CHEMCOMM
Communication
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Se,*Se′*-Diphenyl carbonodiselenoate: preparation and characterization of its molecular structure and thermal reactivity

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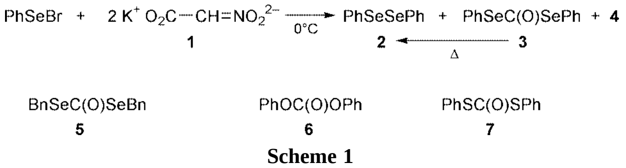
Received (in Corvallis, OR, USA) 10th April 2001, Accepted 6th June 2001
First published as an Advance Article on the web 3rd July 2001

Reaction of dipotassium nitroacetate with benzeneselenenyl bromide produces the title compound as a thermally unstable product, which has been characterized by X-ray crystallography.

Dipotassium nitroacetate, **1**, was first synthesized by Steinkopf[1] in 1909. Since that time the yield and simplicity of preparation of **1** has been improved a number of times.[2] The reported utility of employing this easily prepared dianionic organic salt in reaction with electrophilic reagents has been somewhat limited however. Reaction with electrophilic reagents such as the halogens,[3] the strong mineral acids,[4] and several transition metal salts[5] have been noted but our preliminary attempts to directly react **1** with organo-electrophilic reagents proved frustrating.† One exception, we discovered, was the direct reaction of benzeneselenenyl bromide with **1** in methanol,‡ which produced CO_2 and diphenyl diselenide, **2**, along with two other organic products, **3** and **4**. This communication thus reports our characterization of one of these three organic products, **3**, and additionally elaborates upon its easy thermolytic conversion to produce **2**. (The chemical characterization of **4** is still under investigation.§)

Addition of **1** to an ice-cold solution of benzeneselenenyl bromide in methanol resulted in three TLC separable organic compounds after effervescence of CO_2 had subsided. Separation of the three organic compounds using silica gel chromatography could be achieved by elution with hexane–methylene chloride mixtures. The initial band off the column was easily identified as **2**. The compounds **3** and **4** were then eluted in sequence, with both compounds decomposing to **2** if strict cooling conditions were not maintained (see Scheme 1). Compound **3** could be crystallized by slow evaporation of the elution solvent at 0 °C to deliver X-ray quality crystals. Initial observations on crystals of **3** indicated that yellow crystals of **2** began to grow from the colorless crystals if **3** was allowed to sit at room temperature or above for any extended period of time. (Storage in the refrigerator was mandatory.)

Spectral analysis of compound **3** yielded the following important information: (1) the solution IR spectrum (CCl_4) exhibited a carbonyl stretch at 1711 cm^{-1} in addition to bands similar to those exhibited by **2**. Attempts to obtain the IR spectrum of **3** as a KBr pellet resulted in a spectrum identical to that of **2**. (2) The ^1H-NMR spectrum of a solution ($CDCl_3$) of **3** exhibited phenyl resonance lines only. (3) The ^{13}C-NMR spectrum ($CDCl_3$) of **3** exhibited a carbonyl resonance at δ = 182.7 in addition to four resonance lines in the aromatic region. (4) The ^{77}Se-NMR spectrum ($CDCl_3$) of **3** exhibited a single resonance line at δ = 749 relative to dimethyl selenide.[6] (5) The CI/MS spectrum of **3** exhibited a molecular ion centered at 343 amu with appropriate isotopic satellite peaks for a compound having two selenium atoms in its molecular structure. Major fragment peaks were observed at 312, 237 and 159 amu as well as the base peak at 78 amu. The EI/MS spectrum was identical to that of **2**. (Carbonodithioates fragment in a similar manner in the EI/MS.[7]) (6) The UV-VIS spectrum of **3** exhibited no absorbance above 300 nm in contrast to **2** which has a characteristic thermochromic[8] band at 337 nm (log ε = 3.1). While this spectral information was indicative that **3** had a molecular structure that contained two phenyl selenium moieties, in addition to a carbonyl group, we were uncertain whether our compound was similar to *Se*,*Se′*-dibenzyl carbonodiselenoate (**5**) prepared by Devillanova *et al.*[9] (Reported spectral information available for **5** consisted only of an IR band at 1680 cm^{-1} which was attributed to a carbonyl band.) Consequently we determined the X-ray crystal structure for **3** which confirmed our suspicions that we had isolated *Se*,*Se′*-diphenyl carbonodiselenoate as a rather unstable molecular entity. We hoped that the reasons for the instability of **3** might then become apparent.



Scheme 1

A perspective view of the molecular structure obtained for **3** is shown in Fig. 1. (We had to collect the data at 173 K because of the instability of **3** in the X-ray beam.¶) The space group was found to be *C*2/*c* with a twofold axis passing through the carbonyl function.‖ The unit cell contained four molecules of **3**. The bond lengths for the phenyl selenium moieties were found to be almost identical[10] to those of **2** including the Se–C_{ipso} bond length = 191.5(3) pm. The bond angles around the carbonyl function of **3** are somewhat different from those of diphenyl carbonate (**6**);[11] for **3** Se–C(O)–Se is 110.2(2)°, Se–C = O is 124.9(1)°, and C(O)–Se–C_{ipso} is 97.1(1)° while for **6** O–C(O)–O is 104.6°, O–C = O is ~127.5° and C(O)–O–C_{ipso} is ~118.5°. The bond lengths around the carbonyl function of **3** appeared to be normal, and similar to those of **6** when comparable: for **3** Se–C(O) is 193.5(2) pm, and C = O is 118.5(5) pm while for **6** C = O is 119.1 pm.

There are several interesting interactions within **3**. That exhibited between the two intramolecular selenium atoms is one of them. These two selenium atoms are separated by a distance of 319 pm which is well within the sum of two Van der Waals radii for selenium (~400 pm). Whether there is a partial

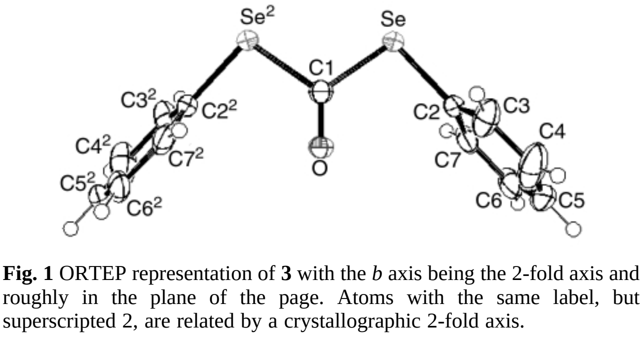


Fig. 1 ORTEP representation of **3** with the *b* axis being the 2-fold axis and roughly in the plane of the page. Atoms with the same label, but superscripted 2, are related by a crystallographic 2-fold axis.

intramolecular bond between the two selenium atoms of **3**, implying some hypervalency,[12] is not immediately obvious. Secondly, while the overall molecular structure for **3** is similar to that exhibited by **6**, the comparative bond angles around the carbonyl function are different implying that any interaction between selenium atoms in **3** is very different from those manifested by the oxygen atoms in **6**. It was therefore of interest to determine the thermodynamic activation parameters associated with the thermal conversion of **3** to yield **2**.

Dilute solutions of **3** could be quantitatively converted to **2** while monitoring changes in the visible spectrum at 350 nm. (A clean isosbestic point was observed at ~ 300 nm.) Compound **3**, which is colorless, smoothly and completely converted to yellow **2** in ethylene glycol solvent within 2 h at 60 °C and ½ h at 90 °C. The first order (or pseudo-first order) kinetics were linear over the entire temperature range studied, after taking into account the thermochromic properties of **2**.[8] The thermodynamic activation values of E_a = +65.8 kJ mol^{-1} and ΔS_a = -227 J deg^{-1} could be derived using the method of Arrhenius. The low activation energy for the thermolysis reaction thus indicated that the process of forming the 229 pm bond in **2** may be partially on the way to completion within the molecular structure of **3** itself. Consequently the preliminary conclusion that there may be a partial Se–Se bond in **3** seems plausible. (See footnotes ** and †† which were added in proof.)

The negative entropy of activation generated during the thermolysis reaction of **3**, where one molecule fragments to two molecular products, may imply that the associated disorder in the overall reaction can be offset, to some extent, by some factors of orderliness in the activated complex. The first factor implied is that the solvent (ethylene glycol) could be involved in creating more order during the thermolysis process. This possibility is buttressed by our observation that thermolysis of **3** in hydrocarbon solvent requires higher temperatures and is thus slower than in $HOCH_2CH_2OH$.** A second factor implicated is that a shorter than usual movement of the phenyl selenium substituents, during the extrusion of CO, may be inherent in **3**. As the crystal structure‖ of **3** shows the angle between the phenyl selenium groups is compressed in comparison to a normal sp^2 hybridized situation around a carbonyl group. (It has to be noted here that the compression of the analogous angle in **6** is even greater.[11]) And a third possible factor is the proposed hypervalent interaction between the selenium atoms of **3**. This proposal bolsters a hypothetical mechanistic process where the thermolytic transition state structure is a loosely organized diselenacyclopropanone ring structure. Consequently contrasting the thermal lability of **3** with the thermal stability of **6** suggests that these factors may not be available during analogous bond formation processes associated with the parent chalcogen.†† Comparing the molecular structures of *Se*,*Se′*-diphenyl carbonodiselenoate, **3**, and *S*,*S′*-diphenyl carbonodithioate (**7**) to that of diphenyl carbonate,[11] **6**, should prove interesting.‡‡

We (ROD and AC) would like to thank NSF (CHE-9974648) and the University of Massachusetts for funds to purchase the Nonius KappaCCD diffractometer. JTL and WR would like to thank the URI Foundation for partial support to fund this research and to Michael Callahan for recording the CI/MS for us.

Notes and references

† For example: reaction of **1** with simple alkyl halides in methanol (or other solvents) produced no identifiable materials other than the starting compounds.

‡ *Preparation of* **3**: 1.0 g of benzeneselenenyl bromide was dissolved in 15 ml of cold (0 °C) methanol and placed in a round bottom flask containing a stir bar. Solid, freshly prepared **1**, 0.77 g, was added in a controlled manner so that effervescence did not become too vigorous. Monitoring of progress was done by TLC over the duration of the ~ 1 h reaction. During the course of the reaction the color changed from dark red to a light yellow. Rotary evaporation of the resultant mixture was done under vacuum at approximately 0 °C after adding some silica gel. The product, adsorbed onto silica gel, was then mixed with 70:30 hexane–CH_2Cl_2 and added to the top of a chromatography column. Elution was commenced and the fractions were monitored using TLC. The organic products were eluted from the column in sequence (numerically). The fractions containing **3** were combined and allowed to evaporate in the cold until clear colorless crystals had formed. % Yield of **3** = 19%; mp = 48–50 °C.

§ The molecular characterization of **4** has proven difficult since it more readily decomposes to **2** than even **3**. We believe **4** may be either a hydrate or hemihydrate of **3**, since **4** exhibits CI/MS data with ion peaks centered around major masses, having two and four selenium atoms respectively, at 359 and 699 amu.

¶ The compound **3** decomposed in the X-ray beam within 5 min at rt.

‖ *X-Ray study of* **3**: Data was collected on a Nonius KappaCCD diffractometer. Satisfactory crystal stability was obtained by mounting the crystal inside of a sealed, thin walled glass capillary and by collecting the data at 173(2) K. *Crystal data for* **3**: $C_{13}H_{10}OSe_2$, *FW* = 340.13, monoclinic space group *C*2/*c*, a = 2140.38(5), b = 523.60(2), c = 1291.76(4) pm, β = 119.960(2)°, V = 1.25423(7) × 10^9 pm^3, Z = 4, *D*calc = 1.801 g cm^{-3}, μ = 5.871 mm^{-1}. Intensities were obtained for 2055 reflections ($2\theta_{max}$ = 50.1°) of which 1104 were unique. Refinement on F^2 was based on all of the data. The final agreement factors for the 941 unique reflections with $I > 2\sigma_I$ are R = 0.0262 and Rw = 0.0595. CCDC 163698.

** As pointed out by referee K this observation '…strongly argues for a polar transition state…' that is '…hydrogen bonded resulting in increasing order in the transition state.' We agree with this comment and note that a diselenacyclopropanone molecular entity would most likely be polar and H-bonded in ethylene glycol.

†† This same referee K has stated: '…the factors that the authors ascribe to the thermal lability of **3** are said to be not available for thermally stable **6**. A more obvious difference for this differing reactivity is that the thermodynamic driving force is substantially different *i.e.* a C(O)–O bond is stronger than a C(O)–Se bond and an O–O bond is much weaker than an Se–Se bond.' We again agree and we wish to thank this referee for these cogent ideas lending further support to our diselenacyclopropanone transition state proposal.

‡‡ Thermolytic studies of carbonodithioate esters have been referenced[13] to **7** but the molecular structure of **7** has not been determined as far as we are aware.

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