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ELECTROCHEMICAL HYDROXYSELENENYLATION AS A NEW METHOD FOR ONE-STEP PREPARATION OF α-ARYLSELENO-α,β-UNSATURATED ALDEHYDES FROM 3-HYDROXYALKYNES

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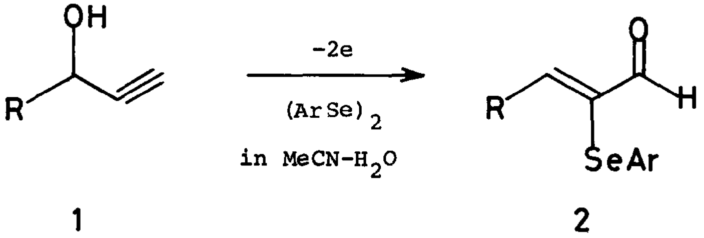
SUMMARY: Electrochemical oxidation of 3-hydroxyalkynes in the presence of diaryl diselenides in MeCN-H_2O provided α-arylseleno-α,β-unsaturated aldehydes 2 in 62 - 94% yields via hydroxyselenenylation of alkynes.

Inspite of many useful oxyselenenylation of olefins,[1] very few are known for selenation of triple bonds [2-6] and attempt on hydroxyselenenylation of acetylenic compounds leading to α-selenocarbonyl compounds has not appeared yet. Here, we describe an electrochemical one-step preparation of α-arylseleno-α,β-unsaturated aldehydes 2 [7] from 3-hydroxyalkynes 1 as a first successful hydroxyselenenylation of alkynes. So far as selenenylation of alkynes is concerned, rather strong selenenylating reagents such as phenylselenenyl chloride,[2, 3, 4] trifluoroacetate,[5] and hexafluorophosphate [6] have been employed because of the low reactivity of the triple bond. While phenylselenenic acid generated by hydrogen peroxide oxidation [8] is useless for the purpose although it affects smooth hydroxyselenenylation of olefins.[9] In contrast, the electrochemical procedure is effective since phenylselenenic acid can be generated gradually by controlling the current density so as to avoid the undesirable disproportionation of the acid [11] and furthermore the electrolysis can be conducted at the higher temperature where the triple bond is reactive enough.

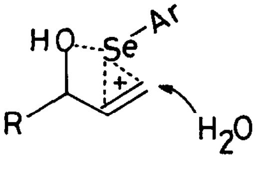


A typical electrolysis procedure is as followed; A mixture of 7 (190mg, 1.5mmol), p-chlorophenyl diselenide (57 mg, 0.15 mmol), tetraethylammonium perchlorate (9 mg, 0.4 mmol), and conc. sulfuric acid (30 mg, 0.3 mmol) dissolved in MeCN (6 mL) and H_2O (1 mL) was electrolyzed at 65 °C under constant current (3.3 mA/cm^2) for 14 h (35 F/mol) using platinum foils as electrodes in an undivided cell, affording 15 (81% based on p-chlorodiphenyl diselenide).[12]

In contrast to the smooth hydroxyselenenylation of olefins, the electrolysis of 1 at room temperature resulted in a poor yield of 2.[8] However, the yield increased sharply as the reaction temperature was raised (45% at 17 °C, 62% at 50 °C, and 81% at 65 °C for 7). The substituent on the phenyl ring of aryl diselenide also affected remarkably the yield since the electron withdrawing chlorine atom on para position provided a satisfactory result [81% (p-Cl), 52% (H), and 39% (p-MeO) for 7]. The result obtained with p-chlorophenyl diselenide is summarized in Table 1. Most of the example of 1 provided 2 in reasonable yields. On the contrary, the reaction of 1 with p-chlorophenylselenenic acid generated by hydrogen peroxide oxidation failed to give 2.[9] Likewise, electrolysis of disubstituted alkynes (9, 10, 12) afforded the corresponding ketones.

The regiochemistry of the selenenylation is strictly controlled by the hydroxyl group. The triple bond of 1 is attacked in an anti-Markownikoff fashion by the electrooxidatively generated selenenylating reagent followed by hydrolysis of the selenirenium type cation 3 from the less hindered side to give the enol 4, which undergoes dehydration yielding 2. Interaction between hydroxyl group and selenenic acid is responsible both for the regioselectivity[13] and the reaction rate of 1 since hydroxy compound 7 (X = OH) is more reactive than the nonsubstituted alkyne 23 (X = H),[14] and it provides anti-Markownikoff product sharply in contrast with 23, which gives Markownikoff product 25 (X = H).[15] Acetoxyl and methoxyl groups (X = AcO and MeO in Table 2) are less effective for the reactivity and the regioselectivity.[16]

It was found that 2 is an excellent dienophile while the related α-seleno-α,β-unsaturated carbonyl compounds have been known to be Michael acceptors and radicophiles. Thus, Diels-Alder reaction of 13 with butadiene at 115 °C provided 26 (81%), while crotonaldehyde gave the corresponding adduct in a poor yield (40%). The usual deselenation of 26 afforded cyclic dienal 27. The detailed results of the Diels-Alder reaction of 2 and deselenation of the adducts will be reported elsewhere.



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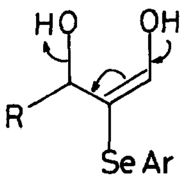

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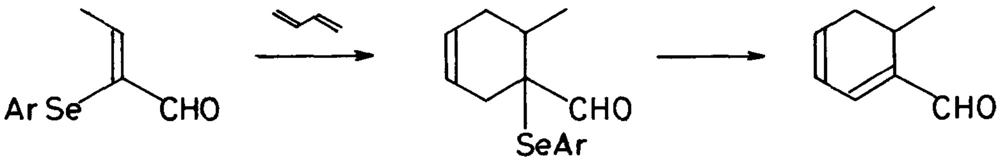
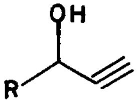
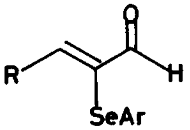
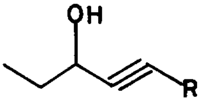
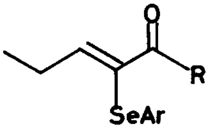
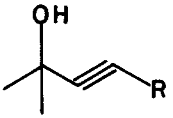
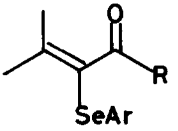


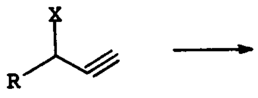
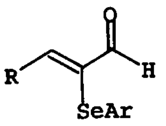
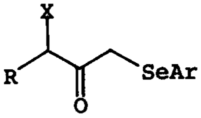
13 26 27

Table 1. Electrooxidative Hydroxyselenenylation of 3-Hydroxyalkynes and its Relatives.

Substrate		R	F/mol	Product		Yield % [a]
	5 [b]	CH_3	15		13	87
	6 [b]	CH_2CH_3	26		14	81
	7 [b]	$(CH_2)_4CH_3$	35		15	81
	8 [b]	Ph	36		16	74 [e]
	9 [b]	Ph	19		17	90
	10 [b]	$(CH_2)_3CH_3$	30		18	94
	11 [d]	H	30		19	62 [f]
	12 [c]	Ph	16		20	65

a) Isolated yield based on p-chlorophenyl diselenide. b) Et_4NClO_4 was employed as an electrolyte. c) Et_4NBr was used as an electrolyte. d) Et_4NOTs was an electrolyte. e) 1-Phenylpropyn-1-one (12%) was produced as a byproduct. f) 2,3-Epoxy-3-methyl-1-phenylbutanone (3%) was obtained as a byproduct.

Table 2. Effect of Substituent on C-3 in Electrochemical Hydroxyselenenylation [a]

					Recovered $(ArSe)_2$
	R	X	24 (%)	25 (%)	(%)
7	$(CH_2)_4CH_3$	OH	81	0	9
21		OAc	21	21	42
22		OMe	55	0	32
23	$(CH_2)_2CH_3$	H	0	33	56

a) Isolated yield based on p-chlorophenyl diselenide after 35 F/mol of electricity was passed.

References and Notes

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

2) E. G. Kataev; T. G. Mannafov; Y. Y. Samitov, J. Org. Chem. (U.S.S.R.), 1975, 11, 2366.

3) C. N. Filer; D. Ahern; R. Fazio; J. E. Shelton, J. Org. Chem., 1980, 45, 1313.

4) G. H. Schmid; D. G. Garratt, Chemica Scripta, 1976, 10, 76.

5) H. J. Reich, J. Org. Chem., 1974, 39, 428.

6) G. H. Schmid; D. G. Garratt, Tetrahedron Lett., 1975, 3991.

7) Alternative preparation of 2 and its related compounds; (a) From propargyl selenoxide rearrangement, H. J. Reich; S. K. Shah, J. Am. Chem. Soc., 1977, 99, 263. (b) H. J. Reich; S. K. Shah; P. M. Gold; R. E. Olson, Ibid., 1981, 103, 3112. (c) From the reaction of unsaturated cyclic ketones with PhSeCl-pyridine complex, G. Zima; D. Liotta, Synthetic Commun., 1979, 9, 697.

8) (a) O. Behaghel; H. Seibert, Chem. Ber., 1933, 66, 708. (b) T. Hori; K. B. Sharpless, J. Org. Chem., 1978, 43, 1689. (c) H. J. Reich; S. Wollowitz; J. E. Trend; F. Chow; D. F. Wendelborn, J. Org. Chem., 1978, 43, 1697.

9) p-Chlorophenylselenenic acid generated by hydrogen peroxide reacts easily with olefins to give the corresponding hydroxyselenides although 3 mole equivalents of the reagents are required to complete the reaction.[8] In contrast, the yield of 15 was only 17% and 38% of 7 was recovered after stirring at room temperature for 18 h. At the higher temperature(40°C) TLC of the reaction mixture was complex and the yield of the desired compound was poor.

10) (a) S. Torii; K. Uneyama: M. Ono, Tetrahedron Lett., 1980, 21, 2741. (b) S. Torii; K. Uneyama; M. Ono, Ibid., 1980, 21, 2653. (c) S. Torii; K. Uneyama; M. Ono; T. Bannou, J. Am. Chem. Soc., 1981, 103, 4606.

11) (a) H. J. Reich; J. M. Renga; I. L. Reich, J. Am. Chem. Soc., 1975, 97, 5434. (b) ref. 9a,c.

12) The structure of 2 was identified with H^1, and C^{13} NMR, and IR spectra. The stereochemistry of 15 (trans) was assigned on the basis of the relative induced shifts of protons of 15 and crotonaldehyde using $Eu(fod)_3$ in $CDCl_3$.

13) A similar type interaction between hydroxyl group and benzene selenenic anhydride has been proposed by Kuwajima. M. Shimizu; R. Takeda; I. Kuwajima, Tetrahedron Lett., 1979, 3461.

14) In spite of the expected deactivation of the triple bond through electron-withdrawing inductive effect of 3-hydroxy group, 7 reacts faster than 23 (X = H) since competitive reaction between 7 and 23 (1 : 1 mixture) afforded 15 preferentially (15 : 25 = 2 : 1).

15) The stereochemical course (Markownikoff type) of hydroxyselenenylation of unsubstituted 1-alkynes is contrary to that of chloroselenenylation reported by Schmid.[4]

16) The acetoxy compound gave regioisomer 24 and 25 (X = AcO, Table 2). The isomer 25 would be derived from the transition state as illustrated in 28 and 29. The compound 24 may arise in part from 7 since 24 was hydrolyzed in the reaction condition.

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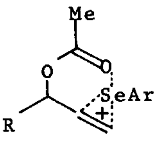

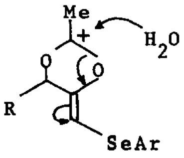

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