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REACTIONS OF DIMETHYLSELENADIAZOLE AND ALKYLTIN DERIVATIVES

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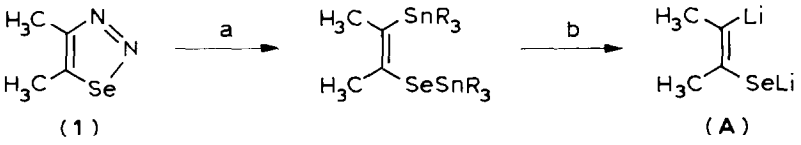
Summary

Reactions of 4,5-dimethyl-1,2,3-selenadiazole with hexaalkylditins or trialkyltin anion followed by quenching with trialkyltin chloride affords only dimethylacetylene and bis(trimethyltin) selenide. Implications of these results in relation to possible syntheses of selenatellurafulvalenes are discussed.

The relatively recent discovery of superconductivity in tetramethyl tetraselenafulvalene salts [1] has spurred interest in attempts to prepare the tellurium analog [2]. Whereas the synthesis of hexamethylenetetratellurafulvalene was successful, the same methodology could not be extrapolated to the covetted tetramethyl derivative. We thought that it could be possible to prepare a diselenaditellura analog according to Schemes 1–3.



(1) (A)

(a = R_3SnSnR_3 , b = BuLi)

SCHEME 1

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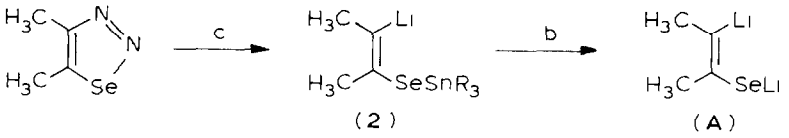
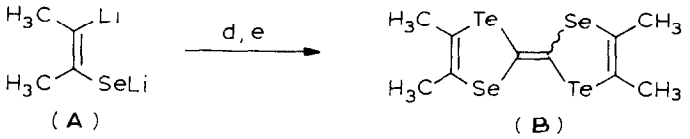


(b = BuLi, c = Me_3SnLi)

SCHEME 2



(d = Te, e = $Cl_2C{=}CCl_2$)

SCHEME 3

Scheme 1 was based on work of Cava and others [3] where an intermediate resulting from loss of nitrogen was successfully trapped to produce other heterocycles. In this article we describe the results of reactions of heterocycle **1** according to the Schemes and with strong nucleophiles and reducing agents.

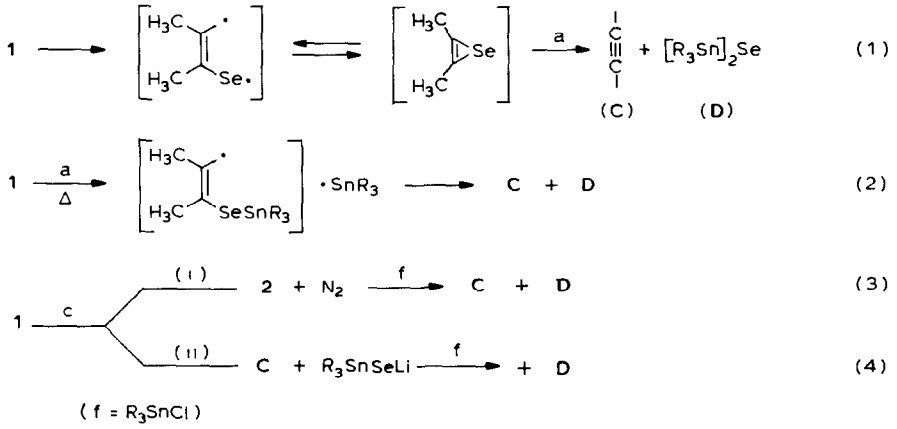
Heterocycle **1** was prepared according to literature procedures [4], but was always found contaminated with the isomeric 4-ethyl-1,2,3-selenadiazole. Purification was best accomplished by taking advantage of the difference in reactivity of the two isomers with strong base [5]; i.e., the ethyl isomer is converted to 1-propyne selenolate which can be easily removed (see Experimental).

When **1** was allowed to react with hexaalkylditins or with trimethyltin lithium, the only characterizable products which could be obtained were 2-butyne and bis(trimethyltin) selenide.

On pyrolysis in the presence of hexaalkylditin, evolution of gas was observed and a clean reaction took place yielding dimethylacetylene and bis(trialkyltin) selenide. This result implies that (a) the intermediate resulting from loss of nitrogen reacts with the hexaalkylditin probably to produce the desired product which is unstable under the reaction conditions (reaction 1, Scheme 4), or (b) alternately, an intermediate vinyl radical is relatively long lived to decompose to 2-butyne and the selenyltin radical which eventually gets trapped to produce the observed product (reaction 2, Scheme 4), (c) a possible intermediate selenirene is degraded via the previously mentioned vinyl radical (reaction 1, Scheme 4), and (d) the decomposition of **1** to 2-butyne and selenium is faster than reaction with hexaalkylditin; the reaction of the latter two to produce the observed **D** (cf. Scheme 4, in which reagents a–c are the same as in Schemes 1–3) is facile under these conditions [6].

As can also be seen in Scheme 4, the expected intermediate, vinyllithium (**2**), is apparently not generated (path i, Scheme 4), or if it is, it appears to be unstable toward elimination of trimethylstannyl selenolate. Alternately, **1** could also decompose in a concerted reaction with a strong nucleophile (path ii, Scheme 4); for example, when **1** was allowed to react with phenyllithium, lithium naphthalenide, or lithium dispersion, the only organic product characterizable was 2-butyne.

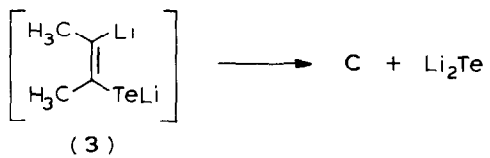
In summary, the most important inference from all the above work is that the



SCHEME 4

reactions exploited by Spencer [3] must indeed be concerted because it is difficult to believe that carbon disulfide would be so much more efficient a trap for the intermediates described in equation 1 than the hexaalkyltins employed in this study [9].

Another conclusion from the above observations is that perhaps even intermediates such as **3**, will be unstable and may not offer viable routes to tetramethyltetratellurafulvalene.



Experimental

Preparation of 4,5-dimethyl-1,2,3-selenadiazole (1)

(1) Semicarbazide HCl (60 g) and sodium acetate (60 g) were dissolved in water (400 ml). Methyl ethyl ketone (50 ml) was added and the solution was stirred for 1 h. The white precipitate was filtered and washed with water. The yield (60 g) is ~ 100%; m.p. 146–147°C.

Methyl ethyl semicarbazone (75 g, 0.58 mol) and glacial acetic acid (500 ml) were placed in a 2-necked 1 l flask which was equipped with a magnetic stirrer and a connection to argon. Finely powdered SeO_2 (64.5 g, 0.58 mol) was added slowly (a slight cooling was needed in order to keep the reaction at room temperature). The deep red solution was allowed to stir overnight at room temperature. It was filtered and diluted with water (1 l). The solution was extracted with CH_2Cl_2 (~ 500 ml) and the organic layer separated, washed with water and dried over $MgSO_4$ (anhydrous). The residue, after removal of the solvent (27 g, 30% yield), was found to contain 30% of 4,5-dimethyl-1,2,3-selenadiazole and 70% of 4-ethyl-1,2,3-selenadiazole. Trials to separate the two isomers by distillation did not give good

separation. The components were separated by preparative HPLC (Waters Porasil columns) using 4.5% ethyl acetate in hexane as eluant. Four fractions of 200 ml were collected. Distillation of the residue from fraction 2 afforded a colorless liquid (b.p. 34–35°C, 0.01 Torr) which was identified as the 4-ethyl-1,2,3-selenadiazole [4,5]. ^{1}H NMR ($CDCl_3$, TMS): 8.92 (s, 1H) 3.23 (q, J 7.5 Hz, 2H) 1.41 (t, J 7.5 Hz, 3H). Each pattern of peaks was accompanied by two identical patterns with J 56 Hz. These originate from the coupling with ^{77}Se. ^{13}C ($CDCl_3$, TMS): 164.8, 137.0, 22.65, 13.82 ppm.

Distillation of the residue of fraction 4 afforded a colorless liquid (b.p. 64°C, 0.08 Torr) which was identified as the 4,5-dimethyl-1,2,3-selenadiazole [4,5].

^{1}H NMR ($CDCl_3$, TMS): 2.56 (S, 3H), 2.65 (S, 3H). Two doublets J 63 Hz are observed in the spectrum, owing to ^{77}Se.

^{13}C NMR ($CDCl_3$, TMS): 156.24, 153.72, 12.70, 12.57 ppm.

Purification of 4,5-dimethyl-1,2,3-selenadiazole (1)

According to the procedure described by Lalezari et al. [5], the following experiment was performed.

In a 2-necked 100 ml flask equipped with a dropping funnel and a connection to an argon line were placed potassium ethoxide (16.8 g, 0.2 mol) and dry ether (50 ml). A mixture of the selenadiazoles (3.5 g, 0.02 mol) dissolved in ethanol (10 ml) was added dropwise and the mixture was stirred for 1 h while evolution of gas was observed. It was filtered under anhydrous conditions, the solid residue was washed with dry ether and the washing solution was combined with the filtrate. Water (100 ml) was added to the combined organic solution and the layers separated. The organic layer was washed with water (until neutral) and dried over $MgSO_4$. The residue after evaporation of the solvent was found to contain 4,5-dimethyl-1,2,3-selenodiazole (0.63 g, 65% of the compound present in the original solution).

Reaction between 4,5-dimethyl-1,2,3-selenadiazole (1) and hexamethylditin (a)

In a 3-necked, 5 ml flask equipped with a magnetic stirrer, a connection to a Dry-Ice/acetone cooled trap (which contained 1 ml of $CDCL_3$) and a serum septum 4,5-dimethyl-1,2,3-selenadiazole (0.5 g) and hexamethylditin (0.85 ml) were placed. The flask was heated to 150°C and kept at this temperature for 0.5 hour. The NMR of the compound collected in the cold trap showed a singlet at δ 1.6 ppm which is the signal of the methyl groups in dimethylacetylene. The spectrum of the reaction product showed singlets at δ 0.5 ppm for its ^{1}H absorption and at δ −2.36 ppm for its ^{13}C absorption.

The product was distilled under reduced pressure (b.p. 48°C, 0.01 Torr) and the product was identified as bis(trimethyltin) selenide. (lit. [7] b.p. 72°C, 0.1 Torr). The ^{1}H chemical shift, δ 0.5 ppm, and $J(^{119}Sn–C–^1H)$ 50.8 Hz is in agreement with the value for this compound [8]. X-ray fluorescence spectroscopy indicated that the compound contains Se and Sn. Mass spectrum: m/e 408.1 (M + 1)rel. int. 31%, 391.4 (M − Me)rel. int. 100%, 165 [$Sn(CH_3)$]rel. int. 100%; typical multiple lines due to different Sn and Se isotopes were observed in these m/e regions.

Reaction between 4,5-dimethyl-1,2,3-selenadiazole (1) and hexabutylditin (a)

The heterocycle (0.5 g) and 2 ml of hexabutylditin were heated in a 5 ml flask under argon. Evolution of gas was observed at 120°C and the mixture was heated to

155°C for 1 h. Analysis of the reaction mixture (NMR) showed that it contained none of the heterocycle, but a mixture of a new product and the excess of hexabutylditin. The two components were separated by column chromatography. First fraction (50 ml) was eluted with hexane and contained the reagent, the product (third fraction) was eluted with 5% ethyl acetate in hexane and was shown to be bis(tributyltin) selenide (^{13}C NMR ($CDCl_3$, TMS) δ 13.52, 15.42, 27.04, and 28.99 ppm).

Reaction between trimethyltinlithium (c) and 4,5-dimethyl-1,2,3-selenadiazole (1)

Methyllithium (2.58 ml, 1.0 *M* in ether, low halide) was dissolved in dry THF (10 ml). The solution cooled to −20°C and hexamethylditin (0.8 ml) was added. The resulting solution, which had a slightly yellow color, was stirred at −20°C for 15 min. This solution was cooled to −78°C and the heterocycle (0.4 ml) was added with a syringe. A vigorous reaction was observed which was accompanied by evolution of gas. The mixture, which became dark brown, was allowed to stir at −78°C for 0.5 hour. Trimethyltin chloride (610 mg dissolved in 5 ml of dry THF) was then added, the cooling bath was removed and the solution allowed to warm to room temperature.

The solvent was removed, water and CH_2Cl_2 were added. The organic layer separated and washed with water. It was dried ($MgSO_4$) and the solvent removed. NMR ($CDCl_3$) of the residue indicated that the mixture contained mainly the heterocycle and bis(trimethyltin) selenide. The X-ray fluorescence spectrum of the spot on the TLC plate which is suspected to be the bis(trimethyltin) selenide indicated the presence of Sn and Se in this compound.

Reaction of 4,5-dimethyl-1,2,3-selenadiazole with the following reagents was tried: lithium (30% on mineral oil), phenyllithium (1.7 *M* in benzene/ethyl ether) and lithium in the presence of naphthalene. In all cases the intermediate which was obtained was found to be unstable and decomposed to dimethylacetylene.

Acknowledgement

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9 The most intriguing implication of this result is that in order to obtain the products of ref. 5 in a concerted fashion, the selenium atom of **1** must attack the carbon of carbon disulfide and the resulting thiocarboxylate anion then simultaneously attacks the 3 position of **1** with concomitant loss of nitrogen. A referee pointed out that CS_2 is smaller than hexamethylditin and that a dipolar form of **1** may lead to the reported product with CS_2 but is forced to sequential displacement with the bulkier tin reagent.