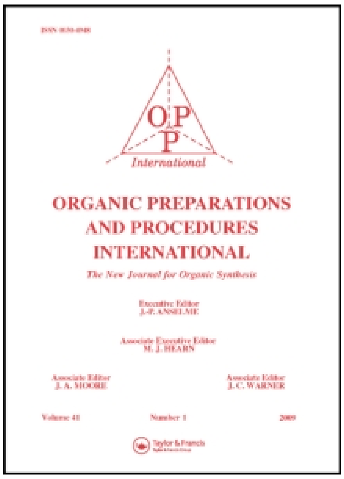

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A NOVEL SYNTHESIS OF ORGANIC DISELENIDES

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A NOVEL SYNTHESIS OF ORGANIC DISELENIDES

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In spite of their importance as intermediates in organic synthesis, many organic diselenides have only been obtained by displacement of halides or tosylates by nucleophilic selenium species.[1] Carbonyl compounds are potentially attractive novel starting materials for such syntheses.[2] Margolis[3] and Cohen[4] found that reacting carbonyl compounds with hydrogen selenide gave diselenides in the presence of triethylamine. Lewicki[2] reported the synthesis of diselenides from aldehydes, (a) by the reaction of aldehydes with sodium hydrogen selenide in the presence of amine and (b) by the reduction of the reaction mixture with sodium borohydride. In order to avoid the use of toxic hydrogen selenide gas, to simplify the procedure and to improve the yields, we developed a facile and efficient method for the synthesis of organic diselenides.

We initially found only small amounts of organic diselenides were obtained upon reaction of aldehydes with sodium hydrogen selenide in ethanol. It was rationalized that the formation of the organic diselenide might result from the attack of the aldehyde by the minute amounts of disodium diselenide present in the solution of sodium hydrogen selenide. Since disodium diselenide already contains the selenium-selenium bond and sodium hydrogen selenide is a selective reducing agent, we used the mixture of these two species to provide the source of selenium-selenium bond efficiently and perform the subsequent reduction selectively. A solution in which disodium diselenide and sodium hydrogen selenide are generated in the desired molar ratio may be obtained by adjusting the amount of selenium and sodium borohydride. Dimethylformamide was used in order to increase the nucleophilicity of disodium diselenide.[5] The results show that in the mixed solvent system of EtOH-DMF (1:2 v:v),aliphatic or aromatic aldehydes react with the mixed solution of Na_2Se_2-NaHSe (1:3 mol:mol) to produce alkyl or aralkyl diselenides respectively in excellent yields (see Table). The products were identified by means of IR,^{1}H NMR and mass spectra.

$$\underset{\mathbf{1}}{RCHO} + Na_2Se_2 + NaHSe \xrightarrow{DMF/EtOH} \underset{\mathbf{2}}{RCH_2SeSeCH_2R} + Se$$

a) R = 4-ClC_6H_4 b) R = 2-BrC_6H_4 c) R = C_6H_5 d) R = 4-$CH_3C_6H_4$
e) R = CH_3 f) R = $CH_3(CH_2)_4$ g) R = $(CH_3)_2CHCH_2$

TABLE. Synthesis of Alkyl and Aralkyl Diselenides

Cmpd	Time (hrs)	Yield (%)	mp (°C)	lit. mp. (°C)	^{1}H-NMR (δ)
2a	7	92	75-76	76^a	3.83 (s, 2H), 7.20 (m, 4H)
2b	6	91	97.5-98.5^b		3.95 (s, 2H), 7.22 (m, 4H)
2c	8	87	91-92	91-93^c	3.78 (s, 2H), 7.20 (s, 5H)
2d	9	85	60.5-61.5	61-62^c	2.32 (s, 3H), 3.78 (s, 2H) 7.08 (s, 4H)
2e	7	90	oil^d		1.46 (t, 3H), 2.90 (q, 2H)
2f	6	93	oil^e		0.89 (t, 3H), 1.34 (m, 6H) 1.73 (m, 2H), 2.92 (t, 2H)
2g	7	95	oil^f		0.90 (d, 6H), 1.42 (m, 1H) 1.72 (m, 2H), 2.91 (t, 2H)

a) Ref. 4. b) *Anal.* Calcd for $C_{14}H_{12}Br_2Se_2$: C, 33.77; H, 2.43; Found: C, 33.81; H, 2.44. c) Ref. 2.
d) Ref. 6. e) *Anal.* Calcd for $C_{12}H_{26}Se_2$: C, 43.91; H, 7.98; Found: C, 43.78; H, 7.97.
f) *Anal.* Calcd for $C_{10}H_{22}Se_2$: C, 40. 01; H, 7.39; Found: C, 40.09; H, 7.40.

The advantages of this method are safer and milder conditions which avoid the use of poisonous hydrogen selenide gas, a simple one-step reaction without the use of amine, and better yields then those previously reported. Thus this reaction provides a general method for the synthesis of organic diselenides.

EXPERIMENTAL SECTION

Melting points were determined on a Delta Series DSC 7 apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on Varian EM-360 (60MHz) using TMS as internal standard. Mass spectra were determined on a Finnigan 8230 mass spectrometer. IR spectra were obtained as neat capillary cells(liquid products) or as KBr disks (solid products) on a Shimadzu IR-408 instrument. Elemental analyses were performed on a Carlo Erba 1106 instrument. All reactions were carried out under nitrogen in an efficient hood.

General Procedure for the Synthesis of Alkyl or Aralkyl Diselenides 2.-To a mixture of selenium powder (6 mmol) and sodium borohydride (5 mmol) cooled by ice-bath was added ethanol (5 mol) under nitrogen.[7] After the vigorous evolution of gas had subsided, the reaction mixture was heated at 60-70° for 1 hr. A solution of aromatic or aliphatic aldehyde (1.5 mmol) in DMF (10 mL) was then injected at 60-70°, and the reaction mixture was stirred at 120-130° (for aromatic aldehydes) or at 60-70° (for aliphatic aldehydes.) After the time indicated in the Table, the reaction mixture was quenched with water (20 mL). It was then filtered, and the filtrate was extracted twice with ligroin (30 mL). Then the combined ligroin extracts were washed with aqueous sodium hydroxide (0.1 M, 2 x 20 mL), dried over magnesium sulfate and evaporated *in vacuo*. The crude product was purified by column chromatography [silica gel 200-300 mesh, ether:ligroin (1:4)] to give alkyl or aralkyl diselenide **2**.

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