New reaction of dithiophosphoric acids with *O*-thioacylhydroxylamines. Nucleophilic substitution or single electron transfer process?†

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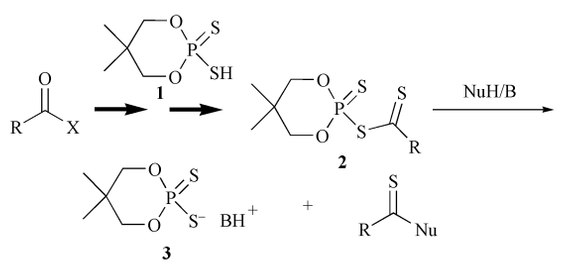
Disubstituted or sterically hindered hydroxylamines react with bulky *S*-thioacyl dithiophosphates yielding *O*-thioacylhydroxylamines. The reaction of *O*-thioacylhydroxylamines with dithiophosphoric acids yields acyl thiophosphoryl disulfides and ammonium dithiophosphates. The influence of radical traps on the reaction yield strongly suggests that radicals are involved in the mechanism of the process. The low redox potential of dithiophosphates, the observed photochemical stability of *O*-thioacylhydroxylamines and the influence of light on acyl thiophosphoryl disulfides yield imply involvement of a single electron transfer process in the investigated reaction.

Introduction

We have recently described[1,2] a convenient method of converting carboxylic acids into thioacyl dithiophosphates **2**, which are excellent thioacylating reagents (see Scheme 1). Thioacyl dithiophosphates **2** react much faster with nitrogen or sulfur nucleophiles than with oxygen ones. This kind of reactivity can find general application in the direct thioacylation of aminoalcohols and mercaptoalcohols having an unprotected hydroxy function. As we proved recently[3] thiohydroxamic acids (*N*-thioacylhydroxylamines) can also be obtained by direct thioacylation of hydroxylamines with thioacyl dithiophosphates **2**.



Scheme 1 *S*-Thioacyl dithiophosphates and their application as thioacylating agents.

However, when we treated *N*-isopropylhydroxylamine **4a** with thiopivaloyl dithiophosphate **2a**, to our surprise, from the reaction mixture[4,5] we isolated pivaloyl thiophosphoryl disulfide **5a** instead of the expected thiohydroxamic acid **6** (Scheme 2). In this paper, we would like to present the details of our research concerning this new reaction effecting the cleavage of the nitrogen–oxygen bond in the hydroxylamine moiety under the action of dithiophosphoric acid.

† Electronic supplementary information (ESI) available: ^{31}P NMR spectra of reaction mixtures formed from *O*-thiopivaloyl-*N*-(1-phenylethyl)hydroxylamine and dithiophosphoric acid in the presence of a radical trap; ^{1}H NMR spectrum of the reaction mixture formed after irradiation of *O*-thiopivaloyl-*N*-(1-phenylethyl)hydroxylamine in the presence of a radical trap and ^{1}H NMR spectra of the reaction mixtures formed after irradiation of *O*-thiopivaloyl-*N*-(1-phenylethyl)-hydroxylamine. For direct access see http://www.rsc.org/suppdata/p2/b2/b203619n/

Results and discussion

In order to explain the very unusual course of the reaction of *N*-isopropylhydroxylamine **4a** with thiopivaloyl dithiophosphate **2a**, we pondered over the difference between this and the other cases of hydroxylamine thioacylation. Both reagents have bulky substituents and, as we showed recently,[3] in the event of greater steric hindrance *O*-thioacylhydroxylamines **7** may be formed instead of the expected thiohydroxamic acids **6** (Scheme 3).

Hence, we made an assumption that *O*-thiopivaloyl-*N*-isopropylhydroxylamine **7a** was the intermediate and disulfide **5a** was formed on further reaction with the dithiophosphate anion. However, the question arose, why in this case it was impossible to isolate the respective *O*-thioacylhydroxylamine and an additional process took place. To answer this question we ran the reaction of another bulky hydroxylamine (*N*-*tert*-butylhydroxylamine **4b**; R′ = Bu^t, R″ = H) with pivaloyl dithiophosphate **2a**. Also in this case we isolated disulfide **5a** from the reaction mixture in 81% yield. Monitoring the reaction with ^{31}P NMR we found that after mixing the reagents, thioacyl dithiophosphate **2a** (δ_P 71 ppm) is consumed, though only dithiophosphate anion (δ_P 106 ppm) production can be observed (using ^{31}P NMR). It means that the formation of disulfide **5a** (δ_P 83 ppm) results from the following acidic work-up of the mixture. Therefore, we presumed that disulfide **5a** should be formed in the reaction of *O*-thioacylhydroxylamines with the dithiophosphoric acid. To verify this hypothesis we treated isolated *O*-thiopivaloyl-*N*-*tert*-butylhydroxylamine **7b** with two equivalents of dithiophosphoric acid **1**. From the reaction mixture we were able to isolate disulfide **5a** and *tert*-butylammonium dithiophosphate **3b** in very good yields (Scheme 4).

In order to check whether other hindered *O*-thioacylhydroxylamines reveal the same reactivity, we treated *O*-thiopivaloyl-*N*-(1-phenylethyl)hydroxylamine **7c** and *O*-thiopivaloyl-*N*-hydroxymorpholine **7d** with dithiophosphoric acid **1**. The formation of disulfide **5a** and the respective ammonium dithiophosphates **3** in each case shows that this kind of reactivity is typical for *O*-thioacylated hydroxylamines. Moreover, as we demonstrated, the reaction of *O*-thiopivaloyl-*N*-*tert*-butylhydroxylamine **7b** with other dithiophosphinic (dithio-

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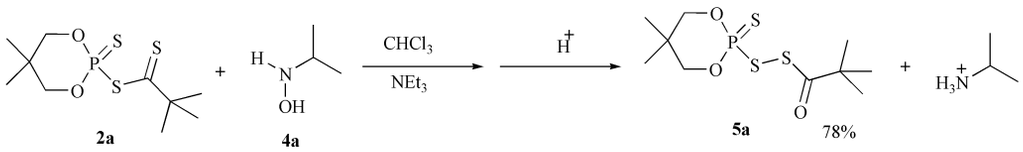
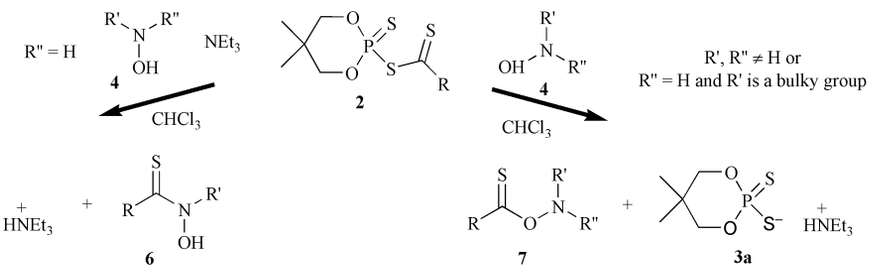
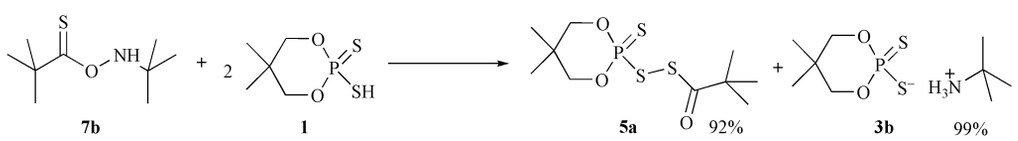


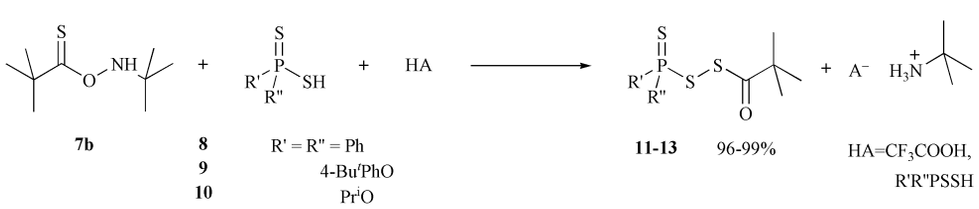
Scheme 2 Reaction of thiopivaloyl dithiophosphate **2a** with *N*-isopropylhydroxylamine **4a**.



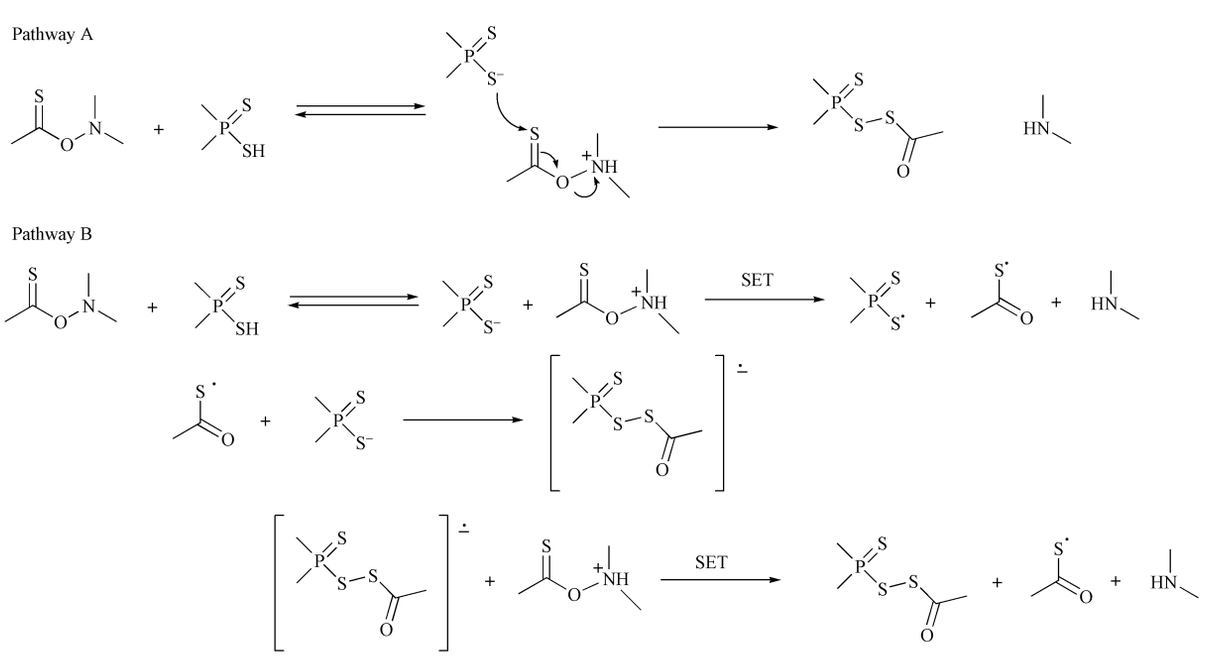
Scheme 3 Reaction of *S*-thioacyl dithiophosphates **2** with *N*-alkylhydroxylamines **4**.



Scheme 4 Reaction of *O*-thiopivaloyl-*N*-*tert*-butylhydroxylamine **7b** with dithiophosphoric acid **1**.



Scheme 5 Synthesis of thiophosphoryl thiopivaloyl disulfides **11**–**13**.



Scheme 6 Reaction of *O*-thioacylhydroxylamines with dithiophosphoric acids; mechanism hypothesis.

phosphoric) acids **8**–**10** yields respective acyl thiophosphinyl (thiophosphoryl) disulfides **11**–**13**. Hence, the reaction is likely to be characteristic not only for cyclic acid **1** but also for other dithioacids of phosphorus (Scheme 5). It is noteworthy that instead of two equivalents of a dithiophosphoric acid, only one can be used together with one equivalent of another strong, weakly nucleophilic acid (trifluoroacetic acid) for protonation of the amine formed in the course of the reaction.

The next interesting area to discuss is the mechanism of the new reaction of *O*-thioacylated hydroxylamines with dithiophosphoric acids.

From the theoretical point of view disulfide **5** can be formed in the discussed reaction as a product of the thiophilic attack of the dithiophosphate anion on the sulfur atom of the thiocarbonyl group in protonated *O*-thioacylhydroxylamine **7** (Pathway A, Scheme 6) (Since *O*-thioacylhydroxylamine is a

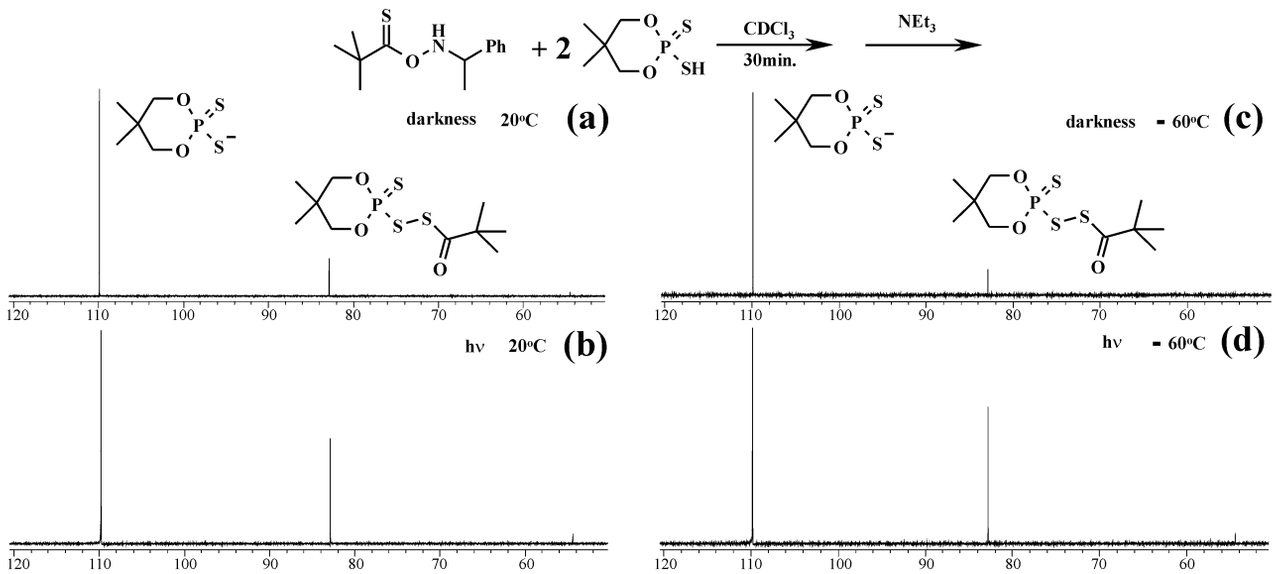


Fig. 1 ^{31}P NMR spectra of reaction mixtures formed from *O*-thiopivaloyl-*N*-(1-phenylethyl)hydroxylamine **7c** and dithiophosphoric acid **1** under different experimental conditions.

base, in the first stage it should be protonated by the strong dithiophosphoric acid.) On the other hand, it is well known that dithiophosphate anions easily undergo one-electron oxidation.[6] Consequently, the dithiophosphate anions can act in the investigated reaction as a single electron donor and disulfide **5** can be formed as a product of the SET process (Pathway B, Scheme 6).

In Pathway B the principal process is the single electron transfer from dithiophosphate anion to the protonated form of *O*-thioacylhydroxylamines producing the amine and acylsulfenyl radical. The key step in the mechanism outlined in Scheme 6 Pathway B is the formation of the disulfide anion radical as a consequence of the reaction between the acylsulfenyl radical and dithiophosphate anion. Subsequent electron transfer from the disulfide anion radical to *O*-thioacylhydroxylamine completes the propagation sequence.

During oxidation of carboxylate anions decarboxylation of the transient carboxyl radicals leads to alkyl radicals (Kolbe reaction). It can be asked why acylsulfenyl radicals formed during the reaction in focus do not undergo this type of transformation. It was demonstrated[7] that during electrooxidation of monothiocarboxylate anions the acylsulfenyl radicals dimerize into diacyl disulfides without decomposition to alkyl radical and carbon monoxide monosulfide.

Light may speed up a radical anion substitution process. Numerous instances of light effects have been found, some of them very substantial. In general, it appears that visible or near ultraviolet light is effective in promoting these reactions and, indeed, all that is required is illumination by ordinary fluorescent light.[8,9]

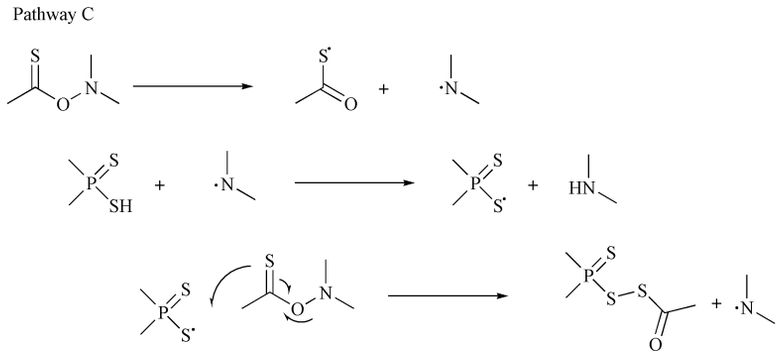
In order to provide evidence for the SET mechanism involvement in the reaction under discussion we monitored the reaction between two equivalents of dithiophosphoric acid **1** and *O*-thiopivaloyl-*N*-(1-phenylethyl)hydroxylamine **7c** (we changed the model compound due to the high volatility of *O*-thiopivaloyl-*N*-*tert*-butylhydroxylamine **7b**). The reaction was carried out for 30 minutes in $CDCl_3$ under a variety of conditions: at −60 °C as well as at 20 °C, in darkness and under irradiation with a 500 W bulb. After 30 min we quenched the reaction mixture with a 10 molar excess of triethylamine to avoid any progress of the reaction after warming up, during analysis *etc.* In these experiments, we observed the formation of disulfide **5a** (δ_P 83 ppm) and we found a substantial influence of light on the yield of the disulfide formation (Fig. 1). As one can see from the presented ^{31}P NMR spectra, the relative signal intensity of the products changes when comparing the reaction mixtures obtained in darkness to the irradiated ones. Especially significant changes can be observed when the reactions were carried out at −60 °C.

Thiophenols are known to be free radical traps. Thus, we decided to perform the reaction between *O*-thiopivaloyl-*N*-phenethylhydroxylamine **7c** and dithiophosphoric acid **1** in the presence of 2,6-dimethylthiophenol **14**, in darkness and under irradiation with a 500 W bulb. After 30 minutes the reaction mixture was quenched with triethylamine and examined using ^{31}P NMR. The spectrum of the reaction mixture formed in darkness exhibited one resonance line at 110 ppm attributed to triethylammonium dithiophosphate **3a**, and no disulfide formation was observed. The spectrum of the reaction mixture formed under irradiation with a 500 W bulb exhibited two resonance lines: at 110 ppm (very intense) and 82 ppm (very weak), attributed to triethylammonium dithiophosphate **3a** and traces of disulfide **5a** respectively (Fig. S1). † These experiments show that 2,6-dimethylthiophenol prevents the formation of disulfide **5a**.

One may argue that formation of disulfide **5** might have been inhibited due to the reaction of the thiophenol with *O*-thioacylhydroxylamine. Therefore we monitored the reaction of *O*-thioacylhydroxylamine **7c** with dithiophosphoric acid **1** in the presence of 2,6-dimethylthiophenol **14** using ^{1}H NMR. After 30 min and even after 20 h we observed only the resonance lines responsible for the starting materials (Fig. S2). † This set of experiments confirms that a radical scavenger like 2,6-dimethylthiophenol completely inhibits the reaction under discussion, hence radical species should be involved in the reaction mechanism.

The fact that *O*-thiopivaloyl-*N*-(1-phenylethyl)hydroxylamine **7c** does not react with dithiophosphoric acid **1** in darkness under the applied reaction conditions, and only irradiation (or daylight exposure) leads to disulfide formation, excludes the possibility of an ionic mechanism (Scheme 6, Pathway A). Also adding a radical scavenger like 2,6-dimethylthiophenol prevents the formation of disulfide **5**. The results of the performed experiments are compatible with the proposed SET mechanism (Pathway B) presented in Scheme 6.

However, at this point one can also argue that during light irradiation of *O*-thioacylhydroxylamines, homolytic cleavage of the N–O bond can lead to aminyl and acylsulfenyl radicals. These radicals can initiate the radical chain process (Scheme 7, Pathway C) leading to disulfide **5**.



Scheme 7 Possible reaction mechanism for the reaction of *O*-thioacylhydroxylamines with dithiophosphoric acids.

Such a hypothesis has two weak points. The intermediate aminyl radicals are relatively unstable, and the reaction should not be stopped by triethylamine addition (there is no step where protonation is necessary). However, experimental proof was required.

To distinguish between Pathways B and C we designed a new set of experiments. The key step in Pathway C is the homolysis process of the N–O bond (initiation step). Therefore, we irradiated the solution of *O*-thiopivaloyl-*N*-(1-phenylethyl)hydroxylamine with a 500 W tungsten lamp for 30 min at −60 °C. In this experiment we did not observe any products of homolysis. Even after 24 h of irradiation at room temperature there was no change in the reaction mixture (^{1}H NMR) and we isolated the starting material (Fig. S3).† The results of these experiments exclude the possibility of Pathway C for the reaction between *O*-thioacylhydroxylamines and dithiophosphoric acid.

Conclusions

To summarize, we found that *O*-thioacylhydroxylamines react with dithiophosphoric (dithiophosphinic) acids yielding acyl thiophosphoryl disulfides and amines. The reaction is inhibited in darkness and in the presence of radical traps. Considering that *O*-thioacylhydroxylamines are resistant to light in the applied reaction conditions, it is very likely that an $S_{RN}1$ mechanism is involved in the reaction under discussion.

Experimental

Reaction of thiopivaloyl (5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphinan-2-yl) sulfide (2a) with *N*-isopropylhydroxylamine (4a) or *N*-*tert*-butylhydroxylamine (4b); general procedure

Triethylamine (0.167 g, 1.65 mmol) was added to a suspension of *N*-isopropylhydroxylammonium oxalate (0.083 g, 0.5 mmol) in 1 cm^3 of chloroform (or 0.056 g, 0.55 mmol of triethylamine was added to a solution of 0.045 g of *N*-*tert*-butylhydroxylamine in 1 cm^3 of chloroform). Next, a solution of thiopivaloyl (5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphinan-2-yl) sulfide (0.149 g, 0.5 mmol) in 2 cm^3 of chloroform was added. The reaction mixture turned pale yellow. The reaction mixture was washed with 5% HCl (aq), then water; dried with $MgSO_4$, and after solvent evaporation was subjected to column chromatography (eluent: hexane–chloroform, 2 : 3) yielding 0.112 g (71.3%) (or 0.128 g, 81%) of pivaloyl (5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphinan-2-yl) disulfide (**5a**) respectively; mp 62–64 °C; ν_{max}/cm^{-1} 2968, 2933, 2883 (C–H), 1730 (C=O), 1045, 955 (P–O–C), 684 (P=S); δ_P($CDCl_3$) 83.18; δ_H($CDCl_3$) 4.38 (2H, dd, J_{H-H} 11.2, J_{P-H} 6.4, Me_2CCH_2O), 3.96 (2H, dd, J_{H-H} 11.2, J_{P-H} 22.9, Me_2CCH_2O), 1.31 (9H, s, Bu^t), 1.24 (3H, s, $(CH_3)_2$-CCH_2O), 0.95 (3H, s, $(CH_3)_2CCH_2O$); δ_C($CDCl_3$) 201.13 (C=O), 78.63 (d, J_{P-C} 9, Me_2CCH_2O), 47.4 ($C(CH_3)_3$), 32.65 (d, J_{P-C} 7.1, Me_2CCH_2O), 22.29 ($(CH_3)_2CCH_2O$), 21.13 ($(CH_3)_2CCH_2O$); *m*/*z* 314.0234 ($C_{10}H_{19}O_3PS_3$ requires 314.02044).

In order to monitor the formation of disulfide **5a** the reaction of hydroxylamine **4b** with anhydride **2a** was repeated and analytical samples were taken after mixing the starting materials and after washing the reaction mixture with HCl solution. Before washing the reaction mixture with aqueous HCl, only the signal of the 5,5-dimethyl-2-sulfanyl-2-thioxo-1,3,2-dioxaphosphinan salt (δ_P 106) was present in the ^{31}P NMR spectrum; after washing the reaction mixture with aqueous HCl, only the signal of pivaloyl (5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphinan-2-yl) disulfide (**5a**) δ_P 83.2 was observed.

Reaction of *O*-thiopivaloyl-*N*-*tert*-butylhydroxylamine (7b) with 5,5-dimethyl-2-sulfanyl-2-thioxo-1,3,2-dioxaphosphinan (1)

A solution of 5,5-dimethyl-2-sulfanyl-2-thioxo-1,3,2-dioxaphosphinan (0.396 g, 2 mmol) in 2 cm^3 of $CDCl_3$ was added to a solution of *O*-thiopivaloyl-*N*-*tert*-butylhydroxylamine (0.189 g, 1 mmol) in 2 cm^3 $CDCl_3$. After 15 min a ^{31}P NMR spectrum was taken showing the presence of the *tert*-butylammonium salt of 5,5-dimethyl-2-sulfanyl-2-thioxo-1,3,2-dioxaphosphinan δ_P 108.53 and pivaloyl (5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphinan-2-yl) disulfide (**5a**) δ_P 83.19. Next, D_2O (10 cm^3) was added. After stirring for 20 min, the organic layer was separated, dried with $MgSO_4$ and the solvent was removed yielding 0.29 g (92%) of pivaloyl (5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphinan-2-yl) disulfide (**5a**). The water layer was subjected to NMR analysis: δ_P 103.1 and δ_H 3.85 (4H, d, *J* 15), 1.23 (9H, s), 0.87 (6H, s) and subsequent evaporation yielded 0.27 g (99%) of the *tert*-butylammonium salt of 5,5-dimethyl-2-sulfanyl-2-thioxo-1,3,2-dioxaphosphinan.

Reaction of *O*-thiopivaloyl-*N*-alkylhydroxylamines (7a–d) generated *in situ* with 5,5-dimethyl-2-sulfanyl-2-thioxo-1,3,2-dioxaphosphinan (1); NMR identification of the products

Triethylamine (0.051 g, 0.5 mmol) was added to a solution (suspension) of *N*-alkylhydroxylamine (**4a**–**d**) (0.5 mmol) in $CDCl_3$ (1 cm^3). (When *N*-alkylhydroxylammonium oxalate was used then 0.152 g (1.5 mmol) of triethylamine was used.) Next a solution of thiopivaloyl (5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphinan-2-yl) sulfide (0.149 g, 0.5 mmol) in $CDCl_3$ (2 cm^3) was added. After 15 min the ^{31}P NMR spectrum was taken, and only the signal of 5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphinan-2-thiolate (δ_P 106–110 ppm) was present. Next 5,5-dimethyl-2-sulfanyl-2-thioxo-1,3,2-dioxaphosphinan (**1**) (0.198 g, 1 mmol) was added. After 5 min the ^{31}P NMR spectrum was taken: besides the signal of acid **1** salt, the signal of pivaloyl 2-(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphinanyl) disulfide (**5a**) (δ_P 83.16–83.22) was also present. After a further 5 min D_2O (5 cm^3) was added. Then after 10 min of intensive stirring the ^{1}H NMR spectrum of the water layer was taken: signals of the respective *N*-alkylammonium 5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphinan-2-thiolate (**3b**–**e**) were present (as confirmed by original sample addition) and traces of the respective hydroxylamine (dithiophosphate salts) were detected as well.

Pivaloyl thiophosphoryl disulfides 11–13; general procedure

A solution of dithiophosphoric (dithiophosphinic) acid (2 mmol) in methylene chloride (3.5 cm^3) was added to a solution of *O*-thiopivaloyl-*N*-(1-phenylethyl)hydroxylamine (0.173 g, 1 mmol) in methylene chloride (3.5 cm^3). After 15 min the reaction mixture was filtered through a short pad of silica gel. Solvent removal yielded pure product.

Diphenylthiophosphinoyl pivaloyl disulfide (11). Yield 98.1%; mp 107–108 °C; $\delta_P(CDCl_3)$ 71.73; $\delta_H(CDCl_3)$ 7.98 (4H, dd, J_{P-H} 14.2, J_{H-H} 7.8; *o*-C_6H_5), 7.55 (2H, td, J_{H-H} 7.3, J_{P-H} 2, *p*-C_6H_5), 7.45 (4H, td, J_{H-H} 7.3, J_{P-H} 3.9, *m*-C_6H_5), 1.19 (9H, s, Bu^t); $\delta_C(CDCl_3)$ 200.5 (C=O), 133.09 (d, J_{P-C} 82.9, *C*$(CHCH)_2CH$), 132.58 (d, J_{P-C} 3.2, $C(CHCH)_2$*C*H), 132.54 (d, J_{P-C} 11, $C(CH$*C*$H)_2CH$), 128.79 (d, J_{P-C} 13.3, $C($*C*$HCH)_2CH$), 47.48 ($C(CH_3)_3$), 27.57 ($C($*C*$H_3)_3$); *m*/*z* 366.03312 ($C_{17}H_{19}OPS_3$ requires 366.03356).

Bis(4-*tert*-butylphenoxy)thiophosphoryl pivaloyl disulfide (12). Yield 95.7%; $\delta_P(CDCl_3)$ 81.25; $\delta_H(CDCl_3)$ 7.41 (4H, d, *J* 7.3, $OC(CH$*C*$H)_2CBu^t$), 7.26 (4H, d, *J* 7.3, $OC(CHC$*H*$)_2CBu^t$), 1.35 (18H, s, $Bu^tC_6H_4$), 1.34 (9H, s, Bu^tCO); $\delta_C(CDCl_3)$ 199.59 (C=O), 148.9 (Bu^t*C*$(CHCH)_2CO$), 148.38 (d, J_{P-C} 9.2, $Bu^tC(CHCH)_2$*C*O), 126.75 ($Bu^tC($*C*$HCH)_2CO$), 121.62 (d, J_{P-C} 5.1, $Bu^tC(CH$*C*$H)_2CO$), 37.51 ($(CH_3)_3$*C*CO), 34.75 ($(CH_3)_3$-*C*C_6H_4), 31.69 ((C*H*$_3)_3CC_6H_4$), 27.53 ((C*H*$_3)_3CCO$); *m*/*z* 468.10205 ($C_{22}H_{29}O_3PS_3$ requires 468.10164).

Diisopropoxythiophosphoryl pivaloyl disulfide (13). A solution of triethylammonium *O*,*O*-diisopropyl dithiophosphate (0.315 g, 1 mmol) was used instead of 2 mmol of the free acid, and subsequently trifluoroacetic acid (0.228 g, 2 mmol) was added dropwise. Yield 99.1%; $\delta_P(CDCl_3)$ 81.25; $\delta_H(CDCl_3)$ 4.86 (2H, m, C*H*), 1.37 (6H, d, *J* 5.9, $(CH_3)_2CH$), 1.35 (6H, d, *J* 6.3, $(CH_3)_2CH$), 1.31 (9H, s, Bu^t); $\delta_C(CDCl_3)$ 200.58 (C=O), 74.64 (d, J_{P-C} 5.5, *C*H), 47.32 ($C(CH_3)_3$), 24.01 (d, J_{P-C} 4.1, $(CH_3)_2CH$), 23.61 (d, J_{P-C} 5.9, $(CH_3)_2CH$), 27.57 ($C(CH_3)_3$) *m*/*z* 330.05451 ($C_{11}H_{23}O_3PS_3$ requires 330.05469).

Reaction of *O*-thiopivaloyl-*N*-(1-phenylethyl)hydroxylamine (7c) with 5,5-dimethyl-2-sulfanyl-2-thioxo-1,3,2-dioxaphosphinan (1) under a variety of reaction conditions; general procedure

A $CDCl_3$ solution of 5,5-dimethyl-2-sulfanyl-2-thioxo-1,3,2-dioxaphosphinan (400 mM, 0.5 cm^3) was added to a solution of *O*-thiopivaloyl-*N*-(1-phenylethyl)hydroxylamine (200 mM, 0.5 cm^3). The reaction mixture was stirred for 30 min and triethylamine (0.101 g, 1 mmol) was added to prevent further reaction. Next, the ^{31}P NMR (^1H NMR) spectrum was taken. The reaction was repeated at room temperature, at −60 °C; in darkness (reaction flask tightly covered with aluminium foil), on irradiation (500 W tungsten lamp at 30 cm distance from the reaction vessel); and in the presence of 2,6-dimethylthiophenol (0.014 g, 0.1 mmol). The reaction flask was dipped in methanol for easier temperature control. The results are shown in Fig. 1, S1, S2†.

The stability of *O*-thiopivaloyl-*N*-(1-phenylethyl)hydroxylamine (7c) under the influence of light

A solution of *O*-thiopivaloyl-*N*-(1-phenylethyl)hydroxylamine (0.024 g, 0.1 mmol) in $CDCl_3$ (0.7 cm^3) placed in an NMR tube was dipped in methanol and was irradiated with a tungsten lamp (500 W, 30 cm distance from the reaction vessel) maintaining a temperature of −60 °C. After 30 min the solution was warmed up to room temp. and the ^1H NMR spectrum was taken. Next spectra were taken after 30 min and 24 h of irradiation at rt. Finally, the solvent was evaporated off yielding quantitatively unchanged starting material.

Acknowledgements

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