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On the Reaction of Bis(phosphothioyl)disulfanes with Hydroxamic Acids, Part I: Ionic versus Radical Reaction Pathways

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ABSTRACT: *Among sodium N-alkyl-4-chlorobenzohydroxamates treated with bis(phosphothioyl)disulfanes >P(S)SSP(S)< (where >P(S) is phosphorothioyl, phosphonothioyl, and phosphinothioyl), only the N-methyl one yields quantitatively the respective O-phosphothioyl derivatives exhibiting complete inversion of configuration at phosphorus in a reaction whose products are inert toward dithiophosphate arising in the reaction. For branched N-alkyl benzohydroxamates, products of a SET process predominated. The mechanism of the title reaction is discussed.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:271–282, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20423

INTRODUCTION

Disulfanes **1** have found wide practical application and are involved in some important technical processes. They are used as stabilizers for polymer compositions [1], vulcanization accelerators [2], antioxidant and antiwear additives in engine lubricant oil additives [3], and as highly effective sulfurizating agents [4] in organic synthesis. Some of them are physiologically active compounds with both insecticidal and fungicidal activity [5]. Phostex—a mixture of bis(dialkoxyphosphinethioyl)disulfanes—is the only one representative of disulfanes **1** among commercial organophosphorus pesticides in use.

Chemical properties of bis(phosphothioyl)disulfanes **1** are not nearly as well documented as those of other phosphothioyl derivatives, but it is known that in **1**, like in other phosphorus pseudohalogens, the reactive disulfane unit exhibits strong sulfur cationoid properties. The S—S bond is readily cleft by nucleophiles [6] and metal species [7] with formation of stable dithioacid anion or its metal complexes, respectively. Amines, cyanide, and organometallic compounds react in this manner. It should be emphasized that this mechanism is not exclusive. In situ generated dithioacid anion or an external nucleophile can dealkylate the disulfane when an alkoxy group is attached to the phosphorus. Thus, primary amines are able to dealkylate both methoxy- and isopropoxy-substituted disulfanes **1**.

There is still a pressing need to develop effective methods for detoxification of neurotoxic organophosphorus compounds. The reaction with supernucleophiles is one of the most frequently studied. For the first time, it was found that benzohydroxamic acids accelerate the hydrolysis of diisopropyl fluorophosphates (DFP) and isopropyl methylphosphonofluoridate (sarin) by the factor of 100 and even more at higher pH [8]. Also other phosphoric acid derivatives (mainly esters) hydrolysis mediated by hydroxamate **2** was investigated except for bis(phosphothioyl)disulfanes **1**. It was postulated that the corresponding *O*-phosphorylated hydroxamic acids are the primary products of hydroxamate-catalyzed hydrolysis, but they were never detected or isolated from aqueous media [9].

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According to HSAB theory, a hydroxamate anion **2**, being a hard base, should react preferably with a hard electrophilic phosphorus atom of disulfane **1** rather than with a soft sulfur atom. On the other hand, *O*-phosphothioylated hydroxamic acids **3**, that is, the potential products of hydroxamate attack on phosphorus in **1**, are an unexplored class of compounds. Only one patent deals with the preparation of *N*-methyl-*N*-diethoxyphosphinthioyloxy acetamide starting from *N*-chloro-*N*-methylacetamide in moderate yield [10]. Recently, we isolated *N*-isopropyl-*N*-[methoxy)(4-methoxyphenyl)-phosphinothioyloxy]benzamide from the reaction mixture of the corresponding hydroxamic acid and Lawesson's reagent (LR) [11].

The reactivity of hydroxamic acid mixed anhydrides exemplified by **3** toward nucleophiles can be complex and should depend not only on the relative electrophilicity of both centers (localized at nitrogen or phosphorus atoms) and on steric hindrance but also on the acidity of the leaving group and on the nature of the nucleophile. For example, the sulfur nucleophile attack at the nitrogen atom of **3** gives products with a weak N—S bond. On the other hand, *O*-thioacylated hydroxamic acids are known to undergo rearrangement to unstable *S*-acylthiolobenzamides, which decompose further to benzamides [12]. *O*-Phosphothioylated hydroxamic acids **3** are structural analogs of the corresponding *O*-(thio)acylated and *O*-sulfonylated hydroxamic acids. It would, therefore, be interesting to compare their chemical properties.

The purpose of this paper is to report a new reaction of various disulfanes **1** with *N*-alkyl-4-chlorobenzohydroxamates **2**. Effects of chemical structure and reaction conditions have been studied. Some preliminary results concerning the reactivity of *O*-phosphothioylated hydroxamic acids **3** as sole products of the title reaction are also presented.

RESULTS AND DISCUSSION

To investigate the effect of substituents at the phosphorus atom, a series of disulfanes **1a–h**, derivatives of phosphoro-, phosphono-, and phosphinodithioic acids, have been prepared (Table 1). 4-Methoxyphenylphosphonodithioic acid derivatives (**1e, 1g, 1h**) are new compounds and have been fully characterized. **1e** was isolated as a pure (S$_P$, S$_P$) diastereomer. The X-ray crystal structure analysis (Fig. 1) of compound **1e** shows that the geometry and absolute configuration at both phosphorus atoms are the same as that of a related bis[(−)-menthyloxyphenylphosphinothioyl]disulfane [13].

TABLE 1 Disulfanes **1** Used in the Reaction with Hydroxamates **2**

Compound	*Y^1*	*Y^2*	*δ_P (ppm)*
1a	O*i*Pr	O*i*Pr	82.7
1b	Ph	Ph	62.2
1c	Ans[a]	OMe	92.8, 93.0
1d	Ans	OiPr	85.8
1e	Ans	(–)-O-Menthyl	86.1
1f	Ans	$>C(CH_2O)_2$	88.7
1g	Ans	NH*i*Pr	72.2, 74.2
1h	Ans	N(*i*Pr)$_2$	87.7

[a] Ans = 4-Methoxyphenyl.

It was observed that bis(phosphonothioyl)disulfanes **1c–h** were more labile than the corresponding bis[phosphoro(ino)thioyl]disulfanes **1a, 1b** and slowly lost sulfur during their storage. The nature of this behavior is not clear yet. In addition, it was found that repeated crystallization might cause transesterification. When **1e** was recrystallized three times from isopropanol, it quantitatively transformed into **1d**.

Disulfanes **1** were treated with benzohydroxamate salts **2** in THF at room temperature. Using tertiary amines or nonnucleophilic amidines (DBU) as bases should be avoided because they do not fully deprotonate the starting hydroxamic acid and are not inert toward the disulfanes **1** under study. Therefore, it was observed that disulfanes **1a** and **1b**

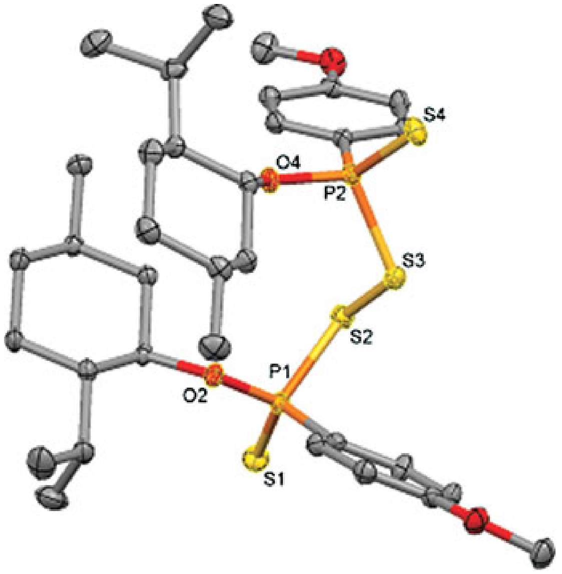


FIGURE 1 X-ray structure of **1e**. Selected bond lengths (Å) and angles (°): P(1)–S(1) 1.9353(5), P(1)–S(2) 2.112596), S(2)–S(3) 2.0786(5), P(1)–O(2) 1.585(1), P(1)–C(5) 1.795(1), S(1)–P(1)–S(2) 105.16(2), S(3)–S(2)–P(1) 104.44(2), S(1)–P(1)–S(2)–S(3) 161.74(2), P(1)–S(2)–S(3)–P(2) −112.68(2).

TABLE 2 Products of the Reaction of Disulfanes **1** with Hydroxamates **2**

Entry	**3**[a] *(Yield)* δ_P *(ppm)*	**4** δ_P (ppm)	*Other Products (Yield)*
1	**3aa** (92) 70.0	**4a** 109.8	–
2	**3ab** (89) 94.2	**4b** 62.7	–
3	**3ac** (82) 97.7	**4c** 111.4	**5** (12)
4	**3ad** (95) 94.0	**4d** 110.6	–
5	**3ae** (90) 93.7	**4e** 111.2	–
6	**3af** (100)[b] 96.0/103.3		**3af′** (98)[c]
7	**3ag** (91) 88.2	**4g** 72.8	–
8	**3ah** (nd)[d] -	-	–
9	**3ba** (30) 72.9	**4a** 109.8	**1a** (28); **9b** (7); **10b** (8); **11** (3)
10	**3be** (35) 94.2 and 96.2	**4e** 110.0	**1e** (12); **9b** (9); **10b** (10)
11	**3ca** (nd)[d] -	**4a** 109.8	**9c** (9); **10c** (30)

[a] The two letters in the designation for **3** refer first to the identity of R and second to the identity of Y^1 and Y^2.
[b] Determined by ^{31}P NMR.
[c] After quenching with CH_3I.
[d] Not detectable after 6 h.

underwent fast decomposition upon DBU action in chloroform solution (browning). ^{31}P NMR analysis confirmed the formation of DBU salts of the corresponding phosphodithioic acids besides unidentified phosphorus products. Hence, the best results (total consumption of **1**) were achieved if sodium hydroxamate **2a** was generated by the use of NaH and was taken in the excess as a solution or as a solid (Table 2, entries 1–7). The reaction was completed in 20 min using 2 equivalents of **2a**. Disulfanes **1a, 1b**, and **1d–g** afforded products **3** in nearly quantitative yield. In the case of **1c** (entry 3) by-product, namely *O*,*S*-dimethyl (4-methoxyphenyl)phosphonodithioate **5** (δ_P 99.8 ppm) was isolated in 12% yield. Its formation was probably resulted from dealkylation of **3ac** by phosphonodithioate salt **4c** arising in the reaction, but the presence of the corresponding dealkylation product was not confirmed experimentally because of its instability. It is interesting that the presence of the acidic hydrogen atom and the nitrogen atom in disulfane **1** structure does not influence the course of the reaction. It is obvious that the negative charge at the nitrogen atom in **1g** should repel the attacking **2** and lone electron pairs at the nitrogen in **1g** and **1h** decrease the electrophilic character of the phosphorus center. But both these electron effects playing substantial role in **1g** and **1h** seem to have no importance in this particular reaction, and the total inertness of **1h** is likely due to steric factors.

The reaction was also studied using optically pure disulfane /S$_P$, S$_P$/–**1e**. X-ray analysis showed that the product /S$_P$/–**3ae** (Fig. 2) was formed with a complete inversion of configuration. Therefore, the reaction has an ionic character and proceeds via an S_N2P mechanism at the phosphorus atom. CCDC-635363 (for **1e**) and CCDC-635364 (for **3e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

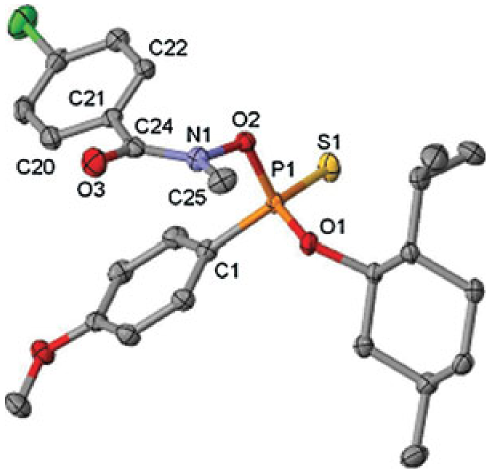
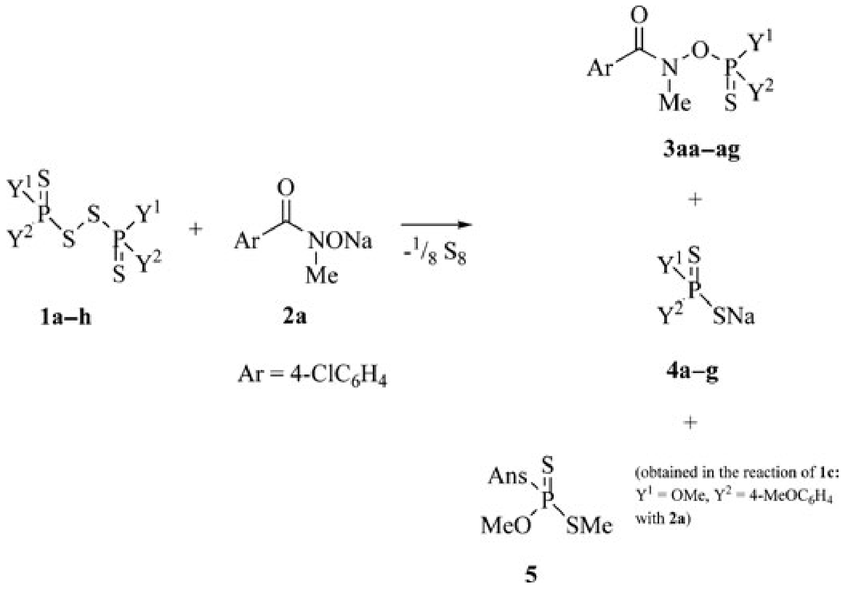


FIGURE 2 X-ray structure of **3ae**. Selected bond lengths (Å) and torsion angles (°): P(1)–S(1) 1.9169(8), P(1)–O(1) 1.576(1), P(1)–O(2) 1.648(2), N(1)–O(2) 1.420(2), C(24)–O(3) 1.229(3), O(2)–N(1)–C(24)–O(3) −179.4(2), C(25)–N(1)–C(24)-O(3) −7.4(4), C(20)–C(21)–C(24)–O(3), −32.5(3).

In all the reactions under study, phosphodithioate salts **4** and sulfur always accompany the main product **3** (Scheme 1). According to a proposed reaction mechanism (Scheme 2), hydroxamate **2** could attack both electrophilic centers, that is, the phosphorus and sulfur atoms.

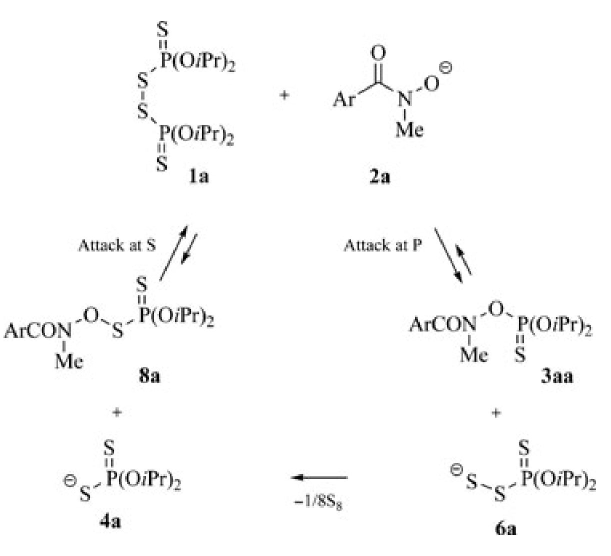
It should be noted that the attempts to detect the presence of (phosphothioyl)disulfane anion **6a** failed. Immediately after mixing the reagents, an additional resonance at δ_P 83.2 ppm (2% of **1a** intensity) was observed, but quenching with methyl iodide gave only the signal of the corresponding phosphorodithioic acid *O*,*O*-diisopropyl *S*-methyl ester **7** (δ_P 92.0 ppm) in place of the signal of **4a**. Therefore, it is clear that the signal at δ_P 83.2 ppm cannot correspond to (phosphothioyl)disulfane anion **6a** due to its expected high nucleophilicity, but rather to an additional by-product, likely with the "NOSP" unit (**8a**).

Performed experiments clearly indicate that only *N*-methyl hydroxamate **2a** gives products **3** quantitatively. **2b** produces **3** with lower yields (30%–35%), and **2c** does not yield any detectable amounts of **3**. A deep green coloration appears immediately after



SCHEME 1

mixing hydroxamate **2c**, and disulfanes **1** indicates the formation of acylaminoxyl radical **2c**′, which was detected by EPR. As is seen from Fig. 3, EPR spectrum of the above-mentioned reaction mixture consists of a broad and intense three-line signal with parameters correspond to radical **2c**′ ($a_N = 0.79$ mT, $g = 2.0068$). Its linewidth does not exclude the presence of other transient species such as benzoyl, phosphothyil, or aminoxyl radicals, besides the most persistent acylaminoxyl **2c**′ that was still observed even after 20 h. During the course of the reaction, the coloration turns blue due to the formation of 2-methyl-2-nitrosopropane and remains unchanged. It indicates that 2-methyl-2-nitrosopropane is not an efficient trap for above-mentioned radicals.



SCHEME 2

Isolation of *N*-alkyl-4-chlorobenzamides (**9b, 9c**), *N*-alkyl-*N*,*O*-bis(4-chlorobenzoyl)hydroxylamines (**10b, 10c**), and *O*-(4-chlorobenzoyl)acetoxime **11** (Table 2, entries 9–11) provides additional, strong evidence for radical intermediates and a SET pathway. Therefore, it is reasonable to assume that an electron transfer from hydroxamate **2**

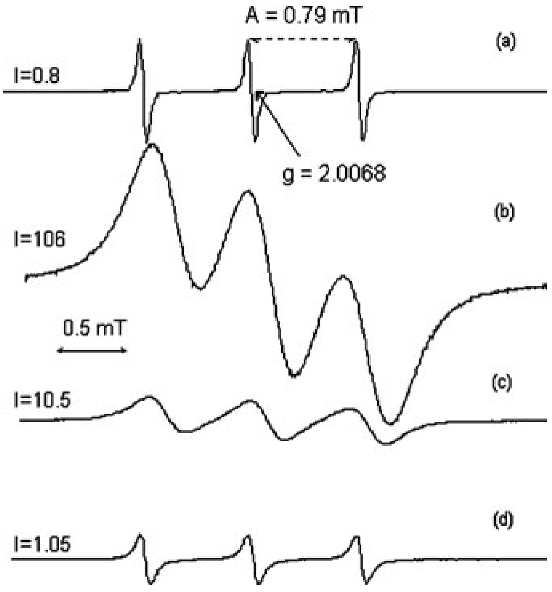
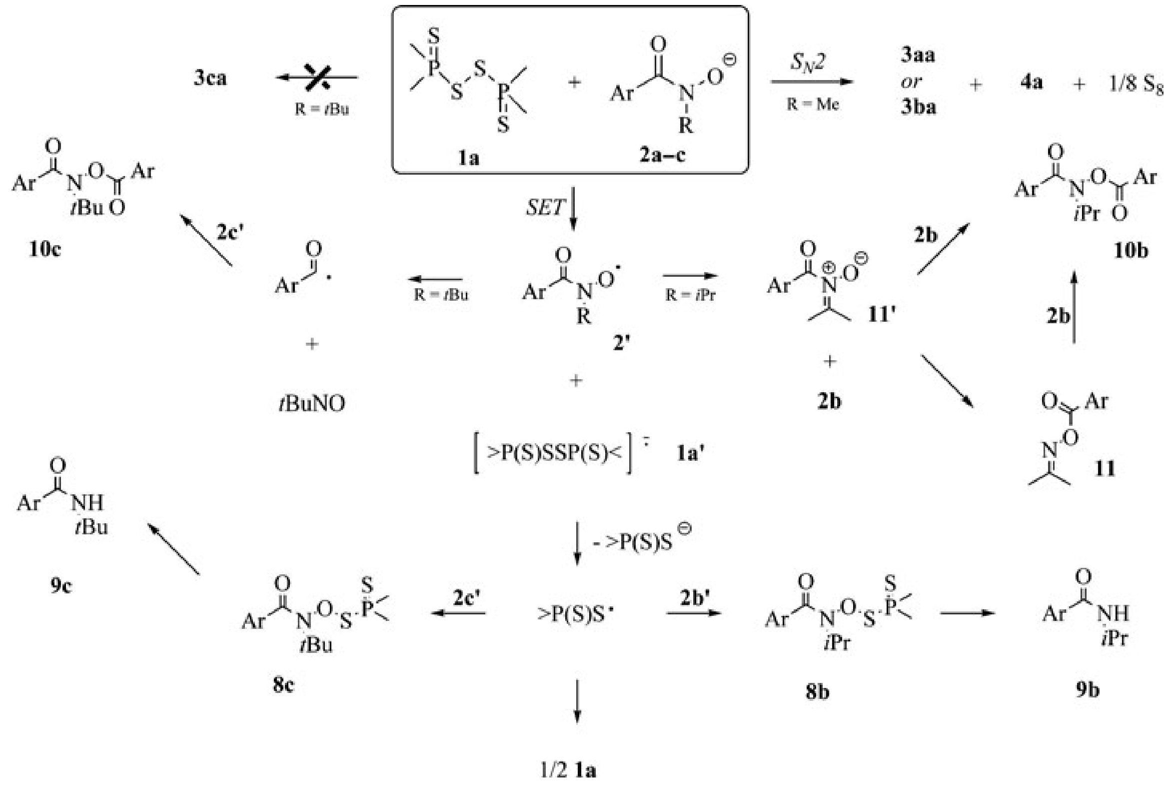


FIGURE 3 (a) EPR spectrum of acylaminoxyl radical **2c**′ spontaneously formed from **2c** in THF solution (17×10^{-3} M) exposed to air; (b) broad and strong EPR signals obtained immediately after treating **2c** with disulfane **1a**; (c) and (d) the decrease of intensity of the triplet observed after 25 min and 20 h, respectively, following disulfane addition.



SCHEME 3

affords the corresponding bis(phosphoyl)disulfane radical anion $[>P(S)SSP(S)P<]^-$ **1′** and *N*-alkylacylaminoxyl **2′**. **2′** undergoes a disproportionation to yield hydroxamate **2b** and *N*-acylnitrone **11′** or cleaves into 2-methyl-2-nitrosopropane and acyl radical. Next, subsequent self-reactions lead to *N*-acyloxybenzamides **10** [14]. Isomerization of **11′** and its reaction with acetoxime give *O*-(4-chlorobenzoyl)acetoxime **11** exclusively. Benzamides **9b** and **9c** are presumably formed from the corresponding **8** precursors, because it is well known that acylaminoxyl radicals do not decompose into amides, and in addition we found that derivatives **10** are stable and are not cleaved by nucleophilic **4a** (4 days at room temperature). Bis(phosphothioyl)disulfane radical anion **1′** splits into a thyil radical (dimerizes to **1**) and an anion **4** (Scheme 3). The recovery of a diastereomeric mixture of **1e** (Fig. 4; Table 2, entry 10) in the reaction of optically pure **1e** with **2b**, which exhibits the considerably decreased optical rotation value (from +228.6 to +2.5) and isolation of **3be** as two diastereomers in a 2:1 ratio, confirms unambiguously the participation of thyil radicals in the reaction under investigation.

Therefore, on the basis on the structure of the identified products, it can be deduced that an ionic, a mixed ionic radical, and a pure radical mechanism exist for the reaction of **1** with **2a, 2b**, and **2c**, respectively.

Obviously, this contrasting behavior of hydroxamates **2** under investigation is caused by their oxidation potential differences and the steric hindrance around the oxygen atom. Among *N*-alkyl benzohydroxamates, the most crowded *N-tert*-butyl one **2c** has the lowest oxidation potential (according to the literature data $E_{ox} = +0.25$, [15], -0.77 and -0.88 V [16] versus F_c/F_{c+} for *N*-methyl, *N-i*-Pr, and *N-t*-Bu benzohydroxamate, respectively).

In the previous report, we found that phosphorodithioates **4** caused the N—O bond cleavage in *O*-thioacylohydroxyloamines [17]. Additional experiments showed that **3a** did not react with phosphodithioate salts **4a** at all (^{31}P NMR analysis). Likewise, no intramolecular nucleophilic substitution (on a nitrogen or phosphorus atom) occurred if the additional phosphodithioate was tethered in the structure of **3af** (the formation of **3af** was as a result of the cyclic disulfane **1f** opening) (Scheme 4). ^{31}P NMR spectrum of the reaction mixture (entry 6) contained only two signals of **3af′**. Its derivative, *S*-methyl ester **3af′**, was isolated in quantitative yield after treating the above-mentioned reaction mixture with methyl iodide.

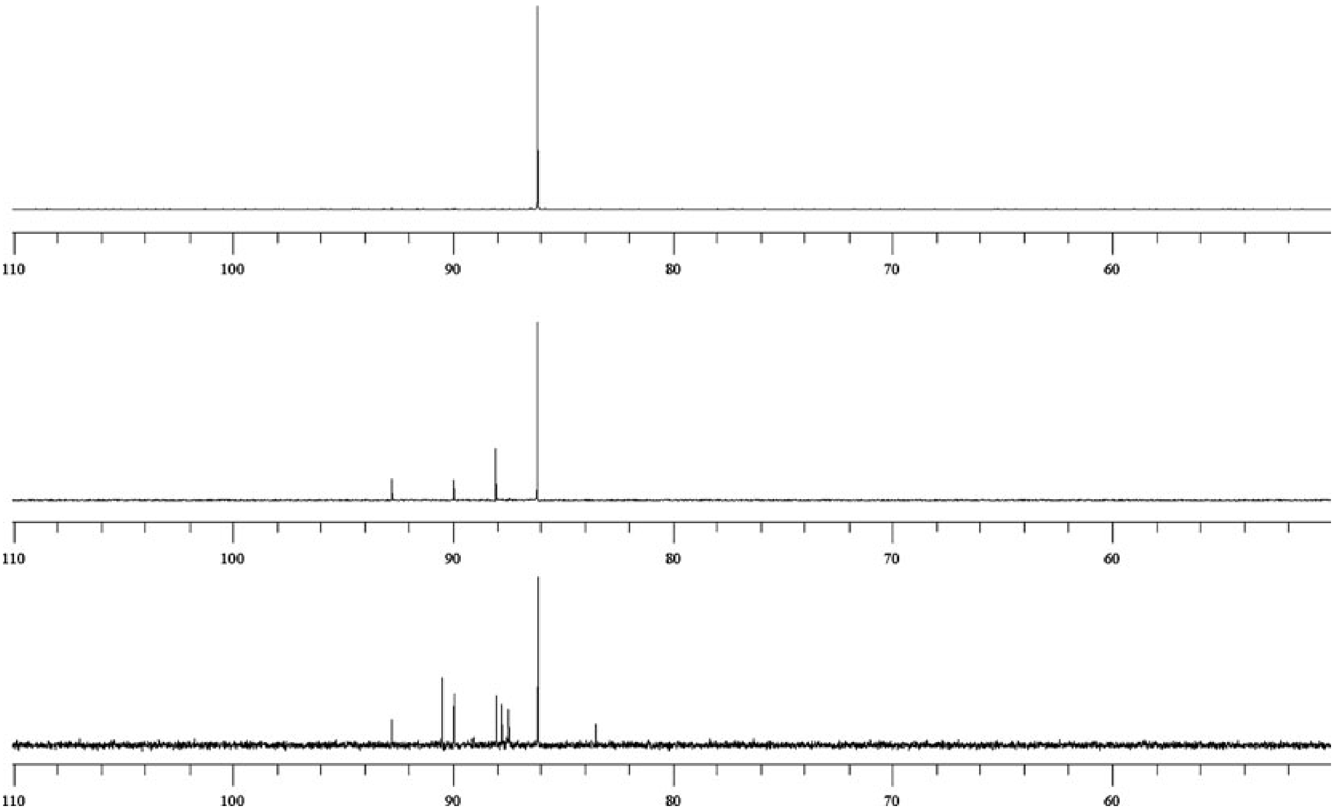
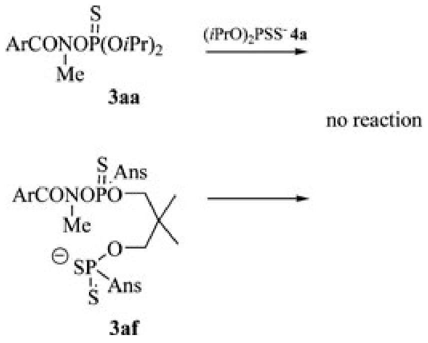


FIGURE 4 ^{31}P NMR spectra of disulfane **1e**: (a) optically pure form; (b) diastereomeric mixture obtained by oxidation of **4e** with iodine; (c) product isolated in the reaction of **2c** with **1e**.

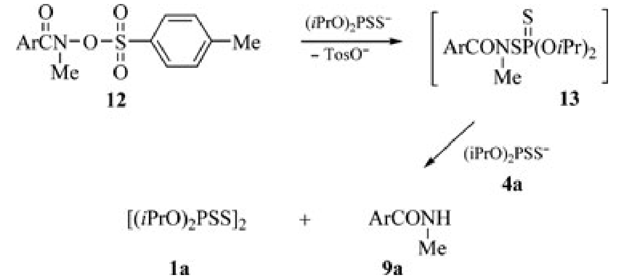
On the other hand, it was expected that *N*-phosphorothioyl thiolbenzamide **13** could be formed from *N*-methyl-*O*-tosyl-4-chlorobenzohydroxamic acid **12** as a product of nucleophilic substitution at the nitrogen atom by phosphodithioate salt **4a**. But attempts to detect the corresponding **13** failed (5 min, the NMR tube reaction). The reaction lead only to one phosphorus product, that is, disulfane **1a** (81%) accompanied by benzamide **9a** (80%), triethylammonium tosylate, and unreacted phosphodithioate salt **4a**. According to the proposed mechanism (Scheme 5), this reaction must run with **13** intermediacy, but based only on these results it is difficult to establish its ionic or radical character. The experiment described above showed that the tosylate in **12** and the phosphodithioate in **13** were much better leaving groups than the phosphothioate in **3aa** and 4-chlorobenzoate in **10**.

It was also found that, unlike *O*-thioacyl hydroxamic acids derivatives (vide supra), product **3aa** was not prone to isomerization to *S*-phosphoyl derivative **3aa**′ and subsequent homolysis leading to benzamide **9a** (chloroformic solution, 60°C, 4 days). This might appear surprising at first, as the energetic balance of such transformation seems to be more advantageous ($\Delta G_{\mathrm{P=S}\rightarrow\mathrm{P=O}} > \Delta G_{\mathrm{C=S}\rightarrow\mathrm{C=O}}$).



SCHEME 4

Comparison of the X-ray structure of **3ae** (Fig. 2) with that of the corresponding *N*-methyl-4-methylbenzohydroxamic acid [18] and **1e** (Fig. 1) revealed some significant differences in bond lengths. In compound **3ae**, the N—O bond is longer (1% relative to hydroxamic acid), the P—O bond is shorter (4.5% relative to **1e**) as well as the P=S bond (1.917Å) (1% relative to **1e**), which length is similar to that found for phosphothioyl chlorides [19]. Thus, the resulting data may suggest enhanced reactivity of



SCHEME 5

O-phosphothioylhydroxamic acids **3** toward nucleophilic attack.

CONCLUSIONS

In summary, with a set of disulfanes **1** as substrates, it was shown that the reaction demonstrated good generality only for *N*-methyl benzohydroxamate **2a**. For branched *N*-alkyl benzohydroxamates **2b** and **2c**, products of a SET process predominated. It was shown that *O*-phosphothioylated hydroxamic acids **3** neither react with phosphodithioate salts **4** arising in the reaction (in contrast to *O*-tosyl derivative **12**) nor isomerize into labile N—S derivatives (in contrast to *O*-thioacyl derivatives).

EXPERIMENTAL

General Remarks

All NMR spectra were recorded on a Varian Unity 500 Plus spectrometer operating at 500 MHz (^{1}H), 202.4 MHz (^{31}P), and 125.7 MHz (^{13}C) in $CDCl_3$. Mass spectra were measured with an AMD-604 double-focusing mass spectrometer (the EI method) and a MARINER (ESI-TOF) PerSeptive Biosystems spectrometer (the ESI method). EPR spectra of thoroughly degassed solutions (17×10^{-3} M) of the reactants were recorded on a Varian E4 spectrometer. The *g* values were measured using DPPH as reference ($g = 2.0036$). The TLC analysis was performed on aluminum foil plates precoated with silica gel (60F 254, Merck). Silica gel, 230–400 mesh (Merck AG, Darmstadt, Germany), was used for column chromatography. THF was distilled from potassium/benzophenone ketyl. Commercial LR (Lancaster Synthesis, Lancashire, England) was recrystallized from chlorobenzene prior to use. Disulfanes **1a** [20], **1b** [21], **1c** [22], **1d** [22], and **1e** were obtained from the corresponding phosphodithioate salts by using the reported method [23]. *N*-Methyl- [24], *N*-isopropyl- [25], *N*-*tert*-butyl-4-chlorobenzohydroxamic acid [26], and the corresponding benzamides **9b–c** [27] are known compounds and were prepared by acylation of the respective *N*-alkylhydroxylamine or alkylamine with 4-chlorobenzoyl chloride. Diisopropylphosphorochloridothioate was obtained according to the described procedure [28].

Authentic samples of *N*-alkyl-4-chloro-*N*-(4-chlorobenzyloxy)benzamides **10b** and **10c** [29] were obtained from the reaction between the corresponding benzohydroxamic acid and 4-chlorobenzoyl chloride. Authentic sample of *O*-(4-chlorobenzoyl)acetoxime **11** was prepared from acetoxime.

*Bis[isopropoxy(4-methoxyphenyl)phosphinothioyl)disulfane (***1d***).* Yield 61%. White crystals from ethyl acetate–hexanes. Melting point (mp) 118–120°C. ^{1}H NMR, δ: 1.34 and 1.44 ($2 \times$ d, $J = 6.5$ Hz, 6H, CH_3C), 3.83 (s, 3H, OCH_3), 4.98 (dspt, $J = 10$ and 6.5 Hz 1H, CHC), 6.67 (dd, $J = 3.9$ and 8.8 Hz, 2H, H-3/5), 7.55 (dd, $J = 8.8$ and 14.2 Hz, 2H, H-2/6) ppm. ^{13}C NMR, δ: 23.66, 23.70, 24.14, 24.16 (CH_3C), 55.2 (OCH_3), 72.16 (d, $J = 6.5$ Hz, $CHCH_3$), 113.3 (d, $J = 17$ Hz, C-3/5), 123.3 (d, $J = 132$ Hz, C-1), 133.2 (d, $J = 14$ Hz, C-2/6), 162.7 (C-4) ppm. ^{31}P NMR, δ: 85.8 ppm (lit. [11] δ_P: 85.8 and 89.2 ppm).

*(R_P, R_P)-bis[(–)-menthyloxy(4-methoxyphenyl)-phosphinothioyl)disulfane (***1e***).* To a suspension of LR (0.505 g, 1.25 mmol) in THF (8 mL), (–)menthol (0.39 g, 2.5 mmol) was added in one portion. After 15 min, to a clear solution *tert*-butyl amine (0.26 mL, 2.5 mmol) was added dropwise with cooling. Next, thus formed *tert*-butylammonium salt was treated with an iodine solution in THF (0.16 g in 2 mL). ^{31}P NMR analysis showed that the crude product **1e** was obtained as a mixture of three diastereoisomers (**1e** δ 86.1, **1e**′ δ 88.0, and **1e**″ δ 89.91 and 92.8) in 3:1:1 ratio. Removal of the solvent and crystallization from ethanol afforded 0.36 g (42%) of the major (R_P, R_P)−diastereoisomer **1e** as white needles. mp 124–126°C. $[\alpha]_D^{20} = +228.6$ ($c = 0.84$ in CH_2Cl_2). ^{1}H NMR, δ: 0.70 (d, 3H), 0.83 (d, 3H), 0.92 (m, 1H), 1.01 (d, 3H), 1.07 (m, 1H), 1.37 (q, 1H), 1.45 (t, 1H), 1.52 (m, 1H), 1.70 (m, 2H), 1.88 (dt, 1 H), 2.45 (m, 1H), 3.88 (s, OCH_3, 3H), 4.65 (dq, $J = 4.5$ and 10 Hz, 1H, CHO), 6.72 (dd, $J = 3.9$ and 8.8 Hz, 2H, H-3/5), 7.57 (dd, $J = 8.8$ and 14.0 Hz, 2H, H-2/6) ppm. ^{13}C NMR, δ: 16.2, 21.3, 22.4, 23.2, 25.7, 31.9, 34.3, 42.5, 48.8, 48.9, 55.50, and 55.3 (OCH_3), 79.6 (d, $J = 7.7$ Hz, OCH), 113.7 (d, $J = 16$ Hz, C-3/5), 124.5 (d, $J = 133$ Hz, C-1), 133.5 (d, $J = 13$ Hz, C-2/6), 162.9 (C-4) ppm. ^{31}P NMR, δ: 86.1 ppm. HRMS (ESI): Calcd for $C_{34}H_{52}O_4P_2S_4Na$ [M + Na$^+$]: 737.2116; found 737.20961.

*Bis[isopropylamino(4-methoxyphenyl)phosphinothioyl)disulfane (***1g***).* Oxidation of isopropylammonium isopropylamido(4-methoxyphenyl)phosphonodithioate [30] with an iodine solution in THF and subsequent column chromatography in chloroform afforded **1g** as a mixture of two nonseparable diastereoisomers in a 66:34 ratio. Yield 19%. mp 117–121°C. ^{1}H NMR, δ: 1.12 and 1.43 (2 × d, 6H, minor), 1.18 and 1.30 (2 × d, 6H, major), 3.11 (t, $J = 8.8$ Hz, NH, 1H, minor), 3.19 (t, $J = 8.8$ Hz, NH, 1H, major), 3.52 (tspt, $J = 6.5$ and 10 Hz, 1H, minor), 3.66 (tspt, $J = 6.5$ and 10 Hz, 1H, major), 3.85 (s, OCH_3, 3H, major), 3.89 (s, OCH_3, minor), 6.80 (dd, $J = 3.3$ and 8.8 Hz, 2H, H-3/5, major), 7.00 (dd, $J = 3.0$ and 8.8 Hz, 2H, H-3/5, major), 7.85 (dd, $J = 8.8$ and 13.7 Hz, 2H, H-2/6, major), 7.98 (dd, $J = 8.8$ and 13.7 Hz, 2H, H-2/6, minor) ppm. ^{13}C NMR, δ: 21.7 (broad, CH_3, minor), 25.4 and 25.6 (CH_3, major), 45.1 (CH, major), 45.3 (CH, minor), 55.6 (OCH_3, major), 55.8 (OCH_3, minor), 114.0 (d, $J = 15$ Hz, C-3/5, major), 114.3 (d, $J = 15$ Hz, C-3/5, minor), 125.2 (d, $J = 113$ Hz, C-1, major), 125.9 (d, $J = 115$ Hz, C-1, minor), 133.5 (d, $J = 13$ Hz, C-2/6, major), 133.8 (d, $J = 14$ Hz, C-2/6, minor), 163.2 (C-4, major), 163.4 (C-4, minor) ppm. ^{31}P NMR, δ: 72.2 (major) and 74.2 ppm (minor). HRMS (ESI): Calcd for $C_{20}H_{30}N_2O_2P_2S_4Na$ [M + Na$^+$]: 543.05576; found 543.05683.

*Bis[diisopropylamino(4-methoxyphenyl)phosphinothioyl)disulfane (***1h***).* Prepared as above from LR and diisopropylamine and obtained as a mixture of three diastereoisomers (**1h** δ_P 87.7, **1h**′ δ_P 86.9 and 87.9, **1h**″ δ_P 89.4 and 89.5) in 13:15:1 ratio. Crystallization from ethanol afforded (12%) of one diastereoisomer **1h**′ as white powder. MP 113–115°C. ^{1}H NMR, δ: 1.15 (d, 3H), 1.23 (d, 3H), 3.72 (d spt, $J = 6.5$ and 12.7 Hz, 2H), 3.73 (s, OCH_3, 3H), 6.49 (dd, $J = 3$ and 8.3 Hz, 2H, H-3/5), 7.86 (dd, $J = 8.3$ and 14.6 Hz, 2H, H-2/6) ppm. ^{13}C NMR, δ: 23.3 (CH_3), 23.6 (CH_3), 49.0 (CH), 55.3 (OCH_3), 112.9 (d, $J = 17$ Hz, C-3/5), 127.3 (d, $J = 111$ Hz, C-1), 134.6 (d, $J = 14$ Hz, C-2/6), 162.0 (C-4). ^{31}P NMR, δ: 87.7 ppm. HRMS (ESI): Calcd for $C_{26}H_{42}N_2O_2P_2S_4Na$ [M + Na$^+$]: 627.14966; found 627.15275.

*N-Methyl-O-phosphothioylbenzohydroxamic Acids (***3aa–3ag***)*

General Procedure. To a stirred solution of *N*-methyl-4-chlorobenzohydroxamic acid (0.058 g, 0.313 mmol) in THF (5 mL), NaH (0.01 g, 0.39 mmol) was added and the mixture was stirred under argon. When hydrogen evolution was ceased, the mixture was refluxed for 1.5 h and next disulfane **1** (0.25 mmol) was added in one portion at room temperature. After 20 min, the reaction was completed as judged by TLC and the mixture was concentrated in vacuo. The residue was subjected directly to column chromatography. Elution with chloroform afforded elemental sulfur as the first fraction, and next the pure **3** was collected. In the reaction of **1c** with **2a** (entry 3), the second fraction was compound **5**, namely *O*,*S*-dimethyl(4-methoxyphenyl)phosphonodithioate [11] (yield: 0.015 g, 12%; ^{1}H NMR, δ: 2.18 (d, $J = 15.0$ Hz, 3H, SCH_3), 3.82 (d, 3H, $J = 15.1$ Hz, $POCH_3$), 3.99 (s, 3H, $ArOCH_3$), 6.99 (dd, $J = 3.4$ and 8.8 Hz, 2H, H-3′/5′), 7.89 (dd, $J = 8.8$ and 13.7 Hz, 2H, H-2′/6′) ppm; ^{31}P NMR, δ: 99.8 ppm).

In the reaction of **1f** with **2a** (entry 6) after 16 h, the crude mixture was treated with methyl iodide (0.009 mL, 0.138 mmol) and the corresponding *S*-methyl ester **3af**′ was isolated as a mixture of two diastereomers, which separation was not successful.

*N-Methyl-N-diisopropoxyphosphinothioyloxy-4-chlorobenzamide (***3aa***).* Yield 0.042 g (92%). A colorless oil. ^{1}H NMR, δ: 1.27 and 1.31 (2 × d, $J = 6$ Hz 12H, CH_3CH), 3.49 (s, 3H, NCH_3), 4.71 (dspt, $J = 6.5$ and 10 Hz, 2H, OCH), 7.40 (d, $J = 8.8$ Hz, 2H, ArH), 7.63 (d, $J = 8.8$ Hz, 2H, ArH) ppm. ^{13}C NMR, δ: 23.5, 23.60, 23.65, and 23.7 (CH_3), 40.3 (NCH_3), 75.2 (d, $J = 6$ Hz, CH), 128.7 (C-3/5), 130.4 (C-2/6), 132.5 (C-1), 137.5 (C-4), 170.9 (C═O) ppm. ^{31}P NMR, δ: 70.05 ppm. MS (EI), *m/z* (%): 365 (3) M$^+$, 185 (2) [M-P(S)(OiPr)$_2$]$^+$, 168 (3) [M-OP(S)(OiPr)$_2$]$^+$, 139 (100) ArC≡O$^+$, 111 (13) $ClC_6H_5^+$. HRMS (EI): Calcd for $C_{14}H_{21}NO_4PS^{35}Cl$: 365.06175; found 365.06189.

*N-Methyl-N-diisopropoxyphosphinothioyloxy-4-chlorobenzamide (***3aa***) from Diisopropylphosphorochloridothioate.* To a stirred solution of *N*-methyl-4-chlorobenzohydroxamic acid (0.19 g, 1 mmol) and DBU (0.165 mL, 1.1 mmol) in CH_2Cl_2 (5 mL), diisopropylphosphorochloridothioate (0.22 g, 1 mmol) in CH_2Cl_2 (2 mL) was added dropwise at −10°C. After 2 h, the reaction mixture was concentrated in vacuo and the residue was subjected to column chromatography (chloroform) to yield 0.30 g (82%) of **3aa**.

*N-Methyl-N-diphenylphosphiothioyloxy-4-chlorobenzamide (***3ab***).* Yield 0.045 g (89%). A colorless oil. ^{1}H NMR, δ: 3.46 (s, 3H, NCH_3), 7.27 (d, $J = 8.8$ Hz, 2H, ArH), 7.40 (d, $J = 8.8$ Hz, 2H, H–), 7.44 (2 × t, 4H, H-4′), 7.53 (t, 2H), 7.90 (dd, $J = 8$ and 13.7 Hz, 4H, H-2′) ppm. ^{13}C NMR, δ: 42.2 (NCH_3), 128.6 (d, $J = 13.7$ Hz, C-3′/5′), 128.8 (C-3/5), 130.3 (C-2/6), 131.9 (C-1), 132.1 (d, $J = 11.4$ Hz, C-2′/6′), 132.5 (d, $J = 91$ Hz, C-1′), 132.8 (d, $J = 3$ Hz, C-4′), 137.5 (C-4), 171.7 (C=O) ppm. ^{31}P NMR, δ: 94.2 ppm. MS (EI), *m/z* (%): 401 (0.5) M$^+$, 234 (17) $[Ph_2P(S)OH]^+$, 217 (95) $[Ph_2P(S)]^+$, 168 (24) $[M\text{-}OP(S)Ph_2]^+$, 139 (100) ArC≡O$^+$, 111 (43) $ClC_6H_5^+$. HRMS: Calcd for $C_{20}H_{17}NO_2PS^{35}Cl$ 401.04062; found 401.03906.

N-Methyl-N-[methoxy)(4-methoxyphenyl)phosphinothioyloxy]-4-chlorobenzamide (**3ac**). Yield 0.079 g (82%). A colorless oil. ^{1}H NMR, δ: 3.36 (s, 3H, NCH_3), 3.78 (d, $J = 14.1$ Hz, 3H, $POCH_3$), 3.85 (s, 3H, OCH_3), 6.89 (dd, $J = 3.4$ and 8.8 Hz, 2H, H-3′/5′), 7.30 (d, $J = 8.3$ Hz, 2H, ArH), 7.47 (d, $J = 8.3$ Hz, 2H, ArH), 7.72 (dd, $J = 8.8$ and 13.7 Hz, 2H, H-2′/6′) ppm. ^{13}C NMR, δ: 40.6 (NCH_3), 53.9 (d, $J = 6$ Hz, $POCH_3$), 55.7 (OCH_3), 114.0 (d, $J = 17$ Hz, C-3′/5′), 121.9 (d, $J = 156$ Hz, C-1′), 128.6 (C-3/5), 130.3 (C-2/6), 132.2 (C-1), 133.8 (d, $J = 13$ Hz, C-2′/6′), 137.4 (C-4), 163.6 (d, $J = 3$ Hz, C-4′), 170.7 (C=O) ppm. ^{31}P NMR, δ: 97.7 ppm. MS (EI), *m/z* (%): 385 (3) M$^+$, 218 (9) $[AnsP(S)(OMe)OH]^+$, 201 (100) $[AnsP(S)OMe]^+$, 185 (11) $[M\text{-}P(S)(OiPr)_2]^+$, 168 (9) $[M\text{-}OP(S)(OiPr)_2]^+$, 139 (46) ArC≡O$^+$, 111 (18) $ClC_6H_5^+$. HRMS (EI): Calcd for $C_{16}H_{17}NO_4PS^{35}Cl$: 385.03045; found 385.02983.

N-Methyl-N-[isopropoxy)(4-methoxyphenyl)phosphinothioyloxy]-4-chlorobenzamide (**3ad**). Yield 0.049 g (95%). A colorless oil. ^{1}H NMR, δ: 1.24 and 1.38 (2 × d, $J = 6.5$ Hz, 6H, CH_3C), 3.44 (s, 3H, NCH_3), 3.85 (s, 3H, OCH_3), 4.89 (dspt, $J = 6.5$ and 11 Hz, 1H, CHC), 6.88 (dd, $J = 3.4$ and 8.3 Hz, 2H, H-3′/5′), 7.30 (d, $J = 8.3$ Hz, 2H, ArH), 7.48 (d, $J = 8.3$ Hz, 2H, ArH), 7.69 (dd, $J = 8.3$ and 14.1 Hz, 2H, H-2′/6′) ppm. ^{13}C NMR, δ: 23.84, 23.88, 24.03, 24.06 (CH_3C), 40.5 (NCH_3), 55.7 (OCH_3), 73.8 (d, $J = 6.5$ Hz, $CHCH_3$), 113.8 (d, $J = 16$ Hz, C-3′/5′), 123.4 (d, $J = 155$ Hz, C-1′), 128.5 (C-3/5), 130.4 (C-2/6), 132.4 (C-1), 133.7 (d, $J = 14$ Hz, C-2′/6′), 137.2 (C-4), 163.5 (C-4′), 170.7 (C=O) ppm. ^{31}P NMR, δ: 94.0 ppm. MS (EI), *m/z* (%): 413 (0.5) M$^+$, 246 (6) $[AnsP(S)OiPrOH]^+$, 229 (28) $[AnsP(S)OiPr]^+$, 187 (100) $[AnsP(S)OH]^+$, 171 (30) $[AnsP(S)+1]^+$, 139 (89) ArC≡O$^+$, 111 (37) $ClC_6H_4^+$. HRMS (EI): Calcd for $C_{18}H_{21}NO_4PS^{35}Cl$: 413.06175; found 413.06054.

(S_P)-N-Methyl-N-[(–)-menthyloxy(4-methoxyphenyl)phosphinothioyloxy] 4-chlorobenzamide (**3ae**). Yield 0.057 g (90%). White crystals from acetonitrile. MP 105–107°C. $[\alpha]_D^{20} = -29.3^\circ$ ($c = 0.58$ in CH_2Cl_2).^{1}H NMR, δ: 0.80 (d, 3H), 0.82 (m, 1H), 0.89 (d, 3H), 0.94 (d, 3H), 0.96 (m, 1H), 1.04 (m, 1H), 1.36 (m, 1H), 1.45 (t, 1H), 1.66 (m, 2H), 1.88 (m, 1H), 2.24 (m, 1H), 3.50 (s, NCH_3), 3.85 (s, OCH_3, 3H), 4.51 (dq, $J = 4.4$ and 10.7 Hz, 1H), 6.85 (dd, $J = 3.4$ and 8.8 Hz, 2H, H-3/5), 7.27 (d, $J = 8.3$ Hz, 2H, ArH), 7.43 (d, $J = 8.3$ Hz, 2H, ArH), 7.67 (dd, $J = 8.8$ and 13.7 Hz, 2H, H-2/6) ppm. ^{13}C NMR, δ: 16.1, 21.3, 22.1, 23.0, 25.5, 31.7, 34.2, 40.9 (NCH_3), 42.9, 48.6, 48.7, 55.6 (OCH_3), 81.0 (d, $J = 7.6$ Hz, OCH), 113.7 (d, $J = 16$ Hz, C-3′/5′), 124.2 (d, $J = 153$ Hz, C-1′), 128.4 (C-3/5), 130.4 (C-2/6), 132.3 (C-1′), 133.8 (d, $J = 14$ Hz, C-2′/6′), 137.2 (C-4), 163.4 (d, $J = 3$ Hz, C-4′), 170.9 (C=O) ppm. ^{31}P NMR, δ: 93.8 ppm. MS (EI), *m/z* (%): 493 (1) $[M - 15]^+$, 341 (3) $[AnsP(S)OMenOH]^+$, 171 (40) $[AnsP(S)+1]^+$, 139 (76) ArC≡O$^+$, 111 (30) $ClC_6H_4^+$. HRMS (ESI): Calcd for $C_{25}H_{33}NO_4PS^{35}ClNa$ $[M + Na^+]$: 532.14487; found 532.1474.

O-{3-[(4-Methoxyphenyl)methylsulfanylphosphinothioyloxy]-2,2-dimethylpropyl}, O′-(N-methyl-4-chlorobenzamido)-4-(methoxyphenyl)phosphonothioic Acid (**3af′**). Obtained as a mixture of two diasteroisomers in 53/47 ratio with 98% yield. ^{1}H NMR, δ: 0.97, 0.99, 1.00, and 1.02 (4 × s, 6H), 2.05 (d, $J = 14.6$ Hz, 1.41H, SCH_3), 2.17 (d, $J = 15.1$ Hz, 1.59H, SCH_3), 3.29 (s, 1.41H, NCH_3), 3.37 (s, 1.59H, NCH_3), 3.76, 3.82, 3.98, 4.03, 4.11 (8 × dd, 4H, OCH_2), 3.83, 3.85, 3.86, 3.87 (4 × s, OCH_3, 6H), 6.86, 6.91, 6.93, 6.98 (4 × dd, $J = 3.4$ and 8.8 Hz, 4H, H-3/5), 7.27 (d, $J = 8.8$ Hz, 1.41H, ArH), 7.31 (d, $J = 8.8$ Hz, 1.59H, ArH), 7.45 (d, $J = 8.8$ Hz, 1.41H, ArH), 7.49 (d, $J = 8.3$ Hz, 1.59H, ArH), 7.72–7.89 (4 × dd, $J = 8.8$ and 13.7 Hz, 4H, H-2/6) ppm. ^{13}C NMR, δ: 15.4 (d, $J = 3$ Hz, SCH_3), 21.7, 21.8 (C-3), 36.4 (2 × d, $J = 8.4$ Hz, C-2), 40.6 and 40.8 (NCH_3), 55.7 (OCH_3), 69.2 and 69.6 (2 × d, $J = 6.9$ Hz, OC), 71.3 and 71.8 (2 × d, $J = 6.9$ Hz, OC), 114.1 and 114.2 (2 × d, $J = 16$ Hz, C-3′/5′), 122.0 and 122.2 (2 × d, $J = 156$ Hz, C-1′), 125.65 and 125.71 (2 × d, $J = 128$ Hz, C-1′), 128.6 and 128.7 (C-3/5), 130.37 and 130.41 (C-2/6), 132.9 and 133.0 (C-1), 133.8 and 133.9 (2 × d, $J = 14$ Hz, C-2′/6′), 137.36 and 137.42 (C-4), 163.0 and 163.6 (2 × s, C-4′), 170.77 and 170.81 (C=O) ppm. ^{31}P NMR, δ: 95.7 and 96.2 (PO_2), 97.3 and 97.8 (POS) ppm. HRMS (ESI): Calcd for $C_{28}H_{34}NO_6P_2S_3ClNa$ $[M + Na^+]$: 696.06043; found 696.06283.

N-Methyl-N-[isopropylamino(4-methoxyphenyl)-phosphinothioyloxy]-4-chlorobenzamide (**3ag**). Yield 0.094 g (91%). White crystals from ethyl acetate–hexanes. MP 143–144°C. ^{1}H NMR, δ: 1.10 and 1.11 (2 × d, $J = 6.5$ Hz, 6H, CH_3C), 3.28 (br s, 1H, NH), 3.49 (s, 3H, NCH_3), 3.66 (d spt, 1H, CH), 3.86 (s, 3H, OCH_3), 6.95 (dd, $J = 3.4$ and 8.6 Hz, 2H, H-3′/5′), 7.40 (d, $J = 8.3$ Hz, 2H, ArH), 7.56 (d, $J = 8.8$

Hz, 2H, ArH), 7.91 (dd, $J = 8.6$ and 13.5 Hz, 2H, H-2′/6′) ppm. ^{13}C NMR, δ: 25.5–25.7 (4 × s, CH_3C), 42.5 (CH), 45.0 (NCH_3), 55.7 (OCH_3), 114.0 (d, $J = 16$ Hz, C-3′/5′), 125.4 (d, $J = 145$ Hz, C-1′), 129.0 (C-3/5), 130.0 (C-2/6), 132.5 (C-1), 133.4 (d, $J = 13$ Hz, C-2′/6′), 137.6 (C-4), 163.1 (C-4′), 171.2 (C=O) ppm. ^{31}P NMR, δ: δ_P: 88.2 ppm. MS (EI), *m/z* (%): 354 (1) [M-NHiPr]$^+$, 228 (100) [AnsP(S)NHiPr]$^+$, 186 (25) [AnsP(S)OH]$^+$, 169 (6) [AnsP(S)]$^+$, 139 (33) ArC≡O$^+$, 111 (13) $ClC_6H_4^+$. HRMS (ESI): Calcd for $C_{18}H_{22}N_2O_3PSClNa$ [M + Na$^+$]: 435.06750; found 435.06832.

Reaction between **1a** *and N-Isopropyl-4-chloro-benzohydroxamic Acid Sodium Salt (***2b***)*

To a stirred solution of **2b** (0.42 g, 1.78 mmol) in THF (10 mL), **1a** (0.39 g, 0.89 mmol) was added in one portion. After 16 h the solvent was stripped off under vacuum and the residue was chromatographed with chloroform to provide: **1a** (0.12 g, 28%), **3ba** (0.11 g, 30%), two nonpolar compounds, namely *N*-isopropyl-4-chloro-*N*-(4-chlorobenzyloxy)benzamide **10b** (0.023 g, 8%), *N*-isopropyl-4-chlorobenzamide **9b** (0.012 g, 7%) and *O*-(4-chlorobenzoyl)acetoxime **11** (0.005 g, 3%).

*Characterization of N-Isopropyl-N-diisopropoxy-phosphinothioyloxy-4-chlorobenzamide (***3ba***).* A colorless oil. ^{1}H NMR, δ: 1.30 (d, $J = 6.5$ Hz, 6H), 1.36 (d, 6.5 Hz, 6H), 2.38 (d, 6.5 Hz, 6H), 4.14 (spt, 1H, NCH), 4.86 (dspt, $J = 6$ Hz, $J = 10$ Hz, 2H, OCH), 7.42 (d, $J = 8.8$ Hz, 2H, ArH), 7.63 (d, $J = 8.8$ Hz, 2H, ArH) ppm. ^{13}C NMR, δ: 19.9 ($NCCH_3$), 23.60, 23.65, 23.68, and 23.71 (CH_3), 56.4 ($NCCH_3$), 74.8 (d, $J = 6$ Hz, OCH), 129.1 (C-3/5), 130.0 (C-2/6), 133.2 (C-1), 137.9 (C-4), 172.2 (C=O) ppm. ^{31}P NMR, δ: 72.9 ppm. HRMS (ESI): Calcd for $C_{16}H_{25}NO_4PS^{35}ClNa$ [M + Na$^+$]: 416.08227; found 416.08415.

*Characterization of N-Isopropyl-4-chloro-N-(4-chlorobenzyloxy)benzamide (***10b***).* ^{1}H NMR, δ: 1.29 (d, $J = 6.5$ Hz, 6H), 4.68 (spt, 1H, NCH), 7.34 (d, $J = 8.8$ Hz, 2H, ArH), 7.44 (d, $J = 8.8$ Hz, 2H, ArH), 7.56 (d, $J = 8.8$ Hz, 2H, ArH), 7.94 (d, $J = 8.8$ Hz, 2H, ArH) ppm. ^{13}C NMR, δ: 19.9 (CH_3), 52.7 ($NCCH_3$), 125.5, 128.9 (CH), 129.2 (CH), 129.4 (CH), 131.5 (CH), 132.8, 137.3, 141.1, 164.0 (C=O), 169.1(C=O) ppm. HRMS (EI): Calcd for $C_{17}H_{15}NO_3Cl_2$: 351.04290; found 351.04304.

*Characterization of O-(4-Chlorobenzoyl)aceto-xime (***11***).* White flakes from ethyl acetate–hexanes. MP 89–90°C. ^{1}H NMR, δ: 2.13 and 2.14 (2 × s, 6H), 7.46 (d, $J = 8.8$ Hz, 2H, ArH), 8.02 (d, $J = 8.8$ Hz, 2H, ArH) ppm. ^{13}C NMR, δ: 17.4 and 22.3 (CH_3), 127.9 (C-1), 129.1 (CH), 131.2 (CH), 139.9 (C-4), 163.3 (C=N), 165.1(C=O) ppm. HRMS (EI): Calcd for $C_{10}H_{10}NO_2Cl$: 211.04001; found 211.04013.

Reaction between **1e** *and N-Isopropyl-4-chloro-benzohydroxamic Acid Sodium Salt (***2b***)*

To a stirred solution of **2b** (0.42 g, 1.78 mmol) in THF (10 mL), **1e** (0.60 g, 0.89 mmol) was added in one portion. After 16 h, the solvent was stripped off under vacuum and the residue was chromatographed with chloroform to provide **1e** (0.07 g, 12%) with $[\alpha]_D^{20}$ +2.5° ($c = 0.86$ in CH_2Cl_2), **3be** (0.17 g, 35%), **10b** (0.03 g, 10%), and **9b** (0.015 g, 9%).

*Characterization of N-Isopropyl-N-[(–)-menthyl-oxy(4-methoxyphenyl)phosphinothioyloxy]-4-chloro-benzamide (***3be***).* A colorless oil. $[\alpha]_D^{20} = -23.0°$ ($c = 2.86$ in CH_2Cl_2); ^{1}H NMR, δ: 0.56–2.10 (complex multiplets, 18H), 2.33 (m, 0.67H), 2.44 (m, 0.33H), 3.87 (s, 3H, OCH_3), 4.12 (2 × spt, NCH, 1H), 4.55 (dq, $J = 4.4$ and 10.7 Hz, 0.33H), 4.71 (dq, $J = 4.4$ and 10.7 Hz, 0.67H), 6.92 (dd, $J = 3.4$ and 8.8 Hz, 1.34H, H-3/5), 6.93 (dd, $J = 3.4$ and 8.8 Hz, 0.66H, H-3/5), 7.35 (d, $J = 8.8$ Hz, 1.34H, ArH), 7.37 (d, $J = 8.8$ Hz, 0.66H, ArH), 7.53 (d, $J = 8.8$ Hz, 1.34H, ArH), 7.56 (d, $J = 8.8$ Hz, 0.66H, ArH), 7.88 (dd, $J = 8.8$ and 13.7 Hz, 1.34H, H-2/6), 7.93 (dd, $J = 8.8$ and 13.7 Hz, 0.66H, H-2/6) ppm. ^{31}P NMR, δ: 94.2 and 96.2 ppm (intensity ratio: 2.2:1). HRMS (ESI): Calcd for $C_{27}H_{37}NO_4PS^{35}ClNa$ [M + Na$^+$]: 560.17617; found 560.17867.

Reaction between **1a** *and N-tert-butyl-4-chloro-benzohydroxamic Acid Sodium Salt (***2c***)*

To a stirred solution of sodium *N-tert*-butyl-4-chlorobenzohydroxamate **2c** (0.25 g, 1 mmol) in THF (4 mL) **1a** (0.22 g, 0.5 mmol) was added in one portion. Immediately a deep green coloration appeared due to aminoxyl formation. After 16 h, the solvent was stripped off under vacuum and the residue was chromatographed with chloroform to provide two nonpolar compounds, namely *N-tert*-butyl-4-chloro-*N*-(4-chlorobenzyloxy)benzamide **10c** (0.055 g, 30%) and *N-tert*-butyl-4-chlorobenzamide **9c** (0.01 g, 9%).

*Characterization of N-tert-butyl-4-chloro-N-(4-chlorobenzyloxy)benzamide (***10c***).* ^{1}H NMR, δ: 1.59 (s, 9H), 7.24 (d, $J = 8.3$ Hz, 2H, ArH), 7.40 (d, $J = 8.3$ Hz, 2H, ArH), 7.50 (d, $J = 8.3$ Hz, 2H, ArH), 7.78 (d, $J = 8.3$ Hz, 2H, ArH) ppm. ^{13}C NMR, δ: 27.9

(NCCH3), 63.6 ($NCCH_3$), 125.1 (C—H), 128.4 (C—H), 129.0 (C—H), 129.5 (C—H), 131.2 (C—H), 134.6 (C-1), 136.5, 141.2, 164.9 (C=O), 170.6 (C=O) ppm.

*Characterization of N-tert-butyl-4-chlorobenzamide (**9c**).* ^{1}H NMR, δ: 1.49 (s, 9H), 7.40 (d, $J = 8.3$ Hz, 2H, ArH), 7.68 (d, $J = 8.3$ Hz, 2H, ArH) ppm.

*N-Methyl-N-tosyloxy-4-chlorobenzamide (**12**)*

To a stirred solution of **2** (0.371g, 2 mmol) in CH_2Cl_2 (5 mL), NaH (0.053 g, 2.2 mmol) was added. When hydrogen evolution was ceased, the mixture was refluxed under argon atmosphere for 1.5 h and next tosyl chloride (0.381 g, 2 mmol) in CH_2Cl_2 (3 mL) was added dropwise at –5°C. After 16 h, the reaction mixture was evaporated and chromatographed on silica gel with ethyl acetate–*n*-hexane (1:7) to provide 0.61 g (90%) of **12** as white solid (mp 88–90°C). ^{1}H NMR, δ: 2.38 (s, 3H, $ArCH_3$), 3.53 (s, 3H, NCH_3), 7.15 (d, $J = 8.5$ Hz, 2H, ArH), 7.21 (d, $J = 8.8$ Hz, 2H, ArH), 7.26 (d, $J = 8.8$ Hz, 2H, ArH), 7.54 (d, $J = 8.8$ Hz, 2H, ArH) ppm. ^{13}C NMR, δ: 22.0 ($ArCH_3$), 40.2 (NCH_3), 128.4 (C—H), 129.3 (C—H), 130.0 (C—H), 130.2 (C—H), 130.3, 131.0, 137.7, 146.7, 170.1 (C=O) ppm. MS (EI), *m/z* (%): 339 (4) M$^+$, 168 (3) ArCON $(CH_3)^+$, 155 (19) $ArSO_2^+$, 139 (100) $ArC{\equiv}O^+$, 111 (18) $ClC_6H_4^+$, 91 (17) $C_7H_7^+$. HRMS (EI): Calcd for $C_{15}H_{14}NO_4S^{35}Cl$: 339.03321; found 339.03203.

*Reaction between N-Methyl-N-tosyloxy-4-chlorobenzamide (**12**) and Triethylammonium Diisopropoxyphosphinodithioate (**4a**). In $CDCl_3$*: A solution of **12** (0.068g, 0.2 mmol) and triethylammonium diisopropoxyphosphinodithiate **4a** (0.063 g, 0.2 mmol, 1 equiv.) in deuteriochloroform (0.7 mL) was placed in and NMR tube. ^{31}P NMR spectra recorded after 5 min and 1.5 h contained only two signals (intensity ratio 1:4), which corresponds to **1a** (δ_P 82.6 ppm) and diisopropoxyphosphinodithioate **4a** (δ_P108.9 ppm), respectively.

In THF: A solution of **12** (0.136 g, 0.2 mmol) and **4a** (0.252 g, 0.8 mmol, 2 equiv.) in THF (3 mL) was stirred for 1.5 h at room temperature. ^{31}P NMR analysis showed that **1a**/**4a** ratio was raised to 6. The deposited crystals of triethylammonium tosylate were filtered off [^{1}H NMR, δ: 1.28 (t, $J = 6.5$ Hz, 9H), 2.32 (s, 3H, $ArCH_3$), 3.09 (dq, $J = 6.5$ and 5 Hz, 6H), 7.13 (d, $J = 8.5$ Hz, 2H, ArH), 7.72 (d, $J = 8.8$ Hz, 2H, ArH), 10.3 (br s, 1H, NH) ppm], and the solvent was stripped under vacuum. The residue was chromatographed in chloroform to afford **1a** (0.138 g, 81%), unreacted **12** (0.010 g, 7%), and benzamide **9a** (0.054 g, 80%).

Crystal data for **1e** [7]: $C_{34}H_{52}O_4P_2S_4$, $M = 719.94$, orthorhombic, $a = 11.8388(4)$, $b = 17.4852(5)$, $c = 18.1602(5)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $U = 3761.4(2)$ Å^3, $T = 120(2)$ K, space group $P2_12_12_1$, $Z = 4$, $D_c = 1.262$ g cm^{-3}, Mo Kα (λ $1 = 0.71073$ Å), 34,051 reflections measured, 10947 unique, $R(I > 2\sigma(I)) = 0.0337$, R_w(all reflections) $= 0.0858$. Absolute structure parameter (Flack parameter) –0.03(4).

Crystal Data for **3ae** [7]: $C_{25}H_{33}ClNO_4PS$, $M = 510.03$, monoclinic, $a = 7.2401(3)$, $b = 13.9561(6)$, $c = 12.9788(5)$ Å, $\alpha = 90^\circ$, $\beta = 90.667(3)^\circ$, $\gamma = 90^\circ$, $U = 1311.34(9)$ Å^3, $T = 120(2)$ K, space group $P2_1$, $Z = 2$, $D_c = 1.292$ g cm^{-3}, Mo Kα ($\lambda = 0.71073$ Å), 7341 reflections measured, 4108 unique, $R(I > 2.00\sigma(I)) = 0.034$, R_w(all reflections) $= 0.0865$. Absolute structure parameter (Flack parameter) 0.15(6).

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