possibility of catalyzing the water–gas shift reaction. Indeed, we discovered that $RhHL_3$ compounds and related species such as **1**, **6**, **4a**, and **7**, etc. serve as active catalysts. The details will be described separately.[13]

Transition-metal compounds would provide a low-energy system for the catalytic photodissociation of water, which is one of the intensive current research interests.[14] Although a Rh(I) dimer, tetrakis(1,3-diisocyanopropane)dirhodium(2+),[15] was proposed as such a system, hydrogen evolution remains stoichiometric. Therefore, the present study should contribute to our fundamental knowledge for the water-splitting systems.

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(11) Anal. Calcd for $C_{24}H_{42}O_6P_2Rh_2$: C, 41.40; H, 6.37. Found: C, 41.61; H, 6.28. IR (Nujol), ν(CO) ~1950 cm^{-1}; ^{1}H NMR (benzene-d_6 under CO) 0.9 (br, CH_3), ~1.6 (br, CH).

(12) A similar formation of rhodium(0) carbonyl compounds [Rh(CO)$_2$L$_2$]$_2$ and [Rh(S)(CO)L$_2$]$_2$ (S = solvent) from a hydrido complex RhH(CO)L$_3$ (L = PPh_3) was reported: Evans, D.; Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2660–2665.

(13) Yoshida, T.; Okano, T.; Otsuka, S., to be published.

(14) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Gleria, M. *Science (Washington D.C.)* **1975**, *189*, 852–856.

(15) Mann, K. M.; Lewis, L. S.; Miskowski, V. M.; Erwin, D. K.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *99*, 5525–5526. Miskowski, V. M.; Sigal, I. S.; Mann, K. R.; Gray, H. B.; Milder, S. J.; Hammond, G. S.; Rayson, P. R. *Ibid.* **1979**, *101*, 4383–4385.

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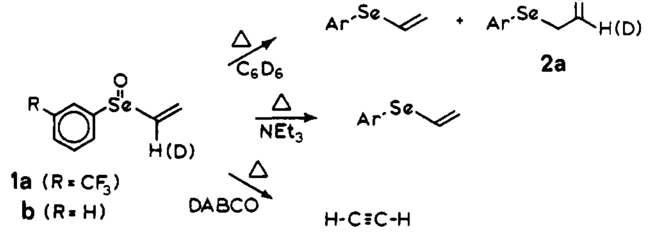
Organoselenium Chemistry. Formation of Acetylenes and Allenes by Syn Elimination of Vinyl Selenoxides[1]

Sir:

The syn elimination of alkyl selenoxides to give olefins is one of the most important applications of selenium in organic synthesis.[2] We report here that under the proper conditions this reaction also takes place with vinyl selenoxides to give acetylenes and, in certain situations, allenes.

Thermolysis of *m*-trifluoromethylphenyl vinyl selenoxide[3] (**1a**) in benzene forms no acetylene. The products are variable amounts of the reduced selenide and arylselenoacetaldehyde **2a**. The latter

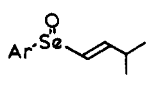


1a (R = CF$_3$)
b (R = H)
2a

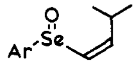
is presumably formed by reaction of vinyl selenide or vinyl selenoxide with selenenic acid.[5] An alternative mechanism involving addition of ArSeOH to acetylene[1b] was ruled out when it was found that deuterated **1a** gave **2a** with deuterium only at the aldehyde position. If the thermolysis of **1a** is carried out with triethylamine present, the formation of **2a** is completely suppressed, but reduction is still the major process. On the basis of the theory that triethylamine is now the reductant, other amines not as easily oxidized to immonium cations were tried. These included 1,4-diazabicyclo[2.2.2]octane (Dabco), quinuclidine, and hexamethyldisilazane. In the presence of 1–2 equiv of these amines, vinyl selenoxides are smoothly thermolyzed to acetylenes at 95 °C. Of the amines used, Dabco is most effective in preventing both selenenic acid addition and reduction. A pericyclic syn elimination mechanism for the acetylene formation is consistent with all of the experimental results:

(1) The rate of elimination of **1a** is the same when 0.5, 2.9, or 5.1 equiv of Dabco are present. The reaction, thus, is not an E2 elimination.

(2) The selenoxides **3a** and **4a**[1c,3] show very different behavior. Compound **3a** gives a 63% (by NMR) yield of 3-methylbutyne in 20 h at 95 °C whereas **4a** gives only a trace (<5%) of acetylene after 60 h, together with about 50% of reduced selenide.

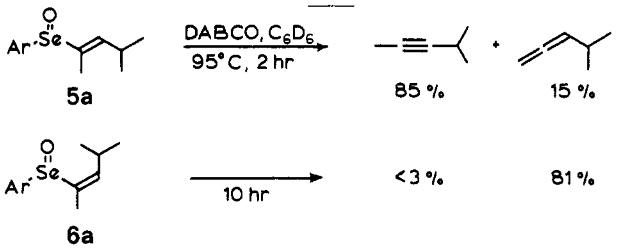


3a



4a

(3) Compounds **5a** and **6a**[3] were thermolyzed at 95 °C, with the results shown below. The (*Z*)-selenoxide **6a**, which cannot undergo syn elimination to an acetylene like the *E* isomer **5a**, reacts more slowly and gives predominantly allene.



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[1] For previous papers in this series see: (a) H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow, and D. F. Wendelborn, *J. Org. Chem.*, **43**, 1697 (1978); H. J. Reich and J. E. Trend, *ibid.*, **41**, 2503 (1976); (b) H. J. Reich, *ibid.*, **39**, 428 (1974); (c) H. J. Reich, F. Chow, and S. K. Shah, *J. Am. Chem. Soc.*, **101**, 6638 (1979); (d) *ibid.*, **101**, 6648 (1979); (e) H. J. Reich and S. K. Shah, *ibid.*, **99**, 263 (1977); H. J. Reich, P. M. Gold, and F. Chow, *Tetrahedron Lett.*, 4433 (1979); H. J. Reich, J. M. Renga, and I. L. Reich, *J. Org. Chem.*, **39**, 2133 (1974); H. J. Reich, J. J. Rusek, and R. E. Olson, *J. Am. Chem. Soc.*, **101**, 2225 (1979); H. J. Reich and S. K. Shah, *J. Org. Chem.*, **42**, 1773 (1977).

(2) For recent reviews see: (a) H. J. Reich in "Oxidation in Organic Chemistry. Part C", W. Trahanovsky, Ed., Academic Press, New York, 1978, p 1; (b) H. J. Reich, *Acc. Chem. Res.*, **12**, 22 (1979); (c) D. L. J. Clive, *Tetrahedron*, **34**, 1049 (1978).

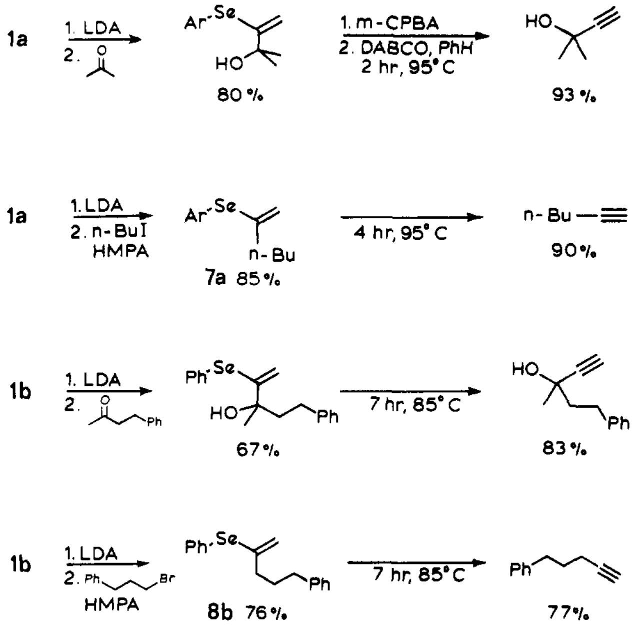
(3) Selenoxides were prepared by oxidation with *m*-chloroperoxybenzoic acid[4] in dichloromethane. Compounds in the **a** series have Ar = *m*-$CF_3C_6H_4$ whereas those in the **b** series have Ar = C_6H_5.

(4) M. Sevrin, W. Dumont, and A. Krief, *Tetrahedron Lett.*, 3835 (1977). These authors also observed that vinyl selenoxides give selenides on thermolysis.

(5) The reaction of olefins with PhSeOH is a common side reaction during selenoxide syn eliminations.[1a,6] It can usually be prevented by carrying out the elimination in the presence of alkylamines.[1a]

(6) T. Hori and K. B. Sharpless, *J. Org. Chem.*, **43**, 1689 (1978).

Scheme I



The observation, independently made by us,[7] Raucher,[8] and Krief,[9] that some vinyl selenides can be deprotonated, coupled with the syn elimination reported here, allows α-lithio vinyl selenides[10] to be used as lithium acetylide equivalents (see Scheme I, in which yields of the volatile acetylenes from **1a** were determined by NMR and those from **1b** were of isolated and purified materials).

Rough rate measurements show that the reactions follow first-order kinetics, with the following relative rates at 95 °C in benzene-d_6 (half-lives in brackets): **1a**, 1.0 (2.3 h); **1b**, 0.83 (2.8 h); **7a**-selenoxide, 9.7 (0.24 h); **3a**, 0.3 (7.4 h); **5a**, 5.4 (0.43 h); **6a**, 1.0 (2.3 h). The substituent effects are strikingly similar to those observed for syn elimination of aryl alkyl selenoxides.[1a] Thus, substitution of a m-CF_3 group on the aryl ring (**1a** vs. **1b**) increases the rate by 1.3 while for the aryl ethyl selenoxides the rate is increased by 1.5. Replacement of the α hydrogen by methyl for alkyl selenoxides (i.e., ethyl vs. isopropyl selenoxide) increases the rate by 9.5 whereas factors of 10 (**1a** vs. **7a**, α-butyl) and 18 (**3a** vs. **5a**, α-methyl) are observed here. β substitution in alkyl selenoxides (i.e., propyl vs. isobutyl) retards the rate of elimination by 0.36; in the vinyl compounds (**1a** vs. **3a**), the rate is decreased by 0.3. The extent of allene formation which occurs for **5a** is also compatible with these rates: **6a** gives only allene with a relative rate of 1.0 whereas **5a** gives 15% of allene, with a partial rate for allene formation of 0.8. No allene was observed during the thermolysis of the selenoxides derived from **7a** and **8b**.[3] These compounds lack the β-alkyl substituent of **5a** which retards acetylene formation.

A range of procedures is available for the preparation of vinyl selenides.[1c,e,4,8,10,11] It seems likely that many of these can now be used to prepare acetylenes although the geometric requirements for a syn elimination will limit the range of compounds that can be prepared. We have been able to find no other examples of acetylene-forming pericyclic eliminations involving sulfoxides and amine oxides, with the possible exception of a fragmentation involving a β-boron-substituted vinyl sulfoxide.[12] Enol acetates give acetylenes upon pyrolysis at 760 °C, but the mechanism does not appear to be a concerted cycloelimination.[13] Other pyrolytic routes to acetylenes have been reported.[14]

Acknowledgments. We thank the National Science Foundation and the National Institutes of Health for research support and Peter D. Clark for preliminary work on the pyrolysis of vinyl selenoxides.

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(7) H. J. Reich, "21st Annual Report on Research, PRF", 1976; H. J. Reich, W. W. Willis, Jr., and P. D. Clark, unpublished results. The selenides were deprotonated in THF as follows: **1a**, LDA, −78 °C, 5 min; **1b**, LDA, −78 °C, 2 h or LDA/HMPA, −78 °C, 5 min; **3** and **4**, lithium 2,2,6,6-tetramethylpiperidide, −50 °C, 3 h.

(8) S. Raucher and G. A. Koolpe, *J. Org. Chem.*, **43**, 3794, 4252 (1978).

(9) M. Sevrin, J. N. Denis, and A. Krief, *Angew. Chem.*, **90**, 550 (1978).

(10) α-Lithio vinyl selenides have also been prepared by Li/Se exchange: B.-T. Gröbel and D. Seebach, *Chem. Ber.*, **10**, 852, 867 (1977).

(11) E. G. Kataev, T. G. Mannafov, A. B. Remizov, and O. A. Kamarovskaya, *J. Org. Chem. USSR* (*Engl. Transl.*), **11**, 2363 (1975); E. G. Kataev, G. A. Chmutova, A. A. Musina, and E. G. Yarkova, *Dokl. Akad. Nauk SSSR, Ser. Khim.*, **187**, 673 (1969); J. Hooz and R. Mortimer, *Tetrahedron Lett.*, 805 (1976); N. Petragnani, R. Rodrigues, and J. V. Comassetto, *J. Organomet. Chem.*, **114**, 281 (1976); B. Harirchian and P. Magnus, *J. Chem. Soc., Chem. Commun.*, 522 (1977); S. Raucher, *J. Org. Chem.*, **42**, 2950 (1977); S. Raucher, M. R. Hansen, and M. A. Colter, *ibid.*, **43**, 4885 (1978); I. Kuwajima and M. Shimizu, *Tetrahedron Lett.*, 1277 (1978); G. Zima and D. Liotta, *Synth. Commun.*, **9**, 697 (1979).

(12) M. Naruse, K. Utimoto, and H. Nozaki, *Tetrahedron*, **30**, 2159 (1974).

(13) J. J. Harrison, *J. Org. Chem.*, **44**, 3578 (1979).

(14) (a) Selenadiazole pyrolysis: See ref 2a, p 119 for a review. (b) Oxidation of 1,2-bishydrazones: W. Schlenk and E. Bergmann, *Justus Liebigs Ann. Chem.*, **463**, 76 (1928); T. Curtius, *Chem. Ber.*, **22**, 2161 (1889). (c) α-Ketophosphorane pyrolysis: G. Märkl, *ibid.*, **94**, 3005 (1961). (d) Thermolysis of vinylenephosphorane: T. Mukaiyama, H. Nambu, and T. Kumamoto, *J. Org. Chem.*, **29**, 2243 (1964). Deoxygenation of vinylene thiocarbonate: D. P. Bauer and R. S. Macomber, *ibid.*, **41**, 2640 (1976). (e) Pyrolysis of cyclopropenones: R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1326 (1965).

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Low-Temperature Ozonation of Alkenes Adsorbed on Silica Gel

Sir:

The ozonation of compounds on silica gel has received considerable recent attention.[1-13] Particularly interesting reports include (i) regiospecific formation of tertiary alcohols from tertiary alkanes;[1,3,5,11] (ii) formation of nitroalkanes in high yield from primary amines;[4] (iii) carbon–carbon cleavage of alkanes;[9] and (iv) high yields of α-carbonylation products from alkylcyclopropanes.[6,7] This technique, called "dry ozonation", has been used to achieve carbonylation and epoxidation of triterpenes[12] as well as selective oxidation of the aromatic nucleus of arylalkanes.[8]

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(1) (a) Cohen, Z.; Keinan, E.; Mazur, Y.; Varkony, T. H. *J. Org. Chem.* **1975**, *40*, 2141–2142. (b) Varkony, H.; Pass, S.; Mazur, Y. *J. Chem. Soc., Chem. Commun.* **1974**, 437–438.

(2) Keinan, E.; Mazur, Y. *Synthesis* **1976**, 523–524.

(3) Cohen, Z.; Keinan, E.; Mazur, Y.; Ulman, A. *J. Org. Chem.* **1976**, *41*, 2651–2652.

(4) Keinan, E.; Mazur, Y. *J. Org. Chem.* **1977**, *42*, 844–847.

(5) Cohen, Z.; Mazur, Y. *J. Org. Chem.* **1979**, *44*, 2318–2320.

(6) (a) Proksch, E.; de Meijere, A. *Angew. Chem.* **1976**, *88*, 802. (b) *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 761–762. (c) *Tetrahedron Lett.* **1976**, 4851–4854.

(7) Preuss, T.; Proksch, E.; de Meijere, A. *Tetrahedron Lett.* **1978**, 833–836.

(8) Klein, H.; Steinmetz, A. *Tetrahedron Lett.* **1975**, 4249–4250.

(9) Tal, D.; Keinan, E.; Mazur, Y. *J. Am. Chem. Soc.* **1979**, *101*, 502–503.

(10) (a) Trifilieff, E.; Bang, L.; Ourisson, G. *Tetrahedron Lett.* **1977**, 2991–2994. (b) Trifilieff, E.; Bang, L.; Narula, A. S.; Ourisson, G. *J. Chem. Res., Synop.* **1978**, 64–65.

(11) (a) Beckwith, A. L. J.; Bodkin, C. L.; Duong, T. *Aust. J. Chem.* **1977**, *30*, 2177–2188; *Chem. Lett.* **1977**, 425. (b) Beckwith, A. L. J.; Duong, T. *J. Chem. Soc., Chem. Commun.* **1978**, 413–414; *Ibid.* **1979**, 690–691.

(12) (a) Akiyama, E.; Tada, M.; Tsuyuki, T.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 164–169; *Chem. Lett.* **1978**, 305–306. (b) Suokas, E.; Hase, T. *Acta Chem. Scand., Ser. B* **1978**, *32*, 623–624.

(13) The colored transient species arising during room-temperature ozonation of aryl alkenes and acetylenes have been described; see: Desvergne, J-P.; Bouas-Laurent, H. *J. Catal.* **1977**, *51*, 126–130. These authors report that the "usual products" were obtained in their experiments. Ozonation of solid stilbene is reported to give benzaldehyde and benzoic acid; see: Desvergne, J-P.; Blackburn, E. V.; Bouas-Laurent, H.; Lapouyade, R. *Tetrahedron Lett.* **1974**, 947–950.