

New thermal rearrangement of 2,4,6-triarylthio(seleno)pyrylium salts

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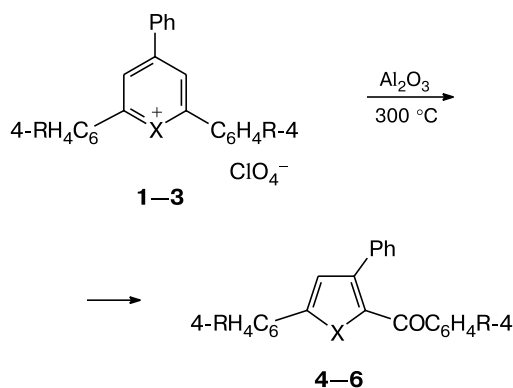
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It is known that^{1–3} 4H-thio(seleno)pyrans and thio-pyrylium salts can be oxidized into the corresponding aroylfurans, -thiophenes, and -selenophenes. In addition, when analyzing pyrylium, thiopyrylium, and selenopyrylium perchlorates by the GC-MS method, we have found that the mass spectra and retention times of the compounds under analysis are completely identical with those of aroylselenophenes, -thiophenes, and -furans.⁴ This is in conflict with the previous⁵ MS data for 2,4,6-triphenylpyrylium perchlorate: analogous spectra have been explained by the specific character of fragmentation of the heteroaromatic cation.⁵

We have found that seleno(thio)pyrylium perchlorates **1–3** applied to alumina transform to the corresponding aroylselenophenes and -thiophenes **4–6** (Scheme 1) in 42–65% yields on heating to 300 °C in an inert atmosphere (the yields of crude products reached 85–95%; however, the content of impurities was 10 to 30% (GC-MS data)).

Scheme 1



Compound	X	R
1, 4	Se	H
2, 5	Se	OMe
3, 6	S	H

It should be noted that the reactions with selenopyrylium salts are slightly more selective than those with thiopyrylium salts. When the corresponding pyrylium perchlorates were used, aroylfurans were not isolated in the individual state: they were only detected by GC-MS with aroylfuran as an authentic sample.

Heating of selenopyrylium (**1, 2**) and thiopyrylium perchlorates (**3**) in the absence of an adsorbent gave complex mixtures of products that was not reliably analyzed by GC-MS.

Products were analyzed by GC-MS on an HP5890/5972 instrument ($T_{\text{inj}} = 200\text{ }^\circ\text{C}$; $t_i = 3\text{ min}$; $T_i = 50\text{ }^\circ\text{C}$; $T_f = 280\text{ }^\circ\text{C}$; $\Delta T = 10\text{ }^\circ\text{C min}^{-1}$; helium as a carrier gas, $v = 1\text{ mL min}^{-1}$; HP-5MS capillary column). Preparative TLC was performed with hexane–ether (5 : 1) and hexane–ether–chloroform (3 : 1 : 1) as eluents; spots were visualized with the iodine vapor. IR spectra were recorded on an IKS-29 spectrophotometer (Nujol and hexachlorobutadiene). ¹H NMR spectra were recorded on a Varian FT 80A spectrometer at 30 °C with Me₄Si as the internal standard.

Experimental procedure. An appropriate chalcogenopyrylium perchlorate^{6,7} (2 mmol) was dissolved in a minimum amount of EtOH–CHCl₃ (1 : 2), applied to alumina (10 g), concentrated at ~20 °C, and transferred to a quartz reaction vessel. The system was purged with argon, heated to 300 °C, and then cooled to ~20 °C. The resulting product was thoroughly extracted with diethyl ether (the starting salts are insoluble in ether). The solvent was removed and the residue was purified by column chromatography on alumina with hexane–ether (6 : 1) as an eluent. The ¹H NMR and IR spectra agree with the previous data.¹

2-Benzoyl-3,5-diphenylselenophene (4) was obtained from 2,4,6-triphenylselenopyrylium perchlorate (**1**). The yield of the crude product was 88% (89% purity according to GC-MS data). After the chromatography, the yield was 65%, m.p. 89–90 °C (cf. Ref. 1: m.p. 85.0–86.5 °C).

2-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-3-phenylselenophene (5) was obtained from 2,6-bis(4-methoxyphenyl)-4-phenylselenopyrylium perchlorate (**2**). The yield of the crude product was 85% (90% purity according to GC-MS data). After the chromatography, the yield was 54%, m.p. 134–136 °C (cf. Ref. 1: m.p. 135–137 °C).

2-Benzoyl-3,5-diphenylthiophene (6) was obtained from 2,4,6-triphenylthiopyrylium perchlorate (**3**). The yield of the crude product was 92% (72% purity according to GC-MS data). After the chromatography, the yield was 42%, m.p. 85–87 °C (*cf.* Ref. 1: m.p. 84.0–85.5 °C).

References

1. B. I. Drevko, L. A. Fomenko, and V. G. Kharchenko, *Khim. Geterotsikl. Soedin.*, 1989, 767 [*Chem. Heterocycl. Compd.*, 1989, **25** (Engl. Transl.)].
2. S. Kuthan, P. Sebek, and S. Bohm, *Adv. Heterocycl. Chem.*, 1994, **59**, 179.
3. G. Doddi and E. Gianfranco, *Adv. Heterocycl. Chem.*, 1994, **60**, 65.
4. V. G. Mandych, B. I. Drevko, G. A. Baranchikova, and E. V. Suchkova, *Tezisy dokladov XVII Mezhdunarodnogo Mendelevskogo s'ezda (Kazan', 21–26 sentyabrya 2003 g.)* [*Abstrs. XVII Int. Mendeleev Conf. (Kazan, September 21–26, 2003)*], Kazan, 2003, **4**, 544 (in Russian).
5. G. Hvistendahl, *Org. Mass Spectrom.*, 1974, **9**, 80.
6. Pat. RF 2 276 150; *Byull. Izobret.*, 2006, No. 13.
7. Inventor's Certificate 1 703 649; *Byull. Izobret.*, 1992, No. 1, 98.

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