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A FACILE ACCESS TO α-PHENYLSELENENYL CARBONYL COMPOUNDS BY ELECTROCHEMICAL OXIDATION

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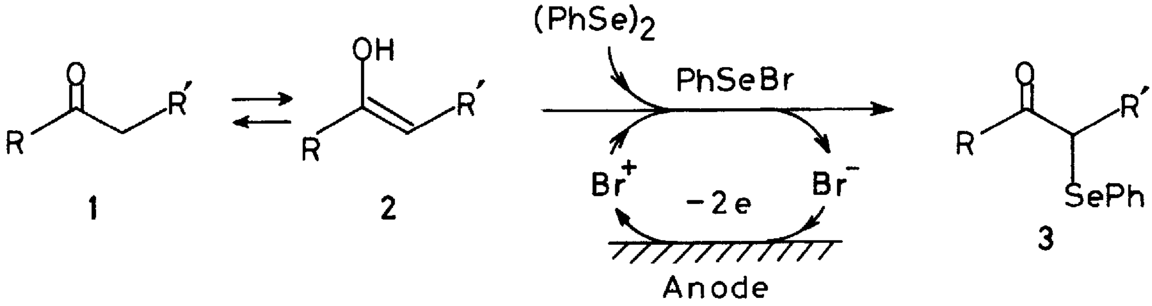
Summary: A novel α-phenylselenenylation of carbonyl compounds has been performed by electrolysis of a solution of ketones, diphenyl diselenide, tetraethylammonium bromide, and magnesium bromide in polar solvents (MeOH, AcOH, MeCN). The electrolysis enables us to prepare the desired seleno-carbonyl compounds without employing strong bases and the activated selenenyl reagents PhSeX.

α-Phenylseleno carbonyl compounds are valuable precursors to α,β-unsaturated and α-exo-methylene carbonyl compounds.1) Reaction of carbonyl compounds with lithium diisopropylamide (LDA) followed by treatment of PhSeX (X=Cl, Br) has been most widely used.1,2) While, selenenylation of enol acetates followed by hydrolysis is a complement of the above method in neutral conditions.3,4) We describe here a straightforward electrolytic α-phenylselenenylation which is characterized by the following facts; (1) neither strong bases such as LDA nor the activated seleno compounds PhSeX (X=Cl, Br, NR_2 etc) are required; (2) pretransformation of the carbonyl compounds to the corresponding enol derivatives is unnecessary.



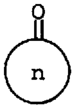
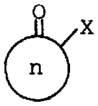
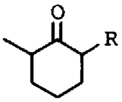
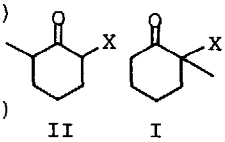
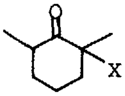
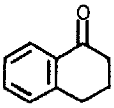
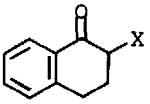
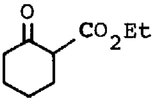
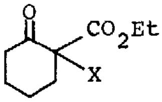
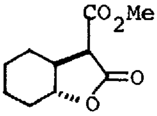
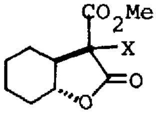
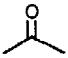
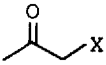
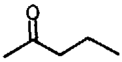
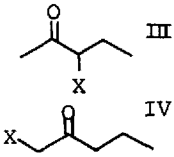
A typical electrolysis is as follows; A solution of cyclododecanone (0.3 mmol), diphenyl diselenide (0.3 mmol), tetraethylammonium bromide (TEAB) (0.15 mmol), $MgBr_2 \cdot 6H_2O$ (1.4 mmol), and H_2SO_4 (0.9 mmol) in MeOH (6 ml) was electrolyzed at room temperature under constant current (30 mA, 12 F/mol) using Pt foils (2×1.5 cm^2) in an undivided cell. The reaction conditions and yields are listed in Table 1 along with the reported yields.

Cycloalkanones (entry 1-4) could be converted into the corresponding seleno compounds in much higher yields than the reported methods which require either strong bases such as LDA and NaH or the enol derivatives and phenylselenenyl halides.[5,6,7] The presence of a small amount of sulfuric acid allows to proceed the selenenylation of the less enolizable ketones (entry, 3,4,10, and 11), whereas the addition of triethylamine assisted the selenenylation of active methine compounds (entry 8 and 9).

The effect of halide ions is remarkable. Thus, bromide is the most effective and iodide is the least (Table 2, entry 1-3). The use of chloride induced α-chlorination of cyclohexanone as a side reaction. Magnesium ion seems to be essential for promoting enolization.[8] Thus, the absence of Mg^{2+} resulted in production of none or very poor yield of the selenides (entry 4 and 6) in spite of the possible formation of the selenenylating agent (PhSeBr) in the electrolysis.[9] Calcium chloride also facilitated the selenenylation , but both $ZnCl_2$ and $BaCl_2$ failed because of low solubility and deposit of metal on the cathode.

The mechanism of the selenenylation would be assumed as follows; Reaction of the electrochemically generated bromonium ion or bromine with diphenyl diselenide produces phenylselenenyl bromide which immediately attacks enol of the carbonyl compounds as it reacts with olefins.[9] However, behavior of tetralone is unusual . The electrolysis in MeOH including TEAB and $MgBr_2$ provided α-bromoketone (ca 30 %, entry 7, X=Br) and seleno compound (7%, X=PhSe). In contrast, the electrolysis in MeOH containing $MgSO_4$ and H_2SO_4 afforded the desired product (71%, entry 7, X=PhSe) along with 2,2-dimethoxytetralone (4%). These results suggest that α-keto radical from tetralone is a possible intermediate although the discussion must wait further detailed studies.

Table 1. Electrolytic α-Phenylselenenylation of Carbonyl Compounds

Entry	Substrate	Solv / Electrolyte & Additive (molar eq to substrate)^a	mA (F/mol)	Product X=SePh	Yield^{b,c} %
1	 n = 5	AcOH/TEAB, $MgBr_2$ (0.12, 1.2)	20 (2.5)		97 (62, A)^d
2	n = 6	AcOH/TEAB, $MgBr_2$ (0.13, 1.2)	20 (2.5)		96 (70, A)^d
3	n = 7	AcOH/TEAB, $MgBr_2$, H_2SO_4 (0.12, 1.3 , 0.29)	10 (7.0)		84 (55,B)^{e,g}
4	n = 12	MeOH/TEAB, $MgBr_2$, H_2SO_4 (0.53, 4.8, 3.2)	30 (12.0)		86 (72,B)^{e,g}
5	 R = H	AcOH/TEAB, $MgBr_2$ (0.26, 1.5)	20 (4.0)	 II I	84 (89, B)^e I/II = 68/32
6	R = Me	AcOH/TEAB, $MgBr_2$ (0.35, 1.0)	5 (7.0)		80 (76,B)^{f,g}
7		MeOH/$MgSO_4$, H_2SO_4 (5.0, 5.4)	20 (10.0)		71
8		MeCN/TEAB, $MgBr_2$, Et_3N (o.17, 2.3 1.0)	10 (1.9)		86 (89,C)^{e,g}
9		MeCN/TEAB, $MgBr_2$, Et_3N (0.40, 2.2 2.2)	7 (3.0)		90
10		AcOH/TEAB, $MgBr_2$, H_2SO_4 (0.01, 0.1, 0.02)	30 (6.0)		88
11		AcOH/TEAB, $MgBr_2$, H_2SO_4 (0.12, 0.73, 0.16)	30 (4.0)	 III IV	94 III/IV=94/6

a) TEAB; tetraethylammonium bromide. b) Isolated yield based on $(PhSe)_2$. c) Reported yield, A; enol acetate and PhSeBr, B; LDA and PhSeX (X=Cl, Br), c) NaH and PhSeX. d) Ref. 5. e) Ref. 3. f) Ref. 6. g) Yield of the corresponding enone after oxidative deselenenylation.

Table 2. Effect of Electrolytes on the α-Selenenylation of Cyclohexanone.

Entry	Electrolyte and Additive (mol. eq to cyclohexanone)		F/mol [a]	Yield [b] %	Recovered $(PhSe)_2$ %
1	Et_4NBr (0.13),	$MgBr_2 \cdot 6H_2O$ (1.2)	2.5	96	4
2	Et_4NCl (0.16),	$MgCl_2 \cdot 6H_2O$ (1.6)	2.5	70	4
3	Et_4NI (0.17),	$MgBr_2 \cdot 6H_2O$ (1.5)	8	9	62
4	Et_4NBr (0.53),	---	3	0	100
5	---	$MgBr_2 \cdot 6H_2O$ (1.3)	4	93	4
6	Et_4NBr (0.14),	NaBr (2.9)	6	11	86
7	Et_4NBr (0.14),	$CaCl_2$ (2.7)	2.5	86	6
8	Et_4NBr (0.14),	$ZnCl_2$ (2.9)	4	37	54
9	Et_4NBr (0.14),	$BaCl_2$ (1.4)	3	20	78

a) Constant current (20 mA) was applied in AcOH. b) Isolated yield based on $(PhSe)_2$

References and Notes

1) D. L. Clive, Tetrahedron, 34, 1049 (1978); H. J. Reich, Acc. Chem. Rec., 12, 22 (1979); P. A. Grieco, Synthesis, 67 (1975).

2) Selenenamides react with β-dicarbonyl compounds without bases although the reagents must be handled in a carefully controlled conditions because of their unstabilities. H. J. Reich and J. M. Renga, J. Org. Chem., 40, 3313 (1975).

3) H. J. Reich, J. M. Renga, and I. L. Reich, J. Am. Chem. Soc., 97, 5434(1975).

4) Several ketones and aldehydes can be converted into the α-phenylseleno compounds in moderate yields on treatment with PhSeCl in ethyl acetate. K. B. Sharpless, R. F. Lauer,and A. Y. Teranishi, J. Am. Chem. Soc., 95, 6137(1973).

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6) H. J. Reich, I. L. Reich, and J. M. Renga, J. Am. Chem. Soc., 95, 5813 (1973).

7) H. J. Reich, J. M. Renga, and I. L. Reich, J. Org. Chem., 39, 2133 (1974).

8) S. Torii, K. Uneyama, and N. Yamasaki, Bull. Chem. Soc. Jpn., 53, 819 (1980).

9) Phenylselenenyl bromide is produced by electrolysis of Br^- in the presence of $(PhSe)_2$ and it can attack olefins in situ providing oxyselenenylated compounds. S. Torii, K. Uneyama, and M. Ono, in contribution.

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