Heteroatom Chemistry
Volume 19, Number 1, 2008

Comparison of the Reactivity of *N*-(*p*-Toluenesulfonyl)-Sulfinimidoyl Fluorides and Chlorides Toward Triphenylphosphine

Valeriy E. Pashinnik, Alexei V. Borovikov, and Yuriy G. Shermolovich

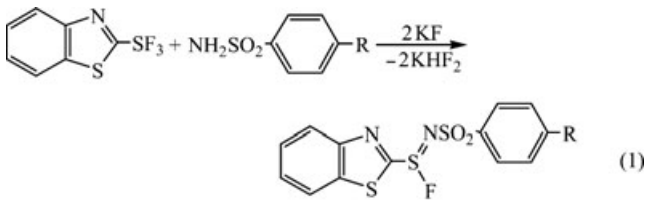
Institute of Organic Chemistry of the National Academy of Sciences of Ukraine, Murmanskaya str. 5, 02094, Kyiv, Ukraine

Received 12 October 2006; revised 10 March 2007

ABSTRACT: *The path of the reaction of aryl-N-(p-toluenesulfonyl)-sulfinimidoyl fluorides and triphenylphosphine is highly dependent on the order of the reactants addition. Addition of triphenylphosphine to aryl-N-(p-toluenesulfonyl)-sulfinimidoyl fluorides results in the formation of triphenyl(arylthio)phosphonium salts of N,N′-bis(p-toluenesulfonyl)aryl-sulfinamidines and triphenyldifluorophosphorane. By changing the reagent addition order, we obtained triphenyldifluorophosphorane, P,P,P-triphenyl-N-(p-toluenesulfonyl)-phosphine imide, and diaryl disulfides. The outcome of the reaction aryl-N-(arenesulfonyl)-sulfinimidoyl chlorides and triphenylphosphine does not depend on the order of addition of the reactants. P,P,P-Triphenyl-N-(arenesulfonyl)-phosphine imides, triphenyldichlorophosphorane, and diaryl disulfides were formed as a result.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:66–71, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20408

INTRODUCTION

In our recent work, we reported the synthesis of the N-substituted sulfinimidoyl fluorides **1a–c** by the treatment of 2-benzothiazolylsulfur trifluoride with sulfonamides (Eq. (1)) [1].



(1)

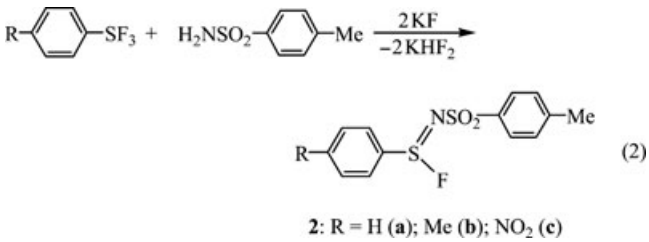
1, R = H (**a**), Me (**b**), Cl (**c**)

In contrast to the well-investigated sulfinimidoyl chlorides [2], the chemistry of the corresponding fluorides remains largely unexplored. In our previous work, we reported the reactivity of the *N*-(*p*-toluenesulfonyl)-sulfinimidoyl fluorides **1a–c** and their analogous chlorides toward *S*-trimethylsilylbenzenethiol. It was shown that the path of the reaction is highly dependent on the nature of the halogen atom: for the chlorides a halogenophilic mechanism is realized, whereas the fluorides reacted with the sulfur atom [1,3]. Similarly, we assumed the possibility of halogenophilic processes for the reactions of sulfinimidoyl chlorides with compounds containing trivalent phosphorus. The goal of this work is to compare the reactivity of N-substituted sulfinimidoyl fluorides and chlorides with triphenylphosphine.

Correspondence to: Yuriy G. Shermolovich; e-mail: iochkiev@ukrpack.net.

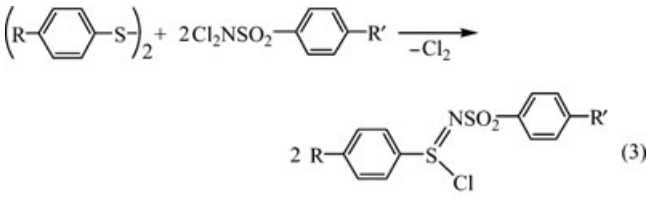
RESULTS AND DISCUSSION

The starting aryl-*N*-(*p*-toluenesulfonyl)-sulfinimidoyl fluorides **2a–c** were synthesized by the methods that have been developed by our group (Eq. (2) [1]. The corresponding chlorides **3,4** were synthesized by the method described earlier (Eq. (3)) [4].



(2)

2: R = H (**a**); Me (**b**); NO_2 (**c**)

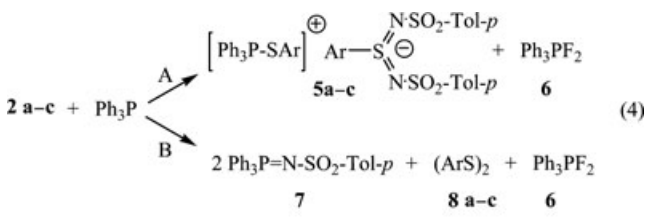


(3)

3: R = NO_2, R′ = Me
4: R = Me, R′ = H

We found that the product formation of the reaction of the fluorides **2a–c** and triphenylphosphine is highly dependent on the order of addition of the reactants (i.e., which reactant is present in the excess in the reaction mixture).

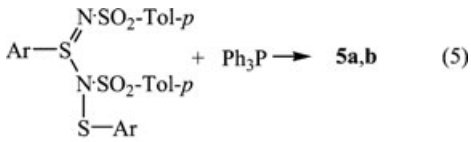
Addition of triphenylphosphine to the fluorides **2a–c** resulted in the formation of triphenyl(arylthio)phosphonium salts of *N*,*N*′-bis(*p*-toluenesulfonyl)aryl-sulfinamidines **5a–c** (pathway A: yield 86%–92% by ^{31}P NMR) and triphenyldifluorophosphorane **6** as the main reaction products along with *P*,*P*,*P*-triphenyl-*N*-(*p*-toluenesulfonyl)-phosphine imide **7** (pathway B: yield 8%–14% based on ^{31}P NMR) and the diaryl disulfides **8a–c** (Eq. (4)) as the byproducts.



(4)

Ar: Ph (**a**), *p*-Tol (**b**), *p*-$NO_2C_6H_4$(**c**)

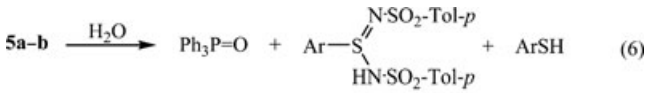
The high sensitivity of the compounds **5a–c** toward moist air did not allow us to separate them from the reaction mixture without hydrolysis. The spectroscopic and analytical data of the hydrolysis products exhibit the formation of **5a–c**, which was further confirmed by the ^{31}P NMR measurement. These data were found to be similar to the ^{31}P NMR spectroscopic and analytical data of the hydrolysis products of the phosphonium salts **5a,b**, which were obtained independently. The compounds **5a,b** were synthesized by the reaction of *N*-arylthio-*N*,*N*′-bis(arenesulfonyl)aryl-sulfinamidines **9a,b** with triphenylphosphine (Eq. (5)).



(5)

9a Ar = Ph
9b Ar = *p*-Tol

The salts **5a–c** obtained are oily in nature, freely soluble in chloroform, and insoluble in benzene and ether. The compounds **5a,b** are easily hydrolyzed by the moist air as similarly observed in the case of other phosphonium salts [5,6]. The ^{31}P and ^{1}H NMR experiments indicate the presence of triphenylphosphine oxide, sulfinamidines **10a,b**, and arenethiols **11a,b** (Eq. (6)) in the reaction mixture.

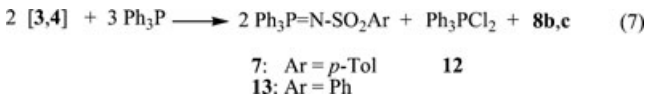


(6)

10a Ar = Ph **11a** Ar = Ph
10b Ar = *p*-Tol **11b** Ar = *p*-Tol

On adding the fluorides **2a–b** to triphenylphosphine (by changing the order of addition of the reactants to keep triphenylphosphine in the excess in the reaction mixture), we obtained **6, 7**, and **8a,b** as the main reaction products (pathway B) (Eq. (4)).

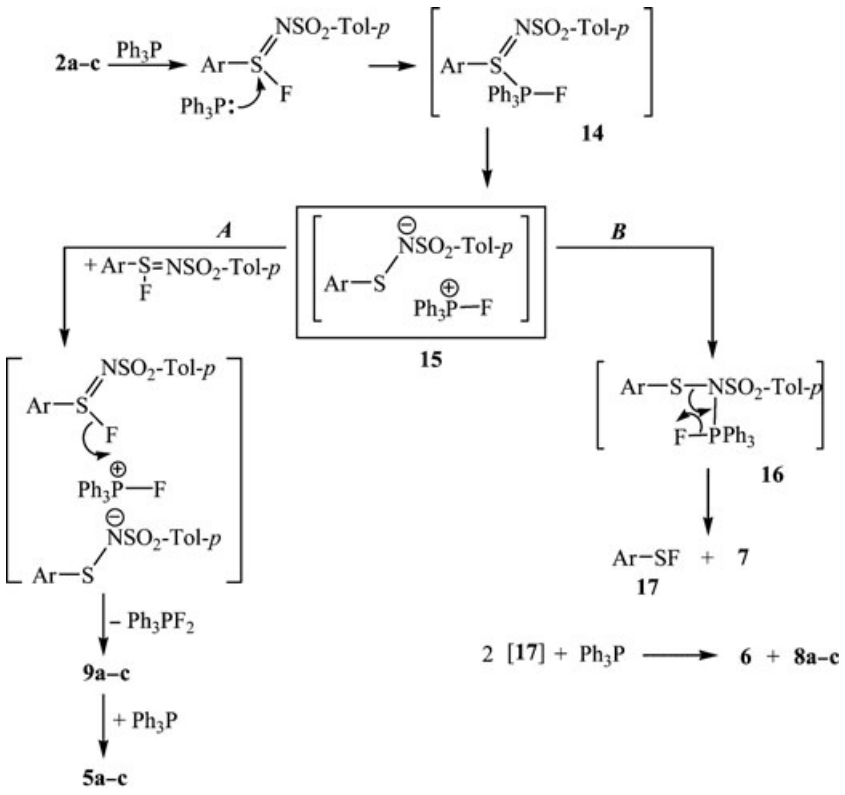
In sharp contrast to the reactivity of the fluorides **2a–c**, the result of the reactions of the sulfinimidoyl chlorides **3,4** with triphenylphosphine showed no influence on the order of addition of the reactants. As a result, the phosphine imides **7** and **13**, triphenyldichlorophosphorane **12**, and the disulfides **8b,c** were formed (Eq. (7); see also [7]).



(7)

7: Ar = *p*-Tol **12**
13: Ar = Ph

The reactions of the compounds **2a–c,3**, and **4** with triphenylphosphine proceed very fast. The final products **5a–c,6,7,13**, and **12**, were observed by ^{31}P and ^{19}F NMR spectra within 5 min after mixing the starting compounds. No other intermediate products were detected.



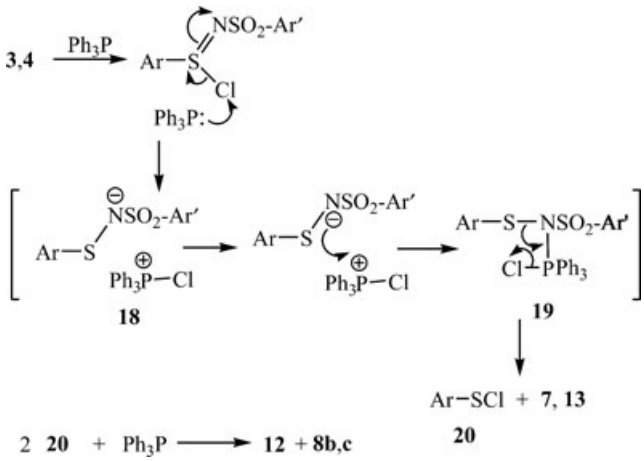
SCHEME 1

In this reaction pathway of the sulfinimidoyl fluorides **2a–c** with triphenylphosphine, we assume that the phosphorus atom attacks the sulfur atom of the fluorides **2a–c** with subsequent formation of the phosphonium salt **15** (probably via phosphorane **14** as an intermediate). A similar type of intermediates to **15** is known [8–10]. The pathways of the transformation of **15** determine the nature of the reaction products (Scheme 1).

The presence of excess fluorides **2a–c** in the reaction mixture (pathway A) leads to the reaction of **15** with another molecule of fluoride **2**, resulting in the formation of triphenyldifluorophosphorane **6** and sulfinamidines **9a–c**, which further react with triphenylphosphine to give salts **5a–c**.

In contrast, the insufficient amount of the fluorides **2a–c** in the reaction mixture (pathway B) results in the decomposition of the salt **15** to the phosphine imide **7** and the arylsulfenyl fluoride **17** (probably via phosphorane **16** as an intermediate). The fluoride **17** reacts with triphenylphosphine to give triphenyldifluorophosphorane **6** and disulfides **8a–c**.

In the reactions of chlorides **3,4** with triphenylphosphine, we observed the formation of salt **18**, which is isostructural to **15** as a result of the halogenophilic attack of triphenylphosphine on the chlorine atom of **3** and **4** (Scheme 2). However, in contrast to the reaction of the fluorides **2a–c**, salt **18** does not react with another chloride molecule because of the positive character of its chlorine atom. Similar to **15**, salt **18** decomposes to give phosphine imides **7,13** and arylsulfenyl chloride **20**



SCHEME 2

(probably via phosphorane **19** as an intermediate). The chloride **20** reacts with triphenylphosphine, resulting in the formation of disulfides **8b,c** and triphenyldichlorophosphorane **12**, which is similarly observed in the previously reported work [11].

CONCLUSION

In this paper, we report the comparison of the reactivity of *N*-(arenesulfonyl)-sulfinimidoyl fluorides **2a–c** and chlorides **3,4** toward triphenylphosphine. Apparently, in both cases, the reaction started with the formation of the phosphonium salt **15** or **18**. The pathways of the transformation of this salt define the nature of the reaction products. In the case of the fluorides **2a–c**, salt **15** formed may either react with another molecule of fluoride resulting in the formation of triphenyldifluorophosphorane (**6**) or decompose to *P*,*P*,*P*-triphenyl-*N*-(*p*-toluenesulfonyl)phosphine imide (**7**). As a consequence, either triphenyl(arylthio)phosphonium salts of *N*,*N*′-bis(*p*-toluenesulfonyl)aryl-sulfinamidines **5a–c** or the diaryl disulfides **8a–c** were formed. In the case of the chlorides **3,4**, only the decomposition of the salt **18** takes place owing to the positive character of chlorine atom in the chloride molecule. Therefore, *P*,*P*,*P*-triphenyl-*N*-(*p*-toluenesulfonyl)-phosphine imide **7**, diaryl disulfides **8b,c**, and triphenyldichlorophosphorane **12** were resulted.

EXPERIMENTAL

The reactions of the substances sensitive to oxygen and air moisture were performed in the atmosphere of dry argon. The solvents were dried by distillation over P_4O_{10} (chloroform, acetonitrile), NaOH (ethanol), and Na (benzene). ^{1}H, ^{19}F, and ^{31}P NMR spectra were recorded on a Varian VRX-300 spectrometer at 299.9, 282.2, MHz, respectively. Chemical shifts (δ) are reported in ppm relative to TMS ($\delta_H = 0.00$) as an internal standard for hydrogen nuclei (in $CDCl_3$ solution), C_6F_6 ($\delta_F = -162.9$) as the internal standard for fluorine nuclei (in $CHCl_3$ or CH_3CN solution), and 85% H_3PO_4 ($\delta_P = 0.00$) as an external standard for phosphorus nuclei (in $CHCl_3$ solution). Mass spectra were obtained on Agilent LC\MSD SL (APCI) spectrometer coupled with Agilent 1100 series chromatograph. IR spectra were taken on KBr disks with UR-20 spectrophotometer. Spray-dried potassium fluoride was used. Evaporation of solutions and drying of compounds were carried out in 0.12 mmHg vacuum.

Starting Materials

Arylsulfur trifluorides were synthesized by treatment of diaryl disulfides **2** with chlorine in acetonitrile in the presence of potassium fluoride in the excess according to [12].

N,*N*′-Bis(arenesulfonyl)aryl-sulfinamidines **10a,b** were synthesized by treatment of diaryl disulfides **8a,b** with chloramine-T in ethanol [13]. *N*-Arylthio-*N*,*N*′-bis(arenesulfonyl)aryl-sulfinamidines **9a,b** were synthesized by treatment of diaryl disulfides **8a,b** with anhydrous chloramine-T in dry acetone [14].

*N-(p-Tolylthio)-N,N′-bis(p-toluenesulfonyl)-(p-tolyl)-sulfinamidines (**9b**).* (It was not described previously). Yield 86%; mp 95–96°C; ^{1}H NMR ($CDCl_3$): $\delta = 2.28$ (s, 6H, CH_3), 2.41 (s, 6H, CH_3), 6.95 (d, 4H, $J_{HH} = 7.60$ Hz, Ar-H), 7.23 (d, 4H, $J_{HH} = 8.10$ Hz, Ar-H), 7.36 (d, 4H, $J_{HH} = 7.60$ Hz, Ar-H), 7.78 (d, 4H, $J_{HH} = 8.10$ Hz, Ar-H). Anal. Calcd for $C_{28}H_{28}N_2O_4S_4$ (584.8): C, 57.51; H, 4.83; N, 4.79; S, 21.93%. Found: C, 57.73; H, 4.87; N, 4.90; S, 22.12.

General Procedure for the Synthesis of **2a–c**

A solution of *p*-toluenesulfonamide (2.47 g, 14.43 mmol) in acetonitrile (15 mL) was added for 1 h to the mixture of arylsulfur trifluoride (14.44 mmol) and KF (44.75 mmol) in acetonitrile (25 mL). The reaction mixture was stirred for 48 h at room temperature. The precipitate was filtered off, washed with acetonitrile (5 mL), dried in vacuum, and extracted with chloroform (40 mL × 4). The solvent was evaporated in vacuum to obtain the residues of **2a–c**.

*Phenyl-N-(p-toluenesulfonyl)-sulfinimidoyl Fluoride (**2a**).* Yield, 64%; mp 70–72°C (decomp.); ^{19}F NMR (CH_3CN): $\delta = -0.38$ (s, 1F); ^{1}H NMR ($CDCl_3$): $\delta = 2.39$ (s, 3H, CH_3), 7.29 (d, 2H, $J_{HH} = 8.10$ Hz, Ar-H), 7.55–7.60 (m, 2H, Ar-H), 7.66–7.71 (m, 1H, Ar-H), 7.87 (d, 2H, $J_{HH} = 8.10$ Hz, Ar-H), 7.92 (d, 2H, $J_{HH} = 7.80$ Hz, Ar-H); IR (KBr): $\nu = 1065$ (S=N). MS: m/z (%) = 297 (M^+, 100), 206 [(M^+ – *p*-Tol), 30], 91 [(*p*-Tol)$^+$, 30]. Anal. Calcd for $C_{13}H_{12}FNO_2S_2$ (297.4): C, 52.51; H, 4.07; N, 4.71; S, 21.57. Found: C, 52.32; H, 4.01; N, 4.85; S, 21.65.

*p-Tolyl-N-(p-toluenesulfonyl)-sulfinimidoyl Fluoride (**2b**).* Yield, 84%; mp 113–114°C (decomp.); ^{19}F NMR (CH_3CN): $\delta = 2.05$ (s, 1F); ^{1}H NMR ($CDCl_3$): $\delta = 2.42$ (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 7.32 (d, 2H, $J_{HH} = 8.10$ Hz, Ar-H), 7.40 (d, 2H, $J_{HH} = 8.10$ Hz, Ar-H), 7.84 (d, 2H, $J_{HH} = 8.10$ Hz, Ar-H), 7.88 (d, 2H, $J_{HH} = 8.10$ Hz, Ar-H); IR (KBr): $\nu = 1070$ (S=N).

MS: *m/z* (%) = 311 (M^+, 100). Anal. Calcd for $C_{14}H_{14}FNO_2S_2$ (311.4): C, 54.00; H, 4.53; N, 4.50; S, 20.59. Found: C, 54.28; H, 4.64; N, 4.32; S, 20.37.

*p-Nitrophenyl-N-(p-toluenesulfonyl)-sulfinimidoyl Fluoride (**2c**).* Yield, 61%; mp 118–120°C (decomp.); ^{19}F NMR (CH_3CN): $\delta = -3.19$ (s, 1F); ^1H NMR ($CDCl_3$): $\delta = 2.44$ (s, 3H, CH_3), 7.35 (d, 2H, J_{HH} = 8.10 Hz, Ar-H), 7.88 (d, 2H, J_{HH} = 8.10 Hz, Ar-H), 8.16 (d, 2H, J_{HH} = 8.60 Hz, Ar-H), 8.45 (d, 2H, J_{HH} = 8.60 Hz, Ar-H); IR (KBr): $\nu = 1060$ (S=N). MS: *m/z* (%) = 342 (M^+, 100). Anal. Calcd for $C_{13}H_{11}FN_2O_4S_2$ (342.4): C, 45.79; H, 3.24; N, 8.18; S, 18.73. Found: C, 45.61; H, 3.18; N, 8.45; S, 18.53.

General Procedure for the Reaction of Triphenylphosphine with Fluorides **2a–c**

(a) A solution of triphenylphosphine (0.60 g, 2.29 mmol) in benzene (10 mL) was added for 0.5 h to **2a–c** (2.05 mmol) in benzene (20 mL). The reaction mixture was stirred for 4 h at room temperature, evaporated in vacuum, and analyzed. In accordance with ^{31}P and ^{19}F NMR ($CHCl_3$) data, the reaction mixture contained triphenyldifluorophosphorane **6** {^{19}F NMR: δ = –41.3 ppm (d, 2F, $J_{PF} = 664$ Hz) [15]; ^{31}P NMR: δ = –58.4 ppm (t, $J_{PF} = 663.5$ Hz) [16]}, phosphine imide **7** (^{31}P NMR: $\delta = 11.9$ ppm (s) [17]), traces of triphenylphosphine oxide (^{31}P NMR: $\delta = 25.9$ ppm (s) [18]), and salts **5a–c**. The reaction mixture was hydrolyzed by stirring the solution for 30 h on air with 1 mL of water. The solvent was evaporated in vacuum. Compounds **8a,b** were extracted from residue with ether (5 mL × 4), and compounds **8c** precipitated after dissolution of evaporated reaction mixture in chloroform (10 mL). Triphenylphosphine oxide was extracted from the residue with ether (20 mL × 3). Insoluble in ether, residue was crystallized from ethanol to obtain compounds **10a–c**. The filtrate was evaporated and washed with benzene (2 mL) to get the residue of **7**.
(b) The suspension of **2a,b** (3.36 mmol) in benzene (20 mL) was added for 0.5 h to triphenylphosphine (1.35 g, 5.15 mmol) in benzene (20 mL). The reaction mixture was stirred at room temperature for 3 h and analyzed. On the basis of ^{19}F and ^{31}P NMR (C_6H_6) data, the reaction mixture contained **6** and **7**. Then, water (1 mL) was added to the mixture, which was stirred for 12 h (hydrolysis of **6**), and evaporated in vacuum. Compounds **8a,b** were extracted from the evaporated residue with ether (10 mL × 4). Then, triphenylphosphine oxide was extracted from the residue with ether (30 mL × 3), and the solvent was evaporated in vacuum. Insoluble in ether, compound **7** was crystallized from benzene.

*The Reaction of Triphenylphosphine with Phenyl-N-(p-toluenesulfonyl)-sulfinimidoyl Fluoride (**2a**).* (a) The ratio of **6**:**7**:**5a** in the reaction mixture was 1:0.24:0.87 (based on ^{31}P NMR). Yield of **5a**: 88% (based on ^{31}P NMR); ^{31}P NMR ($CHCl_3$): $\delta = 46.64$ (s). Yield of **8a**: 78%; mp 60–62°C (from ethanol) (Lit. [19], 62–63°C). Yield of triphenylphosphine oxide: 55%; mp 157–158°C (from benzene) (Lit. [6], 156°C). Yield of **10a**: 53%; mp 152–153°C (from ethanol) (Lit. [13], 152–153°C). ^1H NMR ($CDCl_3$): $\delta = 2.35$ (s, 6H, CH_3), 7.11 (d, 4H, J_{HH} = 8.00 Hz, Ar-H), 7.30–7.42 (m, 3H, Ar-H), 7.56–7.59 (m, 2H, Ar-H), 7.67 (d, 4H, J_{HH} = 8.00 Hz, Ar-H). Yield of **7**, 6%; mp 184–187°C (Lit. [14], 186–188°C); ^{31}P NMR ($CHCl_3$): $\delta = 11.93$ (s); ^1H NMR ($CDCl_3$): $\delta = 2.30$ (s, 3H, CH_3), 7.01 (d, 2H, J_{HH} = 8.10 Hz, Ar-H), 7.42–7.51 (m, 8H, Ar-H), 7.55–7.60 (m, 3H, Ar-H), 7.70–7.77 (m, 6H, Ar-H).
(b) Yield of **8a**: 54%. Yield of triphenylphosphine oxide: 91%. Yield of **7**: 72%.

*The Reaction of Triphenylphosphine with p-Tolyl-N-(p-toluenesulfonyl)-sulfinimidoyl Fluoride (**2b**).* (a) The ratio of **6**:**7**:**5b** in the reaction mixture was 1:0.28:0.86 (based on ^{31}P NMR). Yield of **5b**: 86% (based on ^{31}P NMR); ^{31}P NMR ($CHCl_3$): $\delta = 45.77$ (s). Yield of **8b**: 64%; mp 44–45°C (from ethanol) (Lit. [20], 45–46°C). Yield of triphenylphosphine oxide: 58%. Yield of **10b**: 55%; mp 148–149°C (from ethanol) (Lit. [13], 149°C); ^1H NMR ($CDCl_3$): $\delta = 2.39$ (s, 9H, CH_3), 7.18 (d, 4H, J_{HH} = 8.20 Hz, Ar-H), 7.22 (d, 2H, J_{HH} = 8.50 Hz, Ar-H), 7.54 (d, 2H, J_{HH} = 8.50 Hz, Ar-H), 7.65 (d, 4H, J_{HH} = 8.20 Hz, Ar-H). Yield of **7**: 5%.
(b) Yield of **8b**: 48%. Yield of triphenylphosphine oxide: 96%. Yield of **7**: 61%.

*The Reaction of Triphenylphosphine with p-Nitrophenyl-N-(p-toluenesulfonyl)-sulfinimidoyl Fluoride (**2c**).* The ratio of **6**:**7**:**5c** in the reaction mixture was 1:0.17:0.92 (based on ^{31}P NMR). Yield of **5c**: 91.5% (based on ^{31}P NMR); ^{31}P NMR ($CHCl_3$): $\delta = 44.55$ (s). Yield of **8c**: 79%; mp 180–181°C (from benzene) (Lit. [4], 182–183°C). Yield of triphenylphosphine oxide: 66%. Yield of **10c**: 62%; mp 163–165°C (from ethanol) (Lit. [13], 165–166°C); ^1H NMR ($CDCl_3$): $\delta = 2.39$ (s, 6H, CH_3), 7.18 (d, 4H, J_{HH} = 8.20 Hz, Ar-H), 7.68 (d, 4H, J_{HH} = 8.20 Hz, Ar-H), 7.76 (d, 2H, J_{HH} = 8.90 Hz, Ar-H), 8.12 (d, 2H, J_{HH} = 8.90 Hz, Ar-H). Yield of **7**: 4%.

*The Reaction of Triphenylphosphine with p-Nitrophenyl-N-(p-toluenesulfonyl)-sulfinimidoyl Chloride (**3**).* Either the solution of triphenylphosphine (1.26 g, 4.81 mmol) in benzene(15 mL) was

added for 0.5 h to **3** (1.15 g, 3.20 mmol) in benzene (20 mL) or the solution of **3** in benzene was added to triphenylphosphine in benzene. The results of these reactions and the treatment of the reaction mixtures were equal. The reaction mixture was stirred at room temperature for 0.5 h and analyzed. On the basis of the ^{31}P NMR (C_6H_6) data, the reaction mixture contained **12** (^{31}P NMR: $\delta = -60.13$ ppm (s) [18]) and **7**. Then, water (1 mL) was added to the mixture, which was stirred for 5 h (hydrolysis of **12**), evaporated in vacuum, and washed with chloroform (10 mL). The residue was **8c**. Yield of **8c**: 0.42 g (86%). Chloroform solution was evaporated in vacuum. Triphenylphosphine oxide was extracted with ether (30 mL × 3) and evaporated in vacuum. Yield of triphenylphosphine oxide: 0.42 g (93%). Insoluble in ether, compound **7** was crystallized from benzene. Yield of **7**: 1.13 g (82%).

General Procedure for the Synthesis of **5a,b**

A suspension of triphenylphosphine (2.37 g, 9.04 mmol) and **9a,b** (9.04 mmol) in benzene (75 mL) was stirred at room temperature for 2 h and evaporated in vacuum. The residues were **5a,b** in the form of colorless oils.

*Triphenyl(phenylthio)phosphonium Salt of N,N′-Bis(p-toluenesulfonyl)phenyl-sulfinamidine (**5a**).* Yield of **5a**: 99.1%; ^{31}P NMR ($CHCl_3$): $\delta = 46.30$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 2.36$ (s, 6H, CH_3), 7.11 (d, 4H, $J_{HH} = 8.10$ Hz, Ar-H), 7.33–7.57 (m, 23H, Ar-H), 7.67–7.70 (m, 6H, Ar-H). Anal. Calcd for $C_{44}H_{39}N_2O_4PS_4$ (819.0): C, 64.52; H, 4.80; N, 3.42; S, 15.66%. Found: C, 64.18; H, 4.91; N, 3.48; S, 15.39.

*Triphenyl(p-tolylthio)phosphonium Salt of N,N′-Bis(p-toluenesulfonyl)-(p-tolyl)-sulfinamidine (**5b**).* Yield of **5b**: 99.7%; ^{31}P NMR ($CHCl_3$): $\delta = 45.57$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 2.28$ (s, 12H, CH_3), 6.98–7.11 (m, 10H, Ar-H), 7.44–7.79 (m, 21H, Ar-H). Anal. Calcd for $C_{46}H_{43}N_2O_4PS_4$ (847.1): C, 65.22; H, 5.12; N, 3.31; S, 15.14. Found: C, 64.89; H, 5.17; N, 3.22; S, 14.96.

REFERENCES

[1] Pashinnik, V. E.; Guzyr, I. A.; Borovikov, A. V.; Shermolovich, Yu. G. Heteroat Chem 2005, 16, 352–356.

[2] Levchenko, E. S.; Markovsky, L. N.; Shermolovich, Yu. G. Zh Org Khim 1996, 32, 1447–1459 (in Russian).

[3] Markovsky, L. N.; Shermolovich, Yu. G.; Vasil'ev, V. V.; Boldeskul, I. E.; Trach, S. S.; Zefirov, N. S. Zh Org Khim 1978, 14, 1659–1664 (in Russian).

[4] Levchenko, E. S.; Seleznenko, L. V. Zh Org Khim 1966, 2, 92–95 (in Russian).

[5] Cristau, H. J.; Chêne, A.; Cristol H. J Organomet Chem 1980, 185, 283–295.

[6] Appel, R.; Warning, K.; Ziehn, K.-D. Liebigs Ann Chem 1975, 17, 406–409.

[7] Shermolovich, Yu. G.; Kornuta, P. P.; Gurzhavina, I. G.; Borovikova, G. S.; Markovsky, L.N. Zh Org Khim 1991, 27, 2245–2246 (in Russian).

[8] Mitsch, R. A. J Am Chem Soc 1967, 89, 6297–6303.

[9] Middleton, W. J.; Howard, E. G.; Sharkey, W. H. J Org Chem 1965, 30, 1375–1384.

[10] Rogoza, A. V.; Furin, G. G. Zh Obskch Khim 1998, 68, 798–805 (in Russian).

[11] Zhmurova, I. N.; Yurchenko, V. G.; Pinchuk, A. M. Zh Obskch Khim 1985, 55, 321–323 (in Russian).

[12] Pashinnik, V. E.; Martyniuk, E. G.; Tabachuk, M. R.; Shermolovich, Yu. G.; Yagupolskii, L. M. Synth Commun 2003, 33, 2505–2509.

[13] Dellérba, C.; Corallo, G. P.; Novi, M.; Leandri, G. Phosphorus Sulfur 1981, 12, 123–125.

[14] Barton, D. H. R.; Britten-Kelly, M. R.; Ferreira, D. J Chem Soc, Perkin Trans I 1978, 1090–1100.

[15] Muetterties, E. L.; Mahler, W.; Schmutzler, R. Inorg Chem 1963, 2, 613.

[16] Ramirez, F.; Smith, C. P.; Pilot, J. F.; Gulati, A. S. J Org Chem 1968, 33, 3787–3794.

[17] Laszlo, P.; Polla, E. Tetrahedron Lett 1984, 25, 4651–4654.

[18] Krawczyk, E.; Mikołajczak, J.; Skowrońska, A.; Michalski, J. J Org Chem 1992, 57, 4963–4970.

[19] Yiannios, C. N.; Karabinos, J. V. J Org Chem 1963, 28, 3246–3248.

[20] Pel'kis, N. P.; Levchenko, E. S. Zh Org Khim 1986, 22, 387–391 (in Russian).