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A CONVENIENT METHOD FOR THE PREPARATION OF DIALKYLDITELLURIDES AND DIALKYLDISELENIDES

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ABSTRACT: Dialkylditellurides 3 and dialkyldiselenides 4 were prepared in high yields and in a one-pot procedure reduction of tellurium by the elemental and selenium with phenyl hydrazine in basic medium (NaOH/DMF) followed by treatment with organohalides.

particularly Organotellurium, and organoselenium compounds have received considerable attraction as useful synthetic reagents and intermediates in organic synthesis. Among them, dialkylditellurides and dialkyldiselenides frequently are used as starting materials and reagents in a number of functional group transformations.³ they Since possess particular importance in organotellurium and organoselenium

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chemistry convenient methods for the preparation of them should be readily available. The most general approach preparation of dialkylditellurides for the and dialkyldiselenides alkylation is based on the of ditelluride and diselenide anions with organohalides. Ditelluride anions usually can be generated by the reduction of elemental tellurium with equivalent amounts of a reducing agent such as sodium⁴ and Super Hydride,⁵ and more recently reported with thioureadioxide. 6 Other by the reaction of organolithium approaches, and Grignard reagents with tellurium, have been also reported in the preparation of dialkylditellurides.7.8,9 Similarly, diselenide anions can be prepared by the reduction of selenium with alkali metals, 10, 11 Rongalite, 12 borohydrides¹³ metal and hydrazine Recently, a combination of electrochemical hydrate.¹⁴ reduction and ultrasound has been used to prepare diselenides in aprotic solvents.¹⁵ Though all these methods have their own merits they suffer from one or more disadvantages including the use of expensive reagents, relatively severe reaction conditions and troublesome alkali metals.

Our interest in the syntheses and in the application of organotellurium and organoselenium compounds in organic synthesis prompted us to seek a way to prepare dialkylditellurides and dialkyldiselenides in a more convenient and practical manner. In this communication, we wish to disclose our results which allows the convenient generation of ditelluride and diselenide anions under mild conditions, thus leading to the preparation of dialkylditellurides and diselenides in a one-pot procedure.

We have found that treatment of elemental tellurium with phenyl hydrazine in basic medium using DMF as aprotic solvent readily generates sodium ditelluride **1** as a wine-colored solution. The reaction completes smoothly within a few hours (70 °C, 5 h). Addition of various alkyl halides to the solution smoothly provides the corresponding dialkylditellurides **3**.



Similarly, treatment of elemental selenium with phenyl hydrazine in DMF gives sodium diselenide 2, a result similar to the reduction of selenium using

Preparation of dialkylditellurides and diselenides

Alkyl halide	Product		Yield(%)
CH_3CH_2Br	3 a	(CH ₃ CH ₂ Te) $_2$	77
$CH_3CH_2CH_2Br$	3b	(CH ₃ CH ₂ CH ₂ Te) ₂	81
(CH ₃) ₂ CHBr	3C	[(CH ₃) ₂ CHTe] ₂	59
$CH_3(CH_2)_2CH_2Br$	3đ	$[CH_{3}(CH_{2})_{2}CH_{2}Te]_{2}$	91
$CH_3(CH_2)_2CH_2Cl$		$[CH_{3}(CH_{2})_{2}CH_{2}Te]_{2}$	75
$CH_3(CH_2)_3CH_2Br$	3e	$[CH_3(CH_2)_3CH_2Te]_2$	85
PhCH ₂ Br	4a	(PhCH ₂ Se) ₂	92
PhCH ₂ Cl		(PhCH ₂ Se) ₂	90
$CH_{3}CH_{2}Br$	4b	(CH ₃ CH ₂ Se) $_2$	88
$CH_3(CH_2)_3Br$	4c	$[CH_3(CH_2)_3Se]_2$	93
(CH $_3$) ₂ CHCH ₂ Br	4d	[(CH ₃) ₂ CHCH ₂ Se] ₂	74
$CH_3(CH_2)_5Br$	4e	$[CH_3(CH_2)_5Se]_2$	85
$CH_3(CH_2)_{11}Br$	4 f	$[CH_{3}(CH_{2})_{1}Se]_{2}$	67

hydrazine hydrate.¹⁴ The dianion generated readily reacts with alkyl halides to give the corresponding dialkyldiselenides **4**.

The results summarized in the table show that a variety of alkyl halides, including long and short chains, can react with ditelluride and diselenide anions generated and the yields are generally good (59%-92%).¹⁶ All the compounds are characterized by their ¹H-NMR spectral data in addition to any existing literature data. The ¹H-NMR spectra of dialkylditellurides **3** and dialkyldiselenides **4** show that the chemical shifts of the CH₂ group adjacent to tellurium are in the 3.00-3.10 ppm region and the CH₂ group adjacent to selenium are in 3.00-4.00 ppm region, depending on the structure of the alkyl group. These results are in good accordance with literature data.^{6.14}

Overall, the present method has advantages such as readily available starting materials, straightforward and simple synthetic procedures, mild reaction conditions and good yields of products. In view of the increasing numbers of applications of organotellurium and organoselenium compounds in organic synthesis, we feel that the method described here is a good complement to previously existing procedures for the preparation of dialkylditellurides and dialkyldiselenides.

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- (16) General procedure for the preparation of dialkylditellurides: to a mixture of finely ground elemental tellurium powder (0.64 g, 5 mmol) and sodium hydroxide (0.20 g, 5 mmol) in DMF (20 mL), phenyl hydrazine (0.33 g, 3 mmol) in 15 mL of DMF was added under nitrogen. The mixture was heated to 70 °C and stirred at this temperature for 5 h, until the tellurium powder was completely consumed. The organohalide (5 mmol) in 2 mL of DMF was added dropwise and the mixture was stirred at 70 °C for 30 min. The reaction mixture was cooled down and quenched with water (30 mL) followed with petroleum ether (30 mL). The organic layer was separated and the aqueous layer was extracted with petroleum ether (3 x 15 mL). The combined extract was washed subsequently with aqueous NaOH (2 x 10 mL, 0.1 N) and water and dried over anhydrous MgSO4. After evaporation of the solvent the residue was distilled to give the pure product.

General procedure for the preparation of dialkyldiselenides: to а stirred mixture of elemental selenium powder (0.79 g, 10 mmol) and sodium hydroxide (0.40 g, 10 mmol) in 15 mL of DMF, phenyl hydrazine (0.65 g, 6 mmol) in 15 mL of DMF was added under nitrogen. The mixture was warmed to 50 °C and stirred at this temperature for 5 h, until the selenium powder was completely consumed. The organohalide (10 mmol) in 2 mL of DMF was added dropwise and the mixture was stirred at 50 °C for 30 min. The workup was same as the above. The pure dialkyldiselenide was obtained by distillation or recrystallization from suitable solvent.

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