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LETTERS TO THE EDITOR

FIRST EXAMPLE OF HYDROTHIOPHOSPHORYLATION OF 3-THIOLENE 1,1-DIOXIDE

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Functionalized derivatives of 3-thiolene 1,1-dioxide (**1**) continue to attract attention as building blocks for organic synthesis, intermediates for obtaining biologically active substances, complexing solvents, and models for studying substituent effects in dihydrothiophenes [1-4].

Synthesis of phosphorus-containing sulfolanes based on thiolene **1** opens up new prospects for constructing functionalized extraction and complexing agents as well as special solvents and ligands for metal complex catalysts. Information about reactions of thiolene **1** with PH acids includes data on nucleophilic and radical addition of dialkylphosphites [5, 6], and also addition of primary and secondary phosphines and phosphine oxides [7].

With the aim of further extending our knowledge about the reactivity of 3-thiolene 1,1-dioxide with respect to PH-acids and also in order to obtain new representatives of phosphorus-containing tetrahydrothiophenes, we have studied for the first time the reaction of thiolene **1** with secondary phosphine sulfides, using as an example bis(2-phenylethyl)phosphine sulfide (**2**) which can be readily obtained from the accessible bis(2-phenylethyl)phosphine [[8] and sulfur. Since phosphine sulfides are ambident compounds [9] and prototropism is possible in thiolene **1**, the direction and outcome of the reaction under study were not predictable.

We found that under mild conditions (45-50°C, 1 h, KOH, DMSO), phosphine sulfide **2** can add to thiolene **1** chemospecifically and regiospecifically, forming 3-[di(2-phenylethyl)thiophosphoryl]tetrahydro-1H-thiophene-1,1-dione (**3**) in 72% yield. We did not observe the SH tautomer of phosphine sulfide **2a** in the reaction mixture among the products of hydrothiophosphorylation of thiolene **1**. Without KOH and also under radical initiation conditions (65°C, 6 h, AIBN [azoisobutyronitrile]) and with all other conditions the same, hydrothiophosphorylation of thiolene **1** does not occur. This is support for the nucleophilic nature of this reaction, probably occurring through the electrophilic isomer **1a** formed as a result of a prototropic shift of the double bond in the dihydrothiophene ring [7].

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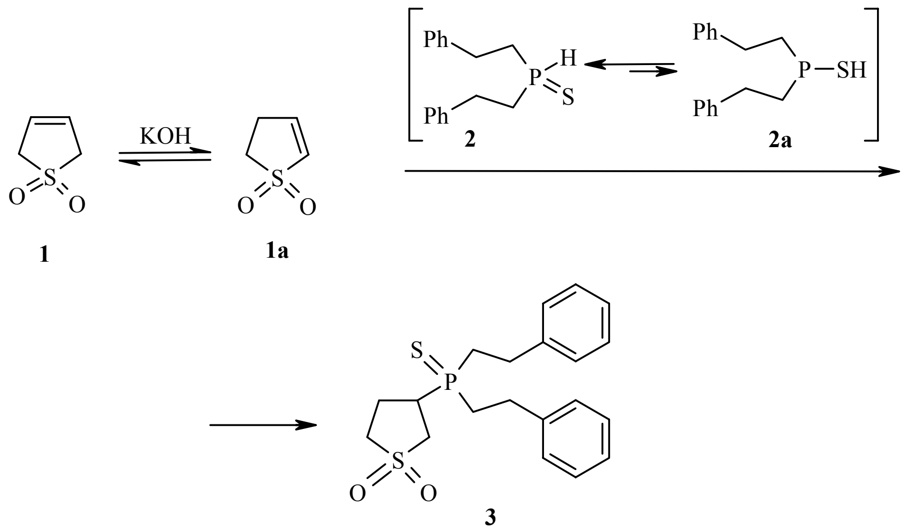

Thus the reaction of the commercially available thiolene **1** with secondary phosphine sulfides opens up a new and convenient approach to atom-economical ("green") synthesis of functionalized tertiary phosphine sulfides, which are already attractive as unique ligands for designing metal complex catalysts [10, 11].

3-[Di(2-phenylethyl)thiophosphoryl]tetrahydro-1H-thiophene-1,1-dione (3). A mixture of thiolene **1** (0.24 g, 2 mmol), bis(2-phenylethyl)phosphine sulfide (0.54 g, 2 mmol), KOH (0.11 g, 2 mmol), and DMSO (7 ml) was purged with argon, stirred at 45-50°C for 1 h, and cooled down. Then water (20 ml) was added and it was extracted with chloroform. The chloroform extract was washed with a saturated aqueous solution of sodium chloride and then dried with sodium sulfate. The chloroform was driven off under reduced pressure; the residue was washed with small portions of acetone and dried under vacuum. We obtained 0.56 g (72%) of phosphine sulfide **3**; mp 151-152°C (benzene). IR spectrum (KBr), ν, cm^{-1}: 3103, 3082, 3064, 3022 ν(C=H); 2967, 2945, 2903, 2867 ν(C–H); 1600, 1582, 1495, 1452 ν(C=C); 1408 δ(CH_2); 1315 $\nu_{as}(SO_2)$; 1295, 1268, 1240, 1201 δ(CH_2); 1121 $\delta_s(SO_2)$; 1071, 943, 908, 887 δ(CH_2); 722 ν(P–C); 753, 741 δ(=CH); 720 ν(P–C); 700 δ(=CH); 604 δ(CCC); 553, 572 ν(P=S); 500 δ(PCC); 468 δ(SO_2). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 2.07-2.26 (4H, m, CH_2P); 2.46 (1H, m, H-3); 2.70-3.02 (8H, m, H-4,5, $C\underline{H}_2Ph$); 3.19-3.3 (2H, m, H-2); 7.14-7.32 (10H, m, C_6H_5). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 21.81 (C-4), 28.28 (CH_2Ph), 31.01 (d, $^1J_{PC} = 47.5$, CH_2P), 31.79 (d, $^1J_{PC} = 47.5$, CH_2P), 34.82 (d, $^1J_{PC} = 50.1$, C-3), 49.95 (C-5), 50.02, C(2), 126.57 (C_p), 127.77 (C_o), 128.53 (C_m), 139.34 (d, $^3J_{PC} = 13.3$, C_{ipso}). ^{31}P NMR spectrum (161 MHz, $CDCl_3$), δ, ppm: 54.72. Found, %: C 61.41; H 6.50; P 7.82; S 16.69. $C_{20}H_{25}O_2PS_2$. Calculated, %: C 61.20; H 6.42; P 7.89; S 16.34.

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