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A DIRECT ARYLSELENENYLATION OF ENONES WITH DIARYL DISELENIDES BY A ELECTROREDUCTIVE PROCEDURE

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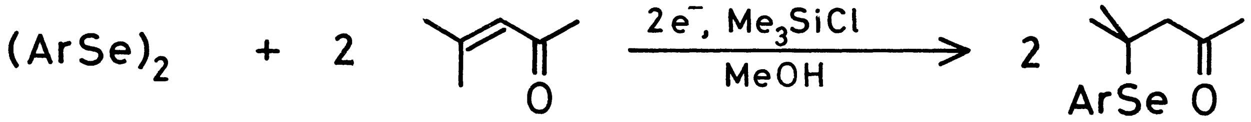
A new procedure for arylselenenylation of enones has been developed by electrolysis with diaryl diselenide and chlorotrimethylsilane in methanol. In the course of the reaction generation of aryl selenols *in situ* is assumed.

There has been much interest in the preparation of benzeneselenol, 1) a useful reagent for selenenylation of α,β-unsaturated carbonyls. 2) Recent papers on methods for the preparation of phenyl trimethylsilylselenide, 3) a potential precursor of benzeneselenol, prompted us to report our results on straightforward arylselenenylation of enones by electrochemical reduction of diaryl diselenide in the presence of chlorotrimethylsilane in methanol. Described here is a convenient procedure for the preparation of aryl selenol *in situ* from the reaction of electrochemically generated aryl selenide anion 4) with chlorotrimethylsilane.

A typical electrolysis procedure is as follows: A solution of mesityl oxide (62 mg, 0.64 mmol), $(PhSe)_2$ (100 mg, 0.32 mmol), and Me_3SiCl (0.3 ml, 3.3 mmol) dissolved in MeOH (17 ml) containing Et_4NOTs (0.055 M) as an electrolyte was electrolyzed using Pt electrode (3 cm^2) under a constant applied voltage of 10 V (7-16 mA/cm^2) in the cathode compartment of a divided cell 5) at room temperature. After 6.6 F/mol of electricity was passed (3.25 h), the mixture was concentrated *in vacuo* and the residue was taken up in benzene-AcOEt (3:1), washed (brine), and dried (Na_2SO_4). Evaporation of the solvent followed by column chromatography (SiO_2, hexane-AcOEt 20:1) gave 142 mg (87%) of 4-methyl-4-phenylseleno-2-pentanone.



Other results of selenenylation of α,β-unsaturated carbonyls are listed in Table. The additive effect of chlorotrimethylsilane is remarkable. Absence and/or use of less than one equivalent of chlorotrimethylsilane caused to recover the starting materials. The excess of chlorotrimethylsilane (ca. 5 eq.) was

Table Electrolytic Aryl Selenenylation of α,β-Unsaturated Carbonyls

Entry	Enone	Diselenide	mA/cm^2 (F/mol)	Yield [a] of adduct (%)
1	Mesityl oxide	$(C_6H_5Se)_2$	7-16 (6.6) [b]	87
2	Mesityl oxide	$(p\text{-}MeOC_6H_4Se)_2$	13-14 (9.1) [b]	92
3	3-Methyl-2-cyclopentenone	$(C_6H_5Se)_2$	5-7 (9.3) [b]	47
4	2-Methyl-2-cyclohexenone	$(C_6H_5Se)_2$	4-10 (12.5) [b]	87
5	Carvone	$(p\text{-}MeOC_6H_4Se)_2$	2-4 (3.4) [c]	78
6	Pulegone	$(p\text{-}MeOC_6H_4Se)_2$	7-15 (3.6) [b]	83
7	1-Methoxycarbonyl-1-cyclohexene	$(p\text{-}MeOC_6H_4Se)_2$	8-13 (16) [b]	62

a) Isolated yield based on enone. b) Carried out at applied voltage of 10 V.
c) Carried out at applied voltage of 5 V.

necessary to complete the reaction. Di-(p-methoxyphenyl) diselenide seems to be more effective for the preparation of arylseleno-adducts rather than diphenyl diselenide (entry 1 and 2). Interestingly, the arylselenenylation of 1-methoxycarbonyl-1-cyclohexene was only affected with di-(p-methoxyphenyl) diselenide in the electrolysis (entry 7).[6)]

The mechanism of this arylselenenylation can be assumed as follows: Reaction of electrochemically generated aryl selenide anion and chlorotrimethylsilane would produce aryl trimethylsilylselenide which undergoes methanolysis to give aryl selenols *in situ*, precursors of arylseleno-adducts.[3c)]

Studies on some synthetic applications of the electrochemical procedure are in progress.

$$\mathrm{ArSe^-} \xrightarrow{\mathrm{Me_3SiCl}} \mathrm{ArSeSiMe_3} \xrightarrow{\mathrm{MeOH}} \mathrm{ArSeH} + \mathrm{Me_3SiOMe}$$

References and Notes

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6) All new compounds indicate the reasonable IR, NMR, and analytical data.

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