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A DIRECT PHENYLSELENENYLATION OF ALKYL HALIDES, ALKENYL SULFONATES, AND EPOXIDES BY AN ELECTROREDUCTION OF DIPHENYL DISELENIDE

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A convenient procedure for phenylselenenylation of alkyl halides, alkenyl sulfonates, and epoxides with phenyl selenide anion was accomplished by electroreduction of diphenyl diselenide in a protic solvent.

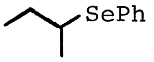
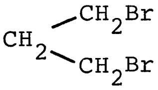
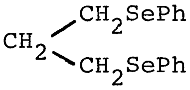
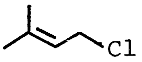
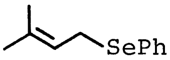
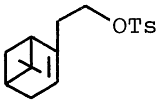
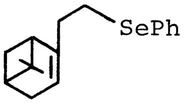
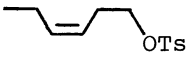
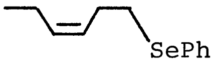
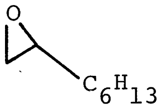
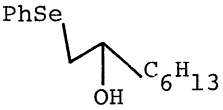
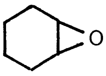
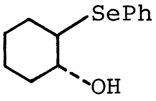
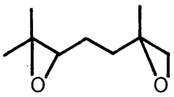
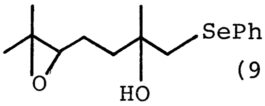
The current interest in the preparation of organo-seleno compounds is due to their versatile transformation to olefins.[1)] Published synthetic procedures using selenide anions are based on the reduction of diselenides with sodium borohydride or sodium metal and on the reaction of selenols with sodium hydride.[1)] In this communication, we report the direct selenenylation of alkyl halides, alkenyl sulfonates, and epoxides, with phenyl selenide anion, which can be produced by electroreduction of diphenyl diselenide without use of reducing agents.

A typical electrolysis procedure for the selenenylation of alkyl halide is as follows: a solution of 1-bromopentane (0.6 mmol) and $(PhSe)_2$ (0.27 mmol) in MeOH (14 ml) containing Et_4NOTs (0.17 M) was electrolyzed using Pt electrodes (3 cm^2) under a constant applied voltage of 10 V (2.6-6.1 mA/cm^2) in the cathode compartment of a divided cell at 3-4 ^oC. After being passed 5.0 F/mol of electricity (10 h), the mixture was worked up in the usual manner to give 108 mg (87%) of phenyl pentyl selenide. Other results of the selenenylation of various electrophiles are listed in Table.

Most of electrophiles could be converted into the corresponding alkyl selenides in good yields. In contrast to an electrochemical sulfenylation of alkyl halides,[2)] protic solvents could be conveniently employed as an electrolysis solvent for the present selenenylation.[3)] The selenenylation of 1,1-diiodomethane and 1,3-dibromopropane produced the corresponding 1,1- and 1,3-diselenoadducts (entries 3 and 4), whereas the reaction of 1,2-dibromoethane did not give rise to the desired selenenylated product. On the other hand, the phenyl selenide anion generated electrochemically also affected the displacement of alkenyl sulfonates at room temperature (entries 7 and 8).

Preferential attack of the selenide anion occurred on the less hindered site of the epoxides, giving β-hydroxyselenides in good yields (entries 9 and 11). These results suggested that the electrochemical preparation of the selenide anion can be used for the preparation of a variety of 1-seleno-2-hydroxy compounds.[4)]Further application for the preparation of some useful compounds is now in progress.

Table. Electrolytic Phenylselenenylation of Halides, Tosylates, and Epoxides

Entry	$(PhSe)_2$ mmol	Electrophile (mmol)	V (mA/cm^2)	F/mol	Product, Yield [a)] (%)
1 [b)]	0.27	$C_5H_{11}Br$ (0.6)	10 (2.6-6.1)	5.0 [c)]	$C_5H_{11}SePh$ (87)
2 [b)]	0.32	sec-C_4H_9Br (0.7)	8 (2.9-5.0)	6.2 [d)]	 (88)
3 [b)]	0.17	CH_2I_2 (0.12)	5 (2.7-3.7)	5.1 [d)]	$CH_2(SePh)_2$ (85) [e)]
4 [b)]	0.43	 $CH_2(CH_2Br)_2$ (0.41)	10 (2.8-6.4)	7.4 [c)]	 $CH_2(CH_2SePh)_2$ (84) [e)]
5 [b)]	1.0	MeO_2CCH_2Br (1. 5)	8 (3.5-9.7)	6.2 [d)]	MeO_2CCH_2SePh (92)
6 [b)]	0.34	 (1.5)	10 (4.0-6.0)	2.7 [c)]	 (94)
7 [b)]	0.37	 (1.14)	5 (1.3-3.2)	4.2 [d)]	 (98)
8 [b)]	0.27	 (0.49)	10 (4.3-10.3)	8.3 [d)]	 (82)
9 [f)]	0.26	 (0.5)	10 (2.9-4.0)	6.7	 (98)
10 [f)]	0.26	 (0.5)	10 (5.4-7.0)	7.3	 (84)
11 [f)]	0.26	 (0.5)	10 (3.6-5.9)	7.4	 (94)

a) Isolated yield based on $(PhSe)_2$. b) Electrolyzed in MeOH-Et_4NOTs (0.17 M).
c) Carried out at 3-4 °C. d) Carried out at room temperature.
e) Isolated yield based on alkyl halide. f) Electrolyzed in EtOH-$NaClO_4$ (0.33 M) at room temperature.

References and Notes

1) D. L. Clive, Tetrahedron, 34, 1049 (1978), and references cited therein.
2) P. E. Iversen and H. Lund, Acta Chem. Scand., B28, 827 (1974).
3) S. Torii, T. Inokuchi, and N. Hasegawa, Chem. Lett., 617 (1980).
4) All products indicated satisfactory IR and ^1H NMR spectra.

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