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INTERMEDIATES IN THE REACTION OF A TRIARYLPHOSPHAETHENE WITH SULFUR

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Summary

The reaction of 2,6-dimethylphenyl(diphenylmethylene)phosphine (**1**) with sulfur in boiling benzene gives the unstable intermediate thioxomethylenephosphorane **4** (which was identified by NMR spectroscopy), and hence the thioxothiaphosphirane **8**. Under more drastic conditions the very unstable dithioxophosphorane **7** is formed, and in the absence of trapping reagents such as ethanol this dimerizes to give the trithiophosphoric double anhydride **12**.

Introduction

We have described oxidation reactions of triarylphosphaalkenes with i.a. oxygen [1], sulfur [1], selenium [2] and tellurium [2]. Similar reactions with sulfur as oxidant have been reported for aminoiminophosphines [3], aminomethylenephosphines [4], and more recently, for phosphaalkenes bearing nitrogen [5] or silicon [6] as a substituent on carbon.

Our previous results on the reaction of 2,6-dimethylphenyl(diphenylmethylene)phosphine ($ArP{=}CPh_2$, **1**) with sulfur are summarized in Scheme 1.

While **1** was inert to sulfur at room temperature in benzene or ethanol, it was completely consumed after heating in ethanol for 2.5 h. Compounds **2** and **3** were together formed practically quantitatively (the yields were 85 and 15%, respectively), along with 15% thiobenzophenone. The formation of **2** and **3** was explained by postulating two modes of reaction of **1**. In pathway A, **1** is oxidized by attack at the lone pair, which is the HOMO [7], to give the thioxomethylenephosphorane **4**; this reaction parallels the well known oxidation of tertiary phosphines to phosphine sulfides. In pathway B, the reaction apparently starts at the P=C double bond, which is the NHOMO, but very close in energy to the lone pair [7], under cleavage to the thioxophosphine **5** and thiobenzophenone; both products are formed in equal yield. The final products **2** and **3** are formed by rapid addition of ethanol to the unstable intermediates **4** and **5**, respectively.

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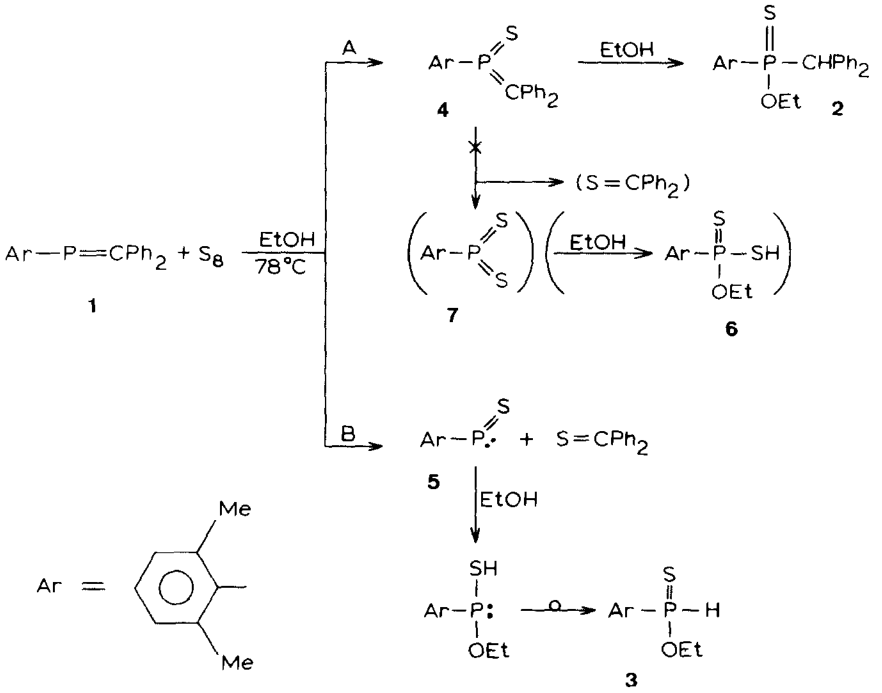


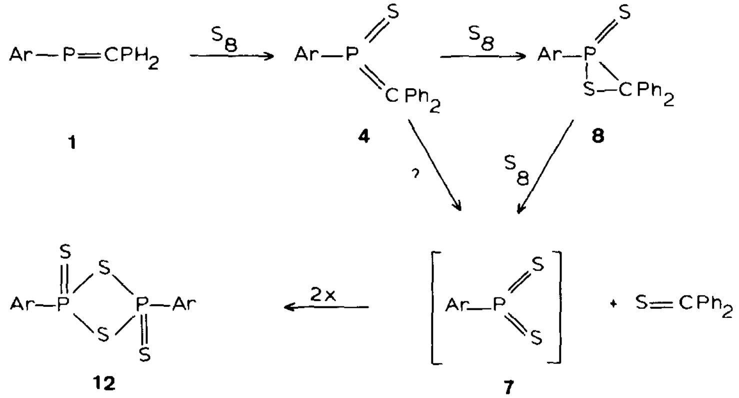
SCHEME 1

A significant feature was the absence of another possible product **6**, which could arise by addition of ethanol to the intermediate dithioxophosphorane **7**; the latter was expected to be formed by oxidative cleavage of the P=C bond in **4**, by analogy to the corresponding reactions with molecular oxygen [1]. The absence of **6** proved that this cleavage reaction does not occur in ethanol, presumably because the reaction of **4** with ethanol is much faster.

We now report that in benzene the unstable intermediate **4** of pathway A can be observed directly by spectroscopic techniques; details of its further reactions with sulfur and oxygen are described [8].

Results and discussion

We previously reported that the reaction of mesityl(diphenylmethylene)phosphine with sulfur in boiling benzene led to a polymer and 50% thiobenzophenone [1]. The same reaction of **1** with an excess of sulfur was not quite complete after 3.25 h refluxing in benzene. The ^{31}P NMR spectrum of the crude reaction mixture indicated that **1** and **4** were present in a ratio of about 1/3, along with small quantities of **8** and decomposition products; the mixture was green, presumably due to the joint presence of **1** (yellow) and small amounts of thiobenzophenone (blue) (Scheme 2). When the reaction was performed with one molar equivalent of sulfur (1/8 S_8 per mol of **1**), the reaction was very slow: after 3 h, a slight green colour indicated a low degree of conversion. Even after 8 h, the conversion of **1** was only 38%, according to the ^{1}H NMR spectrum. This is surprising in so far as in both experiments solid sulfur was discernible throughout; it is thus reasonable to assume that the benzene solution was saturated with sulfur, so that the reaction should be (pseudo) first order in **1**. Possibly, the rate of the reaction is strongly influenced by the presence of sulfur species other than S_8, e.g. S_6 [9].

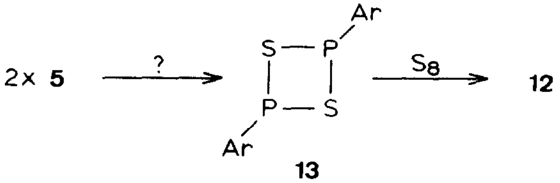


SCHEME 2

Attempts to isolate **4** failed. It was very sensitive to air; attempted crystallization from the reaction mixture under nitrogen was not successful. Attempts to obtain **4** free from **1** by prolonged reaction with sulfur also failed; instead, the amount of **8** increased, and polymeric material was formed, as indicated by broad signals in the *ortho*-methyl region of the ^{1}H NMR spectrum. However, **4** was characterized by its rapid reaction with ethanol to form **2** (cf. Scheme 1), and by its spectral data. Characteristic of **4** is the phosphorus chemical shift (δ 140.5 ppm), which is in the expected range for a thioxomethylenephosphorane, as illustrated by the values for $(Me_3Si)N{-}P({=}S){=}CHSiMe_3$ (**9**) (δ 185.4 ppm [4]) and for $Mes{-}P({=}S){=}C(SiMe_3)_2$ (**10**) (δ 190.9 ppm [6]); the latter two compounds show resonances at lower field due to the effects of the amino and/or trimethylsilyl groups. The signal in the ^{13}C NMR spectrum of **4** at δ 134.6 ppm (J(PC) 91 Hz) is tentatively assigned to the P=C carbon atom (cf. $\delta(^{13}C)$ 97.6 ppm, J(PC) 92.2 Hz for **9** [4], and $\delta(^{13}C)$ 126.0 ppm, J(PC) 34.2 Hz for **10** [6]). Furthermore, **4** was identified by its mass spectrum ($4^{+\cdot}$ (5%); HRMS).

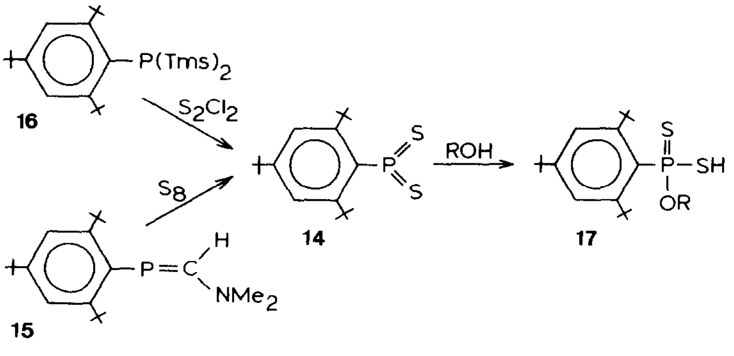
Compound **8** could not be separated directly from reaction mixtures containing also **1**, **4** and minor products, but it was isolated in pure form in the following way. A mixture obtained as above from **1** and 6/8 S_8 was oxidized by bubbling through a stream of dry oxygen, which removed **4** in a rapid reaction (vide infra); **8** crystallized from the resulting mixture, and was isolated in 34% yield. It was not very stable, and partially decomposed on recrystallization from ethanol, yielding, besides **8**, unidentified products and benzophenone. Compound **8** was fully characterized by elemental analysis and NMR spectroscopy, especially by the high field phosphorus chemical shift (δ 1.4 ppm) of the thiaphosphirane ring system (cf. $\delta(^{31}P)$ 2.6 ppm for $Mes{-}P({=}S){-}S{-}C(SiMe_3)_2$ (**11**) [6]. Like **11**, **8** showed hindered rotation around the arylphosphorus bond, as indicated by the presence of two signals from the *ortho*-methyl groups (^{1}H NMR: δ 2.21 ppm (^4J(PH) 2 Hz) and δ 2.89 ppm (^4J(PH) 1.5 Hz); 90 MHz).

The formation of **8** at the expense of **4** indicates that sulfur adds to the P=C bond of **4** with formation of a three-membered ring. This type of reaction has also been reported for **9** [4] and **10** [6]. Further oxidation of **8** (or **4**) with sulfur may be expected to occur by cleavage of the P=C bond with formation of thiobenzophenone and **7** (Scheme 2); indeed, when **8** was isolated and subsequently heated with sulfur, thiobenzophenone was obtained in more than 50% yield. While **7** or **8** are apparently not formed in ethanol (vide supra), the intermediacy of **7**, in benzene was indicated by the isolation of **12** when **1** was heated with 5/8 molar equivalents of sulfur in benzene to 90–100°C in a sealed ampoule. Under these more drastic conditions the reaction proceeded much more rapidly, as indicated by an intense blue colour after 2 h. Compound **12** crystallized from the reaction mixture after cooling to room temperature (46% yield). When heating was continued for 72 h, 60% thiobenzophenone were isolated by sublimation of the residue after evaporation of the solvent from the reaction mixture; the residue left after sublimation contained eleven unidentified phosphorus compounds (^{31}P NMR).



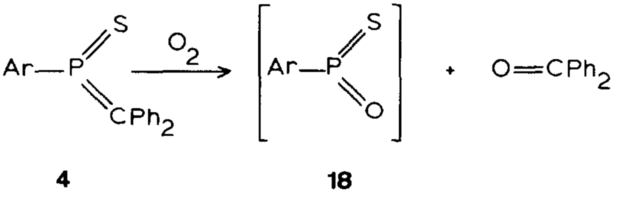
SCHEME 3

Compound **12** was too insoluble for recording of its NMR spectra, and in contact with air one sulfur atom was replaced by oxygen. It was thus characterized by elemental analysis and by its mass spectrum. Compound **12** is an analogue of Lawesson's reagent [10], and must clearly be the dimerization product of the unstable intermediate **7**. An alternative mode of formation by dimerization of **5** to **13**, followed by oxidation to **12** (Scheme 3) is unlikely for the following reason. Pathway B (product **5**, Scheme 1) occurs only to the extent of 15% and cannot account for the 46% yield of **12**, whereas the yield of thiobenzophenone (60%) corresponds nicely with the combined yields of **12** (= product of P=C cleavage from pathway A; 46%) and **5** (= product of P=C cleavage from pathway B, assumed to be approximately 15% as in the ethanol reaction).



SCHEME 4

A stable analogue (**14**) of **7** was recently described (Scheme 4). It was obtained by Navech at al. by treatment of the phosphaalkene **15** with elemental sulfur [5], and by Appel et al. by treatment of **16** with disulfur dichloride. The latter workers confirmed its structure by crystal structure determination [11]. Compound **14** is protected against dimerization by the two bulky *ortho*-t-butyl groups. Reaction of **14** with alcohols gave **17** [5,11], confirming our previous argument [1] that the intermediacy of **7** in the ethanol reaction can be excluded because it would have yielded **6** (Scheme 1).



SCHEME 5

It was mentioned above in connection with the isolation of **8** from a mixture of **1**, **4** and **8** (Scheme 2) that **4** was rapidly destroyed by bubbling dry oxygen (diluted with nitrogen) through the mixture in benzene solution, and, benzophenone (42%) was subsequently isolated. The formation of benzophenone at the expense of **4** must proceed by cleavage of the P=C bond of **4**, presumably with formation of **18**, as illustrated in Scheme 5. Such a cleavage parallels the cleavage by oxygen of triarylmethylenephosphoranes to give triarylphosphine oxides and ketones [12], and of oxomethylenephosphorane $Ar-P(=O)=CPh_2$ [1]; both are analogous to the cleavage by sulfur to triarylmethylenephosphoranes [13], and that of **4** to **7** described in this investigation. Thus, oxidative cleavage of P=C bond seems to be a general reaction of tri- and tetra-coordinate phosphoranes.

Conclusion

The results obtained from this investigation further clarify the course of ractions involved in the oxidation of triarylphosphaethenes of type **1** with sulfur [1]. In pathway A (Scheme 1), the initial step is attack of sulfur at the lone pair under formation of **4**. In ethanol, **4** is quantitatively intercepted to form **2** (Scheme 1). In benzene, further reaction with sulfur first converts **4** into **8** by addition of a sulfur atom to the P=C bond, followed by oxidative cleavage of **8** under more drastic conditions to yield, in the final oxidation stage, compound **7** (Scheme 2), which dimerizes to give **12** (Scheme 2). The mechanism of pathway B remains to be clarified.

Another interesting conclusion concerns the stability of the η^3-phosphoranes $Ar-P(=X)=CPh_2$ (**19**), which increases in the order X = O [1] < X = S (≡ **4**) < X = Se [2]. This order is opposite to that expected from the stability of P=X bonds, and therefore reflects kinetic rather than thermodynamic stability.

Experimental

Reactions were performed under argon or nitrogen. NMR spectra were recorded on a Bruker WH 90 or a Bruker WM 250 spectrometer. Low field NMR signals have a positive sign; references were Me_4Si (^1H, internal), 85% H_3PO_4 (^{31}P, external) and $CDCl_3$ (^{13}C, internal). Melting points are uncorrected. Elemental analyses were performed by the Instituut voor Toegepaste Chemie TNO, Zeist, The Netherlands, under the supervision of Mr. G.J. Rotscheid.

*Reaction of **1** with sulfur in benzene*

(a) At 80°C for 3.25 h. Compound **1** [7] (196 mg, 0.65 mmol) was dissolved in benzene (7 ml) and sulfur (100 mg, 3.13 mmol) was added. After heating under reflux for 3.25 h the solution was green. The ^1H and ^{31}P NMR spectra of a sample indicated the presence of a 3/1 mixture of **4** and **1**; signals of low intensity of **8** and of decomposition products were also present. **4** (2,6-Dimethylphenyl(diphenylmethylene)oxophosphorane): ^1H NMR (C_6D_6) δ 2.61 (d, $^4J(PH)$ 3 Hz, 6H, *o*-Me) 6.73–7.84 ppm (m, 13H + H of **5** and decomposition products, aryl H). ^{13}C NMR (C_6D_6) δ 22.8 (d, $^3J(PC)$ 6 Hz, *o*-Me) 126.8–144.9 (m, aryl C, not assignable), 134.6 ppm (d, $^1J(PC)$ 90.6 Hz, P=C?). ^{31}P NMR (C_6D_6) δ 140.5 ppm. Mass spectrum *m/z* (relative intensity): 334 (5) $[M]^+$, 257 (19) $[M - Ph]^+$, 255 (53) $[M - C_6H_7]^+$, {198 (88) $[Ph_2C{=}S]^+$ }, 165 (100) $[Ph_2CH]^+$, 121 (80). HRMS found 334.0945; $C_{21}H_{19}PS$ calcd. 334.0957. An aliquot of the reaction mixture was added to ethanol. After stirring for 15 min at room temperature, the ^1H NMR spectrum revealed that **2** [1] was formed at the expense of almost all the **4** (**2**/**4** = ca. 4/1).

(b) At 80°C followed by reaction with oxygen. Compound **1** (269.5 mg, 0.89 mmol) was dissolved in benzene (10 ml) and sulfur (163 mg, 5.1 mmol) was added. After 3 h at 80°C the solution was dark green. The excess of sulfur was filtered off, and oxygen/nitrogen was bubbled through the solution, whereupon it became light green. After 22 h **8** and sulfur had crystallized out (110 mg). Evaporation of the solvent gave 290 mg of a green oil; on addition of ethanol another 72 mg of **8** crystallized. After separation of the yellow sulfur crystals (manually) 111 mg pure **8** (2-(2,6-dimethylphenyl)-3,3-diphenyl-2-thioxothiaphosphirane) (34%) remained. Upon recrystallization in air, **8** decomposed partially into benzophenone and unidentified products. After one crystallization 23 mg **8**, m.p. 160–170°C, remained. ^1H NMR ($CDCl_3$) δ 2.21 (d, $^4J(PH)$ 2 Hz, 3H, *o*-Me) 2.89 (d, $^4J(PH)$ 1.5 Hz, *o*-Me) 6.56–7.82 ppm (m, 13H, aryl H). ^{31}P NMR δ 1.4 ppm. Found: C, 68.3; H, 5.9; S, 17.58. $C_{21}H_{19}PS_2$ calcd.: C, 68.82; H, 5.23; S, 17.50%. The ethanol layer (from which **8** was crystallized) was evaporated to dryness; sublimation of the residue (bath temperature 60°C, 10^{-1} mbar) gave benzophenone (35 mg; 40–50% after correction for recovered **8** and for oxidation of **1** present in the reaction mixture).

(c) At 90°C for 2 h. Compound **1** (278 mg, 0.92 mmol) was dissolved in benzene (5 ml) and sulfur (150 mg, 4.7 mmol) was added. After 2 h in a sealed ampoule at 90–100°C, the solution had turned deep blue. Compound **12** (2,4-di(2,6-dimethylphenyl)-2,4-dithioxo-1,3-dithia-2,4-diphosphetane) (85 mg, 46%) crystallized out on cooling to room temperature, m.p. 276–279°C. Attempts to dissolve **12** for NMR spectroscopy failed ($CDCl_3$, $CDCl_3/CF_3COOD$). Mass spectrum *m/z* (relative intensity): 400 (17) $[M]^{+\cdot}$, 384 (100) $[M - S + O]^+$ (vide infra), 304 (31) $[M - 3S]^+$, 217 (50), 200 (54) $[M]^{2+}$ or $[1/2M]^+$, 152 (63) $[C_8H_9PO]^{+\cdot}$. HRMS 399.9779 $C_{16}H_{18}P_2S_4$ calcd.: 399.9767. Found: C, 47.83; H, 4.60; S, 31.02. $C_{16}H_{18}P_2S_4$ calcd.: C, 47.98; H, 4.52; S, 32.02%. Crystalline **12** was oxidized in contact with air; one oxygen replaced one sulfur: HRMS 383.9999. $C_{16}H_{18}OP_2S_3$ calcd.: 383.9995.

(d) At 90°C for 72 h. Compound **1** (166 mg, 0.55 mmol) was dissolved in

benzene-d_6 (1 ml) and sulfur (79 mg, 2.47 mmol) was added. After 72 h in a sealed ampoule at 90–100°C the solution had turned blue. It was evaporated, and on heating of residue (ca. 10^{-2} mbar, 60°C) 65.6 mg (60%) thiobenzophenone, m.p. 43–47°C sublimed out. According to the ^{31}P NMR (C_6D_6) spectrum the light yellow residue contained 11 unidentified phosphorus compounds; ^{1}H NMR ($CDCl_3$) revealed that no **8** was present, but not all the material dissolved in $CDCl_3$ or benzene-d_6 (**12**?).

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