Pergamon

Tetrahedron Vol. 50, No. 6, pp. 1889-1898, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4020/94 $6.00+0.00

0040-4020(93)E0129-4

Structure and Properties of Phosphonium Ylides Obtained by the Reaction of 3-phosphorylated 1,4-dichloro-2-aza-1,3-dienes with Sodium Azide

Luc Van Meervelt*

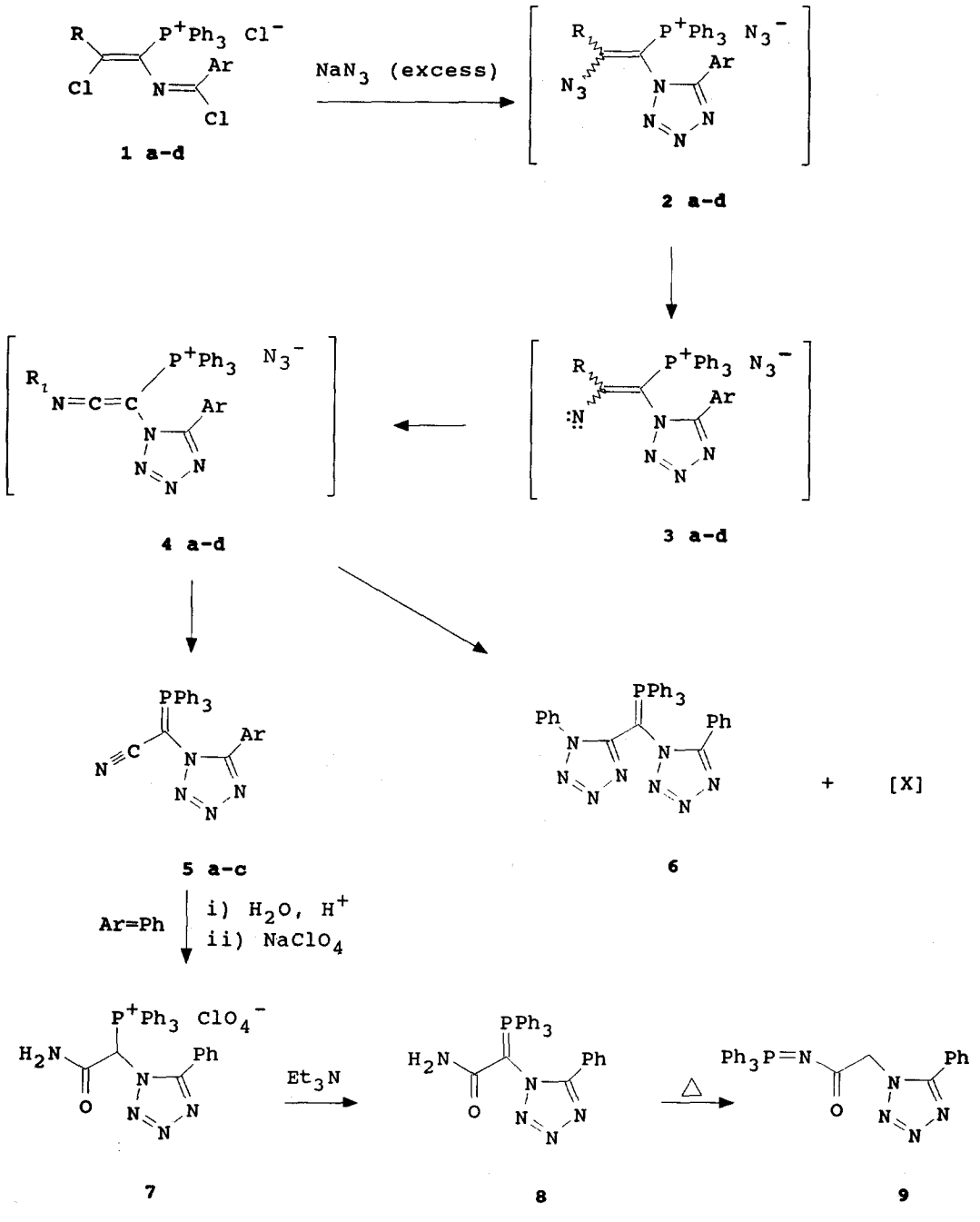
Chemistry Department, K.U. Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium.

Roman N. Vydzhak, Vladimir S. Brovarets, Nikolai I. Mishchenko, and Boris S. Drach

Institute of Bioorganic Chemistry and Petrochemistry, Academy of Sciences of Ukraine, 253660, Kiev, Murmanskaya St., Ukraine.

Abstract: The substituted vinylphosphonium salts of the general formula $RCCl=C(N=CClAr)P^{+}Ph_3\ Cl^{-}$ react with an excess of sodium azide in a peculiar manner. As a result, phosphonium ylides are produced. They are stabilized with a nitrile and a 5-aryltetrazol-1-yl group or with two substituted tetrazolyl residues as confirmed by X-ray structural analysis. All the ylides obtained exhibit low reactivity and do not enter into the Wittig reaction, but one of them was found to undergo the following sequence of transformations: $N{\equiv}C\text{-}\underset{|}{C}{=}P{\leqslant} \rightarrow H_2N\text{-}CO\text{-}\underset{|}{C}{=}P{\leqslant} \rightarrow {\geqslant}P{=}N\text{-}CO\text{-}CH_2\text{-}$.

The available phosphonium reagents with a characteristic fragment $-CCl=C(P^{+}{\leqslant})N=CCl-$ readily react with primary amines, sodium hydrosulfide, and sodium hydroselenide to give the corresponding derivatives of imidazole[1], thiazole[2,3], and selenazole.[2,3] In this communication we report on the cyclocondensation of reagents **1a-d** with sodium azide furnishing new phosphorus-containing tetrazole derivatives (see Scheme). In a first step of the condensation the unstable compounds **2a-d** are presumably formed which are able, even under mild conditions, to eliminate nitrogen due to the effect on the azido function of two strong electron-withdrawing substituents at the C=C bond, i.e.



a: R=H,Ar=C_6H_5 (1-4); Ar=C_6H_5 (5);
b: R=H,Ar=p-$CH_3C_6H_4$ (1-4); Ar=p-$CH_3C_6H_4$ (5);
c: R=H,Ar=p-ClC_6H_4 (1-4); Ar=p-ClC_6H_4 (5);
d: R=Ar=C_6H_5 (1-4).

Scheme

triphenylphosphonium and 5-aryltetrazolyl groups. The resulting substituted vinylnitrenes **3a-d**, like their more simple analogs, can be stabilized through insertion reactions involving C-H or C-C bonds. In the first case, with R = H, the insertion products **4a-c** can eliminate hydrazoic acid in a basic medium that should result in phosphonium ylides **5a-c** stabilized with a nitrile and 5-aryltetrazol-1-yl substituent. For R = C_6H_5 the C≡N bond formation is impossible, and one of the transformation routes for the intermediate ketenimine **4d** might be the addition of an azide ion to the heterocumulene fragment, leading, after intramolecular cyclization, to phosphonium ylide **6** stabilized with two substituted tetrazolyl residues.

The condensation end products **5a-c** and **6** were characterized by IR, ^1H, ^{13}C, ^{31}P NMR and microanalysis. The IR spectra suggest the participation of the 2-aza-1,3-diene moiety in the cyclization. Moreover, the IR spectra of compounds **5a,b** show an intense absorption band at 2150 cm^{-1} due to C≡N stretching. The presence of an ylide center in compound **5a** is verified by the ^{13}C NMR spectrum ($\delta_{C=P}$ 29.23 ppm). However, the most important information on the constitution of ylides **5a** and **6** was obtained by single crystal X-ray analysis (see Fig 1,2 and Tables 1,2). The P=C bond lengths for compounds **5a** and **6** comprise 1.717(3) and 1.719(4)Å respectively in accord with the averaged value 1.716(5)Å found for a number of ylides with a similar structure in the April 1993 release of the Cambridge Structural Database.[4] In addition, the bonds C(2)-C(8) (1.421(4)Å) and C(2)-N(3) (1.427(4)Å) in ylide **5a**,as well as the bonds C(2)-C(3) (1.422(5)Å) and C(2)-N(8) (1.423(6)Å) in ylide **6** are essentially shortened in agreement with the participation of the ylide center in the conjugation with the neighbouring π-systems. All rings in both structures are planar within experimental errors. Both tetrazole rings in **6** make an angle of 95.8° to each other.

Thus the structure of ylides **5a** and **6** is beyond question. Hence, the conversion **2d** → **6** is undoubtedly accompanied with a skeleton rearrangement which is, to a certain extent, similar to the Curtius rearrangement. The rearrangement can also be conceived as a process proceeding without nitrene participation. However additional studies are required to verify alternative mechanisms of conversions **2a** → **5a** and **2d** → **6**. It should be mentioned that the former conversion is the main one and the latter is a side process. In the ^{31}P NMR spectrum of the raw products, formed in the reaction of **1d** with sodium azide, two signals were observed. The minor resonance line at 18.35 ppm was related to the presence of ylide **6** in the mixture, while the more intense NMR signal at 25.00 ppm remains unidentified. It is possible that the identification of all products produced by **1d** and its analogs, on treating with sodium azide, will offer a clearer view of the role played by intermediate nitrenes in this complex reaction.

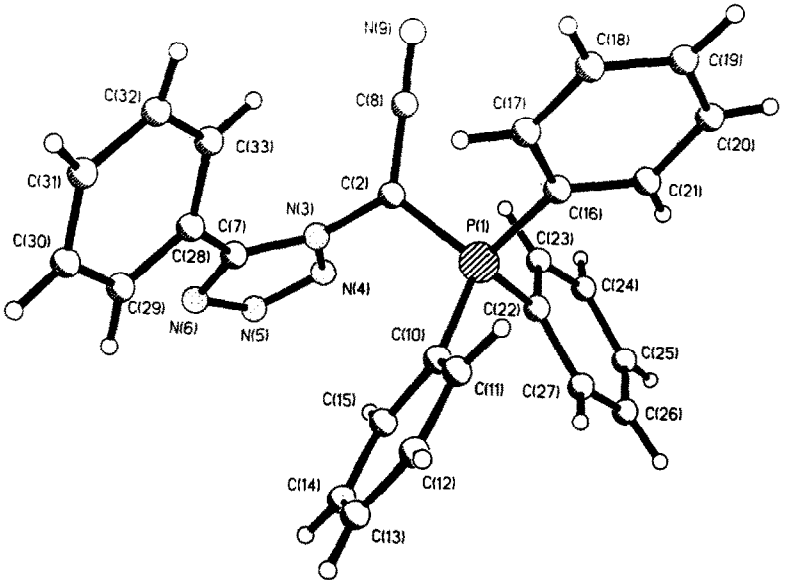


Fig. 1. Molecular Structure of Ylide **5a**.

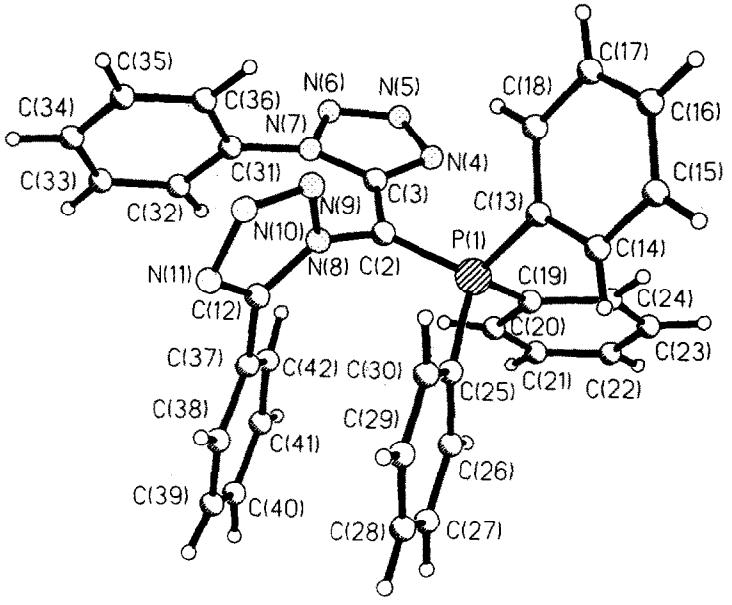


Fig. 2. Molecular Structure of Ylide **6**.

Table 1. Selected Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°) for Ylide **5a**.

P(1)-C(2)	1.717(3)	C(2)-N(3)	1.427(4)
P(1)-C(10)	1.794(3)	N(3)-N(4)	1.372(4)
P(1)-C(16)	1.790(3)	N(4)-N(5)	1.283(4)
P(1)-C(22)	1.795(3)	N(5)-N(6)	1.364(5)
C(2)-C(8)	1.412(4)	N(6)-C(7)	1.318(4)
C(8)-N(9)	1.156(4)	C(7)-C(28)	1.451(5)

C(2)-P(1)-C(10)	108.9(1)	C(2)-N(3)-C(7)	132.0(3)
C(2)-P(1)-C(16)	105.4(1)	N(3)-N(4)-N(5)	106.9(3)
C(2)-P(1)-C(22)	115.6(1)	N(4)-N(5)-N(6)	111.0(3)
P(1)-C(2)-N(3)	118.0(2)	N(5)-N(6)-C(7)	106.4(3)
P(1)-C(2)-C(8)	121.4(2)	N(3)-C(7)-N(6)	108.5(3)
N(3)-C(2)-C(8)	116.9(2)	N(3)-C(7)-C(28)	126.9(3)

C(10)-P(1)-C(2)-N(3)	-48.5(3)
C(10)-P(1)-C(2)-C(8)	153.8(3)
C(16)-P(1)-C(2)-C(8)	33.4(3)
C(2)-P(1)-C(10)-C(11)	-109.6(3)
C(2)-P(1)-C(16)-C(17)	51.6(3)
C(2)-P(1)-C(22)-C(23)	30.7(3)
P(1)-C(2)-N(3)-N(4)	-70.0(3)
C(8)-C(2)-N(3)-C(7)	-98.0(4)
C(2)-N(3)-N(4)-N(5)	174.0(2)
C(2)-N(3)-C(7)-C(28)	6.0(5)
C(22)-P(1)-C(2)-C(8)	-85.3(3)

Table 2. Selected Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°) for Ylide **6**.

P(1)-C(2)	1.719(4)	N(6)-N(7)	1.380(5)
P(1)-C(13)	1.802(4)	C(3)-N(7)	1.357(5)
P(1)-C(19)	1.791(5)	N(7)-C(31)	1.439(6)
P(1)-C(25)	1.812(4)	C(2)-N(8)	1.423(6)
C(2)-C(3)	1.422(5)	N(8)-N(9)	1.371(5)
C(3)-N(4)	1.336(6)	N(9)-N(10)	1.284(6)
N(4)-N(5)	1.357(5)	N(10)-N(11)	1.367(5)
N(5)-N(6)	1.277(6)	N(11)-C(12)	1.325(6)
		C(12)-C(37)	1.456(5)

C(2)-P(1)-C(13)	114.3(2)	C(3)-N(4)-N(5)	106.5(4)
C(2)-P(1)-C(19)	113.3(2)	N(4)-N(5)-N(6)	112.2(4)
C(2)-P(1)-C(25)	106.9(2)	N(5)-N(6)-N(7)	105.7(3)
P(1)-C(2)-C(3)	124.6(3)	C(3)-N(7)-N(6)	108.5(4)
P(1)-C(2)-N(8)	115.2(2)	C(2)-N(8)-N(9)	120.5(3)
C(3)-C(2)-N(8)	118.5(4)	C(12)-N(8)-N(9)	107.8(3)
C(2)-C(3)-N(4)	124.7(4)	N(8)-N(9)-N(10)	106.7(3)
C(2)-C(3)-N(7)	128.1(4)	N(9)-N(10)-N(11)	111.1(4)
		N(10)-N(11)-C(12)	106.3(4)

C(13)-P(1)-C(2)-C(3)	83.9(4)
C(19)-P(1)-C(2)-C(3)	-39.4(4)
C(25)-P(1)-C(2)-C(3)	-158.3(3)
C(13)-P(1)-C(2)-N(8)	-81.2(3)
C(19)-P(1)-C(2)-N(8)	155.5(3)
C(25)-P(1)-C(2)-N(8)	36.6(3)
P(1)-C(2)-C(3)-N(4)	0.5(5)
P(1)-C(2)-C(3)-N(7)	175.2(3)
P(1)-C(2)-N(8)-N(9)	80.7(4)
P(1)-C(2)-N(8)-C(12)	-93.5(4)

Ylides **5a-c** and **6** are rather inactive and do not enter into the Wittig reaction with para-nitrobenzaldehyde. However, ylide **5a** was found to undergo the following sequence of transformations: **5a** → **7** → **8** → **9** (see Scheme). At the last stage of this process a phosphorotropic migration takes place as confirmed by the ^{1}H and ^{31}P NMR spectra (see Experimental Section). A similar rearrangement was observed earlier for other ylides with a characteristic fragment $\geq P=\underset{|}{C}-CONH_2$.[5]

EXPERIMENTAL SECTION

X-ray Structural Analyses of **5a** *and* **6**:[6]

The cell constants and the reflections were measured with a Siemens P4-PC four-circle diffractometer (graphite monochromator, λ(Cu-Kα)=1.541781Å). Lattice parameters were obtained from least-squares of 24 (for **5a**) or 22 (for **6**) reflections with $11<\theta<18^{o}$. The structures were solved by Patterson (for **5a**) or direct methods (for **6**) and refined by full-matrix least-squares to a final R=0.039 (for **5a**) or R=0.046 (for **6**) (H atoms refined with isotropic thermal parameters). The program package SHELXTL PC was used for all calculations and drawings.[7]

(**5a**): $C_{27}H_{20}N_5P$, M=445.5, a light brown crystal of 0.45 x 0.35 x 0.25 mm size, space group $P2_1/c$, Z=4, monoclinic, a=14.688(1), b=8.388(1), c=18.864(2)Å, β=99.878(7)^{o}, V=2289.7(5)Å^3, d_{calc}=1.292 g cm^{-3}, F(000)=928, T=289K, ω-scan, $\Delta\omega$=0.60^{o}, $2.5 \leqslant \omega \leqslant 60.0^{o}$ min^{-1}, $2.0 \leqslant 2\theta \leqslant 100.9^{o}$, 3359 collected reflections ($(\sin\theta/\lambda)_{max}$=0.50), 2407 independent reflections (R_{int}=0.89%), 2054 observed reflections (F>4.0σ(F)). Semi-empirical absorption correction used (μ=1.255 mm^{-1}).

(**6**): $C_{33}H_{25}N_8P$, M=564.6, a white crystal of 0.35 x 0.25 x 0.25 mm size, space group $P2_1/c$, Z=4, monoclinic, a=14.626(1), b=10.145(2), c=20.432(3)Å, β=107.47(1)^{o}, V=2891.9(6)Å^3, d_{calc}=1.297 g cm^{-3}, F(000)=1176, T=289K, ω-scan, $\Delta\omega$=0.60^{o}, $2.0 \leqslant \omega \leqslant 60.0^{o}$ min^{-1}, $2.0 \leqslant 2\theta \leqslant 100.9^{o}$, 3995 collected reflections ($(\sin\theta/\lambda)_{max}$=0.50), 3032 independent reflections (R_{int}=5.33%), 2242 observed reflections (F>6.0σ(F)). No correction for absorption (μ=1.141 mm^{-1}).

IR spectra: Specord M-80; KBr tablets. *^{1}H NMR spectra*: Varian Gemini (200 MHz); δ-scale; internal reference hexamethyldisiloxane. *^{13}C and ^{31}P NMR spectra*: Bruker WP (50.327 and 81 MHz respectively), solutions in DMSO-d_6; coupling constants J in Hz.

Cyano(5-aryltetrazol-1-yl)methylenetriphenylphosphoranes (**5a-c**): General procedure. To a cooled (-10 to -5^{o}C) solution of sodium azide (0.1 mol) in water (40 ml) is added dropwise on intense stirring a solution of an

appropriate reagent **1a-c**[1] (0.01 mol) in methanol (30 ml). The mixture is stirred at 20 to 25°C for 2h and then left for 12 h. The precipitated solid is filtered off, washed with water, and purified by crystallization.

Cyano(5-phenyltetrazol-1-yl)methylenetriphenylphosphorane (**5a**): Yield 75%, mp 198-199°C (from acetonitrile - diethyl ether, 1:1 v/v). IR: 2150 (C≡N) cm^{-1}, no absorption in the region of 1620 to 1750 cm^{-1}. ^{13}C NMR: 29.23 (d, C=P, $^1J_{CP}$ = 106.9), 121.25 (d, C-P, $^1J_{CP}$ = 61.8), 123.33 (i-C, Ph-C^5), 123.54 (d, C≡N, $^2J_{CP}$ = 17.5), 128.62, 128.75 (o,m-C, Ph-C^5), 129.83 (d, o-C, Ph_3P, $^2J_{CP}$ = 8.2), 131.32 (p-C, Ph-C^5), 133.08 (d, m-C, Ph_3P, $^3J_{CP}$ = 7.0), 134.21 (p-C, Ph-C^5), 157.37 (C=N). ^{31}P NMR: +23.72. (Found: C, 72.91; H, 4.58; N, 15.78; P, 7.23. Calc for $C_{27}H_{20}N_5P$ (MW 445.47): C, 72.80; H, 4.53; N, 15.72; P, 6.95%).

Cyano[5-(p-tolyl)tetrazol-1-yl]methylenetriphenylphosphorane (**5b**): Yield 68%, mp 192-193°C (from acetonitrile). IR: 2150 (C≡N) cm^{-1}. (Found: N, 15.08; P, 6.65. Calc for $C_{28}H_{22}N_5P$ (MW 459.49): N, 15.24; P, 6.74%).

Cyano[5-(p-chlorophenyl)tetrazol-1-yl]methylenetriphenylphosphorane (**5c**): Yield 82%, mp 186-187°C (from ethanol). (Found: Cl, 7.35; N, 14.64; P, 6.42. Calc for $C_{27}H_{19}ClN_5P$ (MW 479.91): Cl, 7.51; N, 14.59; P, 6.45%).

5-Phenyltetrazol-1-yl(1-phenyltetrazol-5-yl)methylenetriphenylphosphorane (**6**): To a cooled (-10 to -5°C) solution of sodium azide (0.1 mol) in water (70 ml) is added dropwise on stirring a solution of the reagent **1d**[3] (0.01 mol) in N,N-dimethylformamide (50 ml). The mixture is stirred at 20 to 25°C for 2h and left for 12 h. After addition of water (200 ml), the oily product is separated by decantation, washed with water and dried in a vacuum desiccator over phosphorus pentoxide for a week. The crystalline precipitate formed is separated from the oil on a porous plate and recrystallized from methanol. Yield 10%, mp 177-180°C. A major portion of the product remains in a viscous oil and is difficult to isolate. IR: no intense absorption in the region of 1620 to 2200 cm^{-1}. ^{31}P NMR: +18.35. For the raw oily product: +18.35 and +25.00 in a ca. 1:3 ratio. (Found: C, 70.27; H, 4.46; N, 19.72; P, 5.47. Calc for $C_{33}H_{25}N_8P$ (MW 564.69): C, 70.20; H, 4.46; N, 19.85; P, 5.49%).

Carbamoyl(5-phenyltetrazol-1-yl)methyltriphenylphosphonium Perchlorate (**7**): A suspension of compound (**5a**) (2 mmol) in concentrated sulfuric acid (10 ml) is heated at 40 to 50°C for 3 to 5 min. The solution formed is left for 12 h at 20 to 25°C then poured with caution on stirring into a 5% sodium perchlorate solution (200 ml). The precipitated solid is filtered off, washed with water, and crystallized from acetonitrile. Yield 90%, mp 195-198°C. IR: 1730 (C=O), 3200, 3340 (NH_2 associated) cm^{-1}; no noticeable absorption in the region of 2000 to 2300 cm^{-1}. (Found: C, 57.40; H, 4.38; N, 12.68; P, 5.52. Calc for $C_{27}H_{23}ClN_5O_5P$ (MW 563.94): C, 57.51; H, 4.11; N, 12.83; P, 5.49%).

Carbamoyl(5-phenyltetrazol-1-yl)methylenetriphenylphosphorane (**8**): To a suspension of phosphonium salt (**7**) (1 mmol) in methanol (30 ml) is added triethylamine (1 mmol). The mixture is left at 20 to 25°C for 12 h then the solvent is removed in vacuum, the residue is washed with water, dried, and purified by reprecipitation from methanol with diethyl ether. Yield 90%, mp 176-177°C. IR: 1610 (C=O) 3320, 3480 (NH_2 associated) cm^{-1}. ^{31}P NMR: +17.83. (Found: C, 69.53; H, 4.79; N, 14.96; P, 6.59. Calc for $C_{27}H_{22}N_5OP$ (MW 463.48): C, 69.97; H, 4.78; N, 15.11; P, 6.68%).

Triphenyl(5-phenyltetrazol-1-ylacetylimino)phosphorane (**9**): A suspension of ylide (**8**) (1 mmol) in ethanol (15 ml) is boiled under reflux for 64 h. The precipitate is filtered off and crystallized from ethanol. Yield 85%, mp 205-208°C. IR: 1630 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): 5.25 (s,CH_2), 7.25-7.80 (m, $4C_6H_5$). ^{13}C NMR: 53.56 (d,CH_2, $^2J_{CP}$ = 23.9), 124.37 (i-C, Ph-C^5), 126.60 (d, i-C, Ph_3P, $^1J_{CP}$ = 99.3), 128.35, 128.94 (o,m-C, Ph-C^5), 129.12 (d, m-C,Ph_3P, $^3J_{CP}$ = 2.3), 131.10 (p-C, Ph-C^5), 132.49 (d, o-C, Ph_3P, $^2J_{CP}$ = 10.3), 132.89 (p-C, Ph_3P), 154.63 (C=N), 173.71 (d, C=O, $^2J_{CP}$ = 8.4). ^{31}P NMR: +20.16. (Found: C, 69.65; H, 4.82; N, 14.96; P, 6.52. Calc for $C_{27}H_{22}N_5OP$ (MW 463.48): C, 69.97; H, 4.78; N, 5.11; P, 6.68%).

Acknowledgements: This work was funded by the Research Foundation of Leuven (to LVM and NIM). LVM is a Research Associate of the National Fund for Scientific Research (Belgium).

REFERENCES

1. Brovarets, V.S.; Lobanov, O.P.; Vinogradova, T.K.; Drach, B.S. Zhurn. *Obshch. Khimii* **1984**, *54*, 288-301.
2. Brovarets, V.S.; Drach, B.S. *Zhurn. Obshch. Khimii* **1986**, *56*, 321-325.
3. Brovarets, V.S.; Vydzhak, R.N.; Vinogradova, T.K.; Drach, B.S. *Zhurn. Obshch. Khimii* **1993**, *63*, 87-92.
4. Allen, F.H.; Davies, J.E.; Galloy, J.J.; Johnson, O.; Kennard, O; Macrae, C.F.; Mitchell, E.M.; Mitchell, G.F.; Smith, J.M.; Watson, D.G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187-204.
5. Wanner, M.J.; Koomen, G.-J. *Tetrahedron Lett.* **1992**, *33*, 1513-1516.
6. The list of atomic coordinates has been deposited with the Cambridge Crystallographic Data Centre.
7. SHELXTL PC Manual, version 4.1, Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

(*Received in UK* 11 *October* 1993; *revised* 11 *November* 1993; *accepted* 12 *November* 1993)