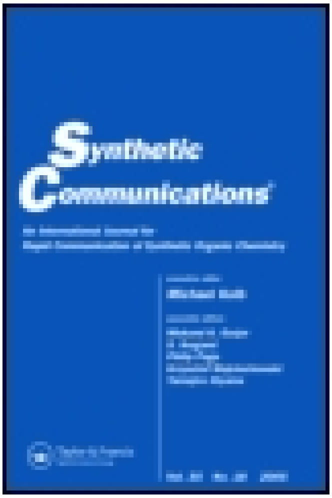

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Synthesis of Organic Diselenide Using Zinc Powder

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SYNTHESIS OF ORGANIC DISELENIDE USING ZINC POWDER

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Abstract: A new synthetic method of diselenide by reducing element selenium with zinc powder in basic environment, and then reacting with electrophiles is described. Nine diselenides are synthesized with yields between 52-90%.

With the development of organoselenium chemistry,much attention has been paid to the synthesis of selenium reagents in recent years[1]. Both arylseleno cation and anion produced by reduction of diselenides are predecessors of many organo-selenium compounds[2]. Several synthetic methods for diselenides have been reported: reaction of M_2Se_2 (M:Li, Na, K) with various electrophiles[3-10]; hydrolysis of RSeMgX[11-14] or ArSeCN[15,16]; reduction of carbonyl compounds with H_2Se and combination of sodium selenophosphoric diethyl ester with

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diazo fluoroborate[10]. However, most of the existing methods of preparation of diselenides are generally troublesome and toxic.

We shall now report a very simple synthetic method for diselenide. Element selenium is reduced by zinc powder in sodium hydroxide to produce disodium diselenide, followed by treatment of various electrophilies(Scheme I).

Scheme I

$$Zn + 2Se + 2NaOH \longrightarrow Na_2Se_2 + Zn(OH)_2$$

$$Na_2Se_2 + 2RX \longrightarrow RSeSeR$$

The reaction time for aryl halide system (12hrs) is longer than for alkyl halides(2hrs). This rule is in according with the activity of alkyl or aryl halide. The characteristic of this synthetic method is one-pot reaction, easy to perform, easy to obtain raw material and to avoid using toxic selenoreagents. The reaction is under room temperature with good yields between 52-90%. It is a useful synthetic method both for aromatic and for aliphatic diselenide.

EXPERIMENTAL SECTION

A mixture of selenium (0.8g, 10mmol), zinc powder(90%, 0.4g 5.5mmol) (washed by acid, base, water and dried in vacuo) and aqueous sodium hydroxide(2.5N, 8ml) was

Table I. The Results of Na_2Se_2 with Various RX

No.	RX	Reaction times(hr)	M. P.		Extract Solvents	Yield (%)	'HNMR(ppm, $CDCl_3$)
			obs.	Ref.			
1a	$BrCH_2CH_2CH_2Br$	2	oil		CH_2Br_2	60	3.90(m,2H) 4.35(m,4H)
1b	C_2H_5Br	2	oil		Et_2O	78	2.90(q,4H,J=7Hz) 1.50(t,6H,J=7Hz)
1c	n-C_4H_9Br	2	oil		Et_2O	82	2.87(t,4H,J=7Hz) 1.30-1.90(m,8H) 0.95(t,6H,J=Hz)
1d	$PhCH_2Cl$	2	90-92 (EtOH)	91-92(21)	Et_2O	87	3.92(s,4H) 7.25(s,10H)
1e	p-$NO_2C_6H_4CH_2Cl$	2	93-94 (EtOH)	a	Et_2O	90	3.97(s,4H) 7.30-7.48(d,4H,J=8Hz) 8.12-8.30(d,4H,J=8Hz)
1f	$PhCOCH_2Br$	2	85-87 (EtOH)	a	CH_2Cl_2	52	2.50(s,4H) 7.30-8.00(m,10H)
1g	p-$NO_2C_6H_4I$	12	175-177(Decomp.) (PhCl)	180(4)	CH_2Cl_2	80	7.54-8.30(m,8H)
1h	o-$NO_2C_6H_4Cl$	12	209-210	21-213 (4)	CH_2Cl_2	85	7.35-8.50(m,8H)
1i	2,4-$2NO_2C_6H_3Cl$	12	260(Decomp.) (DMF/H_2O)	263(4)	CH_2Cl_2	70	7.40-8.30(m,6H)

a: No data is available, the product is checked by E. A..

strirred at 80°C for 2hrs under nitrogen. A deep brown solution was obtained, cooled to room temperature and then added alkyl or aryl halide (10mmol). The reaction time was listed in Table I. After filtration, the residue was washed by solvent (10mlx3) (See Table I), the organic layer was separated, washed by water and dried by anhydrous $MgSO_4$. Concentration the dried solution with Rotavapor to give crude diselenide. We can purify the solid product by recrystallization and chromatography the liquid product on silica gel (pet ether or CH_2Cl_2). The product was examined by 'HNMR, M.p.,and E.A..

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