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CHEMISTRY

Oxidative Dimerization of Sulfenyl Chlorides into Thiosulfonates under the Action of Hexamethylphosphoramide

I. V. Bodrikov, N. V. Nikitina, and A. Yu. Subbotin

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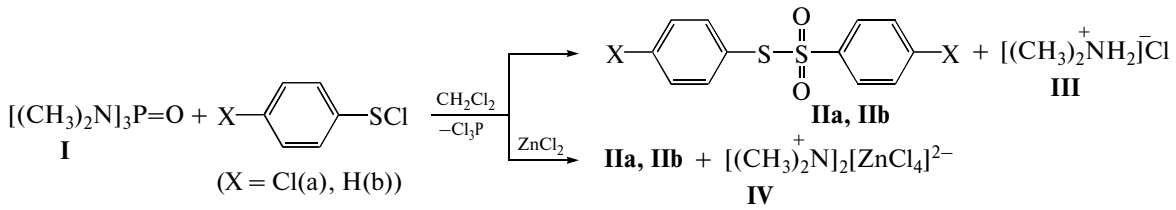
Compounds containing electrophilic sulfur S(II) are mainly known as important reagents in alkene chemistry. Different aspects of reactions of sulfenyl chlorides, sulfur dichloride, and other S(II) reagents with a wide range of unsaturated compounds, including linear and cyclic alkenes, alkynes, etc., are described in the literature [1, 2]. However, in spite of the considerable synthetic and theoretical value of these reagents related in alkene chemistry to weak electrophiles [1, 3], their reactions with *n*-donor substrates have not been studied. There are few reports in the literature on the reaction of this group of electrophiles with typical *n*-donor compounds [4, 5].

It was reported that the reaction of sulfur dichloride with hexamethylphosphoramide (HMPA) leads to elimination of a nitrogen-containing fragment with two alkyl groups that provides cascade processes involving solvent [5].

We have found that HMPA (**I**) in the systems with arenesulfenyl chlorides in methylene chloride promotes unsymmetrical oxidative dimerization of arenesulfenyl chlorides into thiosulfonates **IIa** and **IIb**. This reaction includes the transfer of two oxygen atoms from HMPA molecules and the dimerization of sulfenyl chlorides. The same reaction takes place in this system in the presence of zinc chloride in methylene chloride. However, the yield of thiosulfonate in this reaction is lower.

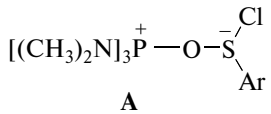
The revealed reaction is accompanied by the cleavage of the dimethylamino fragment from the HMPA molecule, which involves methylene chloride behaving as the source of the hydrogen equivalent in the formation of ammonium salts **III** and **IV** [6].



The structure and composition of reaction products were established on the basis of X-ray diffraction (figure), NMR and IR spectroscopy, and elemental analysis data.

The scheme of thiosulfonate formation was analyzed on the basis of MNDO computations using the PM3 method [6].

According to the computations, the first stage of the revealed reaction is the formation of an HMPA–sulfur-containing electrophile donor–acceptor complex (**A**).



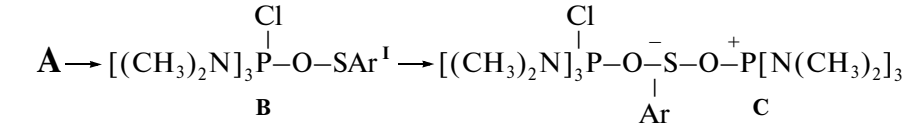
A

The activation barrier of complex formation ($E^{\neq}$) is 12 kcal/mol and the difference between the formation energies for intermediate states and the isolated components of the system (ΔH) is −1.5 kcal/mol.

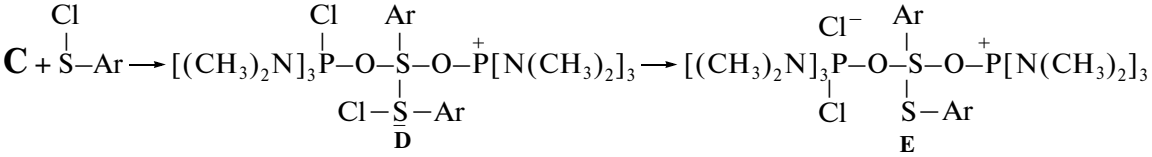
Complex **A** transforms further into complex **B** owing to migration of a chloride anion from the sulfur atom to phosphorus ($E^{\neq}$ = 26 kcal/mol,

State Technical University, ul. Minina 24, Nizhni Novgorod, 603600 Russia

$\Delta H = 7$ kcal/mol). Once the second HMPA molecule has overcome the energy barrier of 10 kcal/mol, it reacts with complex **B** with an energy advantage of 5 kcal/mol to form bipolar ion-type intermediate **C**.

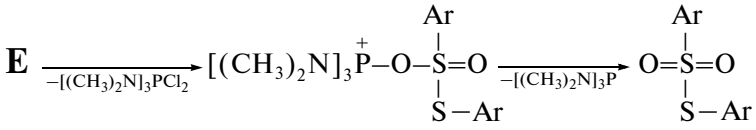


Further development of the cascade process includes the reaction of a second molecule of *p*-chlorobenzenesulfenyl chloride with intermediate **C**. The formation of the S–S bond in this cascade reaction occurs with an activation barrier of 10 kcal/mol to give a metastable species **D** with an S–S distance of 2.2 Å. The cleavage of the S–Cl bond in species **D** requires overcoming an energy barrier of 45 kcal/mol. In the reaction channel under consideration, the reacting system after cleavage of the S–Cl bond spontaneously falls to the global energy minimum of state **E**. The migration of the chloride anion to the phosphorus atom requires overcoming the activation barrier of only 7 kcal/mol, while the system energy decreases by 15 kcal/mol relative to the energy of state **E**.



Thus, the stage involving the cleavage of the S–Cl bond in this reaction channel is the slowest.

Then, two P–O bonds are sequentially broken to give the final reaction product, thiosulfonate. The stage of P–O bond cleavage in complex **E**, where the phosphorus-containing fragment includes two chlorine atoms, has a low energy barrier ($E^{\neq}$ = 3 kcal/mol, $\Delta H = -7$ kcal/mol). The lack of chlorine atoms at phosphorus in complex **E** causes a sharp increase in the activation barrier for the cleavage of the second P–O bond ($E^{\neq}$ = 31 kcal/mol, $\Delta H = 22$ kcal/mol).



EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker DPX 200 spectrometer operating at 200 MHz in DMSO-d_6 solutions using TMS as an internal reference. The IR spectra of the prepared compounds were recorded on a PerkinElmer-180 spectrophotometer in thin film or as Nujol mulls. Substance purity was monitored by TLC on Silufol UV-254 plates with a Silpearl adsorbent using hexane–ether (10 : 1) as an eluent and iodine as a visualization reagent. X-ray diffraction study was carried out on Smart APEX and Smart APEX2 automated diffractometers (MoK_α radiation, graphite monochromator, ω–θ scanning).

The structures were solved by direct methods and refined by least squares on F^2_{hkl} in the anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier syntheses and refined isotropically. All computations were performed using SHELXTL V. 5.10 and SHELXTL V. 6.10 program suites [7, 8].

Crystals of compound **IIa** at 100(2) K are monoclinic, a = 8.1030(3) Å, b = 11.8261(5) Å, c = 13.4437(6) Å, β = 91.4360(10)°, V = 1287.86(9) Å^3, Z = 4, space group $P2(1)/n$. The structure was solved to R = 0.0220 for 2794 independent reflections with

$I > 2\sigma(I)$. Molecular structure of compound **IIa** is shown in the figure.

Reactions of HMPA with sulfenyl chlorides in methylene chloride. A solution of 11.8 mmol of sulfenyl chloride in 5 mL of methylene chloride was added to a solution of 2.1 g (11.8 mmol) of HMPA in 15 mL of methylene chloride at ambient temperature with stirring in a flow of dry nitrogen, and stirring was continued for 4 h. The resultant precipitate of dimethylammonium chloride (**III**) was separated by filtration and recrystallized from acetonitrile. The solvent was removed from the filtrate under reduced pressure. According to IR spectra, the residue consisted of thiosulfonate **IIa** or **IIb** and phosphorus chloride. Thiosulfonates **IIa** and **IIb** were purified by recrystallization from an acetonitrile–carbon tetrachloride mixture.

The yield of compound **IIa** was 2.6 g (70%), mp 134–136°C.

IR (Nujol, ν, cm^{-1}): 750, 810 (out-of-plane bending vibrations of C–H bonds of benzene ring), 1000 (S–O bond vibrations), 1080 ($\overset{\delta+}{S}\cdots\overset{\delta-}{O}$ bond vibrations), 1140–1330 (vibrations of O_2S–S fragment).

For $C_{12}H_8Cl_2O_2S_2$ anal. calcd. (%): C, 45.14; H, 2.51; O, 10.03; S, 20.06; Cl, 22.26.

Found (%): C, 44.82; H, 2.83; O, 10.33; S, 20.16; Cl, 21.86.

The yield of compound **IIb** was 2.1 g (70%), mp 41–43°C.

IR (Nujol, ν, cm^{-1}): 690, 750, 820, 1000 (benzene ring vibrations), 1140, 1620 (vibrations of O_2S–Ph fragment); 1130–1310 (vibrations of O_2S–S fragment).

For $C_{12}H_{10}O_2S_2$ anal. calcd. (%): C, 57.60; H, 4.00; O, 12.80; S, 25.60.

Found (%): C, 56.10; H, 4.50; O, 13.20; S, 26.20.

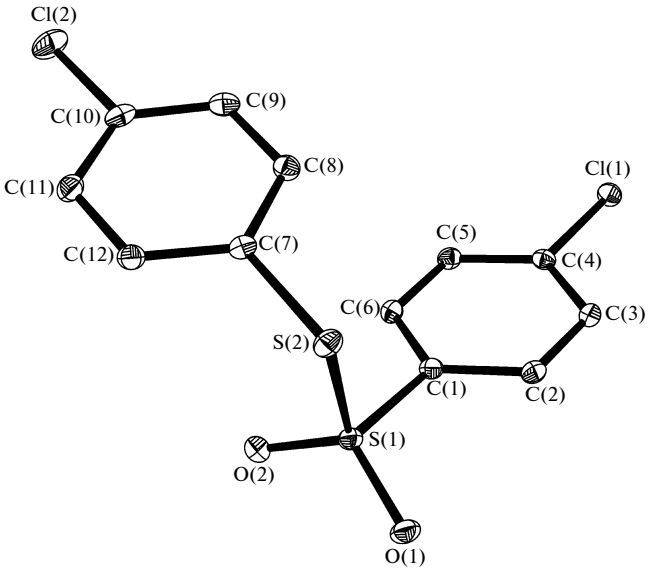
The yield of dimethylammonium chloride (**III**) was 0.24 g (25%), mp 170–171°C.

^{1}H NMR ($CDCl_3$, δ, ppm): 2.74 (s, 3H, CH_3), 2.67 (s, 3H, CH_3).

IR (Nujol, ν, cm^{-1}): 1000–1020 (CH_3 bending vibrations), 1100 (C–N stretching vibrations), 3450 (NH_2 stretching vibrations).

Phosphorus chloride, IR (thin film, ν, cm^{-1}): 550 (P–Cl).

Reactions of HMPA with sulfenyl chloride–$ZnCl_2$ system in methylene chloride. The experiment was carried out under conditions that excluded air moisture access. A solution of 1.4 g (7.9 mmol) of HMPA in 5 mL of methylene chloride was added to a mixture of 1.1 g (7.9 mmol) of zinc dichloride in 10 mL of methylene chloride with stirring at ambient temperature. Then, a solution of 7.9 mmol of sulfenyl chloride in 5 mL of the same solvent was added dropwise. The mixture was stirred for 4 h. The resultant precipitate of dimethylammonium tetrachlorozincate (**IV**) was separated by filtration and recrystallized from acetonitrile. The solvent was removed from the filtrate under reduced pressure. According to IR spectra, the residue consisted of thiosulfonate **IIa** or **IIb** and phosphorus(III) chloride. Thiosulfonates **IIa** and **IIb** were purified by recrystallization from an acetonitrile–carbon tetrachloride mixture.



Molecular structure of *p*-chlorobenzenethiosulfonate **IIa**.

The yields of compounds **IIa** and **IIb** were 0.68 g (27%) and 0.49 g (25%), respectively.

The yield of dimethylammonium tetrachlorozincate (**IV**) was 1.65 g (70%), mp 124–126°C (dec.).

^{1}H NMR (CD_3CN, δ, ppm): 2.72 (s, 3H, CH_3), 2.66 (s, 3H, CH_3).

IR (Nujol, ν, cm^{-1}): 1000–1020 (CH_3 bending vibrations), 1100 (C–N stretching vibrations), 3450 (NH_2 stretching vibrations).

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