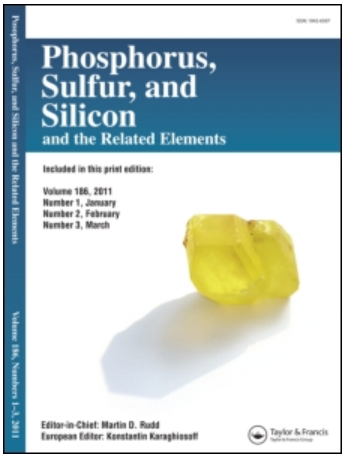

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SYNTHESIS, REACTIVITIES, AND UNIQUE SOLUTION PROPERTIES OF 4,8-BIS(DIETHYLAMINO)-METHYLENE-1,2,3,5,6,7-HEXASELENACYCLOOCTANE

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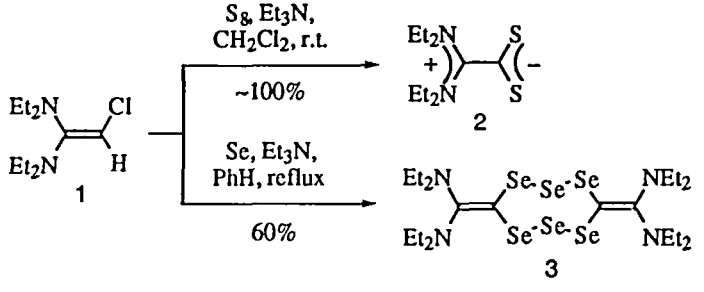
The heading novel heterocycle (3) which contains six selenium atoms in its eight-membered ring was prepared by reaction of 1,1-bis(diethylamino)-2-chloroethene (1) with elemental selenium. The compound 3 showed unique spectroscopic properties behaving as the bis(diethylamino)carbeniumdiselenocarboxylate (4) equivalent in reactivities.

Keywords: elemental selenium, hexaselenacyclooctane, inner salt, spectroscopy, 1,3-dipolar cycloaddition, X-ray diffraction analysis

We have recently reported that the reaction of 1,1-bis(diethylamino)-2-chloroethene (1) with elemental sulfur in the presence of triethylamine at room temperature gives the inner salt, bis(diethylamino)-carbeniumdithiocarboxylate (2), in high yield.[1] We now report that the

reaction of **1** with elemental selenium affords 4,8-bis(diethylamino)methylene-1,2,3,5,6,7-hexaselenacyclooctane (**3**) which shows unprecedented, unique solution properties, thereby behaving as the bis(diethylamino)carbeniumdiselenocarboxylate (**4**) equivalent in reactivities.



Thus, heating **1** with gray metallic selenium in the presence of triethylamine in benzene for 5 h under reflux gave a 60% yield of a dark red crystalline compound that has an empirical formula of $(C_{10}H_{20}N_2Se_3)_n$. Structure of this compound could not be determined unequivocally by spectroscopic means because of its highly complex but unique solution properties which will be discussed below. X-Ray single crystal structure analysis revealed that it has a novel ring system of the hexaselenacyclooctane structure **3** (n=2 in the empirical formula). The compound adopts a typical crown-shaped structure in the crystalline state. Its C=C bond distance (1.384 Å) is longer than those of typical C=C bonds and the torsion angle between N-C-N and Se-C-Se planes is as large as 36.5°, indicating some contribution of the polarized single-bond structure to the ground state.

The ^1H NMR spectrum of **3** shows a highly complex pattern which is dependent on the polarity of the solvent and the temperature. In CD_2Cl_2 at room temperature, the methyl and methylene signals of **3** appeared as two sets of complex multiplets with nearly equal

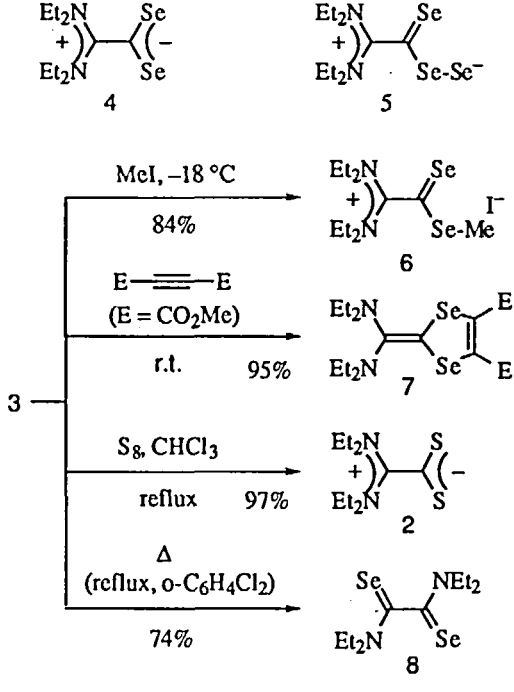
intensities. On lowering the temperature, the intensity of the upper field methyl signal increased with decreasing intensity of the lower field methyl signal and at -50 °C the ratio reached ca. 3:1. Similar phenomena were also observed with methylene signals. In the less polar solvent CCl_4, two sets of methyl and methylene signals are far from being equal intensity at room temperature. The ratio of the upper field and lower field signals of the methyl and methylene is about 6:1. The ^{13}C NMR spectrum gave a large number of signals due to ethyl and methylene carbons and six signals due to olefinic carbons in addition to the signal at δ 235 that should be ascribed to the selenocarbonyl carbon. ^{77}Se NMR gave ten signals in 400-900 ppm region.

UV-Vis spectrum is also highly solvent dependent. Thus, in nonpolar solvents (hexane and CCl_4), the longest absorption maximum appeared at 370 nm, whereas in more polar solvents (CH_2Cl_2, $CHCl_3$, DMF), the maximum moved to 440 nm. The present solvent effect, which is as large as 70 nm, apparently differs from common solvent effects. The IR spectrum also differs between solid and solution states. In CH_2Cl_2, the strong absorption newly appeared at 1545 cm^{-1}, which was not observed in the solid state spectrum (KBr disk) but was observed with the inner salt **2** and related salts.

The most probable explanation that accommodates the above observations is that a large part of **3** dissociates into the charged species such as **4** and **5** in polar solvents. Conformational change of the seven-membered ring of the undissociated **3** should be one of the reasons of the highly complex NMR patterns.

In harmony with the above assumption, **3** behaves as the charged species **4** toward methyl iodide and dimethyl acetylenedicarboxylate (DMAD). Thus, **3** quickly reacted with methyl iodide at -18 °C to give the cabenium iodide **6** bearing a diselenoester moiety. The reaction of **3** with DMAD at room temperature afforded the diselenole **7**, the 1,3-

dipolar cycloadduct of **4** and DMAD. The reaction of **3** with elemental sulfur in refluxing chloroform interestingly afforded the inner salt **2** nearly quantitatively along with elemental selenium. Compound **3** is rather thermally stable and can be kept at room temperature for a long period of time and is recovered from its solution without any appreciable decomposition. However, heating **3** in refluxing *o*-dichlorobenzene for 7 h resulted in the complete decomposition to give the ethanediselenoamide **8** in good yield.



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