1526 Russian Chemical Bulletin, International Edition, Vol. 58, No. 7, pp. 1526—1527, July, 2009

A novel reaction of 2,4,6-triphenyl(thio)selenopyrylium salts leading to benzoyl(thio)selenophenes and 2,4,6-triphenyl(thio)selenopyrans

*B. I. Drevko,** E. G. Bol'shakova, A. F. Almaeva, M. A. Suchkov, V. G. Mandych, and G. A. Shekhter*

Saratov Military Institute of Biological and Chemical Safety,
5 prosp. 50-letiya Oktyabrya, 410037 Saratov, Russian Federation.
Fax: +7 (845) 255 0744. E-mail:svirhbz@overta.ru

Thio- and selenopyrylium salts undergo simultaneous oxidation, leading to the corresponding benzoylselenophene or benzoylthiophene, and reduction reactions leading to 4*H*-selenopyran or 4*H*-thiopyran In the presence of water and triethylamine .

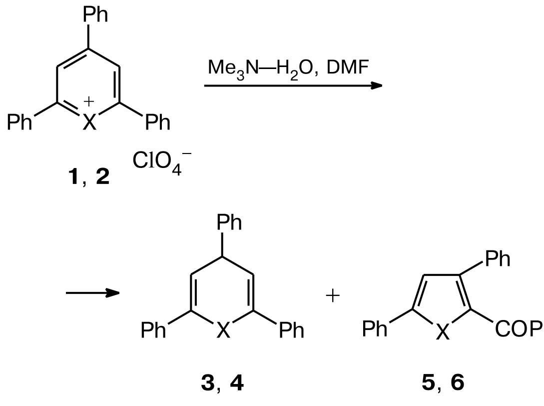
Key words: selenopyrylium salts, thiopyrylium salts, benzoylselenophene, benzoylthiophene, 4*H*-selenopyran, 4*H*-thiopyran.

It is well known that pyrylium, thiopyrylium, and selenopyrylium salts can undergo oxidation or thermal rearrangement resulting in the corresponding aroylfurans, aroylthiophenes, and aroylselenophenes,[1—4] or reduction in the presence of metal hydrides, organometallic reagents, or sodium methoxide leading to the corresponding pyrans, thiopyrans, and selenopyrans.[2,5—8] Thus, heteroaromatic cations can both be oxidized and reduced, which is typical of many disproportionation reactions.

Results and Discussion

We found that aryl-substituted selenopyrylium salts **1** and aryl-substituted thiopyrylium salts **2** undergo disproportionation in the presence of water and triethylamine. The reaction is carried out in DMF and it leads to mixtures of benzoylselenophenes and selenopyrans or benzoylthiophenes and thiopyrans (Scheme 1).

Scheme 1



X = Se (**1**, **3**, **5**); S (**2**, **4**, **6**)

GC-MS data indicate that the ratio of oxidized and reduced forms is 1:1. The product yield of this reaction in the case of 2,4,6-triphenylselenopyrylium perchlorate (**1**) is somewhat higher than in the case of 2,4,6-triphenylthiopyrylium perchlorate (**2**). The product yield of the same reaction with thio- and selenopyrylium bromozincates is less then 50% (GC-MS data). It was not possible to reliably determine the possibility of the disproportination process in the case of pyrylium salts even with the GC-MS method with the use of authentic samples.

When preparative syntheses were carried out, selenopyran **3** and benzoylselenophene **5** crystallized separately from the ethanol-ether solution: compound **3** formed spherical conglomerates of crystals and compound **5** formed needle-like crystals, which were separated manually. Derivatives of thiopyran **4** and benzoylthiophene **6** were separated by column chromatography.

In a similar reaction, 2,6-diphenylselenopyrylium perchlorate **7** gave a more complex mixture of products (Scheme 2), which judging by GC-MS data consists of 2,6-diphenylselenopyran-4-one (**8**, 36%), 2-phenyl-5-benzoylselenophene (**9**, 12%), 4*H*-selenopyran (**10**, 42%), and 2,6-diphenyl-2*H*-selenopyran (**11**, 5%). It is worth mentioning that compound **11** was identified only by mass spectral data (no authentic samples were used).

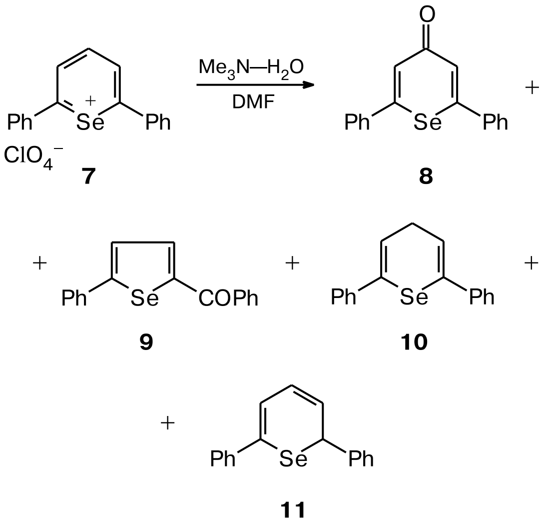
Thus, it was established that thio- and selenopyrylium salts can undergo disproportionation.

Experimental

Analysis by GC-MS was carried out on an HP 5890/5972 instrument, the injector temperature was 200 °C; starting temperature of the column was 50 °C, this temperature was kept for 3 min after the sample injection after that the temperature was raised at a rate of 10 °C min^{-1}; the temperature at the end of the analysis was 280 °C; the carrier gas was helium at a flow rate

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1481—1482, July, 2009.

Scheme 2



of 1 mL min^{-1}, capillary column HP-5MS. Analysis by TLC was carried out on TLC plates using solvent systems hexane—ether 5 : 1 and hexane—ether—chloroform 3 : 1 : 1, visualisation with iodine vapor. IR spectra were recorded on an IRS-29 spectrophotometer in Nujol or hexachlorobutadiene. ^{1}H NMR spectra were recorded with a Varian FT 80A spectrometer at 30 °C using Me_4Si as the internal standard.

Authentic samples were obtained using the known methods of synthesis of 4*H*-selenopyrans,[5,9] 4*H*-thiopyrans,[10] 3,5-diphenyl-2-benzoylselenophene and -thiophene,[1] 5-phenyl-2-benzoylselenophene,[11] and 2,6-diphenylselenopyran-4-one.[12]

Selenopyrylium[13] and thiopyrylium[14] salts were obtained by the described methods.

Aroyl(thio)selenophenes and 2,4,6-triaryl(thio)selenopyrans (general procedure). Halcogenopyrylium salt (2 mmol), H_2O (0.1 mL) and 20% ethanolic solution of triethylamine (1 mL) were added to DMF (10 mL). The reaction was carried out at 60 °C until all the starting salt disappeared from the reaction mixture (TLC). Water (10 mL) and ether (20 mL) were added to the reaction mixture. The etheral layer was washed with water, dried with Na_2SO_4, and analyzed by GC-MS.

After carring out the reaction with 2,4,6-triphenylselenopyrylium perchlorate and work-up, ethanol (20 mL) was added to the etheral solution, and the mixture was concenrated in air. Needle-like crystals of compound **5** and spherical conglomerates of crystals of compound **3** were separated manually. The residual oil consists of a mixture of the mentioned compounds (GC-MS data). **2-Benzoyl-3,5-diphenylselenophene** (**5**). Yield 0.14 g (18%), m.p. 88—89 °C (lit. data[4]: m.p. 89—90 °C), yield by GC-MS 49%. **2,4,6-Triphenyl-4*H*-selenopyran** (**3**). Yield 0.105 g (14%), m.p. 108—109 °C (lit. data[9]: m.p. 107.5—109.0 °C), yield by GC-MS 46%.

After carrying out the reaction with 2,4,6-triphenylselenopyrylium tribromozincate, the etheral solution was analyzed by GC-MS using authentic samples, which showed that the reaction mixture contained 27% of **2-benzoyl-3,5-diphenylselenophene** (**5**) and 22% of **2,4,6-triphenyl-4*H*-selenopyran** (**3**).

After carrying out the reaction with 2,4,6-triphenylthiopyrylium perchlorate, the etheral solution was concentrated. The obtained oil was chromatographed on alumina (hexane—ether, 10 : 1) to give **2-benzoyl-3,5-diphenylthiophene** (**6**). Yield 0.095 g (14%), m.p. 86—87 °C (lit. data[4]: m.p. 85—87 °C), yield by GC-MS 48%. **2,4,6-Triphenyl-4*H*-thoipyran** (**4**). Yield 0.143 g (22%), m.p. 104—105 °C (lit. data[10]: m.p. 104—106 °C), yield by GC-MS 45%.

After carrying out the reaction with 2,4,6-triphenylthiopyrylium tribromozincate, the etheral solution was analyzed by GC-MS using authentic samples, which showed that the reaction mixture contained 24% of **2-benzoyl-3,5-diphenylthiophene** (**6**) and 21% of **2,4,6-triphenyl-4*H*-thiopyran** (**4**).

The reaction of 2,6-diphenylselenopyrylium perchlorate included hexane as a solvent in the work-up, column chromatography on silica gel L (100/400) (hexane—ether, 10 : 1) afforded **2,6-diphenyl-4*H*-selenopyran (10)**, yield 17%, m.p. 50—51 °C (lit. data[12]: m.p. 49.5—51.0 °C), yield by GC-MS 42% (together with supposed **2,6-diphenyl-2*H*-selenopyran** (**11**), which was not described in literature; the peak of putative compound **11** was not completely separated from the peak of compound **10** in GC). The chromatographical yield of 2-**benzoyl-5-phenylselenophene (9)** was 8%, and that of **2,6-diphenylselenopyran-4-one (8)** was 31%.

The ^{1}H NMR and IR spectra of the products obtained correspond to those described earlier .

References

1. B. I. Drevko, L. A. Fomenko, V. G. Kharchenko, *Khim. Geterotsikl. Soedin.*, 1989, 767 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1989, **25**].
2. G. Doddi, E. Gianfranco, *Adv. Heterocycl. Chem.*, 1994, **60**, 65.
3. B. I. Drevko, in *Karbonil´nye soedineniya v sinteze geterotsiklov* [*Carbonyl Compounds in the Synthesis of Heterocycles*], Nauchnaya Kniga, Saratov, 2004, 93 (in Russian).
4. B. I. Drevko, E. V. Sychkova, G. A. Baranchikova, V. G. Mandych, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 1800 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 1867].
5. V. G. Kharchenko, B. I. Drevko, *Khim. Geterotsikl. Soedin.*, 1984, 1634 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1984, **20**].
6. B. I. Drevko, S. N. Petrakov, L. A. Fomenko, O. I. Zhykov, M. I. Smushkin, V. G. Kharchenko, *Zh. Org. Khim.*, 1994, **30**, 115 [*J. Org. Chem. USSR* (*Engl. Transl.*), 1994, **30**].
7. S. Kuthan, P. Sebek, S. Bohm, *Adv. Heterocycl. Chem.*, 1994, **59**, 179.
8. A. T. Balaban, A. Dinnculescu, G. N. Dorofeenko, D. W. Fischer, A. W. Koblic, V. V. Mezheritski, W. Schroth, *Pyrylium Salts: Synthesis, Reactions, and Physical Properties*. Academic Press, New York, 1982, 405 pp.
9. B. I. Drevko, M. A. Suchkov, A. E. Filimonov, V. G. Kharchenko, *Zh. Obsh. Khim.*, 1999, **69**, 84 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 1999, **69**].
10. Pat. RU № 2226192; *Bull. Izobret.*, 2004, No. 9 (in Russian).
11. B. I. Drevko, M. I. Smushkin, V. G. Kharchenko, *Zh. Org. Khim.*, 1995, **31**, 1437 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 1995, **31**].
12. B. I. Drevko, S. N. Petrakov, L. A. Fomenko, V. G. Kharchenko, *Khim. Geterotsikl. Soedin.*, 1991, 996 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1991, **27**, 996].
13. Pat. RU 2276150; *Bull. Izobret.*, 2006, No. 13 (in Russian)
14. Invention certificate USSR 1703649; *Bull. Izobret.*, 1992, No. 1 (in Russian).

Received October 3, 2008;
in revised form March 10, 2009