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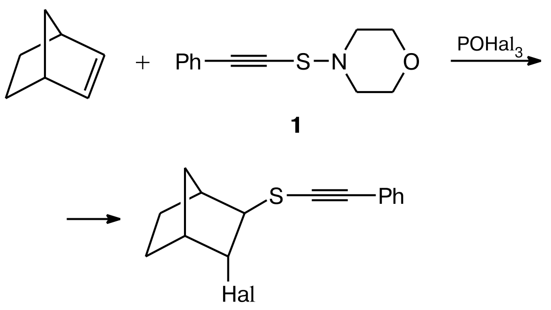
Alkynylsulfenylation of alkenes activated by phosphorus oxohalide

N. V. Zyk, E. K.Beloglazkina, M. A. Belova, and N. S. Dubinina*

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

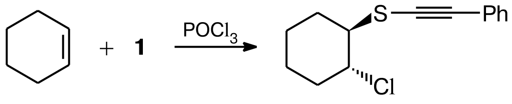
Whereas arylsulfenylation of alkenes with arylsulfenyl chlorides is a well-known electrophilic addition reaction, similar alkynylsulfenylation reactions have not been described so far. We have found that *N*-(2-phenylethynylthio)morpholine (**1**) in the presence of $POHal_3$ (Hal = Cl, Br) acts as an effective donor of the alkynylsulfenylating species.

The reactions of norbornene and cyclohexene with alkynylsulfenamide **1** in the presence of $POCl_3$ and $POBr_3$ were studied. The reactions gave 1,2-*trans*-halosulfenylation products **2**—**4**.



1

2: Hal = Cl, 70%
3: Hal = Br, 65%



4, 67%

The structures of compounds **2**—**4** were determined by ^1H and ^{13}C NMR spectroscopy. The analysis of the spectra and the subsequent structure ascription were based on the data[1] concerning the substituent influence on the chemical shifts and on the ^1H—^1H spin-spin coupling constants. The stereochemistry of compound **4** was determined using the ω-criterion.[2]

We have shown previously that phosphorus oxohalides activate electrophilic addition of arylsulfenylamides[3] and thio and dithio bisamines[4,5] to alkenes. The discovered alkynylsulfenylation reaction confirms the applicability of this activation method to a broad range of compounds containing S—N bonds.

^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 instrument operating at 400 and 100 MHz, respectively.

Alkynylsulfenylation (general procedure). A solution of phosphorus oxohalide (25 mmol) in anhydrous CH_2Cl_2 was added at −40 °C to a solution of *N*-(2-phenylethynylthio)morpholine[6] (0.55 g, 25 mmol) in 20 mL of anhydrous CH_2Cl_2. After 5 min, alkene (25 mmol) dissolved in the same solvent was added at the same temperature. The reaction mixture was heated to 20 °C and stirred until the reaction was complete (TLC monitoring). The solvent was removed *in vacuo* and the residue was passed through a filtering column with silica gel (*h* = 3—4 cm); petroleum ether was used as the eluent.

2-*endo*-Chloro-3-*exo*-(2-phenylethynylthio)bicyclo[2.2.1]heptane (2), R_f 0.86 (EtOAc—petroleum ether, 1 : 10). ^1H NMR ($CDCl_3$), δ: 7.43—7.24 (m, 5 H, C_6H_5); 4.18 (td, 1 H, HCCl, $J_{H(2),H(1)} = J_{H(2),H(3)} = 4.0$ Hz, $J_{H(2),H_{exo}(6)} = 1.8$ Hz); 3.02 (dd, 1 H, HCS, $J_{H(3),H(2)} = 4.0$ Hz, $J_{H(3),H_{anti}(7)} = 2.7$ Hz); 2.51 (t, 1 H, HC(1), $J_{H(1),H(2)} = J_{H(1),H_{exo}(6)} = 4.0$ Hz); 2.40 (d, 1 H, HC(4), $J_{H(4),H_{exo}(5)} = 4.6$ Hz); 2.00 (dddd, 1 H, $H_{endo}(6)$, $J_{H_{endo}(6),H_{exo}(6)} = 13.1$ Hz, $J_{H_{endo}(6),H_{endo}(5)} = 8.8$ Hz, $J_{H_{endo}(6),H_{exo}(5)} = 4.0$ Hz, $J_{H_{endo}(6),H_{syn}(7)} = 2.5$ Hz); 1.90 (dtt, 1 H, $H_{syn}(7)$, $J_{H_{syn}(7),H_{anti}(7)} = 11.0$ Hz, $J_{H_{syn}(7),H_{endo}(5)} = J_{H_{syn}(7),H_{endo}(6)} = 2.5$ Hz, $J_{H_{syn}(7),H(1)} = J_{H_{syn}(7),H(4)} = 1.7$ Hz); 1.72 (tt, 1 H, $H_{exo}(5)$, $J_{H_{exo}(5),H_{endo}(5)} = J_{H_{exo}(5),H_{exo}(6)} = 13.1$ Hz, $J_{H_{exo}(5),H_{endo}(6)} = J_{H_{exo}(5),H(4)} = 4.6$ Hz); 1.53—1.33 (m, 3 H, cage protons). ^{13}C NMR ($CDCl_3$), δ: 131.8 (C arom.); 128.7 (C arom); 128.6 (C arom.); 123.7 (C≡); 94.8 (C≡); 67.0 (CCl); 59.8 (CS); 36.3; 32.4; 30.1; 29.8; 29.5. Found (%): C, 68.57; H, 5.70. $C_{15}H_{15}ClS$. Calculated (%): C, 68.56; H, 5.75.

2-*endo*-Bromo-3-*exo*-(2-phenylethynylthio)bicyclo[2.2.1]heptane (3), R_f 0.87 (EtOAc—petroleum ether, 1 : 10). ^1H NMR ($CDCl_3$), δ: 7.57—7.25 (m, 5 H, C_6H_5); 4.47 (td, 1 H, HCBr, $J_{H(2),H(1)} = J_{H(2),H(3)} = 4.2$ Hz, $J_{H(2),H_{exo}(6)} = 1.9$ Hz); 3.16 (dd, 1 H, HCS, $J_{H(3),H(2)} = 4.2$ Hz, $J_{H(3),H_{anti}(7)} = 2.7$ Hz); 2.55 (t, 1 H, HC(1), $J_{H(1),H(2)} = J_{H(1),H_{exo}(6)} = 4.2$ Hz); 2.38 (d, 1 H, HC(4), $J_{H(4),H_{exo}(5)} = 4.3$ Hz); 1.53—1.33 (m, 6 H, cage protons). ^{13}C NMR ($CDCl_3$), δ: 131.8 (C_{arom}); 129.7 (C_{arom}); 128.7 (C_{arom}); 118.0 (C≡); 94.9 (C≡); 61.4 (CBr); 58.5 (CS); 45.5; 43.8; 36.1; 29.4; 24.3. Found (%): C, 57.76; H, 5.65. $C_{15}H_{15}BrS$. Calculated (%): C, 58.64; H, 4.92.

***trans*-1-Chloro-2-(2-phenylethynylthio)cyclohexane (4)**, R_f 0.84 (EtOAc—petroleum ether, 1 : 10). ^1H NMR ($CDCl_3$), δ: 7.50—7.25 (m, 5 H, C_6H_5); 4.08 (td, 1 H, HCCl, $J = 9.2$ Hz, $J = 4.2$ Hz); 3.04 (td, 1 H, HCS, $J = 9.2$ Hz, $J = 4.1$ Hz); 2.40 (m, 8 H). ^{13}C NMR ($CDCl_3$), δ: 136.7 (C_{arom}); 132.0 (C_{arom}); 129.7 (C_{arom}); 123.8 (C≡); 96.3 (C≡); 62.1 (CCl); 54.5 (CS); 29.5; 25.0; 23.1; 14.6. Found (%): C, 67.06; H, 5.80. $C_{14}H_{15}ClS$. Calculated (%): C, 67.05; H, 6.03.

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