SOCl₂- and POCl₃-activated β -chloroselenenation of alkenes

N. V. Zyk, E. K. Beloglazkina, and R. L. Antipin*

Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory, 119992 Moscow, Russian Federation. Fax: +7 (095) 939 0290. E-mail: antipin@org.chem.msu.ru

At present, selenenamides $PhSeNR_2$ find a limited application as electrophilic agents. Only very reactive olefins such as enamines and enol silyl ethers react with nonactivated selenenamides.¹ Earlier,² electrophilic addition of selenenamides activated by sulfur trioxide to olefins was studied; the reaction products were β -phenylselenenylsulfamates.

Recently, we have proposed phosphorus and sulfur oxyhalides (Refs 3 and 4, respectively) as activating agents in the electrophilic addition of sulfenamides to unsaturated compounds. In the present work, we studied the reaction of diethylbenzeneselenenamide **1** with olefins in the presence of sulfur(v) and phosphorus(v) oxychlorides. The corresponding β -chloro selenides were obtained in 73–99% yields (Scheme 1).



The reaction with cyclohexene is *trans*-stereospecific. The chloroselenenation of the terminal olefin, namely, hex-1-ene, affords a Markovnikov adduct. Apparently, the reaction mechanism is analogous to that reported earlier.³

This reaction affords quantitative yields with the use of $SOCl_2$ and thus can serve as a convenient alternative to direct chloroselenenation with selenenyl chlorides.

¹H and ¹³C NMR spectra were recorded on a Varian VXR-400 instrument (400 and 100 MHz, respectively) in CDCl₃.

N,N-Diethylbenzeneselenenamide (1) was prepared according to a known procedure.²

Addition of diethylbenzeneselenenamide (1) to olefins in the presence of phosphorus(v) or sulfur(v) oxychloride (general procedure). A solution of POCl₃ or SOCl₂ (2.5 mmol) in 10 mL of dry CH₂Cl₂ was added at -30 °C to a stirred solution of compound 1 (2.5 mmol) in 10 mL of anhydrous CH₂Cl₂. The reaction mixture was kept for 10 min and then a solution of an olefin (2.5 mmol) in 10 mL of CH₂Cl₂ was added. After 30 min, the reaction mixture was warmed to ~20 °C and passed through a 5-cm layer of silica gel. The solvent was removed to give yellow oily products.

trans-1-Chloro-2-phenylselenenylcyclohexane (2). ¹H NMR, δ : 1.4, 1.6, 1.7, 2.3 (all m, 2 H each, H(5), H(4), H(6), H(3)); 3.5 (dd, 1 H, HCSe, J = 6.0 Hz, J = 10.1 Hz); 4.15 (dd, 1 H, HCCl, J = 7.0 Hz, J = 10.1 Hz); 7.4 (m, 5 H, H arom.). ¹³C NMR, δ : 22.95, 25.30, 32.67, 34.15, 50.32 (CSe), 64.10 (CCl), 127.85, 129.78, 136.30. MS (EI, 70 eV), m/z (I_{rel} (%)): 274 [M]⁺ (35), 276 [M + 2]⁺ (32).

2-Chloro-1-phenylselenenylhexane (3). ¹H NMR, δ : 0.86 (t, 3 H, Me, J = 7.3 Hz); 1.3 (m, 4 H, CH₂); 1.7, 2.0 (both m, 1 H each, H(3)); 3.17 (dd, 1 H, HCSe, J = 8.5 Hz, J = 12.4 Hz); 3.26 (dd, 1 H, HCSe, J = 5.2 Hz, J = 12.4 Hz); 4.0 (m, 1 H, HCCl); 7.4 (m, 5 H, H arom.). ¹³C NMR, δ : 15.25, 22.85, 29.10, 35.95, 38.50 (CSe), 63.40 (CCl), 127.36, 129.25, 136.65. MS (EI, 70 eV), $m/z(I_{rel}(\%))$: 276 [M]⁺ (43), 278 [M + 2]⁺ (39).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 00-03-32888a), the Foundation "Russian Universities" (Grant No. 05.03.046), and the Presidium of the Russian Academy of Sciences (Program "Theoretical and Experimental Investigation of the Nature of Chemical Bonding and the Mechanisms of Chemical Reactions and Processes").

References

- 1. P. Lerouge and C. Paulimer, Bull. Soc. Chim. Fr., 1985, 1219.
- N. V. Zyk, I. V. Alabugin, A. G. Kutateladze, J. L. Kice, and N. S. Zefirov, *Dokl. Akad. Nauk*, 1994, **337**, 208 [*Dokl. Chem.*, 1994 (Engl. Transl.)].
- N. V. Zyk, E. K. Beloglazkina, R. A. Gazzaeva, V. S. Tyurin, and I. D. Titanyuk, *Phosphorus, Sulfur and Silicon*, 1999, 155, 33.
- 4. N. V. Zyk, E. K. Beloglazkina, and I. D. Titanyuk, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 2516 [*Russ. Chem. Bull.*, 1998, 47, 2434 (Engl. Transl.)].

Received May 12, 2004; in revised form July 13, 2004

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 10, pp. 2250–2251, October, 2004.

1066-5285/04/5310-2352 © 2004 Springer Science+Business Media, Inc.