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An Easy One-Pot Procedure for the Synthesis of *N*-Sulfonyl Phosphorous Ylides and Sulfonyl Iminophosphoranes

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Summary. Reaction of triphenylphosphine and an electron deficient acetylenic ester in the presence of strong N–H acid such as alkyl and aryl sulfamides or acetamide produces phosphorous ylides at room temperature in CH_2Cl_2. The aryl sulfamide phosphoranes undergo a smooth transformation reaction in boiling toluene and produce iminophosphoranes.

Keywords. Iminophosphorane; *N*-Sulfonyl phosphorous ylides; Aza-*Wittig* reaction.

Introduction

The iminophosphoranes (phosphazenes, phosphineimines, phosphazo compounds), which are electronically related to phosphorous are important intermediates in the synthesis of organic compounds [1, 2]. The iminophosphoranes have been synthesized *via* two major routes: (i) The *Staudinger* reaction using tertiary phosphines with organic azides [3] and (ii) the *Kirsanov* reaction constituting an imination of phosphorous pentachloride and its derivatives with compounds containing amino groups [4]. The availability of functionalized iminophosphoranes has been largely expanded through the synthesis of nitrogen heterocycles by intramolecular and intermolecular Aza-*Wittig* reactions. In recent years numerous research papers and several review articles have appeared describing the varied use of iminophosphoranes as powerful tools in organic synthesis strategies directed towards the construction of nitrogen containing hetrocycles [5–8].

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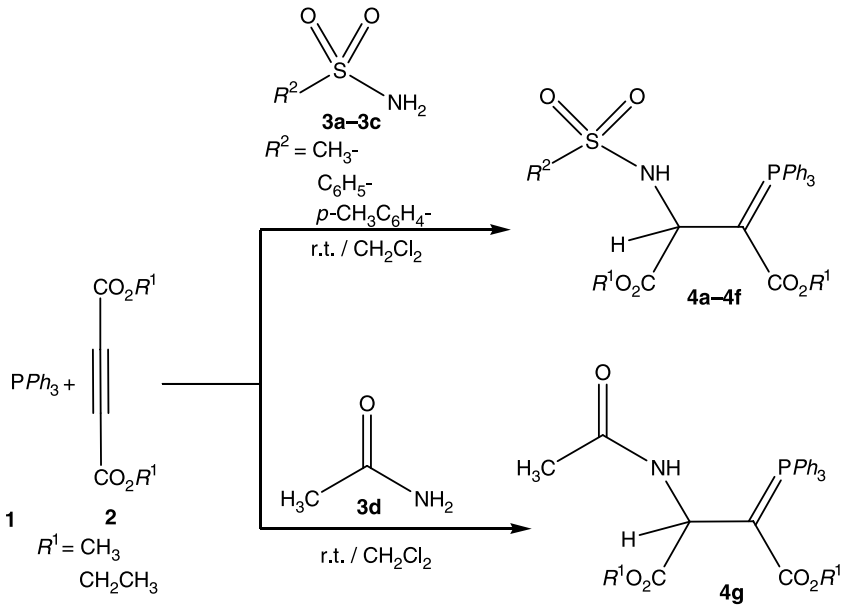
The successful attack by nucleophilic trivalent phosphines on a carbon atom is facilitated when the latter is conjugated with a carbonyl group, or when it is part of an unsaturated bond activated otherwise [9–17]. There have been many studies on reactions between trivalent phosphorus nucleophiles and α,β-unsaturated carbonyl compounds in the presence of a proton source such as an alcohol, phenol, or a CH-acid [9, 17, 18].

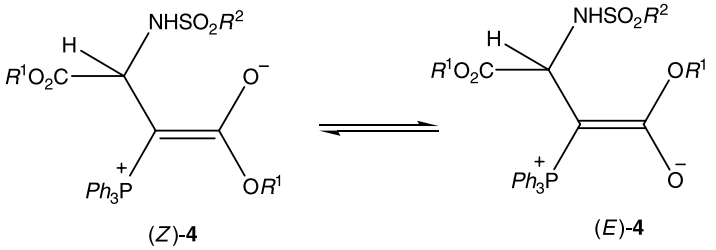
During the course of our studies on the development of new multicomponent reactions [19, 20] we investigated the reaction of triphenylphosphine (**1**) and dialkyl acetylenedicarboxylate **2** in the presence of alkyl and aryl sulfamides **3a–3c** or acetamide **3d** (Scheme 1).

Results and Discussion

The novel three component condensation reaction shown in Scheme 1 produces the stable phosphorous ylides **4a–4g** in excellent yields in CH_2Cl_2 at room temperature without using any catalyst and activator. The structures of **4a–4g** were deduced from their high-field ^1H, ^{13}C, and ^{31}P NMR and IR spectral data. The nature of these compounds as 1:1:1 adducts were apparent from their mass spectra, which displayed the corresponding molecular ion peaks. The ^1H, ^{13}C, and ^{31}P NMR spectra of ylides **4a–4g** are consistent with the presence of two isomers. Selected major and minor diastereomers of **4a–4g** are shown in Scheme 2. The ylide moiety of these compounds is



Scheme 1



Scheme 2

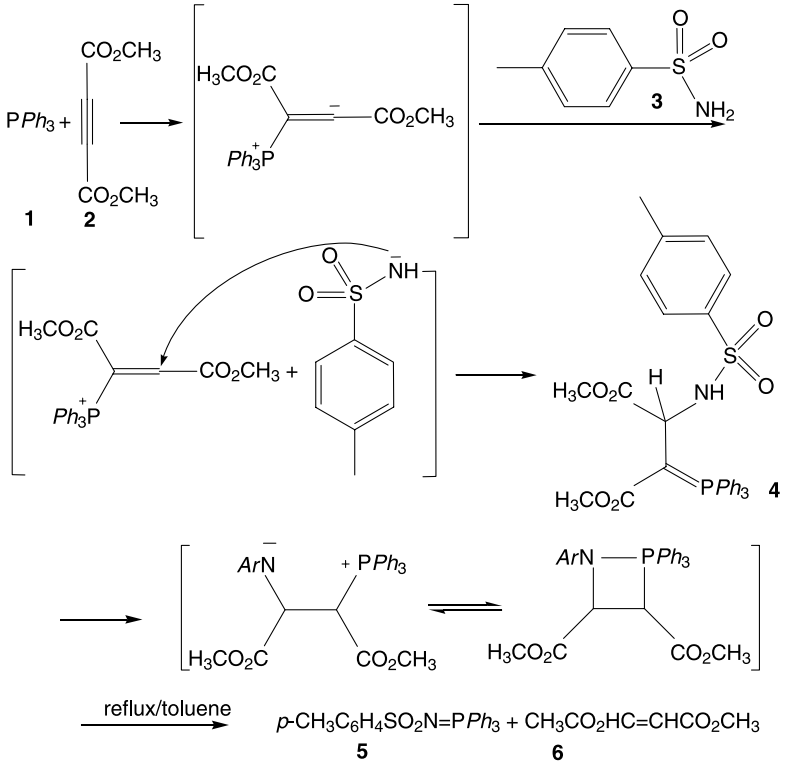
strongly conjugated with the adjacent carbonyl group and rotation about the partial double bond in (*E*)-4 and (*Z*)-4 is slow on the NMR time scale at ambient temperature (see Scheme 2).

On the basis of the well established chemistry of trivalent phosphorus nucleophiles, it is reasonable to assume that phosphorus ylide **4** results from the initial addition of **1** to **2** and subsequent protonation of the 1:1 adduct by the NH-acid **3**. Then, the *Michael* acceptor is attacked by the nitrogen atom of the conjugate base of the NH-acid to form phosphorane **4**. Phosphorus ylides **4a**–**4g** undergo a clean reaction in boiling toluene to produce iminophosphoranes **5** and dimethyl fumarate or dimethyl maleate (Scheme 3).

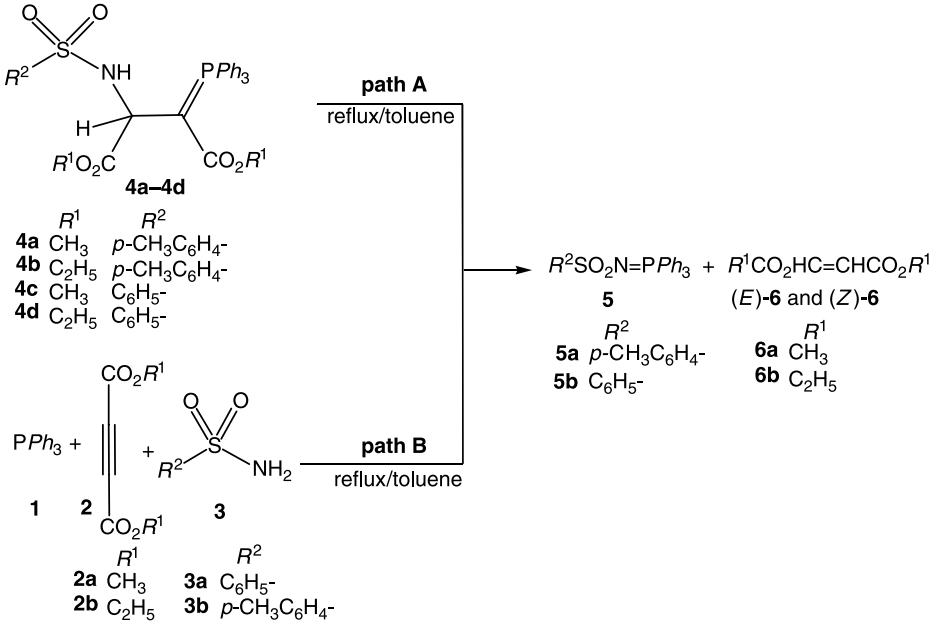
Structures of iminophosphoranes **5a** and **5b** were assigned to the isolated products on the basis of their IR, ^{1}H, ^{13}C, ^{31}P, and mass spectra. Partial assignments of the ^{1}H, ^{13}C, and ^{31}P resonances in the ^{1}H, ^{13}C, and ^{31}P NMR spectra of **5a** and **5b** are given in the exp. part.

It is important to note that the aryl sulfamides **4a**–**4d** undergo a smooth transformation in boiling toluene and produce iminophosphoranes **5** (Scheme 4, **path A**); However, methyl sulfamides **4e** and **4f** and acetamide derivative **4g** did not react under the above mentioned conditions. Thus, the reactions of **1**, **2**, and aryl sulfamide were carried out under reflux conditions in toluene and directly produced **5** (Scheme 4, **path B**).

In conclusion, we introduced a new three-component condensation reaction of triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of alkyl and aryl sulfamides or acetamide for the synthesis of a novel family of stable phosphorous



Scheme 3



Scheme 4

ylide systems. The one-pot nature protocol in the absence of catalyst makes it an interesting approach. In addition, although the present synthesis of iminophosphorans follows the older methods it offers significant advantages for the synthesis of iminophosphoranes from sulfonamides and their ylides.

Experimental

Melting points were measured on an Electrothermal 9100 apparatus. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13, 75.47, and 121.48 MHz. NMR spectra were obtained on solutions in *DMSO*-d_6. All the products are known compounds (except **4e**–**4g**), which were characterized by IR, ^{1}H, ^{13}C, and ^{31}P NMR spectral data and their mps compared with literature [21, 22].

Dimethyl 2-(p-methylsulfonamido)-3-(triphenylphosphoranylidene)butandioate (**4a**)
To a magnetically stirred solution of 0.262 g **1** (1 mmol) and 0.171 g *p*-toluenesolfonamide (1 mmol) in 20 cm^3 CH_2Cl_2 was added dropwise a mixture of 0.142 g dimethyl acetylenedicarboxylate (1 mmol) in 2 cm^3 CH_2Cl_2 at room temperature over 10 min. The reaction mixture was stirred for 5 h at room temperature. After completion of the reaction the solvent was removed under reduced pressure and the residual solid recrystallized from 1:1 acetone:*n*-hexane. Yield 0.495 g (86%); major isomer: 61.8%, minor isomer: 38.2%; pale yellow powder, mp 163–164°C (Ref. [21] 166–167°C).

Diethyl 2-(p-methylsulfonamido)-3-(triphenylphosphoranylidene)butandioate (**4b**)
Yield 0.549 g (91%); major isomer: 59.9%, minor isomer: 40.1%; pale yellow powder, mp 167–168°C (Ref. [21] 168–169°C).

Dimethyl 2-(benzensulfonamido)-3-(triphenylphosphoranylidene)butandioate (**4c**)
Yield 0.488 g (87%); major isomer: 68.2%, minor isomer: 31.8%; pale yellow powder, mp 150–153°C (Ref. [21] 161–162°C).

Diethyl 2-(benzensulfonamido)-3-(triphenylphosphoranylidene)butandioate (**4d**)
Yield 0.548 g (93%); major isomer: 71.9%, minor isomer: 28.1%; pale yellow powder, mp 163–165°C (Ref. [21] 158–159°C).

Dimethyl 2-(methylsulfonamido)-3-(triphenylphosphoranylidene)butandioate (**4e**, $C_{25}H_{26}NO_6PS$)
Yield 0.404 g (81%); pale yellow powder, mp 163–164°C; IR (KBr): $\bar{\nu} = 3315$, 2940, 1744, 1611, 1480, 1429 cm^{-1}; MS: m/z (%) = 354 (15), 340 (30), 277 (15), 201 (25), 183 (70), 152 (30), 122 (50), 51 (100).

Major isomer: 68.5%; ^{1}H NMR: $\delta = 2.88$ (s, OCH_3), 3.13 (s, CH_3SO_2), 3.71 (s, OCH_3), 4.04 (dd, $^{3}J_{HH} = 9.1$ Hz, and $^{3}J_{HP} = 7.78$ Hz, P–C–CH), 6.35 (bd, $^{3}J_{HH} = 9.1$ Hz, NH), 7.48–7.69 (m, $3C_6H_5$) ppm; ^{13}C NMR: $\delta = 42.20$ (CH_3SO_2), 43.91 (d, $^{1}J_{PC} = 127.6$ Hz, P=C), 49.41 (OCH_3), 52.53 (OCH_3), 56.70 (d, $^{2}J_{PC} = 17.4$ Hz, CH–N), 126.12 (d, $^{1}J_{PC} = 92.6$ Hz, P–C^{ipso}), 128.96 (d, $^{2}J_{PC} = 12.4$ Hz, C^{ortho}), 132.47 (C^{para}), 133.88 (d, $^{3}J_{PC} = 9.9$ Hz, C^{meta}), 170.40 (d, $^{2}J_{PC} = 12.7$ Hz, CO), 173.69 (d, $^{3}J_{PC} = 8.5$ Hz, CO) ppm; ^{31}P NMR: $\delta = 22.27$ ppm.

Minor isomer: 31.5%; ^{1}H NMR: $\delta = 2.86$ (s, OCH_3), 3.13 (s, CH_3SO_2), 3.54 (s, OCH_3), 4.10 (dd, $^{3}J_{HH} = 9.1$ Hz, and $^{3}J_{HP} = 16.9$ Hz, P–C–CH), 5.66 (bd, $^{3}J_{HH} = 9.1$ Hz, NH), 7.48–7.69 (m, $3C_6H_5$) ppm; ^{13}C NMR: $\delta = 43.34$ (CH_3SO_2), 44.68 (d, $^{1}J_{PC} = 136.2$ Hz, P=C), 50.36 (OCH_3), 52.52 (OCH_3), 56.07 (d, $^{2}J_{PC} = 17.4$ Hz, CH–N), 125.64 (d, $^{1}J_{PC} = 92.8$ Hz, P–C^{ipso}), 129.02 (d, $^{2}J_{PC} = 12.1$ Hz, C^{ortho}), 132.13 (C^{para}), 133.91 (d, $^{3}J_{PC} = 5.4$ Hz, C^{meta}), 170.03 (d, $^{2}J_{PC} = 18.0$ Hz, CO), 173.83 (d, $^{3}J_{PC} = 12.1$ Hz, CO) ppm; ^{31}P NMR: $\delta = 23.30$ ppm.

Diethyl 2-(methylsulfonamido)-3-(triphenylphosphoranylidene)butandioate (**4f**, $C_{27}H_{30}NO_6PS$)
Yield 0.437 g (83%); white powder, mp 167–169°C; IR (KBr): $\bar{\nu} = 3445$, 3045, 2900, 1733, 1607, 1473, 1435 cm^{-1}; MS: m/z (%) = 454 (25), 408 (30), 303 (20), 262 (30), 183 (80), 99 (100).

Major isomer: 74.1%; ^{1}H NMR: $\delta = 0.83$ (t, $^{3}J_{HH} = 7.1$ Hz, CH_3), 1.16 (t, $^{3}J_{HH} = 7.2$ Hz, CH_3), 1.61 (s, CH), 2.84 (s, CH_3SO_2), 3.63 (t, $^{3}J_{HH} = 7.1$ Hz, CH_2), 3.95–4.14 (m, CH_2), 6.29 (d, $^{3}J_{HH} = 9.1$ Hz, NH), 7.41–7.66 (m, $3C_6H_5$) ppm; ^{13}C NMR: $\delta = 14.12$ (CH_3), 14.21 (CH_3), 42.48 (d, $^{1}J_{PC} = 61.6$ Hz, P=C), 43.30 (CH_3SO_2), 56.57 (d, $^{2}J_{PC} = 17.5$ Hz, CHN), 61.35 (OCH_2), 61.44 (OCH_2), 126.22 (d, $^{1}J_{PC} = 91.5$ Hz, C^{ipso}), 128.53 (d, $^{2}J_{PC} = 12.2$ Hz, C), 128.82 (d, $^{2}J_{PC} = 12.3$ Hz, C), 131.97 (C), 132.10 (d, $^{3}J_{PC} = 10.0$ Hz, C), 133.65 (C), 133.85 (d, $^{2}J_{PC} = 10.0$ Hz, C), 165.65 (C), 169.85 (d, $^{2}J_{PC} = 13.1$ Hz, CO), 173.07 (d, $^{3}J_{PC} = 8.4$ Hz, CO) ppm; ^{31}P NMR: $\delta = 22.21$ ppm.

Minor isomer: 25.9%; ^{1}H NMR: $\delta = 1.13$ (t, $^{3}J_{HH} = 6.8$ Hz, CH_3), 1.21 (t, $^{3}J_{HH} = 7.1$ Hz, CH_3), 2.11 (s, CH), 2.81 (s, CH_3SO_2), 3.91–4.18 (m, $2CH_2$), 5.57 (d, $^{3}J_{HH} = 8.6$ Hz, NH), 7.41–7.70 (m, $3C_6H_5$) ppm; ^{13}C NMR: $\delta = 13.91$ (CH_3), 14.03 (CH_3), 42.13 (CH_3SO_2), 44.18 (d, $^{1}J_{PC} = 61.9$ Hz, P=C), 56.09 (d, $^{2}J_{PC} = 17.2$ Hz, CHN), 61.27 (OCH_2), 61.51 (OCH_2), 125.71 (d, $^{1}J_{PC} = 92.0$ Hz, C^{ipso}), 128.72 (d, $^{2}J_{PC} = 12.4$ Hz, C^{ortho}), 128.72 (d, $^{2}J_{PC} = 12.0$ Hz, C^{ortho}), 131.72 (C^{para}), 132.27 (d, $^{3}J_{PC} = 2.9$ Hz, C^{meta}), 133.10 (C), 165.32 (C), 169.64 (d, $^{2}J_{PC} = 18.7$ Hz, CO), 173.07 (d, $^{3}J_{PC} = 8.3$ Hz, CO) ppm; ^{31}P NMR: $\delta = 23.21$ ppm.

Diethyl 2-(methylsulfonamido)-3-(triphenylphosphoranylidene)butandioate (**4g**, $C_{26}H_{26}NO_5P$)
Yield 0.338 g (73%); white powder, mp 160–163°C; IR (KBr): $\bar{\nu} = 3420$, 2948, 1741, 1668, 1482, 1432 cm^{-1}; MS: m/z (%) = 404 (80), 372 (30), 303 (50), 287 (75), 262 (100), 183 (80), 165 (20).

Major isomer: 61.5%; ^{1}H NMR: $\delta = 1.97$ (s, CH_3CONH), 3.15 (s, OCH_3), 3.70 (dd, $^{3}J_{PH} = 15.2$ Hz, $^{3}J_{HH} = 8.9$ Hz, CHN), 6.27 (d, $^{3}J_{HH} = 8.8$ Hz, NH), 7.47–7.73 (m, $3C_6H_5$) ppm; ^{13}C NMR: $\delta = 49.05$ (OCH_3), 51.54 (d, $^{2}J_{PC} = 17.8$ Hz, Hz, CHN), 52.29 (OCH_3), 126.53 (d, $^{1}J_{PC} = 91.9$ Hz, C^{ipso}), 128.62 (d, $^{2}J_{PC} = 12.3$ Hz, P–C^{ortho}), 133.80 (d, $^{3}J_{PC} = 9.8$ Hz,

P–C^{meta}), 168.75 (C^{para}), 170.41 (CO), 173.77 (CO) ppm; ^{31}P NMR: $\delta_P = 22.21$ ppm.

Minor isomer: 38.5%; ^{1}H NMR: $\delta = 1.96$ (s, CH_3CONH), 3.58 (s, OCH_3), 3.69 (s, OCH_3), 4.57 (dd, $^3J_{PH} = 15.2$ Hz, $^3J_{HH} = 8.9$ Hz, CHN), 6.38 (d, $^3J_{HH} = 8.9$ Hz, NH), 7.47–7.73 (m, $3C_6H_5$) ppm; ^{13}C NMR: $\delta = 42.62$ (OCH_3), 44.32 (OCH_3), 50.92 (d, $^2J_{PC} = 16.5$ Hz, CHN), 125.99 (d, $^1J_{PC} = 8.9$ Hz, C^{ipso}), 128.72 (d, $^2J_{PC} = 12.2$ Hz, P–C^{ortho}), 132.13 (d, $^3J_{PC} = 2.7$ Hz, P–C^{meta}), 168.50 (C^{para}), 170.58 (CO), 173.87 (CO) ppm; ^{31}P NMR: $\delta = 23.51$ ppm.

Typical Procedure for the Preparation of Iminophosphoranes ***5***

Method A. A magnetically stirred solution of 0.563 g **4a** (1 mmol) was refluxed in toluene for 14 h. The solvent and dimethyl fumarate were removed under reduced pressure and the residue recrystallized from acetone and 0.402 g colorless crystals (93%) were obtained.

Method B. To a magnetically stirred solution of 0.262 g **1** (1 mmol) and 0.171 g *para*-toluenesulfonamide (1 mmol) in 20 cm^3 toluene was added dropwise a mixture of 0.142 g dimethyl acetylenedicarboxylate (1 mmol) in 2 cm^3 toluene at room temperature over 10 min. The reaction mixture was refluxed for 14 h. The solvent was removed under reduced pressure and the residual solid recrystallized from acetone (0.371 g, yield 86%).

N-(4-Methylphenylsulfonyl)triphenyliminophosphorane (**5a**)
Yield 0.371 g (86%); colorless crystals, mp 164–165°C (Ref. [22] 168–169°C).

N-(Phenylsulfonyl)triphenyliminophosphorane (**5b**)
Yield 0.343 g (85%); white powder, mp 154–155°C (Ref. [22] 156–158°C).

Acknowledgements

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