Mendeleev Commun., 2027, **37**, JUST ACCEPTED

Received 01.06.26 26/8104

Revised 14.09.26

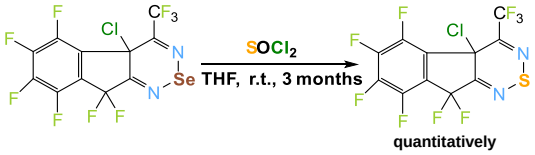
Sulfur–selenium displacement in polyfluoroindene-fused 1,2,6-selenadiazine

Victor M. Karpov, Rodion V. Andreev and Andrey V. Zibarev*

N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: +7 383 330 9752; e-mail: zibarev@nioch.nsc.ru

DOI: 10.71267/mencom.8104

Unprecedented replacement of Se by S in the 1,2,6-selenadiazine ring system under the action of $SOCl_2$ is reported and its possible pathways are discussed on the basis of DFT calculations. Preparative applications of the reaction are envisaged despite its time-consuming character.



Keywords: chalcogen exchange, DFT calculations, organofluorine compounds, reaction pathway, 1,2,6-thia/selenadiazines

Chalcogen-nitrogen chemistry contributes much in fundamentals and applications encompassing materials science and biomedicine. High and varied heteroatom reactivity of chalcogen-nitrogen compounds is frequently unpredictable, whereas reaction products exhibit unusual structures.[1,2]

Of special interest are π-heterocycles such as fused 1,2,5-thiadiazoles, 1,2,3- and 1,3,2-dithiazoles and Se congeners.[3-7] Their reactivity exhibits nontrivial chalcogen exchange exemplified by the S → Se replacement in 1,2,5-thiadiazoles and 1,2,3-dithiazoles under the influence of SeO_2. The Se → S replacement proceeds under the action of S_2Cl_2.[8,9] Their potential towards applications can be improved by fluorination.[10-13]

In contrast to fused 1,2,5-thia/selenadiazoles, fused 1,2,6-thia/selenadiazines are rare and less studied, especially fluorine-containing.[14-17] Here we report on unprecedented Se → S exchange in 1,2,6-selenadiazine ring system under the influence of $SOCl_2$.

The starting material is Cl-containing fluorinated 1,2,6-selenadiazine **1** (Scheme 1). It was found that under the action of air moisture during storage in THF solution compound **1** transforms into HO-containing derivative **2**.[17] With a small molar excess of $SOCl_2$, compound **1** can be recovered, but on prolonged storage at ambient temperature with a large excess of $SOCl_2$ it quantitatively (^{13}C and ^{19}F NMR) transforms into 1,2,6-thiadiazine **3**[†,16] (Scheme 1); moderate heating facilitates the **1** → **3** transformation. Similar to S_2Cl_2,[19] $SOCl_2$ is versatile (chlorinating, oxidizing, condensing, and cyclizing) reagent for organic syntheses,[20] however, it has never been used for the Se → S chalcogen exchange.

For the exchange, the pathways ***a*** and ***b*** assuming the hetero-ring opening and closing can be considered (Scheme 2). The $SeCl_4$ byproduct is common for both ***a*** and ***b***, whereas $SeOCl_2$ (***a***) and the intermediately appeared / disappeared $SeCl_2$[‡,21-23] (***b***) are not. Despite ^{77}Se NMR is very useful in organoselenium chemistry[24,25] encompassing investigation of the S → Se exchange in 1,2,3-dithiazoles,[9] and solution $\delta^{77}Se$ of **3**, $SeCl_4$, $SeOCl_2$, $SeCl_2$, and H_2SeO_3 (below) are known,[17,21,26] here the method is less effective for reliable distinguishing of the pathways of the slow proceeding reaction under discussion.[†] Furthermore, the air moisture converts $SeCl_4$, $SeOCl_2$, and $SeCl_2$ in SeO_2 (and, perhaps, further in H_2SeO_3). For NMR detection of the proposed intermediates (Scheme 2), targeted lower-temperature measurements are most likely needed, together with preliminary calculations of the intermediates' $\delta^{13}C$, $\delta^{19}F$, and $\delta^{77}Se$, which is a separate work.

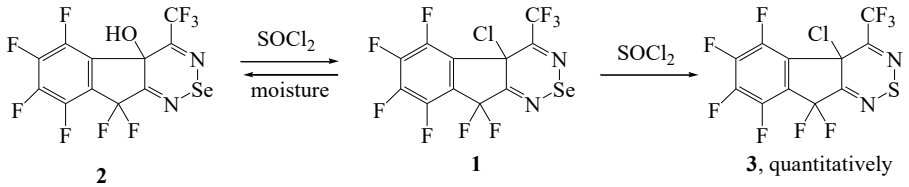
B3LYP/6-31G(d) calculations with account of THF solvent[§,27-30] suggest that the exchange begins with an addition of one or, under conditions of the reagent excess, two molecules of $SOCl_2$ to **1** (the pathways ***a*** and ***b***, respectively) to give the intermediates **A** and **C**, whose structural optimization leads to the intermediates **B** and **D**, respectively, via a cleavage of the Se–N bond. Cyclization of **B** or **D** with elimination of $SeOCl_2$ or SO_2Cl_2, respectively, gives **3** (Scheme 2, Figure 1). Thermodynamically, **3** is less attractive than **1** (calculated total free energies are ~ –2285 and –4289 a. u., respectively). According to the energies (Figure 1), the reaction is kinetically-driven, and the pathway ***a*** seems more realistic than the pathway ***b***. The chalcogen-nitrogen ring-opening addition of reagent to substrate (Scheme 2, Figure 1) may be common for the first stage of the chalcogen exchange (*cf.* the S → Se exchange in 1,2,3-dithiazoles under the action of SeO_2).[13] However, general disclosing of the key mechanistic aspects of the chalcogen exchange under the influence of such different reagents as $SOCl_2$, SeO_2, and S_2Cl_2 (this work and refs 12, 13) requires extensive further research.

The findings of this work confirm earlier conclusion that the chalcogen exchange is a promising new direction of further development of chalcogen-nitrogen heterocyclic chemistry.[8] Mild conditions of the Se → S exchange suppose potential involvement of a broad variety of substrates, including those unstable towards heating, which compensates the

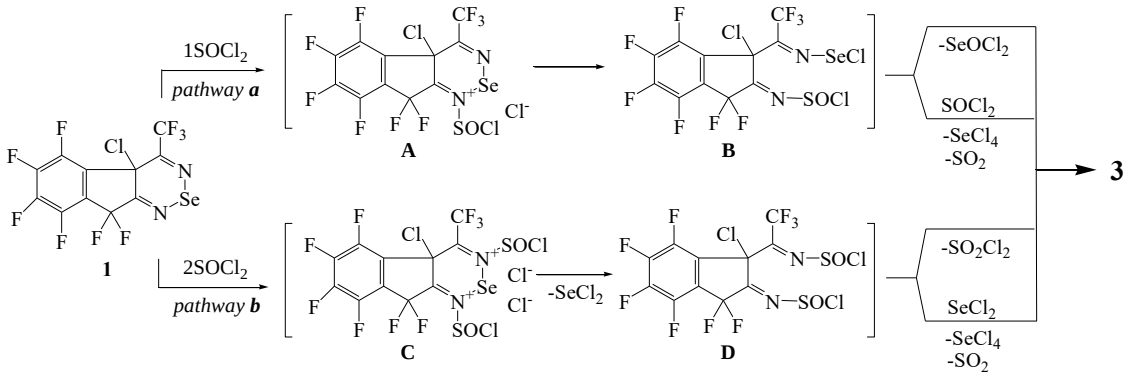
© Mendeleev Communications.

exchange's time-consuming character. Furthermore, in many cases selenium-nitrogen heterocycles are more readily available preparatively (diamine + SeO_2, room temperature) than sulfur-nitrogen ones (diamine + $SOCl_2$, organic base, continuous heating), motivating two-step mild synthesis of sulfur-nitrogen rings via selenium-nitrogen congeners and the Se → S exchange. Overall, the scope of the discovered reaction, particularly possibilities of its catalytic acceleration and transfer into the hydrocarbon series, is worth of further research.

The authors are grateful to the Multi-Access Chemical Research Center of the Siberian Branch of the Russian Academy of Sciences for instrumental and computational facilities.



Scheme 1 Reagents and conditions: The **2** → **1** reaction: THF solvent, ~1.7 molar excess of $SOCl_2$, 1 h at 45°C. The **1** → **3** reaction (i, ii): i, THF solvent, ~1.7 molar excess of $SOCl_2$, 1 h at 45°C and one-month storage at room temperature; ii, ~3.4 molar excess of $SOCl_2$, 1 h at 48°C and two-month storage at room temperature (OSM).



Scheme 2

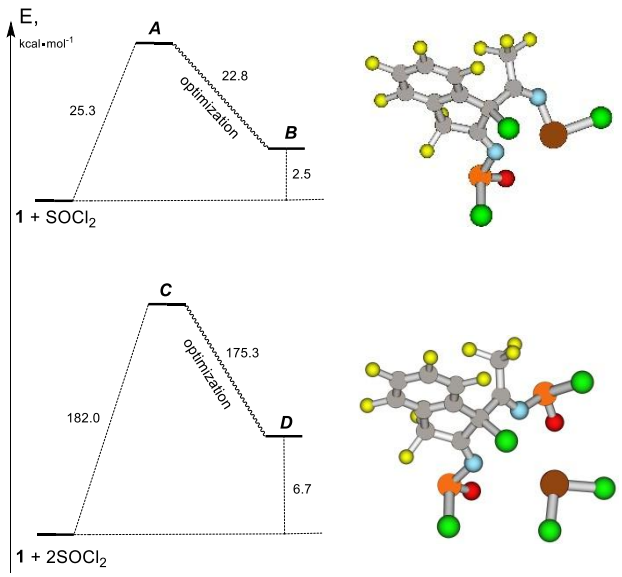


Figure 1 Fragment of the potential energy surface for the pathways ***a*** (above) and ***b*** (below) from B3LYP/6-31G(d) calculations, together with optimized structures of the key intermediates **B** and **D**. Color code: C grey, Cl green, F lemon, N blue, O red, S orange, Se brown.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.8104.

References

1 T. Chivers and R. S. Laitinen, Chalcogen-Nitrogen Chemistry. From Fundamentals to Applications in Biological, Physical and Materials Sciences, World Scientific, 2021; https://doi.org/10.1142/12397.
2 A. Yu. Makarov and A. V. Zibarev, *Adv. Heterocycl. Chem.*, 2026, **150**, 1; https://doi.org/10.1016/bs.aihch.2026.03.001.
3 O. A. Rakitin, *Adv. Heterocycl. Chem.*, 2026, **149**, 327; https://doi.org/10.1016/bs.aihch.2026.01.005.
4 P. A. Koutentis, A. Yu. Makarov, O. A. Rakitin and A. V. Zibarev, *Russ. Chem. Rev.*, 2025, **94**, RCR5146; https://doi.org/10.59761/RCR5146.
5 E. A. Radiush, H. Wang, E. A. Chulanova, D. O. Prima, N. S. Radaeva, Ya. A. Ponomareva, N. A. Semenov and A. V. Zibarev, *Mendeleev Commun.*, 2024, **34**, 297; https://doi.org/10.1016/j.mencom.2024.04.001.
6 O. A. Rakitin and A. V. Zibarev, *Asian J. Org. Chem.*, 2018, **7**, 2397; https://doi.org/10.1002/ajoc.201800536.
7 E. A. Chulanova, N. A. Semenov, N. A. Pushkarevsky, N. P. Gritsan and A. V. Zibarev, *Mendeleev Commun.*, 2018, **28**, 453; https://doi.org/10.1016/j.mencom.2018.09.001.
8 L. S. Konstantinova and O. A. Rakitin, *Mendeleev Commun.*, 2021, **31**, 433; https://doi.org/10.1016/j.mencom.2021.07.002.
9 L. S. Konstantinova, I. V. Baranovsky, E. A. Pritchina, M. S. Mikhailov, I. Yu. Bagryanskaya, N. A. Semenov, I. G. Irtegova, G. E. Salnikov, K. A. Lyssenko, N. P. Gritsan, A. V. Zibarev and O. A. Rakitin, *Chem. – A Eur. J.*, 2017, **23**, 17037; https://doi.org/10.1002/chem.201703182.
10 D. O. Prima, E. V. Vorontsova, A. G. Makarov, A. Yu. Makarov, I. Yu. Bagryanskaya, T. F. Mikhailovskaya, Yu. G. Slizhov and A. V. Zibarev, *Mendeleev Commun.*, 2017, **27**, 439; https://doi.org/10.1016/j.mencom.2017.09.002.
11 Z. Wang, S. Zhu, T. Li, W. Liang and H. Hu, *ACS Mater. Au*, 2025, **5**, 57; https://doi.org/10.1021/acsmaterialau.4c00099.
12 J. Shao, M. Li, G. Chen, Y. Fang, S. Y. Jeong, Y. Ke, X. Yi, H. Y. Woo and B. Huang, *ChemSusChem*, 2025, **18**, e202402226; https://doi.org/10.1002/cssc.202402226.

© Mendeleev Communications.

13 S.-H. Chen, X.-Y. Cao, P.-T. Hu, K. Jiang, Y.-T. Liang, B. J. Xu, Z.-H. Li and Z.-Y. Wang, *Mater. Adv.*, 2023, **4**, 6612; https://doi.org/10.1039/d3ma00876b.
14 A. S. Kologirou, A. Kourtellaris and P. A. Koutentis, *ChemistrySelect*, 2025, **10**, e202405838; https://doi.org/10.1002/slct.202405838.
15 C. Laurent, A. Kourtellaris and P. A. Koutentis, *New J. Chem.*, 2024, **48**, 1206. https://doi.org/10.1039/d3nj04876d.
16 V. M. Karpov, V. E. Platonov, T. V. Rybalova, Yu. V. Gatilov and M. M. Shakirov, *J. Fluor. Chem.*, 2012, **135**, 254; https://doi.org/10.1016/j.jfluchem.2011.12.005.
17 A. Haas, E. Hoppmann, V. M. Karpov, V. E. Platonov and M. M. Shakirov, *J. Fluor. Chem.*, 2000, **102**, 313; https://doi.org/10.1016/S0022-1139(99)00295-X.
18 I. P. Chuikov, V. M. Karpov and V. E. Platonov, *Russ. Chem. Bull.*, 1990, **39**, 1685; https://doi.org/10.1007/bf00961502.
19 L. S. Konstantinova and O. A. Rakitin, *Russ. Chem. Rev.*, 2014, **83**, 225; https://doi.org/10.1070/RC2014v083n03ABEH004354.
20 M. Li, *Synlett*, 2007, 2605. https://doi.org/10.1055/s-2007-986648.
21 A. Maaninen, T. Chivers, M. Parvez, J. Pietikäinen and R. S. Laitinen, *Inorg. Chem.*, 1999, **38**, 4093; https://doi.org/10.1021/ic981430h.
22 M. V. Musalov, V. A. Yakimov, V. A. Potapov, S. V. Amosova, T. N. Borodina and S. V. Zinchenko, *New J. Chem.*, 2019, **43**, 18476. https://doi.org/10.1039/c9nj04707g.
23 M. V. Musalov, S. V. Amosova and V. A. Potapov, *Int. J. Mol. Sci.*, 2023, **24**, 17485; https://doi.org/10.3390/ijms242417485.
24 M. S. Silva, D. Alves, D. Hartwig, R. G. Jacob, G. Perin and E. J. Lenardão, *Asian J. Org. Chem.*, 2021, **10**, 91; https://doi.org/10.1002/ajoc.202000582.
25 L. B. Krivdin, *Russ. Chem. Rev.*, 2021, **90**, 265; https://doi.org/10.1070/RCR4960.
26 H. J. Reich, *Selenium NMR Data*, 2007; http://www.chem.wisc.edu/areas/reich/handouts/nmr/se-data.htm.
27 M. S. Gordon and M. W. Schmidt, in *Theory and Applications of Computational Chemistry: The First Forty Years*; eds. C. E. Dykstra, G. Frenking, K. S. Lim and G. E. Scusaria, Elsevier, 2005, pp. 1167–1190; https://doi.org/10.1016/B978-044451719-7/50084-6.
28 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999; https://doi.org/10.1021/cr9904009.
29 H. Li and J. H. Jensen, *J. Comput. Chem.*, 2004, **25**, 1449; https://doi.org/10.1002/jcc.20072.
30 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378; https://doi.org/10.1021/jp810292n.

† 3-(1-Amino-2,2,2-trifluoroethyliden)-1,1,4,5,6,7-hexafluoro-2-iminoindan[18] was converted in **1**[17] and the later transformed *in situ* in **3** (Scheme 1; Online Supplementary Materials).

‡ Unstable in the individual form, SeX_2 (X = Cl, Br) are long-lived in THF solutions[21] and widely used in organic synthesis (refs[22,23] and refs therein).

§ DFT calculations have been performed at the B3LYP/6-31G(d) level of theory with the *GAMESS* program.[27] Solvation was taken into account by the polarizable continuum model[28-30] using the built-in parameters for THF.

Received: 1st June 2026; Com. 26/8104

© Mendeleev Communications.