A New Performance of the Reaction of PCl₃/AlCl₃ with Anisoles – One-Pot and Multi-Step Syntheses of a New Fused-Ring System [1,2,3]Benzoxadiphospholo[2,3-*b*][1,2,3]benzoxadiphosphole

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Anisoles 4 react with $AlCl_3$ and PCl_3 to yield the new fused bicyclic system derivatives 5 and 6 as major products in a one-pot procedure. An alternative multi-step synthesis of this system is also reported in which bis(o-methoxyaryl)phosphane oxides **11** are treated with $AlCl_3$ and PCl_3 ; the diarylphosphane oxides **11** are obtained by a new simple method.

Introduction

Since the last century the Friedel–Crafts-type reaction using PCl₃ and AlCl₃ has been an excellent method for the direct attachment of a phosphorus atom to an aromatic ring to give aryldichlorophosphanes or diarylchlorophosphanes. However, this reaction is very sensitive to the type of substituents present on the aromatic ring^[1,2] and the literature often gives conflicting results.^[3,4] In particular, it is reported^[4a] that anisole upon treatment with phosphorus trichloride and aluminium chloride, afforded *p*-anisylphosphonous dichloride (I) but in very poor yields and with large amounts of undistillable residues, while in some cases it gave phenylphosphorodichloridite (II) but always in poor yields. In addition, it is reported^[4a,4b] that this phosphonation reaction fails completely when thioanisoles are used (Scheme 1).



Scheme 1. Literature-known results from the reaction between anisole or thio anisole and $\rm AlCl_3/PCl_3$

To increase the yield and the selectivity of this phosphonation reaction on anisoles and thioanisoles, the AlCl₃ catalyst has been replaced^[4a] by SnCl₄ and, very recently,^[4b] by BiCl₃. In contrast to these reported results, in recent years, we discovered^[5] that the reaction of PCl₃ and AlCl₃ with thioanisoles **1** gave, unexpectedly, the new fused bicyclic system^[6] **2** (fused 1,2,3-benzothiadiphosphole) in good yields (see Scheme 2). In addition, we found that the reaction is very dependent on the ratio of the reagents and on the quality of the AlCl₃, which, in this reaction, is not a catalyst, but a reagent. The best yields of **2** were obtained with freshly sublimed AlCl₃ and a ratio 1:0.6:2–4 of thioanisole **1**/AlCl₃/PCl₃ and final quenching with water.



Scheme 2. One-pot synthesis of **2**

The molecular structure of **2** was determined^[5a] by X-ray analysis with the molecule adopting a butterfly-like structure with the phosphorus electron lone pairs in a *cis* configuration and in an eclipsed conformation. Recently, the course of this anomalous reaction has been studied^[5c] by ¹H and ³¹P NMR and it was seen that the benzothiadiphosphole system is formed by a "domino reaction" as reported in Scheme 3. Probably, because of the relative complexity of the structure of **2**, its formation from this simple and well-known reaction was never observed. It should be noted that the final phosphonium salt **G** does not give, after treatment with water, the expected product of hydrolysis **3**, but gives **2a** as a product of reduction. At that time, this result was unexplained.

Results and Discussion

On analysis of the data on anisoles reported^[4] above and our results^[5] on thioanisoles, we decided to reinvestigate the reaction of anisoles **4** with the couple PCl₃/AlCl₃, in order

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Scheme 3. Pathway of the domino reaction giving the benzothiadiphosphole system

to verify whether the reported^[3,4] large amounts of undistillable residues and the conflicting reported results might be due to the formation of heterocyclic compounds related to 2 or of other unexpected products.

At the beginning of this study we noted by GLC-MS that the reaction of PCl₃ and AlCl₃ with *p*-methylanisole (4a) is indeed very complex as it gives a reaction mixture containing several products. We found great variations in these final products and in their relative ratios on varying the ratio of the reagents and reaction conditions. However, we noted, under some reaction conditions, the formation of traces of heterocycle 5a among several other products. The identification of 5a was facilitated by comparison of its mass spectra fragmentations with the fragmentations of 2a.

Recently, after several studies on the structure of the other products, we found^[7] that, when the reaction is carried out under appropriate reaction conditions, an unexpected "insertion" of a phosphorus moiety into the O–Me bond of anisole 4 occurs, to give compound 8 as the major product in place of the expected Friedel–Crafts phosphonation (Scheme 4). The best selective formation of 8 (50–70% yield) was obtained with an anisole 4/AlCl₃/PCl₃

ratio of 1:0.6:1, at 70–80 °C for 7–10 h under dry nitrogen and without solvent.



Scheme 4. Results obtained from the reaction of anisole and $AlCl_3/PCl_3$ in different ratios of the reagents

A suggested mechanism, depicted in Scheme 5, for this phosphorus insertion reaction was also reported.^[7] The insertion of a P moiety is explained by the attack of a molecule of PCl₃ on an anisole–AlCl₃ complex and subsequent migration of the methyl group to the same P atom giving the intermediate \mathbf{A}' . Subsequent nucleophilic attack of free anisole on phosphonium salt \mathbf{A}' gives \mathbf{B}' which, after quenching with water, gives phosphonate 8.



Scheme 5. Pathway of the formation of 8

It should be noted that in the same reagent ratios and reaction conditions thioanisoles 1 did not give formation of P-Me compounds related to 8 and the single product was always 2. This fact may be explained as follows: In the case of thioanisole the S atom can be hypervalent such as in intermediate **B** of Scheme 3, while in the case of anisole the O atom cannot give this hypervalent coordination. In the first step it prefers to expel the Me group which is captured by a phosphorus atom giving stable intermediate **A**' (as de-

picted in Scheme 5) thus explaining the insertion of the P moiety on the O–Me bond.

After repeated attempts varying the reagent ratios and reaction conditions, we have been able to obtain the benzooxadiphosphole system as prevalent product (30-40% yield), as reported in Scheme 4 using a ratio of 4a/AlCl₃/PCl₃ of 1:0.6:7 and refluxing for about 20-25 h without solvent. In contrast with the reaction with thioanisoles 1, the reaction with anisole 4a gives a large amount of its monoxide 6a and only traces of the benzooxadiphosphole 5a. An amount of 10-20% of 8a was also obtained. Presumably, the formation of the benzooxadiphosphole derivatives 5a and 6a is favoured, with respect to the formation of $\mathbf{8}$, by the large excess of PCl₃. Thus, the concomitant methylation of the same phosphorus atom which attacks the oxygen atom of anisole giving the intermediate A' (as reported in Scheme 5) is unfavourable in the first step. This is because the anisole-AlCl₃ complex now presumably undergoes attack by two or more molecules of PCl₃, as depicted in Scheme 6. The subsequent steps of the pathway for the formation of 6 are, tentatively, very similar to the domino reaction reported^[5c] for the formation of 2 (Scheme 3).



Scheme 6. Intermediate 7 to obtain 6

It should be noted that compounds 5a and 6a are very oxygen- and water-sensitive and that their prolonged workup gives oxidation and decomposition products. In addition, chromatographic purification cannot be performed. The proposed structure for 5a is mainly supported by its NMR-spectroscopic data. The ³¹P NMR spectrum shows the presence of two magnetically non-equivalent phosphorus atoms and the presence of a large coupling between them $(J_{PP} = 175 \text{ Hz})$ indicates the presence of a P–P bond. The strongly deshielded doublet at $\delta = 188.0$ can be unambiguously assigned to the phosphorus atom between the two oxygen atoms whereas the other signal at $\delta = -11.8$ as a doublet of triplets ($J_{PP} = 175 \text{ Hz}$, $J_{PH} = 6 \text{ Hz}$) is unambiguously assigned to the other phosphorus atom. In addition, these values are in good agreement with or very close to those reported for related nonfused 1,2,3-benzoxadiphosphole derivatives obtained as decomposition products from the distillation of o-phosphanylphenols.^[8] The mass spectrum of 5a exhibit ion peaks at m/z: 274 [M⁺], 227 (base peak, [M⁺ - PO]), 211, 197, 153, 121, 77, 47 [PO]. It should be noted that the mass spectrum of the related compound **2a** exhibits ion peaks at m/z: 306 [M⁺], 243 (base peak) $[M^+ - PS]$, 211, 197, 153, 121, 77, 63 [PS]. As a consequence of the assignment of 5a, the structure of 6a is easily deduced from its mass and NMR spectra. Its mass peaks are: *m/z*: 290 (base peak) [M⁺], 243 [M⁺ - PO], and 227 [M⁺ – PO₂], 196, 152, 121, 77, 47. The ³¹P NMR spectrum of 6a contains a set of two doublets; the ones at lower field ($\delta = 69.9$, $J_{\rm PP} = 209$ Hz) being assignable to the OP(O)O phosphorus atom while the other as doublet of triplets ($\delta = -112.5$, dt, $J_{PP} = 209$ Hz, $J_{PH} = 7$ Hz) characterises the phosphane phosphorus atom. The configuration of 5a and 6a should be *cis* according to the structure of related benzothiadiphosphole 2 determined by X-ray analysis and as predicted by semi-empirical MM2 calculations. This predicted configuration was ascribed to easier accommodation of the long P-P bond in the *cis* relative to the trans isomer and this preference appears to be general, according to other fused-ring systems.^[9]

When the reaction was carried out with **4b**, products **5b** and **6b** were obtained in minor amounts, 20-25% yield. The ³¹P NMR spectrum of **5b** shows a doublet at $\delta = 186$ $(J_{PP} = 175 \text{ Hz})$ and a doublet of triplets at $\delta = -13$ $(J_{PP} =$ $175 \text{ Hz}, J_{PH} = 7 \text{ Hz})$, while **6b** (as white solid, m.p. 166-167 °C) shows a doublet at $\delta = 69.3$ $(J_{PP} = 211 \text{ Hz})$ and a doublet of triplets at $\delta = -114$ $(J_{PP} = 211 \text{ Hz}, J_{PH} =$ 7 Hz). The mass spectrum of **5b** exhibits ion peaks at *m*/*z*: 246, 199 (base peak) [M⁺ - PO], 183, 170, 152, 107, 69, 47, while the mass spectrum of **6b** exhibits ion peaks at *m*/ *z*: 262 (base peak), 215 [M⁺ - PO], 199, 168, 152, 107, 69, 47.

In order to obtain supporting evidence for a possible pathway of this presumed domino reaction, aliquots of the reaction mixture from 4a, AlCl₃ and PCl₃ were analysed by ³¹P NMR spectroscopy. After 10 h and after removal of PCl₃, the ³¹P(¹H) NMR spectrum showed several signals at $\delta = 178, 158, 104, 69, and 49$ as broad singlets and an intense doublet of doublets at $\delta = 88.3$ (d, $J_{PP} = 262$ Hz), -105.0 (dt, $J_{\rm PP} = 262$ Hz, $J_{\rm PH} = 7.5$ Hz). At the end of the reaction we noted the prevalence of the above doublets over the singlets and after addition of water we noted the disappearance of the above doublets and the appearance of the doublets of 6a. Very small signals of the doublets of 5a were also observed. Thus, the couple of doublets, observed before quenching with water, might be assigned to the final intermediate 7 in Scheme 6. From these data we can affirm that the final intermediate 7 corresponds to the final intermediate G (Scheme 3) observed for the same reaction with thioanisole 1, but the results of the treatment with water are very different. In fact the treatment of phosphonium salt 7 with water gives the expected product of hydrolysis 6while the same treatment of phosphonium salts G gives 2 as an unexpected reduction product.

It should be noted that compounds 5 are very unstable, air- and moisture-sensitive compounds, while the related bicyclic compounds 2 are very stable and air-insensitive solids. This difference is due only to the replacement of two oxygen atoms with the sulfur atoms. We think that this simple substitution might favour a quasi-aromatic structure

FULL PAPER

or a more delocalised structure in the case of compounds 2 in contrast to 5. This stabilization of 2 might also be responsible for its preferred formation with respect to the oxidized derivative 3 in the final hydrolysis of its precursor phosphonium salt G (Scheme 3). In contrast, the oxidised derivative 6 is preferred in the case of 5. The quasi-aromatic structure of 2 might explain also the large difference between the ³¹P NMR spectra of 5a [δ = 188.0 (d, P-6); -11.8 (dt, P-12, ³J_{PH} = 6 Hz, ¹J_{PP} = 175 Hz)] and the ones of 2a [δ = 88.3 (d, P-6); δ = 65.4 (dt, P-12, ³J_{PH} = 7.8 Hz, ¹J_{PP} = 211.5 Hz)] in which we have two signals for the two P atoms in the same region, indicating a possible delocalization of the two P lone pairs.

In order to obtain other data to support the structures of the benzo-fused compound **6** we carried out a multi-step synthesis of this system. As reported in Scheme 7, in the first step *o*-bromoanisole **9** was transformed to its Grignard derivative **10**. In the second step **10** was transformed to diarylphosphane oxide **11** by PCl₃ in high dilution with THF and then hydrolysis. In the last step, again using the couple PCl₃/AlCl₃, demethylation, formation of two O–P bonds, and formation of one P–P bond yield **6** in a one-pot procedure.



Scheme 7. Alternative multi-step synthesis of 6

It should be noted that the described formation of **11** is a new and simple synthesis of this type of phosphorus derivatives. In fact, according to the literature^[10] these compounds are formed in a dry box under nitrogen by reaction of aryllithium compounds with diethyl phosphite.

Conclusion

We have reported that the "domino reaction" which occurs when thioanisole reacts with the couple $PCl_3/AlCl_3$ giving the fused bicyclic system 2 can occur also with anisoles giving the related fused system 5, but with a very large amount of its monoxide 6. However, for anisoles, the best reaction conditions have been more difficult to find because another unexpected reaction (insertion of a P moiety into the O-Me bond) giving diaryl methylphosphonates 8 can also occur. We have, however, been able to control the two different pathways by simple control of the reagent ratios and reaction conditions. These results also give an explanation about the limited success in the phosphonation of anisoles obtained so far with the same reagents. In addition, we have applied the reactivity of the couple $PCl_3/AlCl_3$ to bis(*o*-methoxyaryl)phosphane oxides **11** to form in a onepot procedure two O–P bonds and one P–P bond to yield **6**. Finally, these findings represent a generalisation of a facile one-pot route to obtain benzo-fused systems containing the P–PX₂ unit (X = S, O, etc.). It should be noted that recently the fused-ring compound **2a** has been used^[11] as an efficient phosphorus-donating reagent and **6a** might also be an interesting P=O donating reagent.

Experimental Section

General Remarks: ¹H, ¹³C, and ³¹P NMR spectra were recorded with a Varian Gemini spectrometer at 300 MHz, 75.46 MHz, and 120.75 MHz, respectively, in CDCl₃. Chemical shifts are referenced to internal standard TMS (¹H NMR), to solvent ($\delta = 77.0$ for ¹³C NMR), and to external standard 85% H₃PO₄ (³¹P NMR); J values are given in Hz. - IR spectra were recorded with a Perkin-Elmer spectrophotometer model 1600 FT-IR. IR spectra of compounds **6a** and **6b** showed typical signals: $P=O(1254 \text{ cm}^{-1})$, P-O-C (1086 cm^{-1}) and P-Ph (1466 cm^{-1}) . - MS data were recorded at an ionisation voltage of 70 eV with a VG 7070 E spectrometer. GC-MS analyses were performed with an HP-5890 gas chromatograph equipped with a methyl silicone capillary column and an HP-5970 mass detector. - Thin-layer chromatography was performed on Merck Kieselgel 60 F254. Melting points were measured with a Büchi apparatus and are uncorrected. - THF was distilled from sodium benzophenone ketyl. All reagents were commercial samples (Aldrich). Air- and moisture-sensitive solutions and reagents were handled in a dried apparatus under dry nitrogen. Chemical and physical data of compounds 8a and 8b are in agreement with literature values.[7]

One-Step Synthesis of the [1,2,3]Benzooxadiphospholo[2,3-b][1,2,3]benzooxadiphosphole Systems 5a,b and 6a,b from Anisoles 4a,b and PCl₃/AlCl₃. - Typical Procedure: p-Methylanisole (1a) (5.04 mL, 0.04 mol), AlCl₃ (3.20 g, 0.024 mol), and PCl₃ (24.26 mL, 0.28 mol) were placed in a dried apparatus, filled with dry nitrogen. The mixture was stirred at 80 °C. The reaction was monitored by GC-MS analysis. After about 20-25 h, the reaction mixture was treated quickly with a mixture of water and dichloromethane. After extraction with dichloromethane, the organic layer was dried with anhydrous Na₂SO₄ and the solvent was removed giving a greasy mixture containing 5a, 6a, and 8a in the ratio of about 1:7:2. After removing 8a by bulb-to-bulb distillation at 0.1 Torr at 200 °C, the undistillable residue was crystallised from CH2Cl2/Et2O giving a white solid, containing compounds 5a and 6a in a 1:7 ratio. Fast recrystallization of this solid gave pure 6a (2.13 g, 35%) as a white solid. The procedure shown above was followed using the anisole 4b as reagent. From this reaction, compound 5b was obtained in traces and **6b** in 20-25% yield.

2,10-Dimethyl[1,2,3]benzooxadiphosphole[2,3-*b*][1,2,3]benzooxadiphosphole (5a): ${}^{31}P{}^{1}H{}$ NMR (120.75 MHz, CDCl₃): $\delta = 188.0$ (d, $J_{PP} = 175$ Hz, P-6), -11.8 (dt, $J_{PP} = 175$ Hz, $J_{PH} = 6$ Hz, P-12). - MS (70 eV, EI): m/z (%) = 274 [M⁺] (95), 227 [M⁺ - PO] (100), 211 (45), 197 (26), 153 (18), 121 (20), 77 (28), 63 (35).

2,10-Dimethyl- $6\lambda^5$ -[1,2,3]benzooxadiphosphole[2,3-*b*][1,2,3]benzooxadiphosphol-6-one (6a): M.p. 176-177 °C (from CH₂Cl₂/Et₂O). - ¹H NMR (300 MHz, CDCl₃): δ = 2.30 (s, 6 H, CH₃), 6.95–7.50 (m, 2 H, 3-H, 9-H), 7.10–7.18 (m, 2 H, 4-H, 8-H), 7.32–7.39 (m, 2 H, 1-H, 11-H). - ³¹P{¹H} NMR (120.75 MHz, CDCl₃): δ = 69.9 (d, $J_{PP} = 209$ Hz, P-6), -112.5 (dt, $J_{PP} = 209$ Hz, $J_{PH} = 7.0$ Hz, P-12). - MS (70 eV, EI): m/z (%) = 290 [M⁺] (100), 243 [M⁺ – PO] (75), 227 (45), 196 (26), 152 (7), 121 (11), 77 (9), 47 (32). - HRMS: calcd. for C₁₄H₁₂O₃P₂: 290.0262, found 290.0266; calcd. C 57.95, H 4.17; found C 57.87, H 4.12.

[1,2,3]-Benzooxadiphosphole[2,3-*b*][1,2,3]benzooxadiphosphole (5b): ${}^{31}P{}^{1}H{}$ NMR (120.75 MHz, CDCl₃): $\delta = 186.0$ (d, $J_{PP} = 175$ Hz, P-6), -13.0 (dt, $J_{PP} = 175$ Hz, $J_{PH} = 7.0$ Hz, P-12). - MS (70 eV, EI): *m*/*z* (%) = 246 [M⁺] (95), 199 [M⁺ - PO] (100), 183 (15), 170 (18), 152 (20), 107 (16), 69 (28), 47 (25).

[1,2,3]-Benzooxadiphosphole[2,3-*b*][1,2,3]benzooxadiphosphol-6-one (6b): M.p. 165–166 °C (from CH₂Cl₂/Et₂O). – ¹H NMR (300 MHz, CDCl₃) δ = 7.07–7.19 (m, 4 H, 2-H, 3-H, 9-H, 10-H), 7.35–7.42 (m, 2 H, 4-H, 8-H), 7.58 (dd, $J_{PH} = J_{HH} = 7.1$ Hz, 2 H, 1-H, 11-H). – ³¹P{¹H} NMR (120.75 MHz, CDCl₃): δ = 69.3 (d, $J_{PP} = 211$ Hz, P-6), –114.0 (d, $J_{PP} = 211$ Hz, $J_{PH} = 7.1$ Hz, P-12). – MS (70 eV, EI): *m/z* (%) = 262 [M⁺] (100), 215 [M⁺ – PO] (72), 199 (38), 168 (48), 152 (13), 107 (15), 69 (26), 47 (24). – HRMS: calcd. for C₁₂H₈O₃P₂: 261.9949, found 261.9945; calcd. C 54.98, H 3.08, found C 54.83, H 3.02.

Two-Step Synthesis of Benzooxadiphospholes 6a,b from o-Bromoanisoles 9a,b. - Preparation of 11a and 11b. - Typical Procedure: A solution of PCl₃ (0.654 mL, 0.0075 mol) in THF (30 mL) was placed in a dried apparatus filled with dry nitrogen. A solution of 2-(4-methyl)anisylmagnesium bromide [prepared from 2-bromo-4methylanisole (9a) (2.17 mL, 0.015 mol) and magnesium turnings in THF (30 mL)] was added dropwise and under quick stirring, at 0 °C for 4 h. After the addition, the mixture was left under stirring at room temperature, and the reaction was monitored by GC-MS analysis. After 5 h the reaction mixture was hydrolysed with an aqueous acid solution for almost 30 min. After extraction with dichloromethane, the organic layer was dried with anhydrous Na₂SO₄ and the solvent was removed. The residue was crystallised from CH_2Cl_2/Et_2O giving a white solid containing compound 11a (0.76 g, 70%). The procedure shown above was followed using 2bromoanisole (9b) as reagent. From this reaction compound 11b was obtained in 70% yield.

Bis(2-methoxy-5-methylphenyl)(oxo)phosphorane (11a): $R_{\rm F} = 0.15$ (in Et₂O). $-{}^{1}$ H NMR (300 MHz, CDCl₃) $\delta = 2.31$ (s, 6 H, CH₃), 3.74 (s, 6 H, OCH₃), 6.77–6.85 (m, 2 H, 4-H), 7.27–7.34 (m, 2 H, 3-H), 7.41 (dd, ${}^{3}J_{\rm PH} = 15.3$, ${}^{4}J = 2.4$ Hz, 2 H, 6-H), 8.22 (d, $J_{\rm PH} = 520$ Hz, 1 H, PH). $-{}^{31}$ P{ 1 H} NMR (120.75 MHz, CDCl₃): $\delta = 10.0$ (dt, $J_{\rm PH} = 520$ Hz, $J_{\rm PH} = 15$ Hz). - MS (70 eV, EI): m/z (%) = 290 [M⁺] (100), 259 (52), 241 (39), 135 (95), 105 (54). - HRMS: calcd. for C₁₆H₁₉O₃P: 290.1072, found 290.1067, calcd. C 66.20, H 6.60; found C 66.05, H 6.45.

Bis(2-methoxyphenyl)(oxo)phosphorane (11b): M.p. 136 °C (ref.^[11a] 135–136 °C), $R_{\rm F} = 0.30$ (in Et₂O). $-{}^{1}$ H NMR (300 MHz, CDCl₃) $\delta = 3.76$ (s, 6 H, OCH₃), 6.90 (dd, ${}^{3}J = 8.5$, ${}^{3}J = 6.0$ Hz, 2 H, 4-H), 7.02–7.12 (m, 2 H, 5-H), 7.46–7.56 (m, 2 H, 3-H), 7.67 (qd, ${}^{3}J = 7.5$ Hz, ${}^{3}J_{\rm PH} = 15.0$, ${}^{4}J = 1.8$ Hz, 2 H, 6-H), 8.25 (d, $J_{\rm PH} = 515$ Hz, 1 H, PH). $-{}^{31}{\rm P}{}^{1}{\rm H}$ NMR (120.75 MHz, CDCl₃): $\delta = 8.2$ (dt, $J_{\rm PH} = 515$ Hz, ${}^{3}J_{\rm PH} = 15$ Hz). - MS (70 eV, EI): m/z (%) = 262 [M⁺] (100), 231 [M⁺ - 31] (31), 213 (44), 121 (85), 91 (32). - HRMS: calcd. for C₁₄H₁₅O₃P: 262.0759, found 262.0709.

Reaction of 11a and 11b with AlCl₃/PCl₃. – Typical Procedure: Compound **11a** (0.46 g, 0.0016 mol), PCl₃ (0.96 mL, 0.0075 mol), and AlCl₃ (0.22 g) were placed in a dried apparatus filled with dry nitrogen. The mixture was stirred at 80 °C, and the reaction was monitored by GC-MS analysis. After 4 h, the reaction mixture was quickly treated with a mixture of water and dichloromethane. After extraction with dichloromethane, the organic layer was dried with anhydrous Na₂SO₄ and the solvent was removed. The residue was crystallised from CH₂Cl₂/Et₂O giving **6a** (0.232 g, 50%). The procedure shown above was followed using compound **11b** as reagent. From this reaction compound **6b** was obtained in 53% yield.

Reaction of *p*-Methylthioanisole (1a)/AlCl₃/PCl₃ (1.0:0.6:1.0): A solution of *p*-methylthioanisole (1a) (13.26 mL, 0.1 mol), PCl₃ (8.7 mL), and AlCl₃ (0.6 mol) (sublimed prior to use) was refluxed and stirred under dry nitrogen for 10 h. The reaction mixture was treated with a mixture of ice and dichloromethane; the organic layer was washed with a 5% aq. NaOH solution and twice with water. After removal of the solvent, no traces of methylphosphorylation products were detected, only benzothiadiphosphole 2a.

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