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REACTION OF 3-THIOLENE 1,1-DIOXIDE WITH Ph-ACIDS

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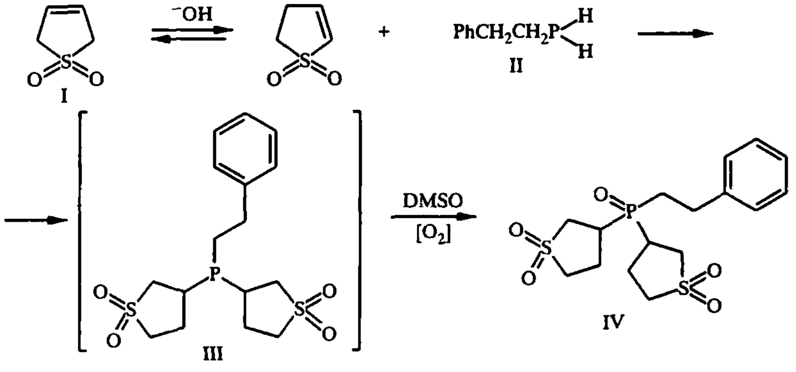
The nucleophilic addition of 2-phenylethylphosphine, bis(2-phenylethyl)phosphine oxide, and bis(2-phenylpropyl)phosphine oxide to 3-thiolene 1,1-dioxide catalyzed by the KOH–DMSO system leads to bis(3-thioanil)(2-phenylethyl)phosphine oxide, bis(2-phenylethyl)(3-thioanil)phosphine oxide, and bis(2-phenylpropyl)(3-thioanil)phosphine oxide, respectively.

3-Thiolene 1,1-dioxide (I) adds various nucleophiles such as ammonia, amines, alcohols, thiols, and CH-acids to give functionalized sulfolanes, which are active complexing solvents and hold promise as synthones and intermediates [1]. However, there is only limited information on the reaction of thiolene I with PH-acids. Bezmenova [1] and McConnell [2] briefly reported the nucleophilic and radical addition of dialkyl phosphites to this compound. Recently, we reported that a secondary phosphine oxide, namely, bis(2-phenylethyl)phosphine oxide, may add to thiolene I [3].

In order to obtain further information on the reactivity of unsaturated cyclic sulfones and develop a convenient synthesis for highly polar nonhydroxyl solvents combining the unique properties of sulfolane and organic phosphine oxides in a single molecule, we studied the reaction of thiolene I with 2-phenylethylphosphine, bis(2-phenylethyl)phosphine, bis(2-phenylethyl)phosphine oxide, and bis(2-phenylpropyl)phosphine oxide, which are readily obtained from red phosphorus or phosphine, styrene, and α-methylstyrene [4]. In this work, we also checked the feasibility of the reaction of thiolene I with phosphorus nucleophiles generated directly from red phosphorus and phosphine in the presence of strong bases.

Thiolene I reacts with a stoichiometric amount of 2-phenylethylphosphine (II) upon heating to 35-40°C for 5 h in a KOH–DMSO superbase system [5] to give bis(3-thioanil)(2-phenylethyl)phosphine oxide (IV) in 40% yield. The expected product, bis(3-thioanil)(2-phenylethyl)phosphine (III) was not identified in the reaction mixture, probably due to its high tendency to undergo oxidation, which could not be prevented even by carrying out the reaction in an inert gas atmosphere. The oxidation agent in this case may not only be atmospheric oxygen but also DMSO. Since the nucleophilic addition reaction is not typical for allylsulfones, thiolene I upon phosphorylation in the KOH–DMSO system apparently initially undergoes prototropic isomerization to give 2-thiolene 1,1-dioxide with a highly electrophilic double bond.



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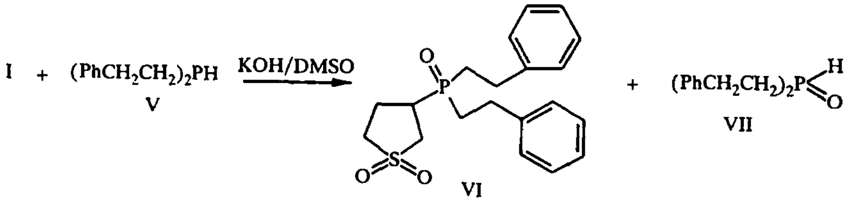
Bis(2-phenylethyl)phosphine (V) is much less active in nucleophilic addition to thiolene I than the corresponding primary phosphine II. Upon heating the reagents at 45-50°C for 6 h in a KOH – DMSO suspension, the conversion of phosphine V was 39% and the yield of bis(2-phenylethyl)(3-thioanil)phosphine oxide (VI) (identified by ^{31}P NMR spectroscopy) was only 6%. The formation of bis(2-phenylethyl)phosphine oxide (VII), which is the product of the oxidation of starting phosphine V, was also detected.

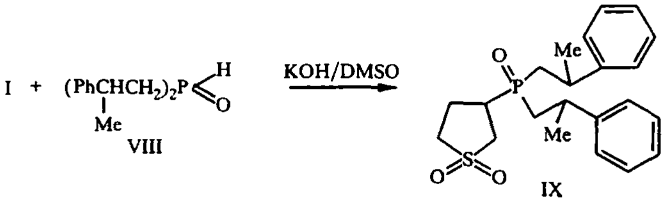


Secondary phosphine oxide VII reacts with thiolene I under analogous conditions to give phosphine oxide VI in 74% yield.

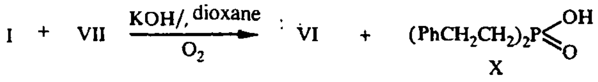
$$\mathrm{I} + \mathrm{VII} \xrightarrow{\mathrm{KOH/DMSO}} \mathrm{VI}$$

The greater reactivity of secondary phosphine oxide VII in comparison with corresponding phosphine V should be attributed to the greater rate of generation of phosphinite anions from the more acidic secondary phosphine oxides relative to the rate of formation of phosphide anions from secondary phosphines in the presence of KOH.

The general nature of the nucleophilic addition of secondary phosphine oxides to thiolene I was indicated by the reaction of I with bis(2-phenylpropyl)phosphine oxide (VIII), which was accomplished by heating of the reagents at 45-50°C for 1.5 h in a KOH – DMSO suspension. The yield of (2-phenylpropyl)(3-thioanil)phosphine oxide (IX) was 47%.



The reaction of thiolene I with phosphine oxide VII in KOH – dioxane at 45-50°C for 4 h proceeds less readily than when the KOH – DMSO superbase system is used and gives phosphine oxide IX in only 31% yield. A significant amount (26%) of bis(2-phenylethyl)phosphinic acid (X) is formed under these conditions as the product of the oxidation of the starting secondary phosphine oxide VII by atmospheric oxygen.



Phosphinic acid X is the only product formed in 94% yield upon heating thiolene I with bis(2-phenylethyl)phosphine oxide in dioxane without KOH at 45-50°C for 4 h. An attempt to phosphorylate thiolene I using red phosphorus and phosphine in the presence of a strong base was unsuccessful. The formation of organophosphorus compounds was not detected in the reaction mixtures obtained upon heating (at 50-53°C) thiolene I with red phosphorus in the KOH – DMSO system or under phase transfer catalysis conditions using 60% aq. KOH – dioxane – benzyltriethylammonium chloride. ^{31}P NMR spectroscopy indicated formation of small amounts (6% of the mass of starting thiolene I) of a phosphorus compound with $\delta_P = -10.3$ ppm, which is probably a tertiary phosphine, upon passing a phosphine – hydrogen mixture generated from red phosphorus by the action of aqueous KOH [6] through a solution of thiolene I in DMSO in the presence of potassium hydroxide at 50°C.

EXPERIMENTAL

The ^1H and ^{31}P NMR spectra were taken on a Jeol FX-90Q spectrometer. The IR spectra were taken on a Specord IR-75 spectrometer.

Bis(3-thioanil)(2-phenylethyl)phosphine Oxide (IV). All the steps of this preparation were carried out in an argon atmosphere. A mixture of 1.08 g (9 mmoles) thiolene I, 0.6 g (4.3 mmoles) 2-phenylethylphosphine, and 0.25 g (4.5 mmoles) KOH in 6 ml DMSO was stirred for 5 h at 35-40°C, cooled, diluted with 6 ml water, and extracted with chloroform. The chloroform extracts were washed with saturated aqueous sodium chloride and dried over sodium sulfate. Chloroform was distilled off in vacuum. The residue was washed with ether and dried in vacuum to give 0.67 g (40%) diadduct IV as a viscous paraffin-like substance. ^1H NMR spectrum in $CDCl_3$: 2.39 (8H, m, $CH_2P=O$; 2H, $CHP=O$; 2H, $CHP=O$; 4H, CH_2), 2.93 (10H, m; 8H, CH_2SO_2; 2H, CH_2PH), 7.25 ppm (5H, m, C_6H_5). ^{31}P NMR spectrum; 45.0, 45.2, 45.4 ppm (11:30:18 relative signal intensity). The finding of three ^{31}P NMR signals may be attributed to the presence of two asymmetric centers in IV. IR spectrum: 1150 (P=O), 1110 cm^{-1} (O=S=O). Found: C, 50.08; H, 6.57; P, 7.17; S, 15.78%. Calculated for $C_{16}H_{23}O_5PS_2$: C, 49.22; H, 5.94; P, 7.93; S, 16.42%.

Bis(2-phenylethyl)(3-thioanil)phosphine Oxide (VI). A mixture of 0.59 g (5 mmoles) thiolene I, 1.29 g (5 mmoles) bis(2-phenylethyl)phosphine oxide, 0.28 g (5 mmoles) KOH, and 10 ml DMSO was stirred at 45-50°C for 1 h, cooled, diluted with 20 ml water, and extracted with chloroform. The chloroform extracts were washed with saturated aqueous sodium chloride and dried over sodium sulfate. Chloroform was distilled off in vacuum. The residue was washed with ether and dried in vacuum to give 1.4 g (74%) phosphine oxide VI, mp 132-134°C (from benzene). ^1H and ^{31}P NMR spectra in $CDCl_3$: 2.25 (7H, m; 4H, $CH_2P=O$; 1H, $CHP=O$; 2H, CH_2), 2.87 (4H, m, CH_2PH), 3.05 (4H, m, CH_2SO_2), 7.20 (10H, m, C_6H_5), 44.8 ppm (P). IR spectrum: 1150 (P=O), 1110 cm^{-1} (O=S=O). Found: C, 63.55; H, 6.84; P, 8.36; S, 8.38%. Calculated for $C_{20}H_{25}O_3PS$: C, 63.81; H, 6.69; P, 8.23; S, 8.52%.

Bis(2-phenylpropyl)(3-thioanil)phosphine Oxide (IX). A mixture of 0.18 g (1.5 mmoles) thiolene I, 0.43 g (1.5 mmole) bis(2-phenylpropyl)phosphine oxide, and 0.084 g (1.5 mmole) KOH in 5 ml DMSO was stirred for 1.5 h at 45-50°C, cooled, diluted with 20 ml water, and extracted with chloroform. The chloroform extracts were washed with saturated aqueous sodium chloride and dried over sodium sulfate. Chloroform was distilled off in vacuum. The residue was washed with ether and dried in vacuum to give 0.28 g (47%) phosphine oxide IX as a paraffin-like substance. ^1H and ^{31}P NMR spectra in $CDCl_3$: 1.18 (6H, m, CH_3), 1.81 (7H, 4H, m, $CH_2P=O$; 1H, $CHP=O$; 2H, CH_2), 3.07 (4H, m, CH_2SO_2), 4.10 (2H, CH), 7.25 (10H, m, C_6H_5), 43.8, 44.6, 45.8 ppm (P). IR spectrum: 1150 (P=O), 1110 cm^{-1} (O=S=O).

Bis(2-phenylethyl)phosphinic Acid (X). A. A solution of 0.1 g (0.85 mmole) thiolene I and 0.22 g (0.85 mmole) bis(2-phenylethyl)phosphine oxide in 4 ml dioxane was stirred for 4 h at 45-50°C, cooled, diluted with 8 ml water, and extracted with benzene. The benzene extracts were washed with saturated aqueous sodium chloride and dried over sodium sulfate. Benzene was distilled off in vacuum. The residue was washed with ether and dried in vacuum to give 0.22 g (94%) phosphinic acid X, mp 98-100°C (from benzene) (mp 98-99°C [7]). This sample proved identical to the sample of phosphinic acid X prepared according to method B.

B. A mixture of 0.22 g (0.85 mmole) bis(2-phenylethyl)phosphine oxide and 0.12 g 30% aqueous hydrogen peroxide in 4 ml acetone was stirred at ~20°C for 3 h and, then, at 50°C for 10 min. The reaction mixture was diluted with water and extracted with chloroform. Then, chloroform was distilled off to give 0.22 g (94%) phosphinic acid X, mp 100-101°C (from benzene). ^1H and ^{31}P NMR spectra in $CDCl_3$: 2.07 (4H, m, $CH_2P=O$), 2.87 (4H, m, CH_2Ph), 6.85 (1H, s, OH), 7.20 (10H, m, C_6H_5), 54.3 ppm (P). IR spectrum: 2670 (OH), 1150, 1105, 1095 cm^{-1} (P=O) [8].

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