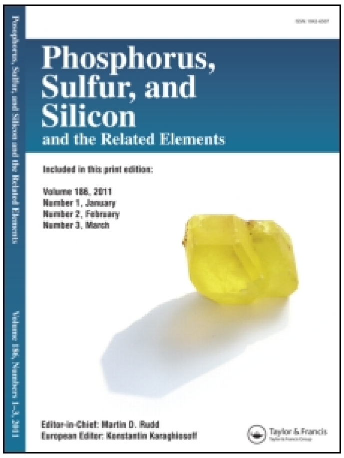

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TRIS[(5-CHLORO-2-THIENYL)METHYL] PHOSPHINE OXIDE FROM ELEMENTAL PHOSPHORUS AND 2-CHLORO-5-(CHLOROMETHYL) THIOPHENE

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TRIS[(5-CHLORO-2-THIENYL)METHYL] PHOSPHINE OXIDE FROM ELEMENTAL PHOSPHORUS AND 2-CHLORO-5-(CHLOROMETHYL) THIOPHENE

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White phosphorus readily reacts with 2-chloro-5-(chloromethyl)thiophene under phase-transfer conditions (KOH, water, dioxane, benzyltriethylammonium chloride, 50–52°C, 3 h) to form tris[(5-chloro-2-thienyl)methyl]phosphine oxide in good yield. This new phosphine oxide undergoes the Wittig – Horner reaction with benzaldehyde ($NaNH_2$/THF system) leading to 2-chloro-5-[(*E*)-2-phenylethenyl]thiophene and bis[(5-chloro-2-thienyl)methyl]phosphinic acid.

Keywords: elemental phosphorus; 2-chloro-5-(chloromethyl)thiophene; phosphorylation; tris[(5-chloro-2-thienyl)methyl]phosphine oxide; Wittig – Horner reaction; 2-chloro-5-[(*E*)-2-phenylethenyl]thiophene; bis[(5-chloro-2-thienyl)methyl]phosphinic acid

INTRODUCTION

Tertiary phosphines or phosphine oxides with thiophene substituent are promising polydentate ligands for metal complex catalysts. Before our investigations such compounds were prepared usually from phosphorus halides and organometallic reagents[1–3]. We have previously reported on

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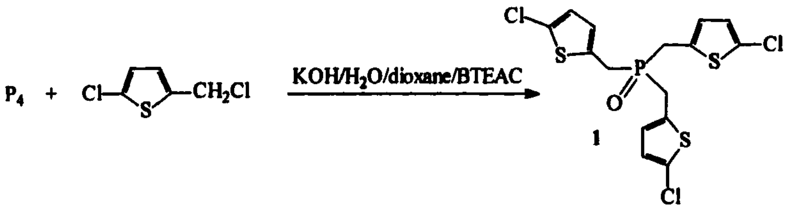
the preparation of tris[2-(2-thienyl)ethyl]phosphine in good yield by nucleophilic addition of potassium phosphide, generated from red phosphorus, potassium and *t*-butanol in liquid ammonia, to 2-thienylethene[4].

In the present work, to develop a new approach to the synthesis of functional tertiary phosphine oxides with the thiophene moiety we have investigated the reaction of elemental phosphorus with readily accessible 2-chloro-5-(chloromethyl)thiophene, prepared by hydrochlorination of commercial 2-chlorothiophene in aqueous formaldehyde[5].

RESULTS AND DISCUSSION

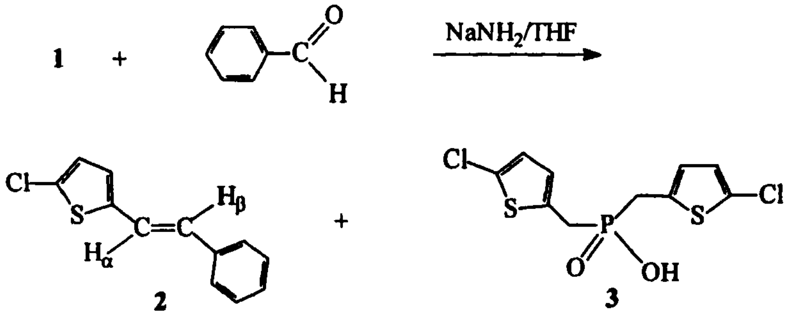
Unlike the reaction of red phosphorus with benzyl chloride, proceeding in the superbase system comprising red phosphorus, 50–60% aqueous KOH, dioxane and benzyltriethylammonium chloride (BTEAC) as a phase transfer catalyst at 80–95°C and giving selectively tribenzylphosphine oxide in 75% yield[6], the phosphorylation of 2-chloro-5-(chloromethyl)thiophene with red phosphorus under analogous conditions proved to be unsuccessful. In this case a mixture of five organophosphorus compounds was formed among which tris[(5-chloro-2-thienyl)methyl]phosphine oxide **1** was identified and its content was only 25% according to integral intensity in the ^{31}P NMR spectrum of the mixture. However, more reactive white phosphorus reacts with 2-chloro-5-(chloromethyl)thiophene under phase-transfer conditions (KOH, water, dioxane, BTEAC, 50–52°C, 3 h) to form tris[(5-chloro-2-thienyl)methyl]phosphine oxide **1** in 56% yield (Scheme 1).



SCHEME 1

This previosly unknown phosphine oxide **1** is of interest as a polydentate ligand for metal complex catalysts as well as a prospective building block.

Thus, it can be involved in the Wittig – Horner reaction. For instance, with benzaldehyde in the $NaNH_2$/THF system it gives selectively 2-chloro-5-[(*E*)-2-phenylethenyl]thiophene **2** (71% yield), a heterocyclic analog of stilbene, and bis[(5-chloro-2-thienyl)methyl]phosphinic acid **3** (Scheme 2).



SCHEME 2

EXPERIMENTAL

^1H, ^1H-^1H NOESY, HMQC and ^{31}P NMR spectra were recorded with a Bruker DPX-400 NMR spectrometer. IR spectra were taken on a Specord IR-75 instrument.

Tris[(5-chloro-2-thienyl)methyl]phosphine oxide 1

A solution of 10 g of KOH in 10 ml of H_2O was introduced into a stirred mixture of 0.53 g (17 mmol) of white phosphorus, 0.1 g of BTEAC and 20 ml of dioxane. Into this mixture heated to 50°C, 2.84 g (17 mmol) of 2-chloro-5-(chloromethyl)thiophene in 1.5 ml of dioxane was added dropwise during 40 min. Then the reaction mixture was stirred at 50–52°C during 3 h, cooled to room temperature, and the organic and aqueous layers were separated. The organic solution was dried over K_2CO_3, dioxane was removed, the residue was washed with Et_2O and dried in *vacuo* to give 1.4 g (56%) of light yellow crystals of **1** (m.p. 146–148°C, from hexane). ^1H-NMR ($CDCl_3$, δ, ppm): 3.25 d (6H, CH_2P, $^2J_{PH}$ 13.15 Hz), 6.74 t (or doublet in ^{31}P decoupled spectrum) (3H, 3-H), 6.78 d (3H, 4-H, $^3J_{HH}$ 3.75

Hz); ^{31}P-NMR 37.0 ppm. IR (KBr, cm^{-1}): $\nu_{P=O}$ 1160. Anal. Calc. for $C_{15}H_{12}Cl_3OPS_3$: C, 40.78; H, 2.74; Cl, 24.07; P, 7.01. Found: C, 40.45; H, 3.13; Cl, 23.51; P, 8.07.

Reaction of tris[(5-chloro-2-thienyl)methyl]phosphine oxide 1 with benzaldehyde

Sodium amide (0.066 g, 1.70 mmol) was introduced into a heated (58–60°C) solution of 0.25 g (0.57 mmol) of tris[(5-chloro-2-thienyl)methyl]phosphine oxide **1** in 35 ml of THF. The mixture was refluxed with stirring for 1 h, and 0.18 g (1.70 mmol) of benzaldehyde was added to it. Then the reaction mixture was refluxed for another 1 h, cooled to room temperature, diluted with 35 ml of water, after which three extractions with Et_2O (10 ml portions) were carried out. The combined ethereal extracts were washed two times with water (8 ml portions), dried over K_2CO_3, the solvent was removed, the residue was dried in *vacuo* to give 0.09 g (71%) of 2-chloro-5-[(*E*)-2-phenylethenyl]thiophene **2** (m.p. 66–68°C). ^{1}H NMR ($CDCl_3$, δ, ppm): 6.79 s, 6.80 s (2 x 1H, 3-H, 4-H), 6.78 d (1H, α-H, $^3J_{HH}$ 15.8 Hz), 7.06 d (1H, β-H, $^3J_{HH}$15.8 Hz), 7.24 t (1H, *p*-H), 7.33 t (2H, *m*-H), 7.43 d (2H, *o*-H). Protons α-H and β-H were assigned with the use of ^{1}H-^{1}H NOESY spectrum showing cross peak corresponding to the interaction of β-H and *o*-H nuclei. Since signs of 3-H, 4-H and one component of the doublet of α-H overlapped in the ^{1}H NMR spectrum, a H,C-correlation experiment (HMQC) was carried out for the assignment of the protons. ^{13}C NMR ($CDCl_3$, δ, ppm): 124.03 (β-C), 128.02 (cross peak with proton at 6.80, 3-C or 4-C), 129.02 (*o*-C), 129.40 (cross peak with proton at 6.79, 3-C or 4-C), 130.54 (*p*-C), 131.22 (α-C), 131.43 (*m*-C).

The combined aqueous extracts were treated with 2 M HCl till pH 2–3, the precipitate formed on the treatment was washed successively with water, EtOH and Et_2O and dried in *vacuo* to give 0.07 g (38%) of bis[(5-chloro-2-thienyl)methyl]phosphinic acid **3** (m.p. 168–170°C). ^{1}H-NMR ($CDCl_3$, δ, ppm): 3.16 d (4H, CH_2P, $^2J_{PH}$ 16.30 Hz), 6.77 t (2H, 3-H), 6.99 d (2H, 4-H, $^3J_{HH}$ 4.0 Hz); ^{31}P-NMR 46.6 ppm. Anal. Calc. for $C_{10}H_9Cl_2O_2PS_2$: C, 36.71; H, 2.77; Cl, 21.67; P, 9.47; S, 19.60. Found: C, 36.83; H, 2.73; Cl, 21.68; P, 9.56; S, 19.43.

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