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Regioselective Oxyselenenylation

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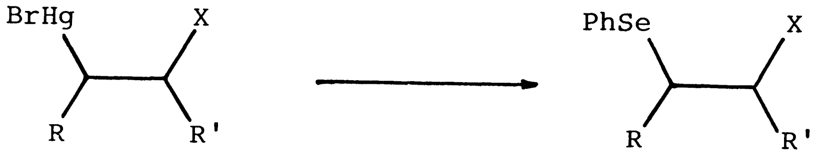
The regioselective oxyselenenylation of terminal olefins or cycloalkenes was achieved via olefin oxymercuration and subsequent radical substitution by selenenylating reagent such as S-benzoyl Se-phenyl selenosulfide, diphenyl diselenide, or phenylselenocyanide. Successful application to intramolecular selenocyclization of a mercurial bearing an α,β-unsaturated ester is also described.

To establish a completely regioselective selenenylation is one of the important requisites in synthesis.[1)] However, electrophilic selenenylations of olefins sometimes give a thermodynamic equilibrated mixture, especially in reactions of terminal olefins.[2)] We have reported the regioselective selenenylation of olefins via a free radical pathway using S-acyl Se-phenyl selenosulfide[3)] [SSe-phenyl (selenothioperoxy)carboxylate], which involves the intramolecular selenothiolactonization[4)] and the intermolecular selenothioesterification,[5)] notably the latter realizing the regioselective selenenylation of terminal olefins. We here describe an overall regioselective selenenylation of olefins via oxymercuration and subsequent radical selenenylation. We also report the selenocyclization of an mercurial bearing an α,β-unsaturated carboxylic ester.

Several 2-hydroxy- and 2-methoxymercurials prepared by the known oxymercuration method[6)] were converted to the corresponding seleno compounds by irradiation with S-benzoyl Se-phenyl selenosulfide [SSe-phenyl benzenecarbo(selenothioperoxoate)]. Diphenyl diselenide was also effective in these reactions. The results are summarized in Table 1.



1 2

a: R=H $R'=C_8H_{17}$ $X=OCH_3$

b: R=H $R'=C_8H_{17}$ X=OH

c: R=H $R'=C_6H_5$ $X=OCH_3$

d: R=H $R'=C_6H_5$ X=OH

e: $R\text{-}R'=-(CH_2)_4-$ $X=OCH_3$

f: $R\text{-}R'=-(CH_2)_4-$ Y=OH

g: $R\text{-}R'=-(CH_2)_3-$ $X=OCH_3$

h: $R\text{-}R'=-(CH_2)_3-$ X=OH

A typical reaction was carried out as follows. A degassed 1 M (1 mol dm^{-3}) benzene solution of organomercury bromide 1 and 1.2 equiv. S-benzoyl Se-phenyl selenosulfide was irradiated under argon atmosphere in a glass tube at a distance of 15 cm from 400 W high pressure mercury lamp. The reaction mixture was filtered, and the filtrate was then concentrated and purified by silica gel chromatography to give the oxyselenenylated compounds 2.

Oxyselenenylated compounds 2a and 2b obtained from 1-decene via oxymercuration were not contaminated with the regio isomers. It was confirmed by GLC and NMR spectra by comparison with the authentic Markovnikov and anti-Markovnikov oxyselenenylated compounds obtained via an ionic pathway. Thus, completely regioselective olefin selenenylation could be achieved. S-Benzoyl Se-phenyl selenosulfide was found to be as effective as diphenyl diselenide7) in most cases, while in reactions of mercurials 1c and 1d selenides 2c and 2d were obtained in lower yields than with diphenyl diselenide. Mercurials 1a and 1b were also irradiated with phenyl selenocyanate to give selenides 2a and 2b, respectively, in moderate yields.

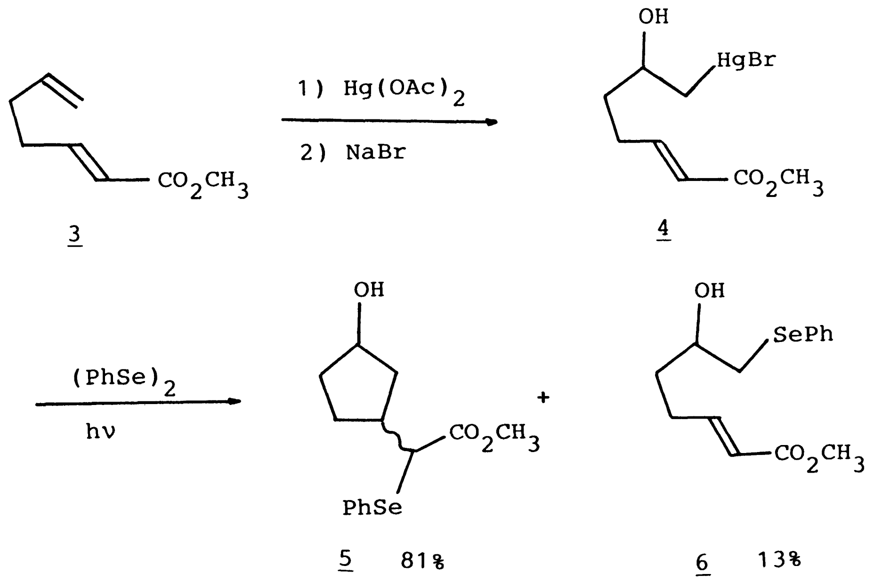
Irradiation of trans cyclohexylmercurials 1e and 1f with S-benzoyl Se-phenyl selenosulfide afforded a significant amount of the cis oxyselenides cis-2e and cis-2f, respectively, in addition to the respective trans isomers trans-2e and trans-2f. Formation of cis isomers cis-2g and cis-2h was also observed in the reaction of trans cyclopentylmercurials 1g and 1h. These features are in accord with the free radical chain process8) and are in contrast to the ionic oxyselenenylation of olefins which leads to the exclusive formation of the trans adduct.

Table 1. Selenenylation of Bromomercurials 1 into 2

Bromomercurial	Reagent	Reaction$^{a)}$ time/h	Selenide	Yield/%
1a	PhCOSSePh	2	2a	95
1a	PhCOSSePh	1.5$^{b)}$	2a	90
1a	(PhSe)$_2$	1	2a	92
1a	PhSeCN	4	2a	64
1b	PhCOSSePh	1.5	2b	92
1b	(PhSe)$_2$	1	2b	95
1b	PhSeCN	1	2b	80
1c	PhCOSSePh	1	2c	56
1c	(PhSe)$_2$	1	2c	90
1d	PhCOSSePh	2	2d	67
1d	(PhSe)$_2$	1	2d	87
1e	PhCOSSePh	1	2e	91 (t/c 60/40)$^{c)}$
1e	(PhSe)$_2$	0.5	2e	95 (t/c 56/44)$^{c)}$
1f	PhCOSSePh	1	2f	97 (t/c 46/54)$^{c)}$
1f	(PhSe)$_2$	0.5	2f	93 (t/c 43/57)$^{c)}$
1g	PhCOSSePh	1	2g	91 (t/c 94/6)$^{c)}$
1g	(PhSe)$_2$	0.5	2g	95 (t/c 92/8)$^{c)}$
1h	PhCOSSePh	1	2h	95 (t/c 97/3)$^{d)}$
1h	(PhSe)$_2$	0.5	2h	97 (t/c 92/8)$^{d)}$

a) All reactions except indicated were carried out by irradiation (400 W Hg lamp) in 1 M benzene solution. b) A 1 M benzene solution was heated under reflux in the presence of AIBN. c) The trans/cis ratios were determined by the NMR spectra.
d) Isolated ratio.

Since the intermediate carbon radical should be nucleophilic,$^{9)}$ we next tried the selenocyclization$^{10)}$ of mercurial 4 bearing an α,β-unsaturated carboxylic ester, prepared from ethyl hepta-2,6-dienoate 3. Irradiation of 4 with diphenyl diselenide (1.1 equiv.) for 1 h gave the selenocyclized product 5$^{11)}$ and selenosubstituted one 6 in 81% and 13% yield, respectively.



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2) For example, S. Rauscher, J. Org. Chem., 45, 2950 (1977); N. Miyoshi, Y. Ohno, K. Kondo, S. Murai, and N. Sonoda, Chem. Lett., 1979, 1309; A. Toshimitsu, T. Aoai, H. Owada, S. Uemura, and M. Okano, J. Chem. Soc., Chem. Commun., 1980, 412.

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4) T. Toru, T. Kanefusa, and E. Maekawa, Tetrahedron Lett., 27, 1583 (1986).

5) T. Toru, T. Seko, and E. Maekawa, Tetrahedron Lett., 26, 3263 (1985).

6) W. Carruthers, "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, Pergamon Press, Oxford (1982), p. 671.

7) Selenenylation of alkylmercury chloride with diphenyldiselenide has been reported by Russell and Tashtoush; G. A. Russell and H. Tashtoush, J. Am. Chem. Soc., 105, 1398 (1983). Their reactions seem to take longer reaction time than ours probably because of the difference of the light sources (275W sunlamp). In addition, alkylmercury chlorides seem to be less reactive than the bromides in these reactions; we found that the irradiation of 2-methoxydecylmercury chloride with S-benzoyl Se-phenyl selenosulfide for 7 h gave the selenide in 62% yield.

8) F. W. Stacey and J. F. Harris, Jr., "Organic Reactions," ed by A. C. Cope, Wiley, New York (1963), Vol. 13, Chap. 4.

9) Cyclohexyl radical reacts with α,β-unsaturated ester 3000 times faster than with 1-hexene, see B. Giese and G. Kretzschmar, Chem. Ber., 116, 3267 (1983).

10) Russell et al. observed that the reaction of hex-5-enylmercury chloride gave a mixture of cyclopentylmethyl and hex-5-enylselenide; see Ref. 7.

11) The stereochemistry has not been determined.

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