C-Phosphorylated *N*-(Trichloroethylidene)sulfonamides: A New Type of Highly Electrophilic Imines

Yuliya V. Rassukana,[a] Petro P. Onys'ko,*[a] Kateryna O. Davydova,[a] and Anatolii D. Sinitsa[a]

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A convenient preparative approach to previously unknown, highly electrophilic *C*-phosphorylated *N*-arylsulfonylimines **1**, based on fairly readily accessible α-phosphorylated sulfonamides **5**, has been developed. Compounds **1** react with trialkyl phosphites or ethyl diphenylphosphinite in the aza-Perkow reaction scheme to give *C*,*N*-diphosphorylated *N*-dichlorovinylsulfonamides **8**. On treatment with O- and S-nucleophilic agents (alcohols, thiols, thiophenols), **1** forms addition products **12** and **15**, the functionalized derivatives of α-aminophosphonic acids, while interaction between **1** and mercaptoacetic acid proceeds with intramolecular cyclization of the intermediate adduct to produce the novel 2-phosphorylated thiazolidinones **17**.

Introduction

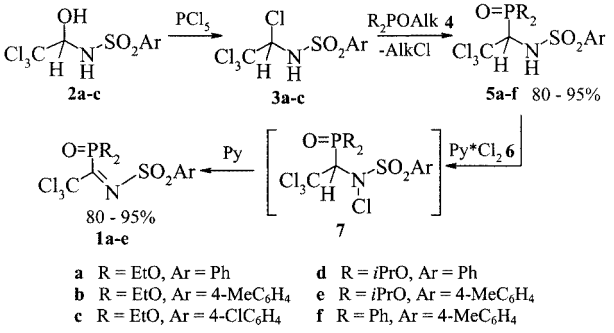
N-(Sulfonyl)haloalkanimines with electron-acceptor substituents are highly reactive and versatile chemical agents. They have found wide application in organic synthesis and can be used as convenient model compounds in the study of chemical reactivity.[1] The recently synthesized derivatives containing a phosphoryl group at the imine carbon atom, imidoylphosphonates, are useful intermediates in the preparation of various acyclic and heterocyclic phosphorus- and nitrogen-containing compounds, in particular the biologically important functionalized α-aminophosphonic acid derivatives.[2] *N*-(Sulfonyl)imidoylphosphonates are so far unknown as single compounds, however. One of the most general methods for the synthesis of imidoylphosphonates is the treatment of imidoyl chlorides with phosphites,[2a] but it is impossible to prepare the desired *N*-(sulfonyl)imidoylphosphonates in this way [e.g., by treatment of *N*-(sulfonyl)trihaloacetimidoyl chlorides with phosphites], as the products undergo fast aza-Perkow or other specific transformations.[3]

In this report we propose a simple and convenient synthetic approach to *N*-(arylsulfonyl)(trichloroacetimidoyl)phosphonates, characterize these compounds for the first time as a new class of *N*-sulfonylimines, and describe some of their chemical transformations, demonstrating their versatility and challenge as novel multifunctional synthons.

[a] Institute of Organic Chemistry, National Academy of Sciences, Kiev, 02094, 5 Murmans'ka St, Ukraine
E-mail: onysko@rambler.ru

Results and Discussion

The proposed string of transformations to provide preparative access to the new type of (trichloroacetimidoyl)phosphonates **1** bearing a sulfonyl group on the nitrogen atom is outlined in Scheme 1.



Scheme 1

Chlorination of the readily available α-(hydroxyalkane)sulfonamides **2**[4] affords the reactive chlorides **3**, which undergo Arbuzov reactions with esters of tervalent phosphorus acids **4** under mild conditions (benzene, 80 °C) to form phosphonates (or phosphane oxides) **5**.

The key step of this reaction sequence is the formal dehydrogenation of **5**, with the formation of imidoylphosphonates **1**. The dehydrogenation was found to proceed almost quantitatively upon treatment of phosphonates **5** with the pyridine−chlorine adduct **6**. Though the oxidation is a complex and multistep process[5] probably involving the chlorination of the nitrogen atom and abstraction of HCl

from the intermediate *N*-chloroamide **7**, only one signal for the final (trihaloacetimidoyl)phosphonate was observed in ^{31}P NMR spectra of the reaction mixture, indicating the absence of any side reactions.

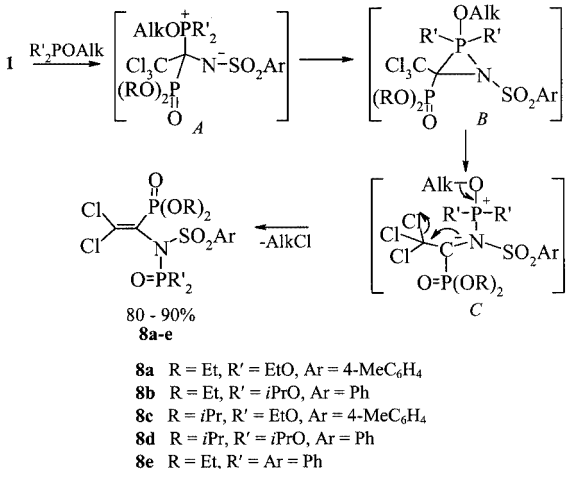
Such a result was not obvious a priori, especially if the complex character of the interaction between the *N*-benzoyl analogue of **5a** and adduct **6** was taken into account.[6] It is likely that the observed course of the oxidation reaction is determined by the substituents both at the nitrogen and at the phosphorus atoms of the substrate **5**. This suggestion is confirmed by the finding that phosphane oxide **5f** does not react with adduct **6** under conditions used for oxidation of the phosphonates.

N-(Arylsulfonyl)(trichloroacetimidoyl)phosphonates **1** are low-melting crystalline solids, stable in anhydrous media but easily hydrolyzable even in humid air. Their elemental analyses and spectroscopic data unequivocally corroborate the proposed compositions and structures of the final products, the imidoylphosphonates **1**. The most important argument in their spectral identification is the position of the ^{31}P NMR signal in the region between $\delta = -3.7$ and -6.5 ppm, which is characteristic of (trihaloacetimidoyl)-phosphonates.[2a,2c,6] No signals for CH or NH protons were observed in the ^{1}H NMR spectra of the products, whereas in their ^{13}C NMR spectra they show a signal for the sp^2-hybridized carbon atom (C=N, δ_C = 164.8−165.4 ppm) with a large one-bond coupling constant ($^{1}J_{C,P}$ = 165−166 Hz). In their IR spectra the compounds also each exhibit a C=N stretching vibration band at 1630−1620 cm^{-1}.

The three strongly electron-withdrawing groups at the azomethine bond make it very polarizable and, as a result, significantly enhance the electrophilicity of the imidoylphosphonates. Because of the high reactivity, compounds **1** were not isolable from the reaction between the corresponding imidoyl chlorides $Cl_3CC(Cl)=NSO_2Ar$ and diethyl trimethylsilyl phosphite, although they were detected spectroscopically in the reaction mixtures: the intermediates successfully competed with the less reactive imidoyl chlorides for the phosphite reagent.[3]

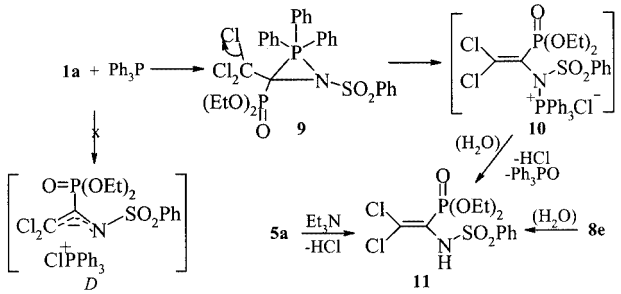
Imidoylphosphonates **1** represent a new type of sulfonylimines containing a phosphoryl group at the imine carbon atom. They can be regarded as phosphorus analogues of *N*-sulfonylimines derived from trihalopyruvates, $X_3CC(COOAlk)=NSO_2Ar$, which have found wide synthetic utility.[1,7] It is interesting to compare the reactivities of these two types of compounds. In particular, a recently disclosed new reaction in the $F_3CC(COOAlk)=NSO_2Ar$ − phosphite system involves an unusual N−C transfer of the sulfonyl group to give *C*-phosphorylated trifluoroalanines.[8] In contrast, reactions between imidoylphosphonates **1** and esters of tervalent phosphorus acids proceed with participation of a chlorine atom of the trichloromethyl group and formation of the *C*,*N*-bis(phosphorylated) sulfonamides **8** (Scheme 2).

It is most probable that the reaction starts with the nucleophilic attack of the phosphorus agent on the most electrophilic center: the imine carbon atom. The subsequent C,N-



Scheme 2

migration of the phosphorus group in the bipolar ion *A* via the unstable phosphorane *B* is promoted by Umpolung of the C and N reaction centers and produces carbanion *C*, which is stabilized through elimination of the alkyl chloride. The validity of Scheme 2 was supported by spectral detection of the intermediate phosphorane **9** in monitoring of the reaction between imidoylphosphonate **1a** and triphenylphosphane. Within 30 minutes of the onset of the reaction (benzene, 20 °C), a pair of signals of equal intensity appears in the ^{31}P NMR spectrum at $\delta = 12.9$ and -43.3 ppm. In all probability they belong to the phosphonate and the phosphorane P atoms, respectively, of the heterocycle **9** (Scheme 3). The position of the phosphonate signal ($\delta = 12.9$ ppm) is characteristic of compounds with a trichloromethyl[9] rather than a dichlorovinyl substituent (in which the phosphorus atoms would be expected to give a signal at $\delta = 7-9$ ppm).[3,6,9] The detection and identification of the intermediate **9** is of basic importance as this excludes the alternative reaction pathway with the initial halophilic attack followed by transformation of the ion pair *D* into compound **11**.



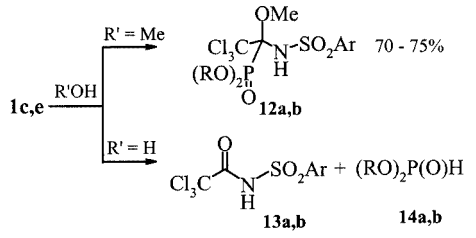
Scheme 3

Azaphosphorine **9** is unstable and, as the ^{31}P NMR spectroscopic data show, it is transformed into the *C*-phosphorylated (dichlorovinyl)sulfonamide **11**, evidently through hydrolysis of the phosphonium salt **10**. The eliminated triphenylphosphane oxide was identified by spectroscopic comparison with an authentic sample of the com-

pound. The *C*,*N*-bis(phosphorylated) sulfonamide **8e** is also easily and selectively hydrolyzed even by atmospheric moisture and eliminates the phosphane oxide, rather than the arylsulfonyl group, to form (dichlorovinyl)phosphonate **11**. This compound was also independently synthesized through dehydrochlorination of phosphonate **5a**.

It should be noted that reactions between imidoylphosphonates **1a**−**e** and esters of P^{III} acids (Scheme 2), irrespective of the substituents on the imine and phosphorus reagents, proceed according to the Perkow reaction scheme, without perceptible contribution of any side processes, and so can be used as a convenient preparative tool for the synthesis of *C*,*N*-bis(phosphorylated) sulfonamides **8**.

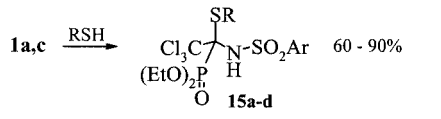
Imidoylphosphonates **1** contain the "oxidized" moiety of α-aminophosphoryl compounds and, owing to the high reactivity, they can be easily functionalized. As already shown, imidoylphosphonates **1** are transformed into *N*-substituted α-(aminodichlorovinyl)phosphonates on treatment with tervalent phosphorus derivatives (Schemes 2, 3). The feasibility of transforming compounds **1** into functionalized α-aminoalkylphosphonic acid derivatives can be demonstrated by their reactions with O- and S-nucleophilic agents. Thus, on treatment with methanol, **1c** and **1e** readily form the corresponding stable addition products **12a** and **12b**, whereas treatment with water affords sulfonamides **13**[3] and dialkyl phosphites **14** (Scheme 4), both identified spectroscopically by comparison with authentic samples of the compounds. In the last case the nucleophilic substitution occurs and the phosphoryl group acts as a nucleofuge. The progress of the reaction with water was monitored by ^{31}P NMR spectroscopy and no signal for the possible intermediate of type **12** was detected. This indicates that the hydrolysis most probably proceeds by the S_N2 mechanism[10] rather than the addition-elimination reaction scheme. Such a difference in the behavior of MeOH and H_2O can be explained in terms of a stronger mesomeric donor effect of the HO group in relation to MeO (σ_p −0.37 and −0.27, respectively).[11] Unlike aliphatic alcohols, 4-chlorophenol and 4-methoxyphenol do not interact with imidoylphosphonates **1** under the same conditions.



a R = Et, Ar = 4-ClC_6H_4
b R = *i*Pr, Ar = 4-$CH_3C_6H_4$

Scheme 4

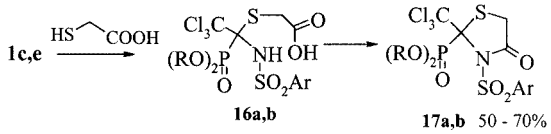
At the same time, thiophenols and thiols react with **1** even in the absence of bases to give stable thioaminals **15** (Scheme 5). The unusually high values of the vicinal coupling constants of the NH protons to the phosphorus nucleus in arylthio derivatives **15c** and **15d** (δ_H = 5.00 ppm, $^3J_{H,P}$ = 18−18.3 Hz) are noteworthy, far exceeding those observed in the benzylthio analogue **15a** (δ_H = 6.1 ppm, $^3J_{H,P}$ = 5.0 Hz) or in aminals **12**.



15a R = $PhCH_2$, Ar = 4-ClC_6H_4
15b R = $HOCH_2CH_2$, Ar = 4-ClC_6H_4
15c R = 4-ClC_6H_4, Ar = Ph
15d R = 4-FC_6H_4, Ar = 4-ClC_6H_4

Scheme 5

The bifunctional agents mercaptoethanol and mercaptoacetic acid first react with imidoylphosphonates **1** as S-centered nucleophiles to give the corresponding addition products **15b** (Scheme 5) and **16** (Scheme 6). The primary products **16** undergo slow cyclization into the *C*-phosphorylated 1,3-thiazolidin-4-ones **17** already at room temperature and were identified spectrally without isolation. The intramolecular cyclization is speeded up and completes upon heating or in the presence of thionyl chloride.



a R = Et, Ar = 4-ClC_6H_4
b R = *i*Pr, Ar = 4-$CH_3C_6H_4$

Scheme 6

Until now, 2-phosphorylated thiazolidinones and thiazoles were unknown. The easy route to heterocycles of type **17** based on imidoylphosphonates **1** is important, as these compounds combine in their structures the fragments of α-aminophosphonic acids and thiazolidinones, known for a wide spectrum of bioactivity.[2a,2d−2f,12]

Schemes 4−6 indicate that the direction of the reactions involving imines **1** is very sensitive even to the smallest changes in structure of the nucleophilic agent.

Conclusion

In summary, we have developed a convenient preparative approach to previously unknown *N*-(sulfonylimidoyl)phosphonates **1**, comprising a new group of activated imines. The presence of "oxidized" α-aminophosphonic acid moieties in these compounds and the high reactivity make imines **1** versatile building blocks in the synthesis of various phosphorus analogues of amino acids. In their reactions with neutral esters of P^{III} acids, the Umpolung of the C- and N-reaction centers in **1** promotes the 1,2-C→N shift of the phosphoryl group and therefore the phosphorylation of the nucleophilic nitrogen atom with the nucleophilic phos-

phorus agents to give *C*,*N*-diphosphorylated *N*-(dichlorovinyl)sulfonamides **8**.

Experimental Section

IR spectra were obtained with an UR-20 spectrophotometer. ^{1}H, ^{19}F, ^{31}P, and ^{13}C NMR spectra were recorded with a Varian VXR 300 spectrometer at 299.95, 282.20, 121.42, and 75.43 MHz, respectively. Chemical shifts are reported relative to TMS (^{1}H, ^{13}C), and $CFCl_3$ (^{19}F) as the internal standards or relative to external 85% H_3PO_4 (^{31}P).

General Procedure for Preparation of the Imidoylphosphonates 1: Pyridine (6.6 mmol), was added dropwise with stirring and cooling (0°C) to a solution of chlorine (3.6 mmol) in CCl_4 (15 mL). The reaction mixture was allowed to warm up gradually to room temperature, and phosphonate **5** (3.3 mmol) was added in portions with stirring. After 8 h, pyridine hydrochloride was filtered off, the solvent was removed in vacuo, and the residue was washed with petroleum ether.

***N*-[2,2,2-Trichloro-1-(diethoxyphosphoryl)ethylidene]benzenesulfonamide (1a):** This compound was prepared from sulfonamide **5a** (1.4 g, 3.3 mmol); white solid; m.p. 46 °C; yield: 1.2 g (86%). IR (Nyol): $\tilde{\nu}$ = 1040 (POC), 1180, 1365 (S=O), 1270 (P=O), 1620 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.48 (t, $^{3}J_{H,H}$ = 7 Hz, 6 H, CH_3), 4.34−4.53 (m, 4 H, CH_2O), 7.59 (t, $^{3}J_{H,H}$ = 8 Hz, 2 H, *m*-C−H, Ph), 7.65 (t, $^{3}J_{H,H}$ = 8 Hz, 1 H, *p*-C−H, Ph), 8.04 (d, $^{3}J_{H,H}$ = 8 Hz, 2 H, *o*-C−H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.4 (d, $^{3}J_{C,P}$ = 6.4 Hz, *C*H_3CH_2), 65.4 (d, $^{2}J_{C,P}$ = 6.3 Hz, CH_2O), 96.2 (d, $^{2}J_{C,P}$ = 49.5 Hz, CCl_3), 127.5, 128.96 (*o*-C, *m*-C, Ph), 133.6 (s, *p*-C, Ph), 140.1 (s, *ipso*-C, Ph), 165.4 (d, $^{1}J_{C,P}$ = 165 Hz, C=N) ppm. ^{31}P NMR ($CDCl_3$): δ = −3.7 ppm. $C_{12}H_{15}Cl_3NO_5PS$ (422.65): calcd. C 34.10, H 3.58, Cl 25.16, N 3.31, P 7.33; found C 34.21, H 3.49, Cl 25.28, N 3.34, P 7.31.

***N*-[2,2,2-Trichloro-1-(diethoxyphosphoryl)ethylidene]-*p*-toluenesulfonamide (1b):** This compound was prepared from sulfonamide **5b** (1.45 g, 3.3 mmol); white solid; m.p. 46 °C; yield: 1.37 g (95%). IR (Nyol): $\tilde{\nu}$ = 1050 (POC), 1180, 1380 (S=O), 1280 (P=O), 1630 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.47 (t, $^{3}J_{H,H}$ = 7 Hz, 6 H, C*H*$_3$CH$_2$), 2.45 (s, 3 H, C*H*$_3$Ar), 4.34−4.51 (m, 4 H, CH_2O), 7.35 (d, $^{3}J_{H,H}$ = 8 Hz, 2 H, Ar), 7.92 (d, $^{3}J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.1 (d, $^{3}J_{C,P}$ = 6 Hz, *C*H_3CH_2), 21.5 (s, 3 H, *C*H_3Ar), 65.4 (d, $^{2}J_{C,P}$ = 6 Hz, CH_2O), 96.3 (d, $^{2}J_{C,P}$ = 49 Hz, CCl_3), 127.6 (s, Ar), 129.6 (s, Ar), 137.1 (s, *C*CH_3), 144.7 (s, CSO_2), 164.8 (d, $^{1}J_{C,P}$ = 166 Hz, C=N) ppm. ^{31}P NMR ($CDCl_3$): δ = −3.7 ppm. $C_{13}H_{17}Cl_3NO_5PS$ (436.68): calcd. C 35.76, H 3.92, Cl 24.36, N 3.21, P 7.09, S 7.34; found C 35.78, H 3.89, Cl 24.40, N 3.22, P 7.10, S 7.36.

4-Chloro-*N*-[2,2,2-trichloro-1-(diethoxyphosphoryl)ethylidene]-benzenesulfonamide (1c): This compound was prepared from sulfonamide **5c** (1.52 g, 3.3 mmol); white solid; m.p. 55 °C; yield: 1.28 g (85%). IR (KBr): $\tilde{\nu}$ = 1040 (POC), 1180, 1370 (S=O), 1280 (P=O), 1630 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.47 (t, $^{3}J_{H,H}$ = 7 Hz, 6 H, CH_3), 4.32−4.53 (m, 4 H, CH_2O), 7.54 (d, $^{3}J_{H,H}$ = 8 Hz, 2 H, Ar), 7.98 (d, $^{3}J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = −3.7 ppm. $C_{12}H_{14}Cl_4NO_5PS$ (457.09): calcd. C 31.53, H 3.09, Cl 31.02, N 3.06, P 6.78, S 7.02; found C 31.69, H 3.08, Cl 31.18, N 3.12, P 6.81, S 6.99.

***N*-[2,2,2-Trichloro-1-(diisopropoxyphosphoryl)ethylidene]benzenesulfonamide (1d):** This compound was prepared from sulfonamide **5d** (1.49 g, 3.3 mmol); white solid; m.p. 56 °C; yield: 1.19 g (80%). IR (Nyol): $\tilde{\nu}$ = 1050 (POC), 1180, 1380 (S=O), 1280 (P=O), 1630 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.47 (d, $^{3}J_{H,H}$ = 6 Hz, 6 H, CH_3), 1.50 (d, $^{3}J_{H,H}$ = 6 Hz, 6 H, CH_3), 5.01−5.12 (m, 2 H, CHO), 7.56 (t, $^{3}J_{H,H}$ = 8 Hz, 2 H, *m*-C−H, Ph), 7.64 (t, $^{3}J_{H,H}$ = 8 Hz, 1 H, *p*-C−H, Ph), 8.04 (d, $^{3}J_{H,H}$ = 8 Hz, 2 H, *o*-C−H, Ph) ppm. ^{31}P NMR ($CDCl_3$): δ = −6.5 ppm. $C_{14}H_{19}Cl_3NO_5PS$ (450.70): calcd. C 37.31, H 4.25, Cl 23.60, N 3.11, P 6.87, S 7.11; found C 37.28, H 4.24, Cl 23.63, N 3.10, P 6.90, S 7.09.

***N*-[2,2,2-Trichloro-1-(diisopropoxyphosphoryl)ethylidene]-*p*-toluenesulfonamide (1e):** This compound was prepared from sulfonamide **5e** (1.54 g, 3.3 mmol); white solid; m.p. 58 °C; yield: 1.24 g (81%). IR (Nyol): $\tilde{\nu}$ = 1020 (POC), 1175, 1380 (S=O), 1275 (P=O), 1630 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.46 (d, $^{3}J_{H,H}$ = 6.3 Hz, 6 H, C*H*$_3$CH), 1.49 (d, $^{3}J_{H,H}$ = 6.3 Hz, 6 H, C*H*$_3$CH), 2.45 (s, 3 H, C*H*$_3$Ar), 5.01−5.11 (m, 2 H, CHO), 7.34 (d, $^{3}J_{H,H}$ = 8 Hz, 2 H, Ar), 7.92 (d, $^{3}J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = −6.4 ppm. $C_{15}H_{21}Cl_3NO_5PS$ (464.73): calcd. C 38.77, H 4.55, Cl 22.89, N 3.01, P 6.66, S 6.90; found C 38.75, H 4.58, Cl 22.91, N 2.99, P 6.74, S 6.91.

General Procedure for Preparation of Chlorinated Sulfonamides (3): A mixture of the appropriate *N*-hydroxyalkylsulfonamide **2** and a 5% molar excess of PCl_5 in benzene (20 mL) was heated at 60 °C for 8 h. The solvent was evaporated in vacuo, and the residue was washed with petroleum ether to give the crystal product.

***N*-(1,2,2,2-Tetrachloroethyl)benzenesulfonamide (3a):** This compound was prepared from sulfonamide **2a** (4.3 g, 14.1 mmol) and PCl_5 (3.08 g, 14.8 mmol); white solid; m.p. 118 °C; yield: 4.46 g (98%). IR (Nyol): $\tilde{\nu}$ = 1175, 1375 (S=O), 3270 (NH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 5.78 (d, $^{3}J_{H,H}$ = 11 Hz, 1 H, NH), 5.98 (d, $^{3}J_{H,H}$ = 11 Hz, 1 H, CHCl), 7.57 (t, $^{3}J_{H,H}$ = 8 Hz, 2 H, *m*-C−H, Ph), 7.67 (t, $^{3}J_{H,H}$ = 8 Hz, 1 H, *p*-C−H, Ph), 7.95 (d, $^{3}J_{H,H}$ = 8 Hz, 2 H, *o*-C−H, Ph) ppm. $C_8H_7Cl_4NO_2S$ (323.02): calcd. C 29.75, H 2.18, Cl 43.90, N 4.34; found C 29.92, H 2.05, Cl 44.12, N 4.28.

***N*-(1,2,2,2-Tetrachloroethyl)-*p*-toluenesulfonamide (3b):** This compound was prepared from sulfonamide **2b** (4 g, 12.6 mmol) and PCl_5 (2.75 g, 13 mmol); white solid; m.p. 98 °C; yield: 4.41 g (98%). IR (Nyol): $\tilde{\nu}$ = 1180, 1375 (S=O), 3280 (NH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.46 (s, 3 H, CH_3), 5.86 (d, $^{3}J_{H,H}$ = 11.4 Hz, 1 H, NH), 5.97 (d, $^{3}J_{H,H}$ = 11.4 Hz, 1 H, CHCl), 7.35 (d, $^{3}J_{H,H}$ = 8 Hz, 2 H, Ar), 7.83 (d, $^{3}J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. $C_9H_9Cl_4NO_2S$ (337.05): calcd. C 32.07, H 2.69, Cl 42.07, N 4.16; found C 32.25, H 2.54, Cl 42.28, N 4.06.

4-Chloro-*N*-(1,2,2,2-tetrachloroethyl)benzenesulfonamide (3c): This compound was prepared from sulfonamide **2c** (6.51 g, 19.2 mmol) and PCl_5 (4.19 g, 20 mmol); white solid; m.p. 129 °C; yield: 6.8 g (99%). IR (Nyol): $\tilde{\nu}$ = 1180, 1380 (S=O), 3280 (NH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 5.83 (d, $^{3}J_{H,H}$ = 11 Hz, 1 H, NH), 5.97 (d, $^{3}J_{H,H}$ = 11 Hz, 1 H, CHCl), 7.55 (d, $^{3}J_{H,H}$ = 8 Hz, 2 H, Ar), 7.88 (d, $^{3}J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. $C_8H_6Cl_5NO_2S$ (357.47): calcd. C 26.88, H 1.69, Cl 49.59, N 3.92; found C 26.93, H 1.72, Cl 49.68, N 3.95.

General Procedure for Preparation of Phosphorylated Sulfonamides 5: A mixture of the appropriate chlorinated sulfonamide **3** and a 10% molar excess of phosphite or phosphinite **4** was heated in benzene at 80 °C for 4 h. The solvent was evaporated in vacuo and the residue was washed with diethyl ether to give the crystal product.

***N*-[2,2,2-Trichloro-1-(diethoxyphosphoryl)ethyl]benzenesulfonamide (5a):** This compound was prepared from sulfonamide **3a** (2 g,

6.3 mmol) and triethyl phosphite (1.1 g, 6.3 mmol); white solid; m.p. 113 °C; yield: 2.42 g (92%). IR (KBr): $\tilde{\nu}$ = 1040 (POC), 1180, 1340 (S=O), 1270 (P=O), 3140 (NH) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.28 (t, $^3J_{H,H}$ = 7 Hz, 3 H, CH_3), 1.32 (t, $^3J_{H,H}$ = 7 Hz, 3 H, CH_3), 3.98−4.22 (m, 4 H, CH_2O), 4.68 (dd, $^2J_{H,P}$ = 19.2, $^3J_{H,H}$ = 9.9 Hz, 1 H, CHP), 6.08 (dd, $^3J_{H,H}$ = 9.9, $^3J_{H,P}$ = 7.5 Hz, 1 H, NH), 7.49 (t, $^3J_{H,H}$ = 8 Hz, 2 H, *m*-C−H, Ph), 7.57 (t, $^3J_{H,H}$ = 8 Hz, 1 H, *p*-C−H, Ph), 7.92 (d, $^3J_{H,H}$ = 8 Hz, 2 H, *o*-C−H, Ph) ppm. ^{31}P NMR ($CDCl_3$): δ = 14.4 ppm. $C_{12}H_{17}Cl_3NO_5PS$ (424.66): calcd. C 33.94, H 4.03, Cl 25.05, N 3.30, P 7.29; found C 33.81, H 3.92, Cl 25.20, N 3.34, P 7.23.

***N*-[2,2,2-Trichloro-1-(diethoxyphosphoryl)ethyl]-*p*-toluenesulfonamide (5b):** This compound was prepared from sulfonamide **3b** (7.85 g, 23.3 mmol) and triethyl phosphite (3.9 g, 23.3 mmol); white solid; m.p. 138 °C; yield: 8.3 g (96%). IR (KBr): $\tilde{\nu}$ = 1050 (POC), 1170, 1340 (S=O), 1260 (P=O), 3140 (NH) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.31 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3CH_2), 1.34 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3CH_2), 2.42 (s, 3 H, CH_3Ar), 4.04−4.25 (m, 4 H, CH_2O), 4.68 (dd, $^2J_{H,P}$ = 19.8, $^3J_{H,H}$ = 9.8 Hz, 1 H, CHP), 5.7 (dd, $^3J_{H,H}$ = 9.8, $^3J_{H,P}$ = 9.8 Hz, 1 H, NH), 7.29 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar), 7.79 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 15.1 ppm. $C_{13}H_{19}Cl_3NO_5PS$ (438.69): calcd. C 35.59, H 4.37, Cl 24.24, N 3.19, P 7.06; found C 35.60, H 4.26, Cl 24.45, N 3.35, P 6.89.

4-Chloro-*N*-[2,2,2-trichloro-1-(diethoxyphosphoryl)ethyl]-benzenesulfonamide (5c): This compound was prepared from benzenesulfonamide **3c** (6.8 g, 19.2 mmol) and triethyl phosphite (3.8 g, 19.2 mmol); white solid; m.p. 117 °C; yield: 8.3 g (94%). IR (KBr): $\tilde{\nu}$ = 1040 (POC), 1180, 1350 (S=O), 1260 (P=O), 3130 (NH) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.31 (t, $^3J_{H,H}$ = 7 Hz, 3 H, CH_3), 1.34 (t, $^3J_{H,H}$ = 7 Hz, 3 H, CH_3), 4.04−4.29 (m, 4 H, CH_2O), 4.68 (dd, $^2J_{H,P}$ = 19, $^3J_{H,H}$ = 10 Hz, 1 H, CHP), 6.40 (dd, $^3J_{H,H}$ = 10, $^3J_{H,P}$ = 7 Hz, 1 H, NH), 7.47 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar), 7.87 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 14.3 ppm. $C_{12}H_{16}Cl_4NO_5PS$ (459.11): calcd. C 31.39, H 3.51, Cl 30.89, N 3.05, P 6.75, S 6.98; found C 31.36, H 3.50, Cl 30.73, N 3.15, P 6.90, S 7.00.

***N*-[2,2,2-Trichloro-1-(diisopropoxyphosphoryl)ethyl]benzenesulfonamide (5d):** This compound was prepared from sulfonamide **3a** (3.2 g, 9.9 mmol) and triisopropyl phosphite (2.06 g, 9.9 mmol); white solid; m.p. 119 °C; yield: 4 g (90%). IR (KBr): $\tilde{\nu}$ = 1020 (POC), 1175, 1350 (S=O), 1275 (P=O), 3140 (NH) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.36 (m, 12 H, CH_3), 4.66 (dd, $^2J_{H,P}$ = 19.8, $^3J_{H,H}$ = 9.6 Hz, 1 H, CHP), 4.76−4.88 (m, 2 H, CHO), 5.82 (dd, $^3J_{H,H}$ = 9.6, $^3J_{H,P}$ = 9.6 Hz, 1 H, NH), 7.50 (t, $^3J_{H,H}$ = 8 Hz, 2 H, *m*-C−H, Ph), 7.58 (t, $^3J_{H,H}$ = 8 Hz, 1 H, *p*-C−H, Ph), 7.92 (d, $^3J_{H,H}$ = 8 Hz, 2 H, *o*-C−H, Ph) ppm. ^{31}P NMR ($CDCl_3$): δ = 12.2 ppm. $C_{14}H_{21}Cl_3NO_5PS$ (452.72): calcd. C 37.14, H 4.68, Cl 23.49, N 3.09, P 6.84; found C 37.21, H 4.62, Cl 23.32, N 3.12, P 6.79.

***N*-[2,2,2-Trichloro-1-(diisopropoxyphosphoryl)ethyl]-*p*-toluenesulfonamide (5e):** This compound was prepared from sulfonamide **3b** (3.1 g, 9.2 mmol) and triisopropyl phosphite (1.92 g, 9.2 mmol); white solid; m.p. 133 °C; yield: 3.8 g (88%). IR (KBr): $\tilde{\nu}$ = 1010 (POC), 1175, 1350 (S=O), 1255 (P=O), 3150 (NH) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.37 (m, 12 H, CH_3CH), 2.42 (s, 3 H, CH_3Ar), 4.65 (dd, $^2J_{H,P}$ = 19.5, $^3J_{H,H}$ = 9 Hz, 1 H, CHP), 4.76−4.88 (m, 2 H, CHO), 5.67 (dd, $^3J_{H,H}$ = 9, $^3J_{H,P}$ = 9 Hz, 1 H, NH), 7.28 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar), 7.80 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 12.2 ppm. $C_{15}H_{23}Cl_3NO_5PS$ (466.75): calcd. C 38.60, H 4.97, Cl 22.79, N 3.00, P 6.64; found C 38.64, H 4.92, Cl 22.67, N 3.12, P 6.71.

***N*-[2,2,2-Trichloro-1-(diphenylphosphanyl)ethyl]-*p*-toluenesulfonamide (5f):** This compound was prepared from sulfonamide **3b** (1.73 g, 5.1 mmol) and ethyl diphenylphosphinite (1.18 g, 5.1 mmol); white solid; m.p. 191 °C; yield: 2.1 g (81%). IR (KBr): $\tilde{\nu}$ = 1170, 1340 (S=O), 1205 (P=O), 3170 (NH) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.34 (s, 3 H, CH_3), 5.27 (dd, $^2J_{H,P}$ = 9.3, $^3J_{H,H}$ = 6 Hz, 1 H, CHP), 6.41 (dd, $^3J_{H,H}$ = 6, $^3J_{H,H}$ = 6 Hz, 1 H, NH), 7.05 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar), 7.44−7.64 (m, 8 H, Ar), 7.82−7.91 (m, 4 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 29.5 ppm. $C_{21}H_{19}Cl_3NO_3PS$ (502.78): calcd. C 50.16, H 3.81, Cl 21.16, N 2.79, P 6.16, S 6.38; found C 50.24, H 3.87, Cl 21.20, N 2.75, P 6.14, S 6.41.

General Procedure for Preparation of Diphosphorylated *N*-Ethenylsulfonamides 8: An equimolar amount of the appropriate phosphite or phosphinite was added to a cooled (ice) and stirred benzene solution of imidoylphosphonate **1**. After 1 h, the solvent was evaporated and the oily residue was washed with petroleum ether and dried in vacuo.

***N*-[2,2-Dichloro-1-(diethoxyphosphoryl)ethenyl]-*N*-diethoxyphosphoryl-*p*-toluenesulfonamide (8a):** This compound was prepared from imidoylphosphonate **1b** (0.19 g, 0.43 mmol) and triethyl phosphite (0.07 g, 0.43 mmol); colorless oil; yield: 0.2 g (87%). IR (film): $\tilde{\nu}$ = 1050 (POC), 1180, 1380 (S=O), 1280 (P=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.30−1.39 (m, 12 H, CH_3CH_2), 2.44 (s, 3 H, CH_3Ar), 4.07−4.38 (m, 8 H, CH_2O), 7.31 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar), 7.93 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. NMR ^{31}P ($CDCl_3$): δ = −3.9 (1 P, PN), 9.5 (1 P, PC) ppm. $C_{17}H_{27}Cl_2NO_8P_2S$ (538.32): calcd. C 37.93, H 5.06, Cl 13.17, N 2.60, P 11.51; found C 37.85, H 5.01, Cl 13.28, N 2.63, P 11.48.

***N*-[2,2-Dichloro-1-(diethoxyphosphoryl)ethenyl]-*N*-diisopropoxyphoslphorybenzenesulfonamide (8b):** This compound was prepared from imidoylphosphonate **1a** (0.17 g, 0.39 mmol) and triisopropyl phosphite (0.08 g, 0.39 mmol); colorless oil; yield: 0.2 g (91%). IR (film): $\tilde{\nu}$ = 1050 (POC), 1175, 1380 (S=O), 1275 (P=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.30−1.34 (m, 18 H, CH_3), 4.19−4.31 (m, 4 H, CH_2O), 4.78−4.89 (m, 1 H, CHO), 5.07−5.17 (m, 1 H, CHO), 7.51 (t, $^3J_{H,H}$ = 8 Hz, 2 H, *m*-C−H, Ph), 7.63 (t, $^3J_{H,H}$ = 8 Hz, 1 H, *p*-C−H, Ph), 8.05 (d, $^3J_{H,H}$ = 8 Hz, 2 H, *o*-C−H, Ph) ppm. ^{31}P NMR ($CDCl_3$): δ = −6.9 (1 P, PN), 8.6 (1 P, PC) ppm. $C_{18}H_{29}Cl_2NO_8P_2S$ (552.34): calcd. C 39.14, H 5.29, Cl 12.84, N 2.54, P 11.22; found C 39.08, H 5.25, Cl 12.91, N 2.53, P 11.19.

***N*-[2,2-Dichloro-1-(diisopropoxyphosphoryl)ethenyl]-*N*-diethoxyphosphoryl-*p*-toluenesulfonamide (8c):** This compound was prepared from imidoylphosphonate **1e** (0.23 g, 0.49 mmol) and triethyl phosphite (0.08 g, 0.49 mmol); colorless oil; yield: 0.24 g (89%). IR (CCl_4): $\tilde{\nu}$ = 1040 (POC), 1185, 1390 (S=O), 1280 (P=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.27−1.39 (m, 18 H, CH_3CH + CH_3CH_2), 2.43 (s, 3 H, CH_3Ar), 4.12−4.34 (m, 4 H, CH_2O), 4.85−4.95 (m, 2 H, CHO), 7.30 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar), 7.94 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. NMR ^{31}P ($CDCl_3$): δ = −3.3 (1 P, PN), 7.7 (1 P, PC) ppm. $C_{19}H_{31}Cl_2NO_8P_2S$ (566.37): calcd. C 40.29, H 5.52, Cl 12.52, N 2.47, P 10.94, S 5.66; found C 40.21, H 5.49, Cl 12.60, N 2.49, P 10.91, S 5.63.

***N*-[2,2-Dichloro-1-(diisopropoxyphosphoryl)ethenyl]-*N*-diisopropoxyphosphorylbenzenesulfonamide (8d):** This compound was prepared from imidoylphosphonate **1d** (0.095 g, 0.21 mmol) and triisopropyl phosphite (0.044 g, 0.21 mmol); white solid; m.p. 60 °C; yield: 0.1 g (86%). IR (CCl_4): $\tilde{\nu}$ = 1040 (POC), 1190, 1390 (S=O), 1280 (P=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.32−1.42 (m, 24 H, CH_3), 4.78−4.99 (m, 3 H, CHO), 5.08−5.19 (m, 1 H, CHO), 7.50 (t, $^3J_{H,H}$ = 8 Hz, 2 H, *m*-C−H, Ph), 7.62 (t, $^3J_{H,H}$ = 8 Hz, 1 H, *p*-

C−H, Ph), 8.06 (d, $^3J_{H,H}$ = 8 Hz, 2 H, *o*-C−H, Ph) ppm. ^{31}P NMR ($CDCl_3$): δ = −6.7 (1 P, PN), 7.7 (1 P, PC) ppm. $C_{20}H_{33}Cl_2NO_8P_2S$ (580.40): calcd. C 41.39, H 5.73, Cl 12.22, N 2.41, P 10.67, S 5.52; found C 41.57, H 5.76, Cl 12.31, N 2.39, P 10.71, S 5.59.

***N*-[2,2-Dichloro-1-(diethoxyphosphoryl)ethenyl]-*N*-(diphenylphosphinoyl)benzenesulfonamide (8e):** This compound was prepared from imidoylphosphonate **1a** (0.12 g, 0.29 mmol) and ethyl diphenylphosphinite (0.07 g, 0.29 mmol); colorless oil; yield: 0.14 g (82%). IR (film): ṽ = 1060 (POC), 1180, 1370 (S=O), 1250 (P=O) cm^{-1}. NMR ^{1}H ($CDCl_3$): δ = 1.24 (t, $^3J_{H,H}$ = 6. 7 Hz, 3 H, CH_3), 1.39 (t, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH_3), 4.01−4.34 (m, 4 H, CH_2O), 7.38−7.81 (m, 12 H, Ph), 7.98−8.12 (m, 2 H, Ph), 8.30−8.37 (m, 1 H, Ph) ppm. ^{31}P NMR ($CDCl_3$): δ = 9.1 (1 P, PC), 33.3 (1 P, PN) ppm. $C_{24}H_{25}Cl_2NO_6P_2S$ (588.38): calcd. C 48.99, H 4.28, Cl 12.05, N 2.38, P 10.53, S 5.45; found C 49.12, H 4.32, Cl 12.18, N 2.34, P 10.47, S 5.40.

***N*-[2,2-Dichloro-1-(diethoxyphosphoryl)ethenyl]benzenesulfonamide (11):** A mixture of sulfonamide **5a** (0.25 g, 0.6 mmol) and triethylamine (0.1 mL, 0.66 mmol) in benzene (5 mL) was heated at reflux for 2 h. The solution was shaken with water, dried ($MgSO_4$), and concentrated in vacuo to give the crystalline product: m.p. 61−62 °C; yield: 0.2 g (84%). IR (KBr): ṽ = 1040 (POC), 1180, 1350 (S=O), 1260 (P=O), 3130 (NH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.31 (t, $^3J_{H,H}$ = 7 Hz, 6 H, CH_3), 4.01−4.16 (m, 4 H, CH_2O), 6.54 (d, $^3J_{H,P}$ = 7.5 Hz, 1 H, NH), 7.52 (t, $^3J_{H,H}$ = 8 Hz, 2 H, *m*-C−H, Ph), 7.61 (t, $^3J_{H,H}$ = 8 Hz, 1 H, *p*-C−H, Ph), 7.95 (d, $^3J_{H,H}$ = 8 Hz, 2 H, *o*-C−H, Ph) ppm. ^{31}P NMR ($CDCl_3$): δ = 8.6 ppm. $C_{12}H_{16}Cl_2NO_5PS$ (388.20): calcd. C 37.13, H 4.15, Cl 18.26, N 3.61, P 7.98; found C 37.25, H 4.21, Cl 18.34, N 3.57, P 8.15.

General Procedure for Preparation of Phosphorylated Sulfonamides 12: Methanol was added in a fivefold molar excess to a solution of the appropriate imidoylphosphonate **1** (0.37 mmol) in benzene (2 mL). The mixture was stirred at room temperature for 8 h and concentrated in vacuo, and the solid residue was washed with petroleum ether.

4-Chloro-*N*-(2,2,2-trichloro-1-diethoxyphosphoryl-1-methoxyethyl)-benzenesulfonamide (12a): This compound was prepared from imidoylphosphonate **1c** (0.17 g, 0.37 mmol) and methanol (0.08 mL, 1.85 mmol); white solid; m.p. 116 °C; yield: 0.13 g (74%). IR (KBr): ṽ = 1040 (POC), 1180, 1350 (S=O), 1260 (P=O), 3120 (NH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.36 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3CH$_2$), 1.37 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3CH$_2$), 3.92 (s, 3 H, CH_3O), 4.18−4.38 (m, 4 H, CH_2O), 6.07 (d, $^3J_{H,P}$ = 5.4 Hz, 1 H, NH), 7.46 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar), 7.87 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 11.6 ppm. $C_{13}H_{18}Cl_4NO_6PS$ (489.14): calcd. C 31.92, H 3.71, Cl 28.99, N 2.86, P 6.33; found C 31.79, H 3.75, Cl 28.81, N 2.91, P 6.28.

***N*-(2,2,2-Trichloro-1-diisopropoxyphosphoryl-1-methoxyethyl)-*p*-toluenesulfonamide (12b):** This compound was prepared from imidoylphosphonate **1e** (0.17 g, 0.37 mmol) and methanol (0.08 mL, 1.85 mmol); white solid; m.p. 85 °C; yield: 0.13 g (69%). IR (KBr): ṽ = 1040 (POC), 1180, 1350 (S=O), 1260 (P=O), 3110 (NH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.39 (m, 12 H, CH_3CH), 2.41 (s, 3 H, CH_3Ar), 3.89 (s, 3 H, CH_3O), 4.78−4.90 (m, 2 H, CHO), 6.02 (d, $^3J_{H,P}$ = 6 Hz, 1 H, NH), 7.26 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar), 7.81 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 10.2 ppm. $C_{16}H_{25}Cl_3NO_6PS$ (496.77): calcd. C 38.68, H 5.07, Cl 21.41, N 2.82, P 6.24; found C 38.54, H 4.97, Cl 21.54, N 2.86, P 6.32.

***N*-[1-Benzylthio-2,2,2-trichloro-1-(diethoxyphosphoryl)ethyl]-4-chlorobenzenesulfonamide (15a):** Benzyl mercaptan (0.05 mL, 0.43 mmol) was added to a stirred solution of imidoylphosphonate **1c** (0.2 g, 0.43 mmol) in benzene (5 mL). After the mixture had been allowed to stand for 24 h at room temperature, the precipitate formed was filtered off and washed with petroleum ether to give the title product as a white powder; m.p. 148 °C; yield: 0.21 g (81%). IR (KBr): ṽ = 1050 (POC), 1180, 1350 (S=O), 1280 (P=O), 3250 (NH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.30 (t, $^3J_{H,H}$ = 7 Hz, 6 H, CH_3), 4.06−4.31 (m, 4 H, CH_2O), 4.46 (d, $^2J_{H_AH_B}$ = 9.9 Hz, 1 H, SCH_A), 4.56 (d, $^2J_{H_BH_A}$ = 9.9 Hz, 1 H, SCH_B), 6.13 (d, $^3J_{H,P}$ = 5 Hz, 1 H, NH), 7.33−7.43 (m, 7 H, Ar), 7.91 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 12.2 ppm. $C_{19}H_{22}Cl_4NO_5PS_2$ (581.30): calcd. C 39.26, H 3.81, Cl 24.40, N 2.41, P 5.33; found C 39.37, H 3.95, Cl 24.62, N 2.39, P 5.28.

4-Chloro-*N*-[2,2,2-trichloro-1-diethoxyphosphoryl-1-(2-hydroxyethylthio)ethyl]benzenesulfonamide (15b): Mercaptoethanol (0.035 mL, 0.50 mmol) was added to a stirred solution of imidoylphosphonate **1c** (0.23 g, 0.50 mmol) in benzene (5 mL) and the mixture was allowed to stand for 24 h at room temperature. The precipitated product was separated by filtration and washed with benzene; white solid; m.p. 135 °C; yield: 0.24 g (90%). IR (KBr): ṽ = 1080 (POC), 1180, 1360 (S=O), 1240 (P=O), 3120 (NH), 3330 (OH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.33 (t, $^3J_{H,H}$ = 7 Hz, 6 H, CH_3), 3.38−3.44 (m, 2 H, CH_2OH), 3.79−3.93 (m, 2 H, CH_2S), 4.11−4.34 (m, 4 H, CH_2OP), 6.45 (d, $^3J_{H,P}$ = 8.7 Hz, 1 H, NH), 7.47 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar), 7.97 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 12.6 ppm. $C_{14}H_{20}Cl_4NO_6PS_2$ (535.23): calcd. C 31.42, H 3.77, Cl 26.50, N 2.62, P 5.79, S 11.98; found C 31.38, H 3.76, Cl 26.55, N 2.60, P 5.76, S 12.03.

***N*-[2,2,2-Trichloro-1-(4-chlorophenylthio)-1-(diethoxyphosphoryl)-ethyl]benzenesulfonamide (15c):** 4-Chlorothiophenol (0.058 g, 0.40 mmol) was added to a solution of imidoylphosphonate **1a** (0.17 g, 0.40 mmol) in benzene (5 mL). After 8 h at room temperature, the solvent was evaporated in vacuo and the solid residue was washed with diethyl ether; white powder; m.p. 87 °C; yield: 0.15 g (65%). IR (KBr): ṽ = 1070 (POC), 1180, 1360 (S=O), 1270 (P=O), 3290 (NH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.33 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.34 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 4.17−4.42 (m, 4 H, CH_2O), 5.00 (d, $^3J_{H,P}$ = 18.3 Hz, 1 H, NH), 7.09 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar), 7.46−7.62 (m, 5 H, Ar), 7.93 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.1 (d, $^3J_{C,P}$ = 6.6 Hz, CH_3), 16.4 (d, $^3J_{C,P}$ = 6 Hz, CH_3), 64.9 (d, $^2J_{C,P}$ = 8.5 Hz, CH_2O), 66.0 (d, $^2J_{C,P}$ = 8 Hz, CH_2O), 80.2 (d, $^1J_{C,P}$ = 163 Hz, CP), 104.2 (d, $^2J_{C,P}$ = 16.1 Hz, CCl_3), 126.8, 128.2, 128.3, 128.8, 132.7, 137.4, 139.9, 141.3 (s, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 11.2 ppm. $C_{18}H_{20}Cl_4NO_5PS_2$ (567.27): calcd. C 38.11, H 3.55, Cl 25.00, N 2.47, P 5.46, S 11.31; found C 38.16, H 3.57, Cl 25.11, N 2.45, P 5.26, S 11.42.

4-Chloro-*N*-[2,2,2-trichloro-1-diethoxyphosphoryl-1-(4-fluorophenylthio)ethyl]benzenesulfonamide (15d): 4-Fluorothiophenol (0.14 g, 1.1 mmol) was added to a solution of imidoylphosphonate **1c** (0.50 g, 1.1 mmol) in benzene (10 mL). After 8 h at room temperature, the solvent was evaporated in vacuo and the solid residue was washed with diethyl ether; white powder; m.p. 112 °C; yield: 0.40 g (64%). IR (KBr): ṽ = 1060 (POC), 1185, 1355 (S=O), 1270 (P=O), 3280 (NH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.35 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 1.36 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 4.18−4.43 (m, 4 H, CH_2O), 4.98 (d, $^3J_{H,P}$ = 18 Hz, 1 H, NH), 6.83−6.89 (m, 2 H, Ar), 7.43 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar), 7.59−7.64 (m, 2 H, Ar), 7.86 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. ^{19}F NMR ($CDCl_3$): δ = −108.19 ppm. ^{31}P NMR ($CDCl_3$): δ = 11.2 ppm.

$C_{18}H_{19}Cl_4FNO_5PS_2$ (585.26): calcd. C 36.94, H 3.27, Cl 24.23, N 2.39, P 5.29; found C 37.11, H 3.30, Cl 24.38, N 2.36, P 5.25.

Reactions between Imidoylphosphonates 1 and Mercaptoacetic Acid. General Procedure: Mercaptoacetic acid (0.3 mmol) was added to a stirred solution of the appropriate imidoylphosphonate **1** (0.3 mmol) in benzene (5 mL). After 2 h at room temperature, the formation of a 4:1 mixture of **16** and **17** was revealed by the ^{31}P NMR spectra. Two or three drops of $SOCl_2$ were added, and the mixture was heated at reflux for 10 min. The solvent was evaporated in vacuo and the solid residue was washed with diethyl ether to give compound **17**.

[2,2,2-Trichloro-1-(4-chlorophenylsulfonylamino)-1-(diethoxyphosphoryl)ethylthio]acetic Acid (16a): ^1H NMR ($CDCl_3$): δ = 1.36 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 1.38 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 4.01 (d, $^2J_{H_AH_B}$ = 16.2 Hz, 1 H, SCH_A), 4.15 (d, $^2J_{H_BH_A}$ = 16.2 Hz, 1 H, SCH_B), 4.13−4.39 (m, 4 H, CH_2O), 6.52 (d, $^3J_{H,P}$ = 9.3 Hz, 1 H, NH), 7.47 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar), 7.97 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 12.0 ppm.

[2,2,2-Trichloro-1-diisopropoxyphosphoryl-1-(*p*-tosylamino)-aethylthio]cetic Acid (16b): ^1H NMR ($CDCl_3$): δ = 1.27−1.48 (m, 12 H, C*H*$_3$CH), 2.41 (s, 3 H, C*H*$_3$Ar), 3.98 (d, $^2J_{H_AH_B}$ = 15.6 Hz, 1 H, SCH_A), 4.16 (d, $^2J_{H_BH_A}$ = 15.6 Hz, 1 H, SCH_B), 4.68−4.98 (m, 2 H, CHO), 6.25 (d, $^3J_{H,P}$ = 8 Hz, 1 H, NH), 7.28 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar), 7.89 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 10.8 ppm.

3-(4-Chlorophenylsulfonyl)-2-diethoxyphosphoryl-2-trichloromethyl-1,3-thiazolidin-4-one (17a): This compound was prepared from imidoylphosphonate **1c** (0.24 g, 0.51 mmol) and mercaptoacetic acid (0.04 mL, 0.51 mmol); m.p. 145 °C (dec.); yield: 0.14 g (51%). IR (KBr): $\tilde{\nu}$ = 1040 (POC), 1190, 1390 (S=O), 1255 (P=O), 1720 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.44 (t, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 3.47 (d, $^2J_{H_AH_B}$ = 16.2 Hz, 1 H, SCH_A), 3.80 (d, $^2J_{H_BH_A}$ = 16.2 Hz, 1 H, SCH_B), 4.28−4.54 (m, 4 H, CH_2O), 7.50 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar), 8.47 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 11.4 ppm. $C_{14}H_{16}Cl_4NO_6PS_2$ (531.197): calcd. C 31.65, H 3.04, Cl 26.70, N 2.64, P 5.83, S 12.07; found C 31.72, H 3.06, Cl 26.92, N 2.63, P 5.79, S 11.95.

2-Diisopropoxyphosphoryl-3-tosyl-2-trichloromethyl-1,3-thiazolidin-4-one (17b): This compound was prepared from imidoylphosphonate **1e** (0.14 g, 0.3 mmol) and mercaptoacetic acid (0.02 mL, 0.3 mmol); m.p. 150 °C (dec.); yield: 73%. IR (KBr): $\tilde{\nu}$ = 1040 (POC), 1180, 1365 (S=O), 1245 (P=O), 1730 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.46 (t, $^3J_{H,H}$ = 7.2 Hz, 12 H, C*H*$_3$CH), 2.42 (s, 3 H, C*H*$_3$Ar), 3.45 (d, $^2J_{H_AH_B}$ = 15.6 Hz, 1 H, SCH_A), 3.76 (d, $^2J_{H_BH_A}$ = 15.6 Hz, 1 H, SCH_B), 4.91−5.01 (m, 1 H, CHO), 5.11−5.21 (m, 1 H, CHO), 7.33 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar), 8.38 (d, $^3J_{H,H}$ = 8 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.7 (s, *C*H$_3$Ar), 23.2 (s, *C*H$_3$CH), 23.3 (s, *C*H$_3$CH), 24.4 (s, *C*H$_3$CH), 24.7 (s, *C*H$_3$CH), 33.1 (s, CH_2S), 75.4 (d, $^2J_{C,P}$ = 8 Hz, CHO), 75.8 (d, $^2J_{C,P}$ = 8 Hz, CHO), 84.7 (d, $^1J_{C,P}$ = 169 Hz, CP), 105.6 (d, $^2J_{C,P}$ = 20 Hz, CCl_3), 129.0 (s, Ar), 131.1 (s, Ar), 135.44 (s, *C*CH$_3$), 145.4 (s, CSO_2), 171.6 (d, $^3J_{C,P}$ = 8 Hz, C=O) ppm. ^{31}P NMR ($CDCl_3$): δ = 10.0 ppm. $C_{17}H_{23}Cl_3NO_6PS_2$ (538.83): calcd. C 37.89, H 4.30, Cl 19.74, N 2.60, P 5.75, S 11.90; found C 38.01, H 4.33, Cl 19.98, N 2.56, P 5.71, S 11.84.

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