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Syntheses and Properties of Eight- and Ten- Membered Selenaradialenes

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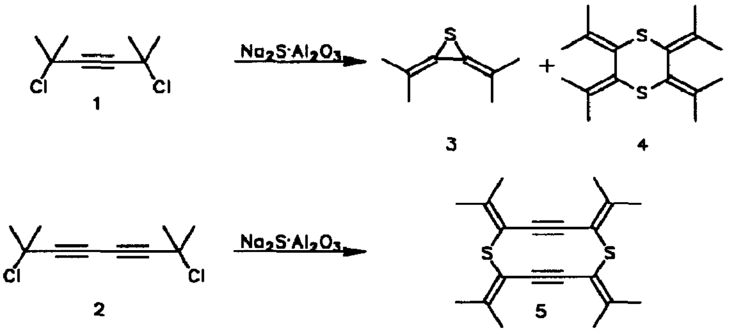
Abstract: Eight- and ten-membered heterocycles with radialenic shape and interesting properties were synthesized by a SN' cyclization reaction.

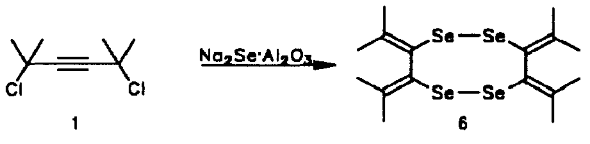
Recently we found that the reaction of Na_2S with 2,5-dimethyl-2,5-dichloro-3-hexyne (**1**) and 2,7-dichloro-3,5-octadiyne (**2**) yields the heteroradialenes **3**-**5**[1]. These results were rationalized by assuming a SN' - mechanism which leads to **3** in an intramolecular and to **4** and **5** in an intermolecular cyclization reaction.

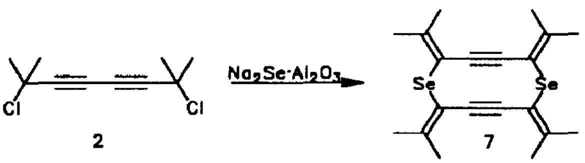


To ascertain, if Na_2Se behaves similarly we have carried out reactions of **1** and **2** with Na_2Se. Treatment of **1** with Na_2Se deposited on Al_2O_3[2] yields neither the three- nor the six-membered ring but the eight-membered heteroradialene **6** in 20 % yield, which is confirmed by spectroscopic data[3]. Evidence for the cyclic tetraselenide - structure is revealed by the mass spectrum which exhibits a M^+ peak at 374 atomic units (^{80}Se) with the correct isotope pattern for four selenic atoms. R. H. Mitchell et al. showed that a cyclic diselenide can be contracted to the cyclic monoselenide when using tris(diethylamino)-phosphine as reactand.[4] This reaction failed with our system, the eight-membered ring could be recovered without isolating any further product.

Ring inversion of the eight-membered ring is hindered at low temperatures. ^{1}H-NMR spectroscopy shows that the two singlets of the methyl groups broaden at 242 K and split into 4 singlets at 202 K. This also is observed in the ^{13}C spectrum where at 202 K four signals (δ = 24.02, 22.90, 22.60, 21.15) appear instead of two (δ = 23.73, 22.86) at room temperature.

In contrast to the reaction of **1** the conjugated dialkyne **2** reacts with Na_2Se in an analogous manner as with Na_2S to yield 2,5,7,10 tetra-isopropylidene-1,6-diselena-cyclodeca-3,8-diyne (**7**) in 10 % yield.

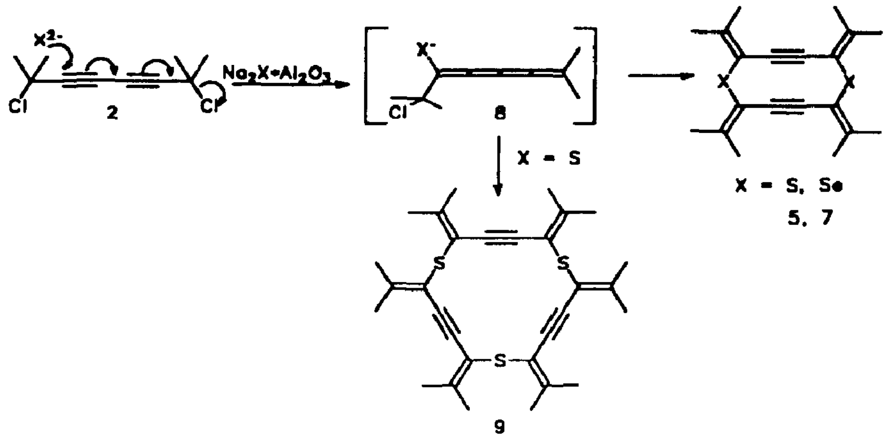




The molecular structure of **7** is confirmed by NMR-spectroscopic data[3]. The mass spectrum shows a M^+ peak at 424 atomic units (^{80}Se) with the correct isotope pattern for two selenic atoms.

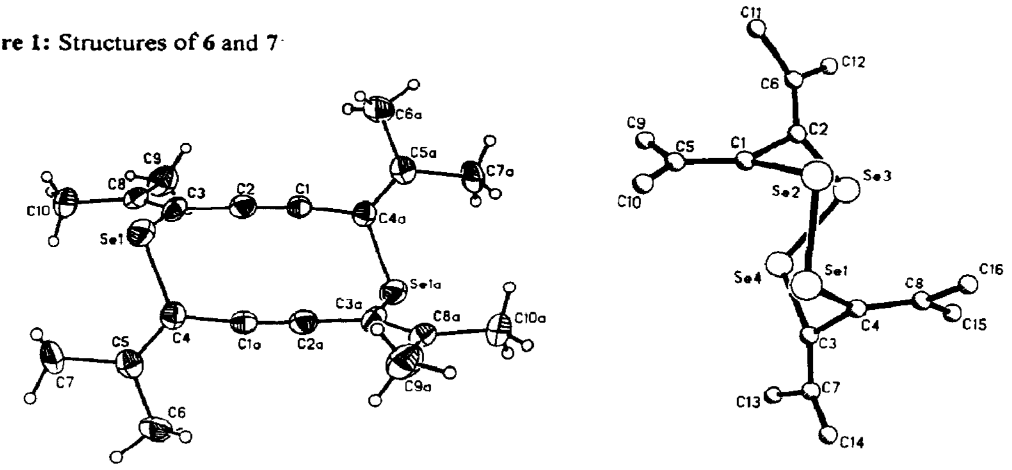
To explain the formation of the cyclic diacetylenes we assume that the first step is the attack of the chalcogene - dianion at the sp-carbon atom adjacent to the tetrasubstituted C-atom, which is activated most for attack by a nucleophile. The intermediately formed [4]cumulene (**8**) then dimerizes to the cyclic diacetylene. The assumption of the existence of **8** is supported by the isolation of the trimer **9** in the case of the sulfur cyclization reaction[3]. However, the equivalent trimer could not be isolated with Na_2Se.

The structures of **6** and **7** have been confirmed by X-ray investigations[5] (Figure 1). The structure of **7** is very much related to that of **5**[1], showing a chair conformation of the ten-membered ring. The transanular distance of the triple bonds amounts to 3.16 Å. The angles at the sp-centers deviate from 180° by 5.0° and 3.9° respectively. The isopropylidene groups are twisted along the $C_3 \cdots C_4$ axis by 97.7°



The eight-membered ring shows a chair like conformation. The dihedral angles around the diselenide unit are 79° and 77°, respectively. This is similar to acyclic diselenides such as diphenyldiselenide which has a dihedral angle of 82.0°.[6] The isopropylidene groups are also twisted. The angles amount to 62° and 64° respectively. The Se - Se bond lengths are 2.335 (7) Å and 2.3001 (9) Å, respectively, and are very similar to the average Se - Se distance of 2.34 Å in many diselenides[7].

Figure 1: Structures of 6 and 7



Cyclic voltammetry studies[8] of this nonplanar electron rich system (6) reveal two reversible oxidation waves at 985 and 1180 mV. In contrast, the oxidation of 7 occurs at 1200 mV in a single irreversible oxidation wave.The same electrochemical behaviour is shown by the thiacyclic species. Compound 4 is oxidized in a reversible one electron transfer to the electrochemically stable radical cation, while **5** shows an irreversible first oxidation step. The stability of the radical cation in **4** and **6** can be rationalized by transanular S··S or Se··Se interactions which lead to delocalization of the positive charge. This is not possible anymore in the elongated systems **5** and **7**, where the heteroatom distances are too long for effective interaction.

Acknowledgements. We are grateful to the Deutsche Forschungsgemeinschaft (Graduiertenkolleg "Selektivität in der Organischen und Metallorganischen Synthese und Katalyse"), the Fonds der Chemischen Industrie and the BASF Aktiengesellschaft, Ludwigshafen for financial support.

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2. R. Gleiter, S. Rittinger, H. Langer, *Chem. Ber.* **1991**, 124, 357 - 363.
3. **6**:^{1}H-NMR: δ = 1.76, 2.06; ^{13}C-NMR: δ = 22.86, 23.73, 126.37, 139.28. **7**: ^{1}H-NMR: δ = 2.01; 2.07; ^{13}C-NMR: δ = 24.19, 24.30 (CH_3-groups), 94.43 (sp - carbon atoms), 106.85, 147.37 (sp^2 - carbon atoms). **9**: ^{1}H-NMR: δ = 1.97; 1.91; ^{13}C: δ = 144.85, 112.06, 91.33, 23.44, 21.56; MS (CI) m/z = 492 (M^+).
4. R.H. Mitchell, *Can. J. Chem.* **1976**, *54*, 238 - 241.
5. X-ray structure analysis of 6: $C_{16}H_{24}Se_4$, $Mr = 532.21$, rhombic, space group C_{2v}^{9} , crystal size: 0.38 × 0.38 × 0.60 mm, $a = 10.1838(4)$, $b = 13.883(9)$, $c = 27.82(2)$ Å, $V = 2932.9$ Å^3, $F(000) = 2048$, $Z = 2*4$, $\rho_{calcd} = 1.80$ g cm^{-3}, $\mu = 7.45$ mm^{-1}, Mo-Kα radiation, $\lambda = 0.7107$ Å. Intensity data were collected on a SYNTEX R3 diffractometer. Of 3927 reflections collected, 2761 were with $I > 2.0\sigma(I)$ and 1104 were considered with $I > 2.5\sigma(I)$. The structure was solved with Patterson-Fourier analysis carried out with SHELXTL PLUS. $R = 0.051$, $R_w = 0.034$. X-ray structure analysis of 7: $C_{20}H_{24}Se_2$, $Mr = 422.33$, monoclinic, space group C_{2h}^{5} , crystal size. 0.30 × 0.40 × 0.45 mm, $a = 8.229(5)$, $b = 12.677(7)$, $c = 9.066(4)$ Å, $\beta = 98.01(4)°$, $V = 936.5$ Å^3, $F(000) = 424$, $Z = 2$, $\rho_{calcd} = 1.50$ g cm^{-3}, $\mu = 3.55$ mm^{-1}, Mo-Kα radiation, $\lambda = 0.7107$ Å. Intensity data were collected on a SYNTEX R3 diffractometer. Of 2869 reflections collected, 1290 were considered with $I > 2.5\sigma(I)$. The structure was solved with Patterson-Fourier analysis carried out with SHELXTL PLUS. $R = 0.069$, $R_w = 0.053$.
6. R.E. Marsh, *Acta Crystallogr.* **1952**, *5*, 458.
7. R.A. Zingaro, W.C. Cooper, *Selenium*, **1974**, V.Nostrand Reinhold Company.
8. The electrochemical measurements were performed with the HEKA potentiostat system PG 28 in a 0.1 M solution of $(n\text{-}Bu)_4N^+PF_6^-$ in CH_2CL_2. As working electrode a METROHM disk electrode was used (r = 0.3 cm).The potential of Fc/Fc^+ was measured at 480 mV with an error of ± 5 mV.

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