(dd, $J = 14.2$, 8.1 Hz, H-7β), 2.75 (dd, $J = 14.2$, 9.0 Hz, H-7α), 3.02 (s, 3 H), 3.20 (d-like m, 2 H-10), 3.40-3.50 (m, 2 H-18), 3.88 (s, 3 H), 4.15 (q, $J = 6.9$ Hz, 2 H), 4.39 (br t, $J = 8.5$ Hz, H-8), 5.05 (s, H-5), 5.90 (m, H-9), 6.69 (s, H-1 and 2), 7.42 (s, H-16). The ^{13}C NMR ($CDCl_3$) spectrum of **7** was very similar to that of **5** except for the new appearance in **7** of a carbonyl signal [δ205.8 (s, C-6)] and a methylene signal δ44.4 (t, C-7)] at the cost of two olefinic signals [δ102.2 (d) and 150.5 (s)] and a methyl signal [δ50.2 (q)] in **5**.

The above results can be most reasonably explained by the stepwise mechanism involving ionic species shown in Scheme I, which was also compatible with the observation of remarkable solvent effects. The reaction may be initiated by the nucleophilic addition of **1** to the electron-deficient acetylenes[14] followed by the cleavage of C(9)–N bond, which is stereoelectronically favored by its almost parallel arrangement to the p orbitals of adjacent C(8)=C(14) double bond. The sterically most favorable ring closure at C(8) position of the resulting intermeidates (A and/or B) leads to the formation of adducts **4** and **5**.

The facile formation of a new type of adduct of **1**, by using polar solvents, is most noteworthy. These results provide a further way for chemical modifications of **1** and stimulate the reexamination of cycloaddition reactions of **1** with various dienophiles in different solvents, which is currently under way in our laboratory.

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[13] Compound **8**: mp 231–233 °C (ethyl acetate); MS, *m/e* 381 (M^+); IR (Nujol) 1735 and 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.68–2.00 (m, 2 H), 2.50 (dd, $J = 13.8$, 8.0 Hz, H-7β), 2.82 (dd, $J = 13.8$, 9.0 Hz, H-7α), 3.00 (s, 3 H), 3.18 (d-like m, 2 H), 3.40–3.60 (m, 2 H), 3.67 (s, 3 H), 3.86 (s, 3 H), 4.37 (br t, $J = 8.5$ Hz, H-8), 5.03 (s, H-5), 5.90 (m, H-9), 6.88 (s, H-1 and H-2), and 7.40 (s, H-16); ^{13}C NMR ($CDCl_3$) δ 29.2 (t), 37.4 (d), 37.4 (s), 41.5 (t), 44.5 (d) 51.1 (q), 53.3 (t), 54.2 (t), 56.5 (q), 89.4 (d), 105.4 (s), 112.8 (d), 119.6 (d), 126.3 (d), 126.3 (s), 132.2 (s), 138.5 (s), 142.3 (s), 143.9 (s), 150.6 (d), 169.4 (s), and 205.7 (s).

[14] Ethyl acrylate was found not to react with **1** in a similar way, but to give the Diels–Alder adduct under more drastic conditions.[3]

Generation and Recycle Use of Selenenylating Reagents in Electrochemical Oxyselenenylation–Deselenenylation of Olefins

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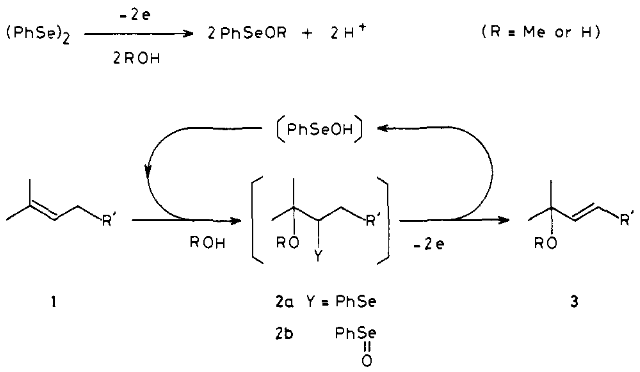
Received March 24, 1981

Oxyselenenylation–oxidative deselenenylation sequence provides double-bond transpositioned allylic alcohols and ethers from olefins.[1] The current method involves two steps: oxyselenenylation with PhSeX (X = Cl, Br, OR, and NR_2) followed by oxidation with O_3, $NaIO_4$, and peroxides (H_2O_2, *t*-BuOOH, *m*-CPBA) where stoichiometric amounts of PhSeX in the former step and large excess amount of oxidative reagents in the latter are required.[1,2] In principle, electrochemical transformation (**1** → **3**) must be realized since both oxyselenenylation and deselenenylation via selenoxide are oxidative processes.[3] Here, we describe a one-step preparation of allylic derivatives **3** from isoprenoids **1**, which is characterized by (1) electrochemical generation and recycled use of selenenylation reagents from a catalytic amount of diphenyl diselenide, (2) one-step preparation of allylic alcohols **3** (R = H) without use of phenylselenenic acid[4] and selenenamide,[5] and finally (3) deselenenylation in the absence of peroxides.

Scheme I



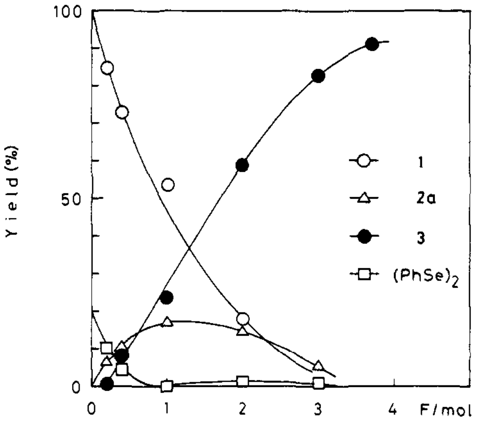


Figure 1. Electricity (F/mol of **1**) and yields of products [**2a** and **3**, R = $CH_2CMe(OAc)C{\equiv}CH$] in the presence of 10 mol % of diphenyl diselenide in MeOH at 60–63 °C.

The reaction procedure requires a mixture of **5** (0.5 mmol), $(PhSe)_2$ (0.05 mmol), and $MgSO_4$ (2.5 mmol) in $MeCN-H_2O$ (5:2) which is electrolyzed under a constant current (6.7 mA/cm^2, 4.2 F/mol) by using Pt foils as electrodes in an undivided cell at 66–68 °C, affording **14** (R = H, 89%). The results of the electrochemical transformation are summarized in Table I. Most of terminal ω double bonds of isoprenoids undergo regioselective oxyselenenylation–deselenenylation to give *trans*-allylic alcohols[6] in aqueous acetonitrile and methyl ethers[6] in methanol. Particularly noteworthy is the fact that the hydroxylative double-bond transposition (**1** → **3**, R = H) takes place efficiently in aqueous acetonitrile, which is an easier access to allylic alcohol **3** (R = H) than the known methods by phenylselenenic acid[4] and phenylselenenamide.[5] Acetoxyl, carbomethoxyl, ethynyl, and sulfonyl groups are inert in the electrolytic conditions. Enol acetate **10** was converted into α,β-unsaturated ketone **19** (81%) by this procedure. β-Pinene **11** provided **20a** and **20b** via oxyselenenylation involving ring opening of the cyclobutane skeleton[3b] → selenoxylation → [2,3]-sigmatropic rearrangement of the selenoxide.[1,7] This electrochemical reaction can be demonstrated by a one-step synthesis of *dl*-dihydroactinidiolide **21** (92%)[8] from

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[1] (a) Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049. (b) Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22.

[2] For instance, the transformation (**1** → **3** for citronellol, R = H) is performed by the action of 3 mol equiv of PhSeOH for hydroxyselenenylation followed by 5 mol equiv of *t*-BuOOH for deselenenylation via selenoxide: Hori, T.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1689.

[3] We reported recently a bromide ion mediated electrochemical oxyselenenylation: (a) Torii, S.; Uneyama, K.; Handa, K. *Tetrahedron Lett.* **1980**, *21*, 1863. (b) Torii, S.; Uneyama, K.; Ono, M. *Ibid.* **1980**, *21*, 2741. (c) Torii, S.; Uneyama, K.; Ono, M. *Ibid.* **1980**, *21*, 2653.

[4] (a) Hölzle, G.; Jenny, W. *Helv. Chim. Acta* **1958**, *41*, 593. (b) Sharpless, K. B.; Lauer, R. F. *J. Org. Chem.* **1974**, *39*, 429. (c) Reich, H. J. *Ibid.* **1974**, *39*, 428. (d) Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1974**, 100.

[5] (a) Nicolaou, K. C.; Claremon, D. A.; Barnette, W. E.; Seitz, S. P. *J. Am. Chem. Soc.* **1979**, *101*, 3704. (b) Reich, H. J.; Renga, J. M. *J. Org. Chem.* **1975**, *40*, 3313.

[6] Purity of **3** was determined by HPLC (μ-Porasil, *n*-hexane–ethyl acetate 5:1). The coupling constants of the newly formed double bond (J, Hz) are as follows: **13**, 15.7; **14**, 15.6; **15**, 15.4; **16**, 15.4; **17** 15.1; **18**, 15.9; **19**, 15.9.

[7] Reich, H. J. *J. Org. Chem.* **1975**, *40*, 2570.

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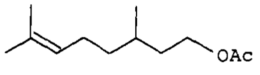
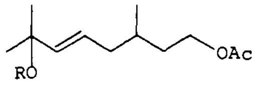
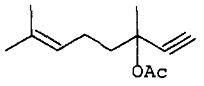
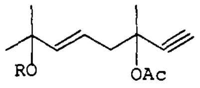
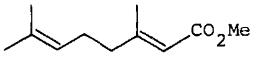
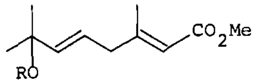
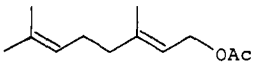
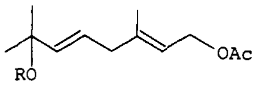
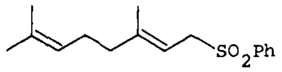
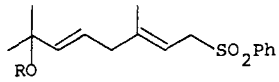
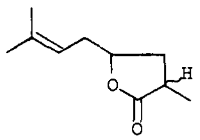
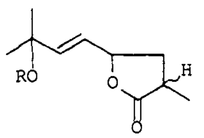
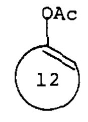
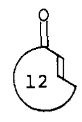
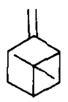
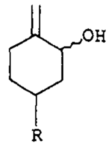
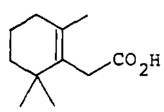
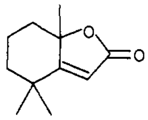
Table I. Electrooxidative Oxyselenenylation-Deselenenylation of Olefins

	substrate	F/mol^a		product	R	yield, %^{b}
4		5.6 3.6	13		Me H	82 80
5		3.7 4.2	14		Me H	91 89
6		3.1 5.9	15		Me H	79 81
7		3.9 6.0	16		Me H	86 69
8		4.8	17		Me	73
9		9.3	18		H	73^c
10		11.9	19		—	81^c
11		4.0	20		a R; C(Me)$_2$OMe b R; C(Me)=CH$_2$	61 13
12		8.2	21			92^d

^{a} Electricity passed during the electrolysis, F/mol of substrate 1. Theoretically, 3 F/mol of electricity is required for the transformation (1 → 3). ^{b} Isolated yield using 10 mol % of diphenyl diselenide. ^{c} 20 mol % of diphenyl diselenide was used. ^{d} 50 mol % of diphenyl diselenide was used.

carboxylic acid **12**. The lactone **21** would be produced by electrochemical intramolecular oxyselenenylation followed by electrochemical selenoxylation and elimination of phenylselenenic acid.[9]

The electrooxidatively generated phenylselenenyl reagents (PhSeOR, R = H or Me, Scheme I)[10] reacts regioselectively with olefins producing oxyselenide **2a** at the first step, followed by the subsequent electrochemical oxidation of **2a** to provide the corresponding selenoxide **2b**, which instantaneously undergoes syn elimination[11] to give the desired product **3**.[12,13] As shown in Figure 1 **2a** [R′ = CH$_2$CMe(OAc)C≡CH] increased gradually, reached the optimum amount near 1 F/mol, and completely disappeared at 3.7 F/mol. Diphenyl diselenide was consumed within 1 F/mol;[14] however, the starting material **1** decreased gradually and the final product **3** increased steadily on further electrolysis. These results suggest that a selenenylation reagent is regenerated in situ and promotes the transformation (**1** → **3**). It is noteworthy that electrooxidation of a mixture [84% of **1** and 16% of **2a**, R′ = CH$_2$CMe(OAc)C≡CH] in the absence of diphenyl diselenide in MeOH provided **3** in 63% yield after 7.6 F/mol, revealing clearly

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[8] (a) Sakan, T.; Isoe, S.; Hyeon, S. B. *Tetrahedron Lett.* **1967**, 1623. (b) Uneyama, K.; Kuyama, M.; Torii, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2108 and references cited therein.

[9] A solution of **12** (0.2 mmol), (PhSe)$_2$ (0.1 mmol), Et$_4$NBr (0.05 mmol), and Na$_2$CO$_3$ (0.2 mmol) dissolved in MeCN (7 mL)-H$_2$O (0.2 mL) was electrolyzed at room temperature (70 mA for 36 min, 8.2 F/mol) giving **21**. While, an intramolecular oxyselenenylation product, 2,2,6-trimethyl-1-(phenylseleno)-7-oxabicyclo[4.3.0]nonan-8-one was prepared by the action of **12** with phenylselenenyl bromide in CH$_2$Cl$_2$ and subjected to electrolysis, providing **21**. The spectral data of synthetic **21** was consistent with those of the authentic sample.[8]

[10] Polarographic analysis showed that diphenyl diselenide is oxidized at 0.96 V vs. Ag/Ag$^+$ in MeCN where olefin **1** could not be oxidized. Bewick, A.; Coe, D. E.; Fuller, G. B.; Mellor, J. M. *Tetrahedron Lett.* **1980**, 3827.

[11] (a) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434. (b) Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow, F.; Wendelborn, D. F. *J. Org. Chem.* **1978**, *43*, 1697.

[12] The presence of small amounts of sulfuric acid using stoichiometric amount of diphenyl diselenide suppresses selenoxylation of **2a** and enabled us to prepare **2a** chemoselectively.[3a,3b]

[13] Although the corresponding selenoxide **2b** derived from **4**–**12** were not isolated due to the fast syn elimination, the selenoxide, 2-methoxy-1-(phenylseleninyl)octane, derived from electrolysis of 1-octene, was actually isolated and identified spectroscopically in comparison with the authentic sample.

[14] At this stage the yellow color of diphenyl diselenide in the reaction solution almost faded away.

that phenylselenenic acid generated from syn elimination of the corresponding selenoxide is recycled during the electrolysis. Therefore, the electricity required for the total conversion is effectively saved.[15]

The effect of salts such as $MgSO_4$, $CaSO_4$ (82%), Na_2SO_4 (86%), K_2SO_4 (65%), $SrSO_4$ (51%), $BaSO_4$ (54%), and $Mg(ClO_4)_2$ (63%) is remarkable for the recycle, since the yield of **14** was only 26% in the absence of these salts and 10 mol % of diphenyl diselenide to **5** was employed. It is reasonable to assume that these salts prevent the conversion of phenylselenenic acid into inert phenylseleninic acid both by disproportionation[16] and in part by electrooxidation,[17] although the detailed mechanism of the effect is not yet clear.[18]

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(15) For instance, electrolysis of **5** in the presence of stoichiometric amount of diphenyl diselenide requires almost twice the amount of electricity (7.8 F/mol) in MeOH although the yield is slightly better (91% → 95%, Table I).

(16) (a) Behaghel, O.; Seibert, H. *Chem. Ber.* **1933**, *66*, 708. (b) Reference 11b.

(17) After electrolysis phenylseleninic acid was extracted with aqueous Na_2CO_3 and was converted into diphenyl diselenide by reduction with $NaHSO_3$.[2]

(18) A study on the mechanism of the recycle and the electrode process of diphenyl diselenide in the present electrolysis system is going on. The details will be reported elsewhere.

Stereomutation at Pentacoordinate Silicon by Intramolecular Ligand Exchange

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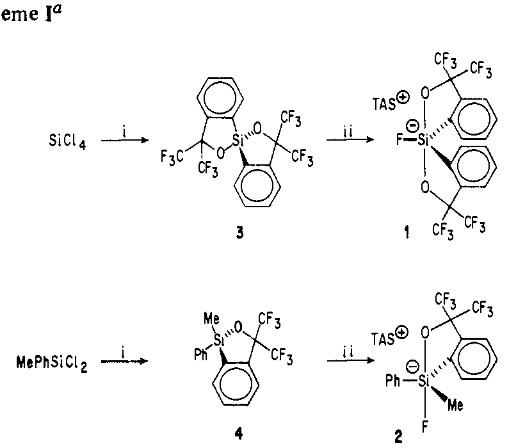
Although anionic, pentacoordinate silicon species have received some attention,[1] detailed studies describing both structure and ligand exchange processes have not been reported. We wish to present the first direct evidence for stereomutation of a pentacoordinate silicon compound by intramolecular ligand exchange.

The spiro siliconate **1**,[2] prepared by reaction of **3**[1a] with tris(dimethylamino)sulfonium (TAS) trimethyldifluorosiliconate[3] (Scheme I), exhibits a temperature-dependent ^{19}F NMR spectrum. The $A_3A_3'B_3B_3'X$ pattern observed in the limiting low-temperature spectrum (−15 °C) is transformed to a simple $A_{12}X$ pattern (at 70 °C) when interchange of diastereotopic trifluoromethyl groups is sufficiently rapid.[4] Visual fit of observed and calculated[5] spectra at various temperatures provided $\Delta G^{\ddagger} = 16.6$ kcal/mol ($\Delta H^{\ddagger} = 14.1$ kcal/mol; $\Delta S^{\ddagger} = -8$ eu) (Figure 1). Spectra were concentration independent and, except for minor differences in $\Delta\nu$, were solvent independent (acetonitrile, 1,2-dichloroethane). The exchange rate was unchanged by addition of either hexamethylphosphoramide or hexamethyldisilazane (HMDS).[6] That

Scheme I[a]



[a] (i) Dilithium reagent from hexafluorocumyl alcohol and 2 equiv of *sec*-butyllithium. (ii) $(Me_2N)_3S^+Me_3SiF_2^-$ in acetonitrile; TAS = $(Me_2N)_3S$.

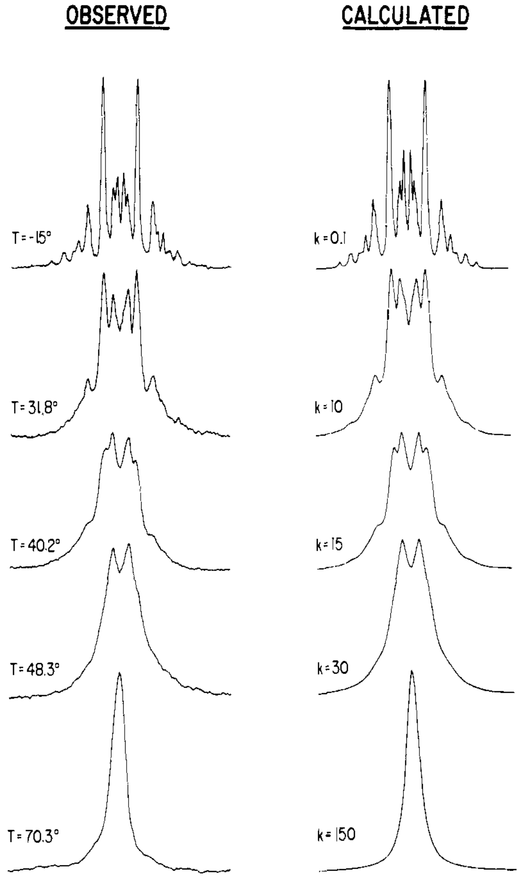


Figure 1. Representative observed and calculated ^{19}F NMR spectra for **1** (CF_3 region). Spectra were recorded while decoupling protons and the silicon-bound fluorine nucleus.

[†] Contribution No. 2904.

(1) (a) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1591. (b) Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1968**, *7*, 155. (c) Marat, R. K.; Janzen, A. F. *Can. J. Chem.* **1977**, *55*, 1167. (d) Corriu, R. J. P.; Royo, G.; De Saxcé, A. *J. Chem. Soc., Chem. Commun.* **1980**, 892. (e) Boer, F. P.; Flynn, J. J.; Turley, J. W. *J. Am. Chem. Soc.* **1968**, *90*, 6973. (f) Boer, F. P.; van Remoortere, F. P. *Ibid.* **1970**, *92*, 801. (g) Daly, J. J.; Sanz, F. *J. Chem. Soc., Dalton Trans.* **1974**, 2051. (h) Sullivan, S. A.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1981**, *103*, 480. (i) Breliere, C.; Carre, F.; Corriu, R. J. P.; De Saxcé, A.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1981**, *205*, Cl. (j) Frye, C. L. *J. Am. Chem. Soc.* **1970**, *92*, 1205.

(2) mp 141–142 °C. Anal. Calcd for $C_{24}H_{26}N_3O_2F_{13}SSi$: C, 41.44; H, 3.77; N, 6.04. Found: C, 41.81; H, 3.84: N, 5.91. Molecular weight determined by osmometry in 1,2-dichloroethane was 650.

(3) Middleton, W. J. (to Du Pont) U.S. Patent 3 940 402. Tris(dimethylamino)sulfonium trimethyldifluorosiliconate was prepared according to the following procedure. Sulfur tetrafluoride (0.12 mol) was condensed in a flask charged with dry ether (150 mL). (Dimethylamino)trimethylsilane (0.37 mol) was added dropwise to the mixture at −78 °C. The mixture was warmed slowly to 25 °C and stirred for 72 h in an atmosphere of dry nitrogen. Filtration under nitrogen provided a nearly quantitative yield of white solid, mp 58–62 °C.

(4) **1**: ^{19}F NMR (−15 °C, CD_3CN) ϕ_A −74.80, ϕ_B −75.05, ϕ_X −130.1, J_{AB} = 9.2 Hz, J_{AX} ~3.5 Hz, J_{BX} ~1.5 Hz; (70 °C) ϕ_A −74.93, ϕ_X −130.1, J_{AX} = 2.5 Hz (13 line pattern).

(5) Spectra were calculated by using LAOCOON 3 and DNMR 3 programs. Kleier, D. A.; Binsch, G. "DNMR3: A Computer Program for the Calculation of Complex Exchange-Broadened NMR Spectra. Modified Version for Spin Systems Exhibiting Magnetic Equivalence or Symmetry," Program 165, Quantum Chemistry Program Exchange, Indiana University, 1970. See also: *J. Magn. Reson.* **1970**, *3*, 146.

(6) HMDS was added to remove trace amounts of water or acid which might be present.

0002-7863/81/1503-4608$01.25/0