

# X-ray crystal structures of ethoxycarbonyl-, diethyl-2-triphenyl- $\lambda^5$ -phosphoranylidene-*N*-phenylimide derivatives

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Phenylisothiocyanate reacts with ethyltriphenylphosphanylideneacetate at room temperature to yield 2-(ethoxycarbonyl)-2-(triphenyl- $\lambda^5$ -phosphanylidene)-*N*-phenylethane thioimidic acid and diethyl-2-(triphenyl- $\lambda^5$ -phosphanylidene)-3-(phenylimino)pentanedioate. The formation of phosphoranes are explained according to mechanism of the Wittig type reaction. The X-ray analysis structures of phosphorane adducts were studied.

**Keywords:** phenylisothiocyanate, phosphonium ylide, phosphanylidene compounds

In 1969, Bestmann and Pfohl reported that the reaction of phenylisothiocyanate **1** with stabilised phosphorus ylides of structure **2** resulted in the formation of the Wittig type reaction product **3**.<sup>1</sup> There have since been several reports of the formation of such adducts between a variety of ylides and both phenylisocyanate and phenylisothiocyanate derivatives.<sup>2,3</sup> Also, it has been found that the reaction of benzonitriloxide,<sup>4</sup> diphenylcarbodiimide<sup>5</sup> with two mole equivalents of phosphonium ylide **2**, yielding phosphorane adduct of type **4** (Scheme 1).

We now present the X-ray crystal structure of the triphenylphosphoranylidene adducts **3** and **4** of phenylisothiocyanate **1** after reaction with Wittig reagent **2** (Scheme 1).

## Results and discussion

When phenylisothiocyanate **1** was allowed to react with one mole equivalent of phosphonium ylide **2** in methylene chloride at room temperature for 8h, phosphorane adduct **3** was obtained as a colourless crystalline compound having a sharp melting point. The structure of isolated phosphorane compound **3** was studied by X-ray crystal structure analysis (Table 1, Fig. 1).<sup>6–10</sup>

The X-ray crystal structure analysis of 2-ethoxycarbonyl-2-(triphenyl- $\lambda^5$ -phosphanylidene)-*N*-phenylethanethioimidic acid **3** confirmed its structure (Fig. 1). The structure of phosphorane adducts of **3** from the Wittig reaction has been reported as structure **3a** and tautomeric form **3b** or cyclic hydrogen bonding formula **3c** (Scheme 2).<sup>1,2</sup>

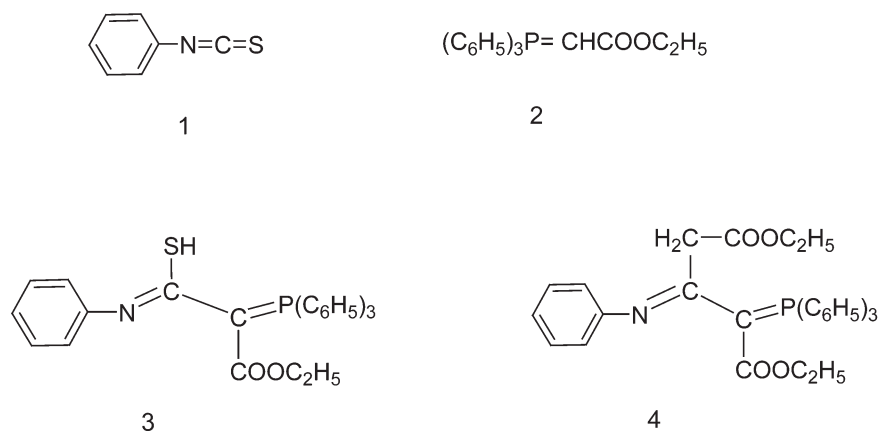
On the other hand, adduct **4** was isolated from the reaction of phenylisothiocyanate **1** with two mole equivalents of Wittig ylide **2** in dry benzene at room temperature. The structure for

diethyl-2-(triphenyl- $\lambda^5$ -phosphoranylidene)-3-(phenylimino)pentanedioate (**4a**) was deduced from its spectroscopic data. The IR spectrum of **4a**, in KBr, revealed the presence of intense bands at 1720, 1735(C=O, ester), 1642, 1594  $\text{cm}^{-1}$  (C=P).<sup>11</sup> The <sup>1</sup>H NMR spectrum of **4a** ( $\text{CDCl}_3$ ,  $\delta$  ppm) gives a triplet at  $\delta = 0.63, 1.28$  ppm,  $J = 6.9$  Hz, due to six protons of two  $\text{CH}_3$ -, and quartet at  $\delta = 3.71, 4.19$  ppm,  $J = 6.9$  Hz, due to four protons of two  $\text{CH}_2$ -ethoxy groups.<sup>11</sup> The spectrum of compound **4a** exhibits a singlet at 3.69 ppm for methylene proton (tautomeric form). Moreover, the structure assigned to **4a** was unambiguously supported by the X-ray analysis (Fig. 2, Table 1).<sup>6–10</sup>

Formation of adducts **3** and **4** can be explained in terms of the Wittig addition reaction to give the stable ylide-phosphorane **3**, followed by olefination of **3** by the ylide reagent with expulsion of triphenylphosphine sulfide to yield phosphorane adduct **4**.<sup>12</sup> X-ray crystal structure analysis confirms the tautomeric structures of **3** and **4a** (Figs 1 and 2).<sup>6–10</sup>

## Experimental

Melting points were determined in open glass capillaries using Electrothermal IA 9000 Series digital melting point apparatus (Electrothermal, Essex, UK) and are uncorrected. The IR spectra were measured in KBr pellets with a Perkin-Elmer Infracord Spectrophotometer Model 157 (Grating). The <sup>1</sup>H spectra were recorded in  $\text{CDCl}_3$  as the solvent on a Joel-500 MHz Spectrometer, and the chemical shifts were recorded in  $\delta$  values relative to TMS. The mass spectra were performed at 70 eV on a Shimadzu GCS-OP 1000 Ex Spectrometer provided with a data system. Elemental analyses were performed using the Elmeuter Varu EL Germany Instrument.



Scheme 1

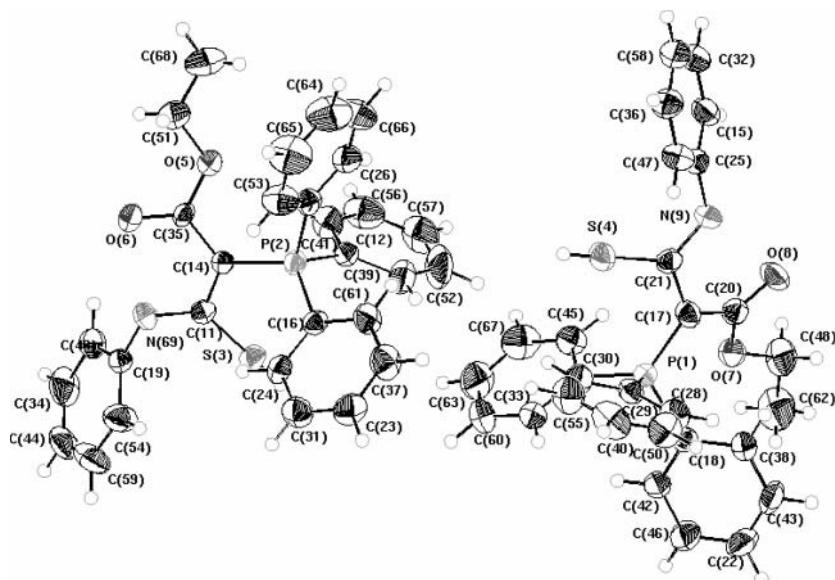
**Table 1** Crystal structure and data refinement parameters

	<b>4</b>	<b>3<sup>a</sup></b>
Empirical formula	C <sub>33</sub> H <sub>32</sub> NO <sub>4</sub> P	C <sub>58</sub> H <sub>52</sub> N <sub>2</sub> O <sub>4</sub> P <sub>2</sub> S <sub>2</sub>
Formula weight (g mol <sup>-1</sup> )	537.596	967.140
Wavelength/Å	0.71073	0.71073
Crystal system/space group	Triclinic	Triclinic
a/Å	10.5233 (5)	11.2217(3)
b/Å	10.9338 (7)	15.1577(4)
c/Å	13.6466 (8)	16.0523(7)
α/°	83.352(4)°	106.5032(8)
β/°	84.053 (5)°	103.2675(9)
γ/°	66.874 (2)°	95.658(2)
V/Å <sup>3</sup>	1431.38 (14)	2508.51(14)
Z	2	4
D <sub>calc</sub> (g cm <sup>-3</sup> )	1.247	2.561
μ (mm <sup>-1</sup> )	0.13	0.44
Colour/shape	Colourless/cube	Colourless/cube
Temperature (K)	298	298
Theta rang for collection	0.998–19.588 °	2.910–30.034
Independent reflections	2549	16569
Data/restraints/parameters	352	613
Goodness of fit on F <sup>2</sup>	0.036	0.077
Final R indices [I>3σ (I)]	R <sub>int</sub> 0.046	R <sub>int</sub> 0.035
R indices (all data)	0.059	0.207
R(gt)	0.036	0.077
wR(ref)	0.102	0.166
wR(all)	0.146	0.287

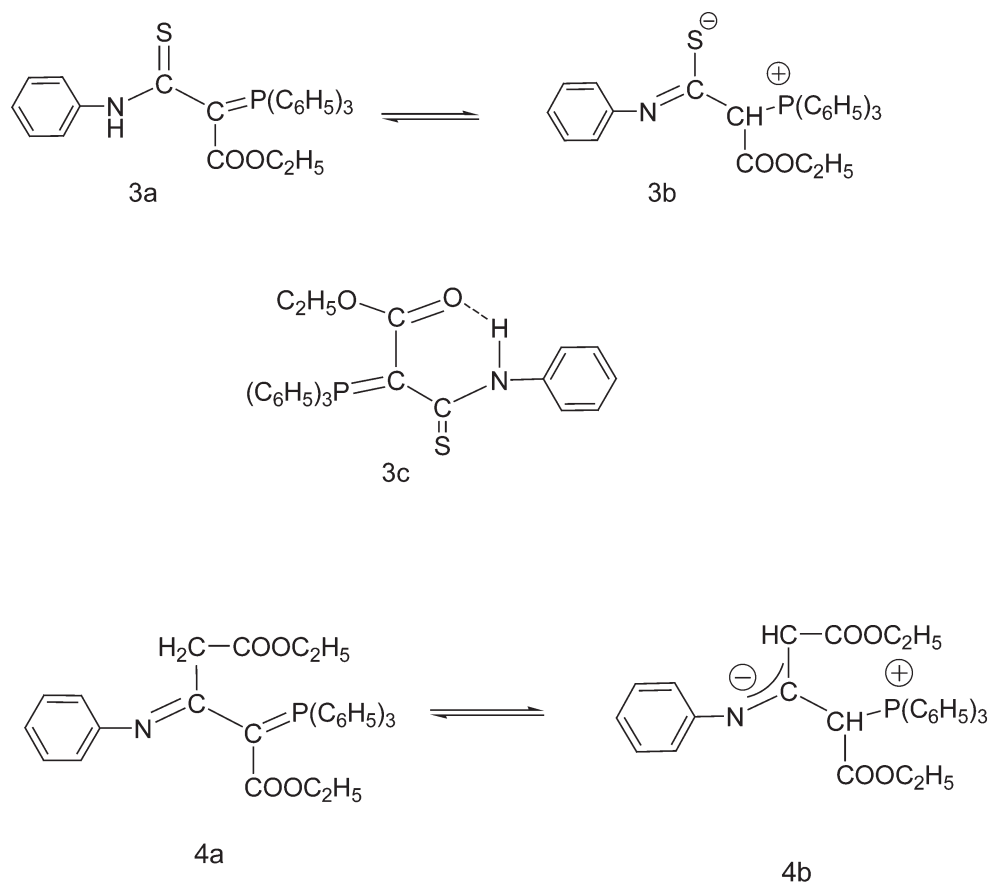
Selected bond lengths (Å) and angles (°)

Compound	<b>4</b>				<b>3</b>			
P1–C8	1.740(3)	O2–C13	1.214 (3)	S4–C21	1.660 (3)	O8–C20	1.231 (3)	
O3–C12	2.334 (3)	O4–C13	1.358 (3)	P1–C17	1.742 (3)	N9–C21	1.370 (4)	
O5–C21	1.208 (3)	N6–C10	1.296 (3)	P1–C29	1.836 (3)	C17–C21	1.453 (4)	
C8–C10	1.447 (4)	C8–C13	1.436 (4)	O7–C20	1.352 (4)	O7–C48	1.460 (4)	
C10–C12	1.525 (4)	C19–C25	1.497 (4)	S4–H4	0.9600 (9)	C48–C62	1.440 (5)	
C7–P1–C8	111.99 (13)	C8–O4–C13	34.0 (2)	P1–C17–C21	116.2(2)	P1–C17–C20	123.9(2)	
C13–O4–C25	116.4 (2)	P1–C8–C10	111.4 (2)	S4–C21–N9	123.6(3)	S4–C21–C17	119.4 (2)	
C8–N6–C10	34.05 (15)	N6–C8–C10	30.09 (13)	N9–C21–C17	117.0 (3)	P1–C29–C28	118.7(3)	
O3–C21–O5	124.2 (3)	O3–C22–C21	30.17 (14)	P1–C29–C30	122.6 (3)	C20–O7–C48	117.2(2)	

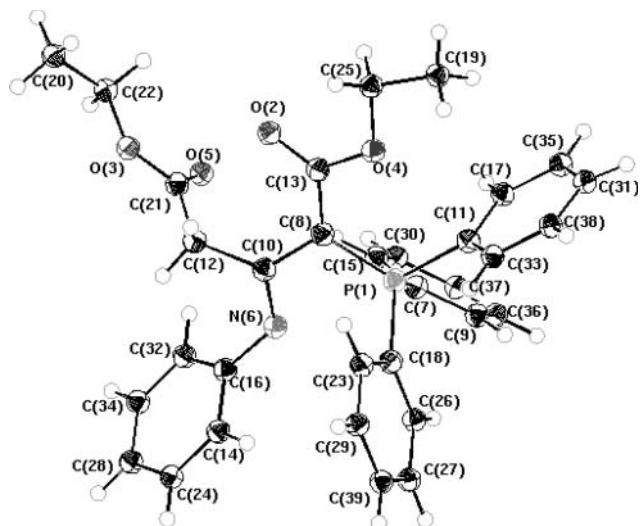
<sup>a</sup>X-ray analysis of compound **3** represented by two molecules of C<sub>29</sub>H<sub>26</sub>NO<sub>2</sub>PS.  
Software used to prepare material for publication: maXus.<sup>6</sup>



**Fig. 1** Molecular structure of **3** with the atomic numbering scheme; anisotropic displacement parameters are drawn at the 30% level, and the hydrogen atoms are shown as spheres of arbitrary radii. X-ray analysis of structure A, represented by two molecules of **3**.



Scheme 2



**Fig. 2** Molecular structure of **4** with the atomic numbering scheme; anisotropic displacement parameters are drawn at the 30% level, and the hydrogen atoms are shown as spheres of arbitrary radii.

*Reaction of phenylisothiocyanate (1) with ethyltriphenylphosphoranylideneacetate (2):* Phenylisothiocyanate **1** (1 mmol) was added to a solution of phosphorane ylide **2** 0.34 g (1 mmol) in methylene chloride (30 cm<sup>3</sup>) and the reaction mixture was stirred at room temperature for 8 h. After the reaction was finished (controlled by TLC), the volatile materials were evaporated on a small amount of silica gel; the mixture was separated on silica gel column chromatography using an eluent mixture of ethyl acetate/n-hexane 5:95% to give **3**.

*2-(Ethoxycarbonyl)-2-(triphenyl-λ<sup>5</sup>-phosphoranylidene)-N-phenyl ethanethioimide (3):* Colourless crystals, yield 80%, m.p.

168–170°C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 0.55 (t, 3H, *J* = 6.85 Hz, CH<sub>3</sub>-ethoxy), 3.64 (q, 2H, *J* = 6.85 Hz, CH<sub>2</sub>-ethoxy), 7.03–7.05 (m, 2H, Ar), 7.41–7.48 (m, 10H, Ar), 7.69–7.70 (m, 3H, Ar), 7.77–7.81 (m, 5H, Ar), 12.31 (s, 1H, SH); MS *m/z*(%) 483 (M<sup>+</sup>, 25). Anal. Calcd for C<sub>29</sub>H<sub>26</sub>NO<sub>2</sub>PS (483.14): C, 72.03, H 5.42, N, 2.90, P, 6.41, S, 6.63. Found: C, 72.16, H 5.30, N 2.98, P, 6.48, S, 6.56%.

*X-ray crystallographic study:*<sup>6–10</sup> A single crystal of **3** was grown by crystallisation from cyclohexane. The crystal structure was solved and refined, using maXus (Nonius, Delft and Mac Science, Japan). MoK<sub>α</sub> (λ = 0.71073 Å) and a graphite monochromator were used for data collection. A summary of the crystal analysis parameters is given in the Table 1, CCDC 748153 contains 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](http://www.ccdc.cam.ac.uk/data_request/cif).

*Reaction of phenylisothiocyanate 1 with phosphonium ylide 2:* **1** (0.001 mol) and **2** (0.002 mol) were stirred in dry benzene (25 mL) at room temperature for 8 h. After the reaction was finished (TLC), the volatile material was evaporated on a small amount of silica gel; the mixture was separated on silica gel column chromatography using an eluent mixture of ethyl acetate/n-hexane. It was found that the first fraction (2:98%) obtained from the column was triphenylphosphine sulfide (TPPS) and the second fraction (8:92%) was the product **4**.

*Diethyl-3-(phenylimino)-2-(triphenyl-λ<sup>5</sup>-phosphoranylidene)pentaedioate (4):* Colourless crystals, yield 60%, m.p. 170–172°C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 0.63, 1.28 (2t, 6H, *J* = 6.90 Hz, 2CH<sub>3</sub>-ethoxy), 3.71, 4.19 (2q, 4H, *J* = 6.90 Hz, 2CH<sub>2</sub>-ethoxy), 3.69 (s, 2H, CH<sub>2</sub>), 7.03–6.09 (m, 2H, Ar), 7.41–7.50 (m, 15H, Ar), 7.76–7.80 (m, 3H, Ar); IR(KBr): ν<sub>max</sub>/cm<sup>-1</sup> 1720, 1735(C=O, ester), 1642, 1594 cm<sup>-1</sup> (C=P); MS *m/z*(%) 537 (M<sup>+</sup>, 45). Anal. Calcd for C<sub>33</sub>H<sub>32</sub>NO<sub>4</sub>P (537.21): C, 73.73, H 6.00, N, 2.61, P, 5.76. Found: C, 73.66, H 6.12, N 2.78, P, 5.84%.

*X-ray crystallographic study:*<sup>6–10</sup> A single crystal of **4** was grown by crystallisation from cyclohexane. The crystal structure was solved and refined, using maXus (Nonius, Delft and Mac Science, Japan). MoK<sub>α</sub> (λ = 0.71073 Å) and a graphite monochromator were used for data collection. A summary of the crystal analysis parameters is given in

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