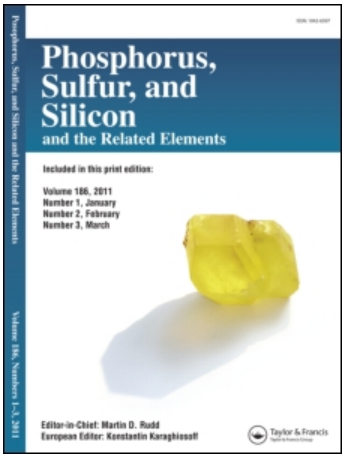

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SYNTHESIS OF SULFUR-CONTAINING ARYLIMINOPHOSPHORANES

Issa Yavari[a]; Nader Zabarjad-Shiraz[b]; Hamid R. Bijanzadeh[a]
[a] University of Tarbiat Modarres, Tehran, Iran [b] Islamic Azad University, Central Tehran Branch, Tehran, Iran

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SYNTHESIS OF SULFUR-CONTAINING ARYLIMINOPHOSPHORANES

Issa Yavari,[a] *Nader Zabarjad-Shiraz,*[b] *and Hamid R. Bijanzadeh*[a]
University of Tarbiat Modarres, Tehran, Iran;[a] *and Islamic Azad University, Central Tehran Branch, Tehran, Iran*[b]

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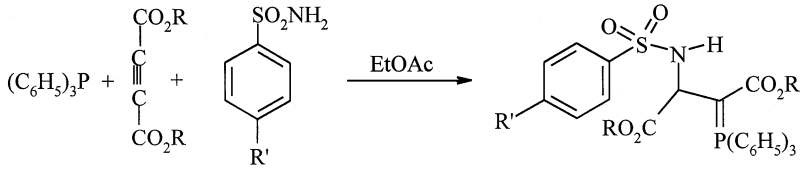
Stabilized phosphoranes, obtained from the three-component reaction between dialkyl acetylenedicarboxylates and arylsulfonamides in the presence of triphenylphosphine, undergo a smooth intramolecular reaction in boiling toluene to produce sulfur-containing iminophosphoranes in excellent yields.

Keywords: Acetylenic esters; iminophosphoranes; stable phosphorus ylides; three-component reaction; triphenylphosphine

Iminophosphoranes, compounds of general structure $R_3P{=}NR'$ with four-coordinate phosphorus and incorporating a formal phosphorus-nitrogen double bond, are reactive species, which take part in many valuable reactions in organic synthesis.[1–5] Iminophosphoranes were first reported by Staudinger and Meyer[6] in 1919 but virtually no additional chemistry was reported until the early 1960s. Much chemistry has been discovered in the last decades with numerous applications to organic synthesis.[1–5] Several methods have been developed for the preparation of iminophosphoranes, although the general procedure is the reaction of triphenylphosphine with azide compounds.[1–10] Reaction of triarylphosphines with dialkyl acetylenedicarboxylates, and on occasion, other acetylenic systems have been discussed.[11,12] We recently described the synthesis of sulfur-containing phosphorus ylides **3** using the three-component reaction of dialkyl acetylenedicarboxylates **1** and arylsulfonamides **2** in the presence of triphenylphosphine.[13] Herein we report that these stable phosphoranes undergo a smooth transformation in boiling toluene to produce sulfur-containing iminophosphoranes **4** in excellent yields (see Scheme 1).

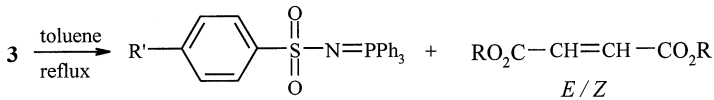
Address correspondence to Issa Yavari, Department of Chemistry, University of Tarbiat Modarres, P.O. Box 14115-175, Tehran, Iran. E-mail: isayavar@yahoo.com



1	R
a	Me
b	Et
c	^{t}Bu

2	R'
a	H
b	Me

3	R	R'	%Yield
a	Me	H	76
b	Et	H	76
c	^{t}Bu	H	73
d	Me	Me	78
e	Et	Me	75
f	^{t}Bu	Me	73
g	Me	Et	72



4	R'	%Yield
a	H	98
b	Me	97
c	Et	98

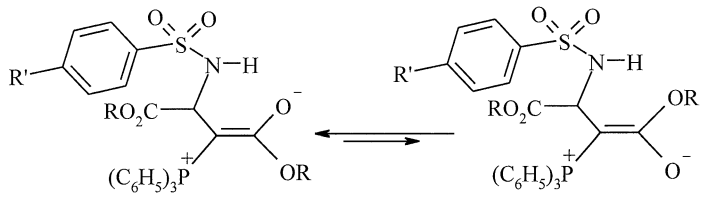
5	R
a	Me
b	Et
c	^{t}Bu

SCHEME 1

RESULTS AND DISCUSSION

The reaction of arylsulfonamides with dialkyl acetylenedicarboxylates in the presence of triphenylphosphine proceeded spontaneously at room temperature in ethyl acetate, and was finished within 3 hours. The ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of phosphoranes **3**. Any other product could not be detected by NMR spectroscopy.

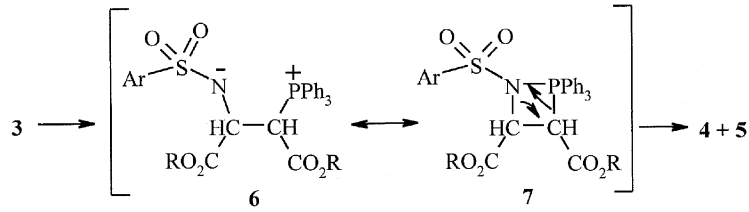
The ^{1}H, ^{13}C, and ^{31}P NMR spectra of ylides **3** are consistent with the presence of two rotational isomers[13] (Scheme 2). During dynamic ^{31}P NMR study of these rotational isomers, a sharp single peak at about 14.6 ppm started to grow as the temperature was increased. In order to identify this new product, phosphorus ylides **3** were refluxed in toluene. The reaction proceeded cleanly and produced iminophosphoranes **4** together with dialkyl fumarates and/or dialkyl maleates **5** (Scheme 1). Structure **4** was assigned to the isolated products on the basis of their elemental analyses, IR, ^{1}H, ^{13}C, and ^{31}P NMR and mass spectral data. The mass spectra of iminophosphoranes **4** confirm their molecular weights.



(*Z*)-**3**; Major (*E*)-**3** ; Minor

SCHEME 2

Although we have not established the mechanism of the formation of iminophosphoranes **4** from ylides **3** in an experimental manner, a possible mechanism is indicated in Scheme 3. It is reasonable to assume that in boiling toluene, the NH-proton shifts to the ylenic carbon and forms the phosphorus betaine **6**. This betaine can be in equilibrium with the azaphosphetane **7**. Iminophosphorane **4** is formed from fragmentation of the azaphosphetane **7**. Formation of dialkyl fumarates and/or dialkyl maleates **5** confirms the proposed mechanism (Scheme 3).



SCHEME 3

In summary, the present synthesis of iminophosphoranes complements older methods and offers significant advantages for the synthesis of iminophosphoranes from sulphonamides. The present method carries the advantage that, not only is the reaction performed under neutral conditions, but also that the substances can be mixed without any modification. The procedure described here may be an acceptable alternative method for the preparation of iminophosphoranes with variable functionalities.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. These data were in good agreement with the

calculated ones. IR spectra were measured on a Shimadzu IR 460 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured with BRUKER DRX-500 AVANCE spectrometer at 500.1, 125.8, and 202.4 MHz, respectively. The mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. Triphenylphosphine and dialkyl acetylenedicarboxylates were obtained from Fluka (Buchs, Switzerland). Phosphoranes **3a**–**3f** have been reported.[13]

Dimethyl 2-(4-ethylbenzenesulfonylamino)-3-(triphenylphosphanylidene)-succinate 3g was prepared according to the previous report.[13] White powder, 0.92 g, yield 80%, m.p.: 172–174°C. IR (KBr) (ν_{max}, cm^{-1}): 3350 (N—H), 1738 (C=O), 1609 (C=C). Anal. Calcd. for $C_{32}H_{32}NO_6PS$ (589.6): C, 65.18; H, 5.47; N, 2.38%. Found: C, 65.3; H, 5.3; N, 2.2%.

Major isomer **3g**-(Z) (65%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.20 (3H,t, $^{3}J_{HH}$ = 7.6 Hz, CH_3), 2.65 (2H, q, $^{3}J_{HH}$ = 7.6 Hz, CH_2), 3.11 and 3.49 (6 H, 2 s, 2 OCH_3), 3.98 (1H, dd, $^{3}J_{HH}$ = 9.3 Hz, $^{3}J_{PH}$ = 15.6 Hz, CH), 6.67 (1H, br d, $^{3}J_{HH}$ = 9 Hz, NH),7.3–7.7 (19H, m, 3 C_6H_5 and C_6H_4).^{13}C NMR (125.7 MHz, $CDCl_3$): δ 15.2 ($CH_2\mathit{CH}_3$) 28.8 (CH_2), 43.6 (d, $^{1}J_{PC}$ = 127.1 Hz, P—*C*=C), 49.5 and 52.6 (2 OCH_3), 56.0 (d, $^{2}J_{PC}$ = 17.3 Hz, N—CH), 126.4 (d, $^{1}J_{PC}$ = 92.6 Hz, P—C_{ipso}), 129.0–134.0 (CH arom), 138.88 (*C*—CH_3), 142.88 (C—S), 170.4 (d, $^{2}J_{PC}$ = 12.2 Hz, P—C=*C*—O), 173.1 (d, $^{3}J_{PC}$ = 7.2 Hz, C=O). ^{31}P NMR (202.4 MHz,$CDCl_3$): δ 21.78 (Ph_3P^+—C).

Minor isomer **3g**-(E) (35%),^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.28 (3H,t, $^{3}J_{HH}$ = 7.6 Hz, CH_3), 2.65 (2H,q, $^{3}J_{HH}$ = 7.6 Hz, CH_2), 3.49 and 3.54 (6H, 2 s, 2 OCH_3), 3.94 (1H, dd, $^{3}J_{HH}$ = 9.3 Hz, $^{3}J_{PH}$ = 13.3 Hz, CH), 6.02 (1H, br d, $^{3}J_{HH}$ = 9 Hz, NH),7.3–7.7 (19H, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 14.8 ($CH_2\mathit{CH}_3$) 25.3 (CH_2), 44.2 (d, $^{1}J_{PC}$ = 135.9 Hz, P—*C*=C), 50.5 and 52.7 (2 OCH_3), 55.2 (d, $^{2}J_{PC}$ = 17.2 Hz, N—CH), 125.8 (d, $^{1}J_{PC}$ = 92.4 Hz, P—C_{ipso}), 129.0–134.0 (CH arom), 138.52 (C—CH_3), 143.05 (C—S),170.3 (d, $^{2}J_{PC}$ = 16.7 Hz, P—C=*C*—O), 173.1 (d, $^{3}J_{PC}$ = 7.2 Hz, C=O). ^{31}P NMR (202.4 MHz,$CDCl_3$): δ 22.73 (Ph_3P^+—C).

Preparation of *P,P,P*-Triphenyl-*N*-phenylsulfonylphosphine Imide 4a

General Procedure

The process for preparation of **4a** is described as an example. A magnetically stirred mixture of 0.56 g phosphorane **3a** (1 mmol) in 30 mL toluene was refluxed for 12 h. The solvent was removed under reduced pressure and the solid residue was washed with 2 × 5 mL cold diethyl ether and the product was obtained as a white powder, 0.40 g, yield 98%,

m.p.: 156–158°C. IR (KBr) (ν_{max}, cm^{-1}): 3050, 1575, 1469, 1429. Anal. Calcd. for $C_{24}H_{20}NO_2PS$ (417.5): C, 69.05; H, 4.83; N, 3.36%. Found: C, 69.15; H, 4.71; N, 3.45%. ^1H NMR (500.1 MHz, $CDCl_3$): [7.23 (2H, dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 7.9 Hz, 2 CH_{meta}), 7.32 (1H, t, $^3J_{HH}$ = 7.2 Hz, CH_{para}), 7.65 (2H, d, $^3J_{HH}$ = 7.9 Hz, CH_{ortho}) (for S—Ph)], 7.48 (6H, ddd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{PH}$ = 2.2 Hz, $6CH_{meta}$), 7.60 (3H, t, $^3J_{HH}$ = 7.2 Hz, $3CH_{para}$), 7.78 (6H, dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{PH}$ = 12.8 Hz, $6CH_{ortho}$). ^{13}C NMR (125.7 MHz, $CDCl_3$): 125.7, 128.1, 130.0, 146.1 (for S—Ph), 127.2 (d, $^1J_{PH}$ = 104 Hz, P—C), 128.8 (d, $^3J_{PH}$ = 13 Hz, C_{ortho}), 132.9 (d, $^5J_{PH}$ = 3 Hz, C_{para}), 133.1 (d, $^4J_{PH}$ = 11 Hz, C_{meta}). ^{31}P NMR (202.4 MHz,$CDCl_3$): δ 14.96 (Ph_3P=N).

P,P,P-Triphenyl-*N*-(toluene-4-sulfonyl)phosphine Imide 4b

White crystals, 0.42 g, yield 97%, m.p.: 165–167°C. IR (KBr) (ν_{max}, cm^{-1}): 3025, 1471, 1422. Anal. Calcd. for $C_{25}H_{22}NO_2PS$ (431.5): C, 69.59; H, 5.14; N, 3.45%. Found: C, 69.40; H, 5.20; N, 3.09%. ^1H NMR (500.1 MHz, $CDCl_3$): δ 2.28 (3H, s, CH_3), 6.99 (2H, d, $^3J_{HH}$=7.8 Hz, $2CH_{ortho}$), 7.49 (2H, d, $^3J_{HH}$ = 7.8 Hz, $2CH_{meta}$), 7.44 (6H, ddd, $^3J_{HH}$ = 7.7 Hz, $^4J_{PH}$ = 3.0 Hz, $^3J_{HH}$ = 7.3 Hz, $6CH_{meta}$), 7.56 (3H, d, $^3J_{HH}$ = 7.3 Hz, $3CH_{para}$), 7.72 (6H, dd, $^3J_{PH}$ = 12.9 Hz, $^3J_{HH}$ = 7.7 Hz, $6CH_{ortho}$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.3 (CH_3), 125.7, 128.8, 140.0 (*C*—CH_3) and 143.5 (C-S) (for S-C_6H_4-), 127.7 (d, $^1J_{PH}$ = 104 Hz, P—C), 128.8 (d, $^3J_{PH}$ = 12 Hz, C_{ortho}), 133.1 (d, $^5J_{PH}$ = 3 Hz, P—C_{para}), 132.8 (d, $^4J_{PH}$ = 11 Hz, C_{meta}). ^{31}P NMR (202.4 MHz,$CDCl_3$): δ 14.62 (Ph_3P=N).

P,P,P-Triphenyl-*N*-(4-ethylbenzenesulfonyl)phosphine Imide 4c

Colorless crystals, 0.42 g, yield 98%, m.p.: 171–173°C. IR (KBr) (ν_{max}, cm^{-1}): 3030, 1476, 1428. Anal. Calcd. for $C_{26}H_{24}NO_2PS$ (445.5): C, 70.09; H, 5.43; N, 3.14%. Found: C, 70.2; H, 5.3; N, 3.0%. ^1H NMR (500.1 MHz, $CDCl_3$): δ 1.18 (3H, t, $^3J_{HH}$ = 7.5 Hz, CH_3), 2.58 (2H, q, $^3J_{HH}$ = 7.5 Hz, CH_2), 6.99 (2H, d, $^3J_{HH}$ = 7.8 Hz, $2CH_{ortho}$), 7.49 (2H, d, $^3J_{HH}$ = 7.8 Hz, $2CH_{meta}$), 7.44 (6H, ddd, $^3J_{HH}$ = 7.7 Hz, $^4J_{PH}$ = 3.0 Hz, $^3J_{HH}$ = 7.3 Hz, $6CH_{meta}$), 7.56 (3H, d, $^3J_{HH}$ = 7.3 Hz, $3CH_{para}$), 7.72 (6H, dd, $^3J_{PH}$ = 12.9 Hz, $^3J_{HH}$ = 7.7 Hz, $6CH_{ortho}$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 15.5 (CH_3), 28.7 (CH_2), 125.7, 128.8, 143.6 (*C*—CH_2) and 146.7 (C—S) (for S—C_6H_4—), 127.7 (d, $^1J_{PH}$ = 104 Hz, P—C), 128.8 (d, $^3J_{PH}$ = 12 Hz, C_{ortho}), 133.1 (d, $^5J_{PH}$ = 3 Hz, P—C_{para}), 132.8 (d, $^4J_{PH}$ = 11 Hz, C_{meta}). ^{31}P NMR (202.4 MHz,$CDCl_3$): δ 14.72 (Ph_3P=N).

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