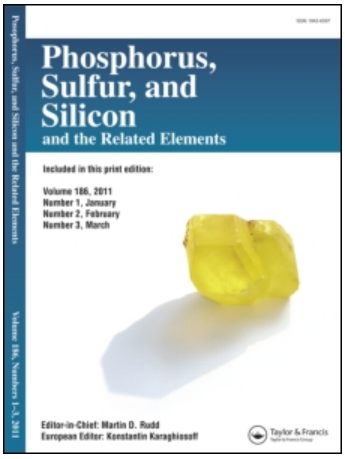

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ZWITTERIONIC SPECIES FROM TRIISOPROPYLPHOSPHINE AND 2-CYANOACRYLATES: SYNTHESIS, STRUCTURE AND PROPERTIES

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ZWITTERIONIC SPECIES FROM TRIISOPROPYLPHOSPHINE AND 2-CYANOACRYLATES: SYNTHESIS, STRUCTURE AND PROPERTIES

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Dedicated to Professor John G. Verkade on the occasion of his 60th birthday

(Received February 27, 1996)

Triisopropylphosphine reacts with 2-cyanoacrylates with formation of the P-zwitterionic species **2a** and **2b**. The reaction of **2b** with trimethylsilyltriflate, in the presence of traces of water, leads to the phosphonium triflate **3**. **2b** is alkylated at the carbon atom with methyl iodide with formation of the phosphonium iodide **4**. The initially formed adducts of the zwitterionic species **2a** and **2b** with tosyl azide and with tosyl isocyanate are thermodynamically unstable. In the first case, the final products of the reaction are tosyl iminotriisopropylphosphine imide **6** and 2-cyanoacrylate polymers. In the second case, the reaction leads to the zwitterionic product **8**, and, in the presence of traces of water, to the molecular complexes **9a** and **9b**. The reaction of the zwitterionic species **2a** and **2b** with methylisocyanate proceeds in an unusual way, resulting in the formation of the zwitterionic species **12a** and **12b**, as a result of the insertion of methylisocyanate into the C—C bond of the starting zwitterionic adducts. The identity and structure of all the new products were established by elemental analysis, IR spectroscopy, ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy, as well as by single-crystal X-ray structure analyses for **2b**, **8**, **9a** and **12b**. The structures of **2b**, **9a** and **12b** are closely similar as regards the molecular backbone. In all four structures there is evidence for some delocalisation of negative charge to the C(:O) and CN group.

Key words: Triisopropylphosphine, 2-cyanoacrylates, zwitterionic species, isocyanates, rearrangement, X-ray crystal structures.

INTRODUCTION

The interest in zwitterionic species with (cationic) phosphonium centers is explained in terms of their practical application (e.g. as polymerisation initiators[1]), and their potential value as reagents in organic synthesis. The general method of preparation of the zwitterionic species involving the groupings **A** and **B** is the reaction of compounds of trivalent phosphorus with aliphatic electrophilic reagents such as substituted alkenes[2] and isocyanates.[3] In many cases such zwitterionic species are unstable compounds especially **A**, that can decompose into their educts, transform into ylides

TABLE I

IR data, ^{31}P-NMR data and selected ^{1}H- and ^{13}C-NMR data for compounds **2a**, **2b**, **3**, **8**, **9a**, **9b**, **12a** and **12b**

Compound	IR ν(CO), cm^{-1} ν(CN), cm^{-1}	δ(^{31}P) ppm	δ(^{1}H), ppm (-CH_2P^+)	δ(^{13}C), ppm		
				-CH_2P^+ (^{1}J(CP), Hz)	-CN	>C(:O)
i-$Pr_3\overset{\oplus}{P}$-CH_2-$\overset{\ominus}{C}$(CN)COOMe **2a**	1627 2146	38.7	3.10, d ^{2}J(HP) = 6.28 Hz	17.4, d (43.5)	129.3	171.5
i-$Pr_3\overset{\oplus}{P}$-CH_2-$\overset{\ominus}{C}$(CN)COOEt **2b**	1602 2136	38.5	3.18, d ^{2}J(HP) = 6.08 Hz	17.3, d (43.4)	129.3	171.5
i-$Pr_3\overset{\oplus}{P}$-CH_2-CH(CN)COOEt $CF_3SO_3^{\ominus}$ **3**	1748 2256	44.9	2.70-3.20, m (CH_AH_BP)	15.9, d (45.5)	115.9, d ^{3}J(CP) = 3.14 Hz	164, d ^{3}J(CP) = 10.4 Hz
i-$Pr_3\overset{\oplus}{P}$-C(=O)-$\overset{\ominus}{N}$-Ts **8**	1614	31.2				160, d ^{1}J(CP) = 95.2 Hz
i-$Pr_3\overset{\oplus}{P}$-CH_2-$\overset{\ominus}{C}$(CN)COOMe $H_3CC_6H_4SO_2NH_2$ **9a**	1595 2144	38.9	3.17, d ^{2}J(HP) = 6.44 Hz	17.6, d (43.9)	129.6	172.1
i-$Pr_3\overset{\oplus}{P}$-CH_2-$\overset{\ominus}{C}$(CN)COOEt $H_3CC_6H_4SO_2NH_2$ **9b**	1591 2141	38.8	3.17, d ^{2}J(HP) = 6.2 Hz	a	a	a
i-$Pr_3\overset{\oplus}{P}$-CH_2-$\overset{\ominus}{C}$(CN)C(=O)-N(Me)-COOMe **12a**	1598, 1690 2158	41.1	3.1, d ^{2}J(HP) = 8.1 Hz	17.1 (44.5)	127.0	152.9 169.5
i-$Pr_3\overset{\oplus}{P}$-CH_2-$\overset{\ominus}{C}$(CN)C(=O)-N(Me)-COOEt **12b**	1592, 1685 2158	41.0	3.17, d ^{2}J(HP) = 8.2 Hz	17.1 (44.0)	126.7	154.7 169.7

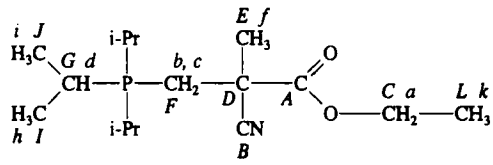
[a] Not recorded

TABLE II

^{1}H- and ^{13}C-NMR data for compound **4**

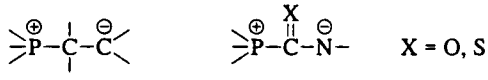
Signal	δ(^{13}C)	No. of protons	J(CP) Hz	^{1}J(HC)-correl. with ^{1}H signal	relative signs: ^{n}J(CP)/$^{n+1}$J(HP)
A	167.9	0		-	
B	118.1	0	3.2	-	
C	64.5	2		a	
D	39.4	0	7.3	-	
E	29.0	3	10.3	f	>0
F	23.8	2	38.4	b + c	<0
G	21.3	1	39.9	d	<0
I	17.6	3	3.4	h	<0
J	17.3	3	3.0	i	<0
L	13.7	3		k	

Signal	δ(^{1}H)	Multiplicity	J(HH) Hz	J(HP) Hz
a	4.38	q	7.1	
b	3.87	dd	16.2	11.5
c	3.18	dd	16.2	12.3
d	3.14	d x sept	7.2	12.3
f	2.14	d		2.5
h	1.57	dd	7.2	16.4
i	1.51	dd	7.2	16.5
k	1.39	t	7.2	



All coupling constants were verified by recording the NMR spectra at both 200 and 400 MHz (^{1}H) and at 50.3 and 100.6 MHz (^{13}C). J(HH) and J(HP) coupling constants were obtained from 2D J-resolved spectra.

(via H-migration) or phosphoranes (via cyclization and formation of a new P—O bond), undergo oligomerization or react with the unsaturated starting compounds.



A **B**

For synthetic purposes those zwitterionic species are, obviously, the most interesting that are thermodynamically stable but sufficiently kinetically active to react with various electrophiles.

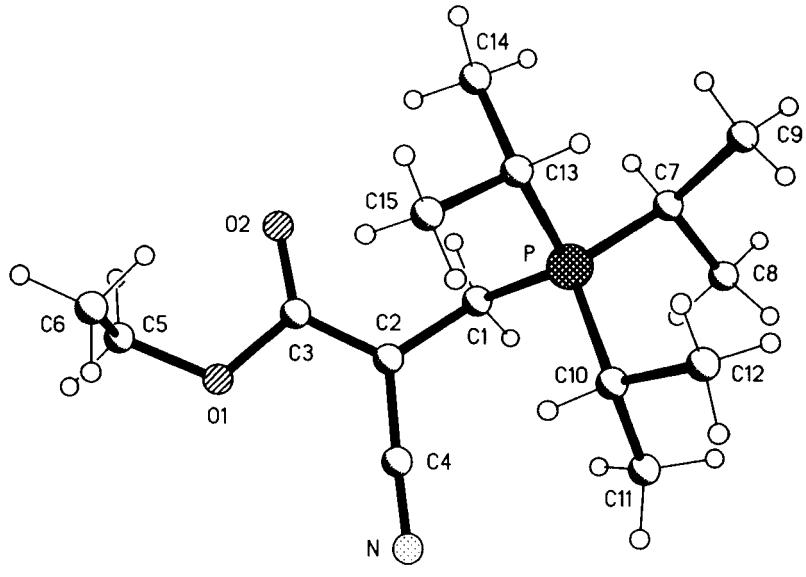


FIGURE 1 The structure of compound **2b** in the crystal. Radii are arbitrary.

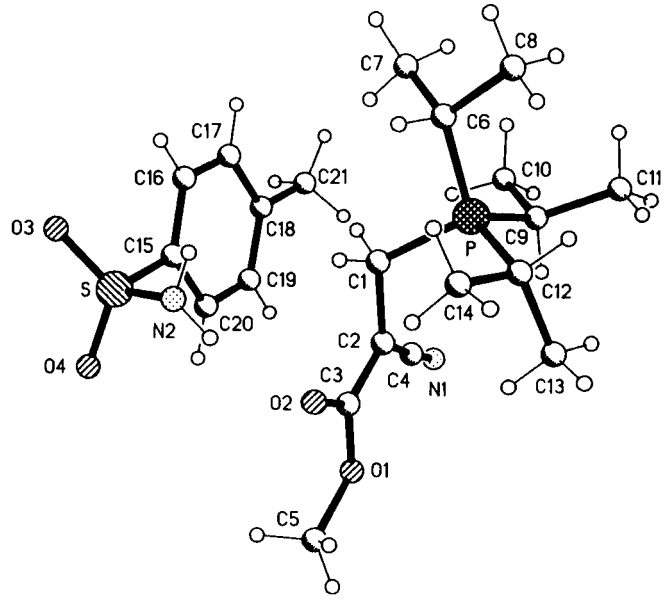


FIGURE 2 The structure of compound **9a** in the crystal. Radii are arbitrary.

RESULTS AND DISCUSSION

2-Cyanoacrylates such as **1b** were described many years ago[4] and are successfully used in polymer chemistry.[5] Recently they were also introduced in organic synthesis.[6] A preliminary communication described[7] the reaction between **1b** and trialkylphos-

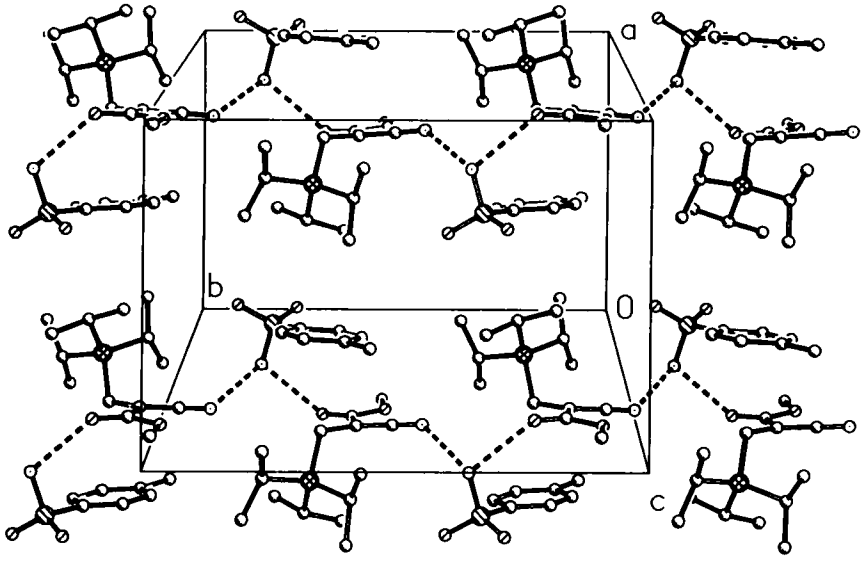


FIGURE 3 Packing diagram of compound **9a**. Hydrogen atoms are omitted. Dashed bonds indicate hydrogen bonding contacts (see text).

phines leading, under special conditions, to zwitterionic species of type **C** (Equation (1)).

$$R_3P + CH_2{=}C(CN)COOEt \rightleftharpoons R_3\overset{\oplus}{P}\text{-}CH_2\text{-}\overset{\ominus}{C}(CN)COOEt \quad (1)$$

1b **C**

R = n-Pr, n-Bu

The process described by Equation (1) is reversible, and between 0 and 20°C the equilibrium can be shifted to the right only in the case of very strong uncharged P-nucleophiles. In the case of relatively weak P-nucleophiles (triarylphosphines, trialkylphosphites, etc.) the equilibrium is shifted to the left and **1b**, which is present in the reaction mixture in large quantities at all times during the reaction, quickly polymerizes by an anionic mechanism.[5] For example, the reaction of **1b** with tetraphenylmethylenediphosphine led only to polymeric substances with phosphonium groups at the end of the chain (Equation (2)).

$$(Ph_2P)_2CH_2 + \mathbf{1b} \longrightarrow Ph_2\overset{\oplus}{P}\text{-}\left(\text{-}CH_2\text{-}\underset{\underset{COOEt}{|}}{\overset{\overset{CN}{|}}{C}}\text{-}\right)_n CH_2\text{-}\overset{\ominus}{\underset{\underset{COOEt}{|}}{\overset{\overset{CN}{|}}{C}}} \quad (2)$$

In contrast, the slow addition of an ether solution of **1a** and **1b** to the solution of triisopropylphosphine in hexane at 0°C resulted in the formation of the crystalline zwitterionic species, **2a** and **2b**, in good yield.

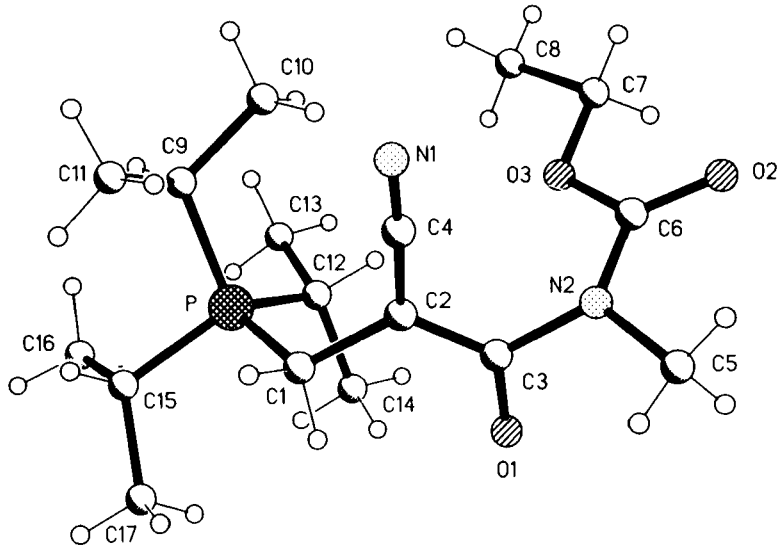


FIGURE 4 The structure of compound **12b** in the crystal. Radii are arbitrary.

$$\text{i-Pr}_3\text{P} + \text{CH}_2{=}\text{C(CN)COOR} \rightleftharpoons \text{i-Pr}_3\overset{\oplus}{\text{P}}\text{-CH}_2\text{-}\overset{\ominus}{\text{C}}\text{(CN)COOR} \qquad (3)$$

1a: R = Me **2a**: R = Me
1b: R = Et **2b**: R = Et

According to the IR spectroscopic data, the negative charge in these compounds is delocalized in the system N—C—C—C—O. As a result of the conjugation the absorption band corresponding to the CN group becomes very intense, and is shifted to the region 2136–2146 cm^{-1} (2200–2250 cm^{-1} for the starting cyanoacrylates). A similar shift to the region 1602–1627 cm^{-1} is observed for the C(:O) absorption bands (1720–1730 cm^{-1} for the starting cyanoacrylates). The $\delta(^{31}P)$ values of these compounds were observed at about 38.5 ppm. In the ^1H NMR spectrum a characteristic doublet, due to the CH_2P protons, is observed (see Table I). In the ^{13}C NMR spectra the resonances due to the C(:O), CN and C^- carbon atoms are observed as singlets (see Table I). The signals of the CH_2P carbon atoms are observed as doublets (see Table I).

The zwitterion **2b** can easily be protonated. Its reaction with $CF_3SO_2OSiMe_3$ in acetone containing traces of water, led to the salt **3** (Equation (4)).

$$\mathbf{2b} \xrightarrow[(H_2O)]{CF_3SO_2OSiMe_3} \text{i-Pr}_3\overset{\oplus}{\text{P}}\text{-CH}_2\text{-CH}(\text{CN})(\text{COOEt})\ \ CF_3SO_3^{\ominus} \qquad (4)$$

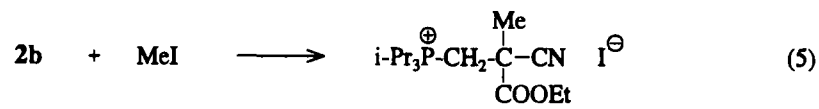
3

The zwitterionic species are nucleophiles strong enough to be alkylated by methyl iodide. The reaction of **2b** with methyl iodide led to the phosphonium salt **4** (Equation (5)).

TABLE III

Summary of X-ray data for compounds **2b**, **8**, **9a** and **12b**

Compound	**2b**	**8**	**9a**	**12b**
Formula	$C_{15}H_{28}NO_2P$	$C_{17}H_{28}NO_3PS$	$C_{21}H_{35}N_2O_4PS$	$C_{17}H_{31}N_2O_3P$
M_r	285.35	357.43	442.54	342.41
Crystal habit	colourless tablet	colourless prism	colourless tablet	colourless tablet
Crystal size (mm)	0.80 x 0.40 x 0.10	0.70 x 0.40 x 0.30	0.80 x 0.60 x 0.25	0.85 x 0.60 x 0.20
Temperature (°C)	-100	-100	-100	-100
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Cell constants				
a (pm)	796.46(10)	859.59(10)	1019.75(10)	1004.7(3)
b (pm)	938.16(8)	1544.2(2)	1469.22(14)	1410.9(4)
c (pm)	1177.10(12)	1469.5(2)	1679.6(2)	1373.6(5)
α (°)	69.038(6)	90	90	90
β (°)	82.651(8)	105.457	105.196(6)	101.38(3)
γ (°)	89.784(8)	90	90	90
U (nm^{-3})	0.8137(2)	1.8801(4)	2.4284(4)	1.9086(11)
Z	2	4	4	4
D_x ($Mg\ m^{-3}$)	1.165	1.263	1.210	1.192
μ (mm^{-1})	0.168	0.271	0.226	0.160
$F(000)$	312	768	952	744
$2\theta_{max}$(°)	55	50	50	50
No. of reflns.:				
measured	3954	4508	4452	3512
independent	3667	3302	4267	3345
R_{int}	0.011	0.018	0.011	0.029
$wR(F^2$, all refl.)	0.089	0.091	0.112	0.123
$R(F,>4\sigma(F))$	0.033	0.034	0.041	0.049
No. of parameters	179	215	276	216
S	1.03	1.02	1.00	0.88
max. Δ/σ	< 0.001	< 0.001	< 0.001	< 0.001
max. $\Delta\rho$ (e nm^{-3})	299	281	639	369



(5)

4

The transformation of the carbanionic center of the zwitterionic species into the sp^3 hybridization state is accompanied by a downfield shift of ca. 5–6 ppm in the ^{31}P NMR spectrum. Associated with the formation of the asymmetric center, the protons of the methylene groups and of the isopropyl groups become magnetically nonequivalent. Detailed ^1H- and ^{13}C-NMR spectroscopic data for compound **4** are presented in Table II.

TABLE IV

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for compound **2b**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
P	2128.9(4)	1479.7(4)	7157.7(3)	19.2(1)
O(1)	-2646.8(13)	-2284.4(12)	8365.8(10)	35.9(3)
O(2)	-979.5(13)	-1896.3(11)	9670.4(8)	33.2(2)
N	-2431(2)	805(2)	5741.4(12)	41.1(3)
C(1)	-31(2)	1189.6(15)	7953.0(11)	21.9(3)
C(2)	-1146(2)	36.4(15)	7749.3(12)	22.6(3)
C(3)	-1532(2)	-1402(2)	8672.5(12)	25.7(3)
C(4)	-1867(2)	428(2)	6656.7(13)	26.6(3)
C(5)	-2949(2)	-3837(2)	9178.3(15)	43.9(4)
C(6)	-1673(3)	-4849(2)	8862(2)	54.6(5)
C(7)	3110(2)	3002(2)	7516.6(13)	27.8(3)
C(8)	2419(2)	4575(2)	6871(2)	44.6(4)
C(9)	5048(2)	3082(2)	7314(2)	39.7(4)
C(10)	2068(2)	1887.0(15)	5532.0(11)	23.7(3)
C(11)	922(2)	3183(2)	4922.5(13)	35.8(3)
C(12)	3836(2)	2143(2)	4780.1(13)	33.2(3)
C(13)	3345(2)	-214.2(14)	7756.1(11)	22.3(3)
C(14)	3344(2)	-676(2)	9148.5(13)	32.2(3)
C(15)	2781(2)	-1581.3(15)	7447.9(13)	27.6(3)

The zwitterionic products **2a** and **2b** readily reacted with tosyl azide with formation of the phosphine imide **6** (NMR experiment). Immediately after the reaction started, a broad signal at 57.5 ppm was seen in the ^{31}P NMR spectrum. It disappeared after a few minutes, and a new intense signal at 58.5 ppm was observed. Apparently the first resonance is due to the initial adduct **5**, and the second one corresponds to the phosphine imide **6** (Equation (6)).

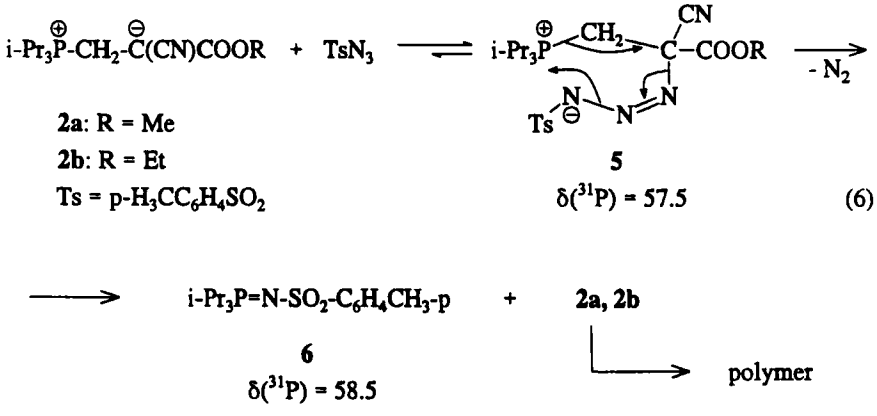


TABLE V

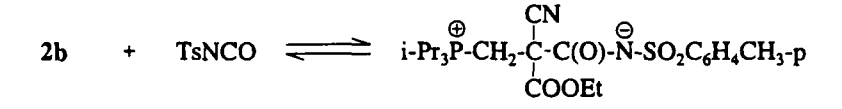
Selected bond lengths [pm] and angles [°] for compound **2b**

P-C(10)	181.95(13)	P-C(1)	182.17(13)
P-C(13)	182.26(13)	P-C(7)	183.12(13)
O(1)-C(3)	138.0(2)	O(1)-C(5)	142.9(2)
O(2)-C(3)	123.7(2)	N-C(4)	115.6(2)
C(1)-C(2)	150.5(2)	C(2)-C(3)	140.2(2)
C(2)-C(4)	140.3(2)	C(5)-C(6)	149.0(3)
C(7)-C(9)	152.9(2)		

C(10)-P-C(1)	109.12(6)	C(10)-P-C(13)	108.60(6)
C(1)-P-C(13)	111.27(6)	C(10)-P-C(7)	115.10(6)
C(1)-P-C(7)	105.83(6)	C(13)-P-C(7)	106.93(6)
C(3)-O(1)-C(5)	116.73(12)	C(2)-C(1)-P	116.27(9)
C(3)-C(2)-C(4)	119.88(12)	C(3)-C(2)-C(1)	120.14(11)
C(4)-C(2)-C(1)	119.91(12)	O(2)-C(3)-O(1)	120.74(12)
O(2)-C(3)-C(2)	126.57(12)	O(1)-C(3)-C(2)	112.69(12)
N-C(4)-C(2)	177.4(2)	O(1)-C(5)-C(6)	111.56(13)

The $\delta(^{31}P)$ value of the product obtained directly by the Staudinger reaction between triisopropylphosphine and tosyl azide was identical to that of **6**.

The reaction of the zwitterionic species **2b** with the highly electrophilic tosyl isocyanate was more complicated. In the first stage of this reaction the adduct **7** was formed (Equation (7)). Its formation was observed by ^{1}H- and ^{31}P-NMR spectroscopy.

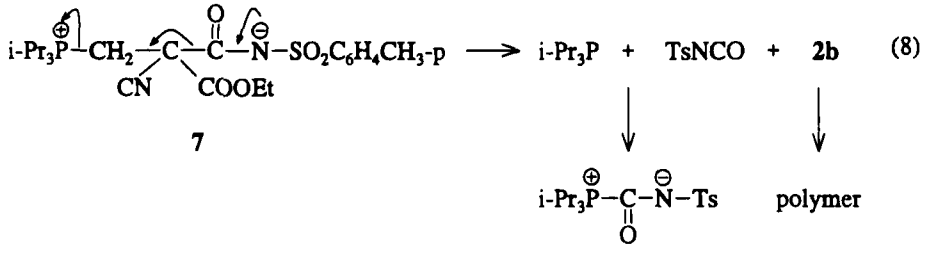


(7)

7

$\delta(^{31}P) = 45.9$

In a few minutes a new signal at δ = 33 ppm was observed in the ^{31}P NMR spectrum, corresponding to the zwitterionic product **8**. The second product of this reaction was, apparently, the polymer of the cyanoacrylate **2b** (Equation (8)). The structure of **8** was confirmed by elemental analysis, IR and NMR spectroscopy and a single-crystal X-ray analysis. It was also obtained by the direct reaction of i-Pr_3P with tosyl isocyanate, similarly to the procedure described in Reference 3.



(8)

7

8

TABLE VI

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for compound **9a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
P	5583.1(6)	7119.2(4)	2925.2(3)	24.6(2)
S	10135.1(6)	8147.3(4)	1389.8(4)	35.9(2)
N(1)	7300(2)	4512.8(14)	2602.6(13)	44.5(5)
O(1)	6787(2)	5429.6(12)	672.1(10)	63.5(6)
O(2)	6634(2)	6960.1(11)	722.2(9)	40.7(4)
O(3)	10908(2)	8957.2(12)	1653.1(12)	52.4(5)
O(4)	10408(2)	7614.4(13)	739.6(10)	52.1(5)
N(2)	8561(2)	8434.3(14)	1105.6(12)	35.3(5)
C(1)	7004(2)	6899.3(15)	2489.0(13)	28.2(5)
C(2)	6887(2)	6089.8(14)	1930.1(13)	27.2(5)
C(3)	6759(2)	6223(2)	1090.0(14)	34.0(5)
C(4)	7105(2)	5216(2)	2277.3(13)	30.6(5)
C(5)	6671(5)	5532(2)	-208(2)	103(2)
C(6)	5992(3)	8183(2)	3493.2(15)	37.8(6)
C(7)	7269(3)	8127(2)	4214(2)	53.9(7)
C(8)	4820(3)	8619(2)	3759(2)	60.2(8)
C(9)	5335(2)	6139.0(14)	3526.5(13)	26.7(5)
C(10)	6576(2)	5885(2)	4229.0(14)	37.3(6)
C(11)	4059(2)	6215(2)	3846(2)	39.9(6)
C(12)	4035(2)	7306(2)	2106.2(14)	34.6(5)
C(13)	3483(2)	6437(2)	1636(2)	43.9(6)
C(14)	4235(3)	8058(2)	1516(2)	51.5(7)
C(15)	10364(2)	7426(2)	2259.8(13)	29.0(5)
C(16)	10607(2)	7803(2)	3042.6(14)	34.4(5)
C(17)	10720(2)	7244(2)	3715.9(14)	37.2(6)
C(18)	10586(2)	6301(2)	3620.3(14)	35.5(6)
C(19)	10353(2)	5943(2)	2831.1(15)	36.0(5)
C(20)	10238(2)	6493(2)	2151.0(14)	32.0(5)
C(21)	10709(3)	5694(2)	4354(2)	55.2(8)

When this reaction was conducted in acetone in the presence of traces of water, the molecular complexes of the original zwitterionic species with tosylamide **9a** and **9b** were formed together with **8** (Equation (9)).

$$\text{i-Pr}_3\overset{\oplus}{\text{P}}\text{-CH}_2\text{-}\overset{\ominus}{\text{C}}\text{(CN)COOR} \xrightarrow[(\text{H}_2\text{O}),\ -\text{CO}_2]{\text{TsNCO}} \begin{matrix} \mathbf{2a}\cdot \text{H}_3\text{CC}_6\text{H}_4\text{SO}_2\text{NH}_2 \\ \mathbf{9a} \end{matrix} + \mathbf{8} \qquad (9)$$

$$\begin{matrix} \mathbf{2b}\cdot \text{H}_3\text{CC}_6\text{H}_4\text{SO}_2\text{NH}_2 \\ \mathbf{9b} \end{matrix} + \mathbf{8}$$

2a: R = Me

2b: R = Et

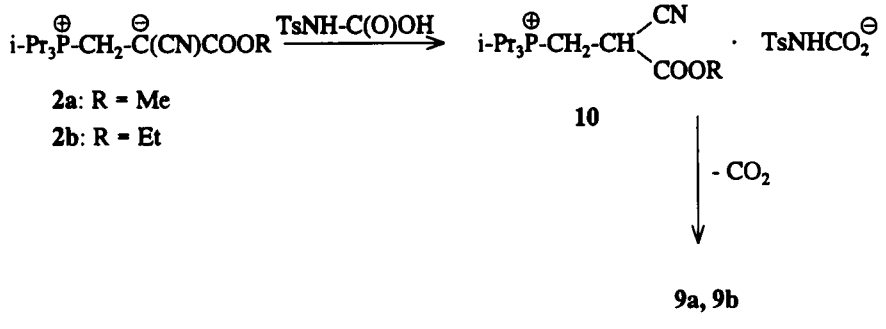
TABLE VII

Selected bond lengths [pm] and angles [°] for compound **9a**

P-C(9)	181.4(2)	P-C(1)	181.6(2)
P-C(6)	182.2(2)	P-C(12)	182.3(2)
S-O(4)	142.9(2)	S-O(3)	143.2(2)
S-N(2)	160.7(2)	S-C(15)	177.1(2)
N(1)-C(4)	116.1(3)	O(1)-C(3)	136.4(3)
O(1)-C(5)	145.9(3)	O(2)-C(3)	123.7(3)
C(1)-C(2)	150.0(3)	C(2)-C(3)	139.6(3)
C(2)-C(4)	140.3(3)		

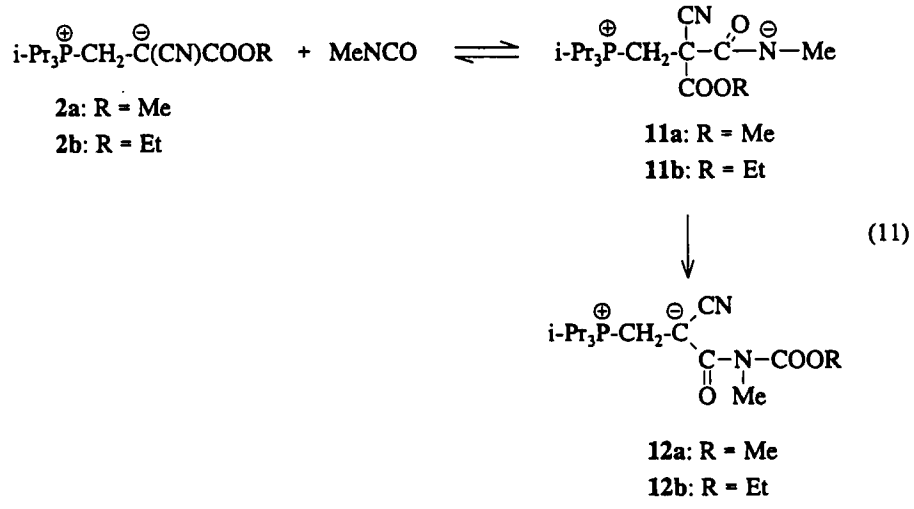
C(9)-P-C(1)	109.01(10)	C(9)-P-C(6)	115.84(10)
C(1)-P-C(6)	105.47(11)	C(9)-P-C(12)	108.66(11)
C(1)-P-C(12)	110.32(11)	C(6)-P-C(12)	107.45(11)
O(4)-S-O(3)	119.33(12)	O(4)-S-N(2)	107.24(11)
O(3)-S-N(2)	107.44(11)	O(4)-S-C(15)	107.02(11)
O(3)-S-C(15)	107.45(11)	N(2)-S-C(15)	107.91(10)
C(3)-O(1)-C(5)	115.2(2)	C(2)-C(1)-P	116.9(2)
C(3)-C(2)-C(4)	120.7(2)	C(3)-C(2)-C(1)	119.5(2)
C(4)-C(2)-C(1)	119.2(2)	O(2)-C(3)-O(1)	120.3(2)
O(2)-C(3)-C(2)	126.7(2)	O(1)-C(3)-C(2)	113.0(2)
N(1)-C(4)-C(2)	176.6(2)		

The structure and identity of **9a** and **9b** were confirmed by elemental analysis, IR-spectroscopy, ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy, and by a single-crystal X-ray analysis (**9a**). Probably tosyl isocyanate is converted into the corresponding acid by reaction with traces of water in the solvent. This acid then reacts with the zwitterionic species **2a** and **2b** resulting in the salts **10**, which are unstable and turn into the amides **9a** and **9b** with loss of CO_2 (Equation (10)).



(10)

With methyl isocyanate, the zwitterionic species, **2a** and **2b**, react differently. In this case the stable zwitterionic products **12a** and **12b** are formed. They are probably the rearrangement products of the initially formed adducts, **11a** and **11b** (Equation (11)).



(11)

TABLE VIII

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for compound **12b**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
P	7552.1(7)	5625.8(5)	1958.2(5)	29.5(2)
O(1)	5746(2)	3468.5(15)	3072(2)	41.0(5)
O(2)	2141(2)	4611(2)	3863(2)	51.3(6)
O(3)	4059(2)	5401.9(14)	3737.1(14)	38.8(5)
N(1)	3045(3)	5556(2)	861(2)	51.7(7)
N(2)	3555(2)	4034(2)	2900(2)	32.2(6)
C(1)	6384(3)	4666(2)	1531(2)	31.3(7)
C(2)	5050(2)	4652(2)	1878(2)	27.7(6)
C(3)	4894(3)	4038(2)	2633(2)	29.3(6)
C(4)	3927(3)	5147(2)	1337(2)	34.0(7)
C(5)	2785(3)	3163(2)	2729(3)	48.2(9)
C(6)	3173(3)	4677(2)	3523(2)	36.1(7)
C(7)	3744(3)	6075(2)	4454(2)	47.8(9)
C(8)	4791(4)	6843(2)	4575(3)	55.6(9)
C(9)	6865(3)	6775(2)	1508(2)	36.6(7)
C(10)	5761(3)	7146(2)	2042(3)	52.4(9)
C(11)	6352(3)	6785(2)	378(2)	51.3(9)
C(12)	7885(3)	5633(2)	3315(2)	37.7(7)
C(13)	8658(4)	6513(3)	3793(3)	60.2(10)
C(14)	8570(3)	4730(2)	3766(2)	44.5(8)
C(15)	9034(3)	5436(2)	1401(2)	39.1(7)
C(16)	10215(3)	6088(2)	1840(3)	50.9(9)
C(17)	9488(3)	4412(2)	1370(3)	45.7(8)

TABLE IX

Selected bond lengths [pm] and angles [°] for compound **12b**

P-C(1)	181.2(3)	P-C(9)	182.2(3)
P-C(15)	182.3(3)	P-C(12)	182.8(3)
O(1)-C(3)	124.0(3)	O(2)-C(6)	122.1(3)
O(3)-C(6)	135.0(3)	O(3)-C(7)	144.7(3)
N(1)-C(4)	114.8(4)	N(2)-C(6)	135.3(4)
N(2)-C(5)	144.7(4)	N(2)-C(3)	146.3(3)
C(1)-C(2)	150.8(3)	C(2)-C(3)	138.4(4)
C(2)-C(4)	140.7(4)	C(7)-C(8)	149.6(4)

C(1)-P-C(9)	112.20(14)	C(1)-P-C(15)	106.51(13)
C(9)-P-C(15)	105.95(13)	C(1)-P-C(12)	108.08(13)
C(9)-P-C(12)	108.77(14)	C(15)-P-C(12)	115.41(14)
C(6)-O(3)-C(7)	115.0(2)	C(6)-N(2)-C(5)	117.5(2)
C(6)-N(2)-C(3)	123.1(2)	C(5)-N(2)-C(3)	116.8(2)
C(2)-C(1)-P	117.8(2)	C(3)-C(2)-C(4)	120.6(2)
C(3)-C(2)-C(1)	118.9(2)	C(4)-C(2)-C(1)	119.8(2)
O(1)-C(3)-C(2)	126.9(2)	O(1)-C(3)-N(2)	117.1(2)
C(2)-C(3)-N(2)	115.9(2)	N(1)-C(4)-C(2)	176.7(3)
O(2)-C(6)-N(2)	124.0(3)	O(2)-C(6)-O(3)	123.2(3)
N(2)-C(6)-O(3)	112.8(2)	O(3)-C(7)-C(8)	107.9(2)

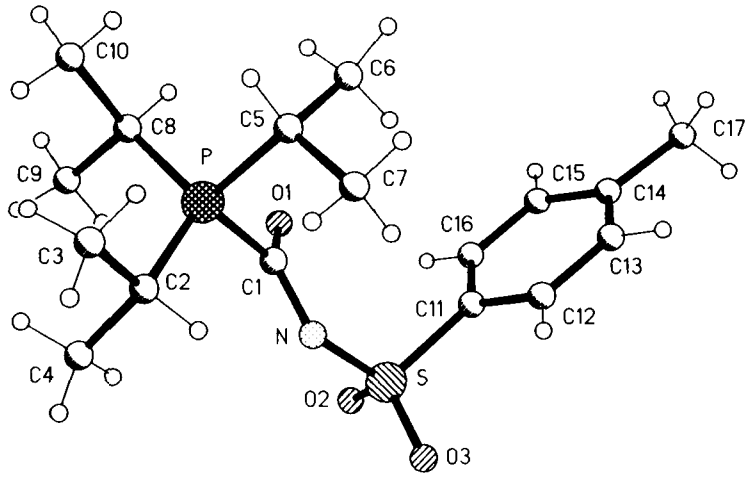


FIGURE 5 The structure of compound **8** in the crystal. Radii are arbitrary.

The structure and identity of **12a** and **12b** were confirmed by elemental analysis, IR-spectroscopy, ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy and by single-crystal X-ray analysis in the case of **12b**. The $\delta(^{31}P)$ values of **12a** and **12b** do not differ significantly from those of the educts **2a** and **2b**. In the ^{1}H NMR spectra of **12a** and **12b**, apart from the signals characteristic of the educts **2a** and **2b**, a singlet due to the CH_3N protons is observed. In the ^{13}C NMR spectra two signals corresponding to

TABLE X

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for compound **8**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
P	572.8(5)	423.0(3)	2231.5(3)	23.8(1)
S	-835.9(6)	2986.2(3)	1522.3(3)	27.2(1)
N	-82(2)	2088.9(10)	2037.0(11)	26.0(4)
O(1)	-270(2)	1320.9(9)	629.4(9)	31.9(3)
O(2)	-13(2)	3288.3(9)	851.5(10)	36.3(3)
O(3)	-911(2)	3571.3(9)	2273.2(10)	37.2(4)
C(1)	27(2)	1417.9(12)	1491.6(13)	24.7(4)
C(2)	1925(2)	688.4(14)	3376.7(13)	32.5(5)
C(3)	2187(4)	-59(2)	4098(2)	59.0(7)
C(4)	3520(3)	1075(2)	3316(2)	55.9(7)
C(5)	-1345(2)	35.6(13)	2391.2(15)	32.5(5)
C(6)	-2628(3)	-2(2)	1445(2)	46.2(6)
C(7)	-1947(3)	578(2)	3108(2)	49.6(6)
C(8)	1298(2)	-359.3(12)	1517.3(13)	27.4(4)
C(9)	2819(3)	-57.3(15)	1255(2)	39.5(5)
C(10)	1536(3)	-1264.7(13)	1950.7(15)	35.8(5)
C(11)	-2851(2)	2742.0(12)	908.6(13)	24.1(4)
C(12)	-4042(2)	2737.9(13)	1390.9(14)	32.0(5)
C(13)	-5626(2)	2583.7(14)	905.6(14)	34.2(5)
C(14)	-6053(2)	2428.5(13)	-60.5(14)	29.9(4)
C(15)	-4850(2)	2402.4(14)	-524.2(14)	33.1(5)
C(16)	-3247(2)	2563.7(13)	-43.9(13)	28.4(4)
C(17)	-7793(3)	2305(2)	-594(2)	45.3(6)

the carbon atoms of two different C(:O) groups, C-*C*(:O)-N and N-*C*(:O)-O, are seen.

Single-crystal X-ray structure determinations of compounds **2b**, **8**, **9a** and **12b** were conducted. Compounds **2b**, **9a** and **12b** differ only in the substituents at C3 and thus their structures are discussed together (Figures 1–4, Tables III–IX). In all the cases the asymmetric unit contains one molecule of the corresponding betaine, although compound **9a** crystallizes as a 1:1 adduct with *p*-toluenesulphonamide.

The negatively charged C2 atoms lie 2.2 pm (**2b**) to 7.0 pm (**12b**) out of the plane of their α-substituents. The angles at C2 are essentially ideal for an sp^2-hybridized atom [from 118.9(2)° (C1—C2—C3, **12b**) to 120.7(2)° (C3—C2—C4, **9a**)]. In all compounds the bond lengths C1—C2 [150.0(3) pm (**9a**) to 150.8(3) pm (**12b**)] and C2—C4 [140.3(2) pm (**2b**, **9a**) to 140.7(4) pm (**12b**)] do not differ significantly, whereas the C2—C3 bond lengths vary over a range of 1.8 pm [138.4(4) pm (**12b**) to 140.2(2) pm (**2b**)]. The C4—N1 triple bond lengths vary from 114.8(4) pm (**12b**) to 116.1(3) pm (**9a**) and are longer than the standard bond length (C—C)≡N of 113.6 pm,[8] while C2—C4 is shorter than the corresponding standard bond length

TABLE XI
Selected bond lengths [pm] and angles [°] for compound **8**

P-C(8)	181.6(2)	P-C(2)	181.9(2)
P-C(5)	182.6(2)	P-C(1)	186.8(2)
S-O(2)	143.59(14)	S-O(3)	144.09(14)
S-N	162.8(2)	S-C(11)	176.8(2)
N-C(1)	132.8(2)	O(1)-C(1)	123.3(2)
C(8)-P-C(2)	116.82(9)	C(8)-P-C(5)	108.48(9)
C(2)-P-C(5)	109.34(9)	C(8)-P-C(1)	106.39(9)
C(2)-P-C(1)	110.64(9)	C(5)-P-C(1)	104.42(9)
O(2)-S-O(3)	116.94(9)	O(2)-S-N	112.79(8)
O(3)-S-N	105.75(8)	O(2)-S-C(11)	108.33(9)
O(3)-S-C(11)	106.64(9)	N-S-C(11)	105.67(8)
C(1)-N-S	117.84(13)	O(1)-C(1)-N	133.3(2)
O(1)-C(1)-P	116.70(14)		

(C—)C≡N of 147.0 pm.[8] In all cases the C3=O double bond is longer than the standard bond length for esters [120.2 pm] or amides [123.1 pm], varying from 123.7 pm (**2b**, **9a**) to 124.0(3) **12b**. This indicates some delocalisation of negative charge to the carboxyl group [C4 is antiperiplanar to the carbonyl oxygen, the largest deviation being observed for **12b** (169.52°)], and to the cyano group. The angle P—C1—C2 between the negatively charged C2 and the positively charged phophorus atom [116.27(9)° (**2b**) to 117.8(2)° (**12b**)] is larger than expected.

All phosphorus atoms display somewhat distorted tetrahedral coordination. The largest deviations from ideal angles are observed for **9a** [105.47(11)° (C1—P—C6) and 115.84(10)° C9—P—C6]. The bond lengths between the secondary carbon atoms of the isopropyl groups and phosphorus vary from 181.4(2) pm [P—C9, (**9a**)] to 183.12(13) pm [P—C7, (**2b**)]. The distances between the phosphorus atoms and carbon atoms of the methylene group are also essentially constant at 181.2(3) pm (**12b**) to 182.17(13) pm (**9a**).

In the case of compound **9a** chains of molecules parallel to the y axis (Figure 3) are formed by hydrogen bonds with the following dimensions: N2—H01···N1 (at 1.5 − x, 0.5 + y, 0.5 − z): 171(2)°, N2—H01 84(2) pm, N2···N1 299.8(3) pm, H01···N1 217(2) pm and N2—H02···O2 165(3)°, N2—H02 87(2) pm, N2···O2 288.1(3) pm, H02···O2 203(2) pm.

In compound **8** the β-position to phosphorus is occupied by the nitrogen atom (Figure 5, Tables III, X, XI). Its structural parameters can be compared to those of $FSO_2\overset{(-)}{N}C(:O)\overset{(+)}{P}(NMe_2)_3$ (**13**),[9] which carries three dimethylamino groups instead of isopropyl groups at phosphorus, and a fluorine atom instead of a tolyl group at sulfur.

The C1—N—S angle is 117.84(13)° and is comparable to that of **13** (118.5°). The N—S bond in **8** [162.8(2) pm] is significantly longer than in **13** (158.3 pm). C1 lies 4.2 pm out of the plane of P, N and O1. However, the angles are markedly different. The P—C1—N angle in **8** is almost tetrahedral 109.72(13)° (**13** 114.4°) whereas O1—C1—N is unusually wide at 133.3(2)° (**13** 131.5°). The C1—O1 bond of **8** [123.3(2) pm] is longer than the corresponding bond in **13** (121.5 pm), but insignificantly shorter than the C3—O2 double bond [123.7(3) pm] in **9a**. Thus, in this

compound also, the oxygen atom participates to some extent in the delocalisation of the negative charge. Phosphorus and sulfur occupy mutually antiperiplanar positions with a torsion angle P—C1—N—S of 169.7°.

As in the case of compounds **2b**, **9a** and **12b** the phosphorus atom in **8** displays distorted tetrahedral coordination; the angles vary from 104.42(9)° to 116.82(9)°. The bond lengths between the phosphorus atom and the carbon atoms of the isopropyl groups do not differ significantly from those in compounds **2b**, **9a** and **12b**.

EXPERIMENTAL

All experiments were carried out with exclusion of air and moisture, unless otherwise stated; solvents were purified and dried according to the usual methods.[10]—All melting points are uncorrected and were determined in sealed capillaries in a Büchi 510 melting point apparatus.—NMR: Bruker AC 200 (^{1}H at 200.1 MHz, ^{13}C at 50.3 MHz, ^{31}P at 81.3 MHz); reference substances were $SiMe_4$ (TMS) int. (^{1}H, ^{13}C), 85% H_3PO_4 ext. (^{31}P); high-field shifts were given negative, low-field shifts positive signs.—IR:—Nicolet FTS 165 Spectrometer; all spectra were obtained in KBr pellets.—Materials: tetraphenylmethylenediphosphine[11] was synthesized according to the literature procedures. Methyl isocyanate was prepared by the reaction between N,N'-dimethylurea and diphenylcarbonate.[12] Triisopropylphosphine, trimethylsilyltriflate and tosyl isocyanate were purchased from Aldrich. 2-Cyanoacrylates were presented by Henkel KGaA. "In vacuo" (i.v.) refers to a pressure of 0.1 Torr, unless otherwise stated.—Yields, melting points and elemental analysis data are presented in Table XII.

Reaction of $Ph_2PCH_2PPh_2$ with **1b**

To a solution of $Ph_2PCH_2PPh_2$ (1.66 g, 4.9 mmol) in 10 ml of diethyl ether a solution of **1b** (2.85 g, 10 mmol) in 10 ml of diethyl ether was added dropwise with stirring at 0°C during 5 min. The amorphous precipitate was separated, and washed with diethyl ether. In the ^{31}P NMR spectrum a complex set of signals (δ(^{31}P) ca. 40–50 ppm) was observed. The ^{1}H NMR spectrum showed multiplets in the region 1.2–1.7 and 2.1–3 ppm, as well as a quartet at 4.2 ppm (CH_2O) and a multiplet, corresponding to the aromatic protons (δ(^{1}H) 7.2–7.6 ppm).

P,P,P-Triisopropyl-(2-cyano-2-alkoxycarbonylethyl)phosphonium Zwitterionic Species **2a** *and* **2b**

To a solution of triisopropylphosphine (50 mmol) in 100 ml of hexane a solution of 2-cyanoacrylate (60 mmol) in 50 ml of diethyl ether was added dropwise with stirring at 0°C over 30 min. (To avoid polymerization the solution of the cyanoacrylate should be added directly to the phosphine solution). The precipitate formed was filtered off, and dissolved in acetone. The product was obtained on slow addition of diethyl ether to this solution at room temperature.

2a: ^{1}H NMR ($CDCl_3$): 1.21–1.33 (m, 18H, $(CH_3)_2$CHP), 2.43–2.61 (m, 3H, $(CH_3)_2CH$P), 3.10 (d, 2H, ^2J(HP) = 6.28 Hz, CH_2P), 3.48 (s, 3H, CH_3O); ^{13}C NMR ($CDCl_3$): 16.53 (d, ^2J(CP) = 3.22 Hz (CH_3)$_2$CHP), 17.4 (d, ^1J(CP) = 43.5 Hz, CH_2P), 20.2 (d, ^1J(CP) = 39.97 Hz, $(CH_3)_2CH$), 32.0 (s, C^-), 49.8 (s, CH_3O), 129.3 (s, CN), 171.5 (s, C(:O)); for ^{31}P-NMR and IR data see Table I.

2b: ^{1}H NMR ($CDCl_3$): 1.11 (t, 3H, ^3J(HH) = 7.04 Hz, CH_3CH_2O), 1.37–1.48 (m, 18H, $(CH_3)_2$CHP), 2.65–2.71 (m, 3H, $(CH_3)_2CH$P), 3.18 (d, 2H, ^2J(HP) = 6.08 Hz, CH_2P), 4.04 (q, 2H, ^3J(HH) = 7.04 Hz, CH_2O). ^{13}C NMR ($CDCl_3$): 15.0 (s, CH_3CH_2O), 16.56 (d, ^2J(CP) = 3.40 Hz (CH_3)$_2$CHP), 17.3 (d, ^1J(CP) = 43.4 Hz, CH_2P), 19.7 (d, ^1J(CP) = 39.80 Hz, $(CH_3)_2CH$P), 32.1 (s, C^-), 57.7 (s, CH_3CH_2O), 129.3 (s, CN), 171.5 (s, C(:O)); for ^{31}P-NMR and IR data see Table I.

Triisopropyl-(2-cyano-2-ethoxycarbonyl)ethylphosphonium triflate **3**

To a solution of **2b** (1.42 g, 5 mmol) in 10 ml of wet acetone trimethylsilyltriflate (1.1 g, 5 mmol) was added with stirring at 0°C during 1 min. After 24 h the solvent was removed i.v., and the product was isolated by crystallization from a mixture of CH_2Cl_2, diethyl ether and THF (1:1:1, 10 ml). ^{1}H NMR ($CDCl_3$): 1.31 (t, 3H, ^3J(HH) = 7.16 Hz, CH_3CH_2O), 1.37–1.50 (m, 18H, $(CH_3)_2$CHP), 2.70–3.20 (m, 5H, CH_2P, $((CH_3)_2CH)_3$P), 3.67–3.75 (m, 1H, PCH_2CH), 4.33 (q, 2H, ^3J(HH) = 7.16 Hz, CH_3CH_2O); ^{13}C NMR: 13.68 (s, CH_3CH_2O), 15.9 (d, ^1J(CP) = 45.5 Hz, CH_2P), 16.89 (d, ^2J(CP) = 3.2 Hz, (CH_3)$_2$CHP), 20.7 (d, ^1J(CP) = 40.5 Hz, $(CH_3)_2CH$P), 30.35 (d, ^2J(CP) = 4.4 Hz, $CHCH_2$P), 64.5 (s, CH_2O), 115.9 (d, ^3J(CP) = 3.14 Hz, CN), 164.0 (d, ^3J(CP) = 10.4 Hz, C(:O)); for ^{31}P-NMR and IR data see Table I.

TABLE XII

Yields, melting points and elemental analysis data for compounds **2a**, **2b**, **3**, **4**, **8**, **9a**, **9b**, **12a** and **12b**

Compound No.	Yield %	m. p. °C	Molecular formula Molecular weight	Elemental analysis, %	
				calcd.	found
2a	48	133-134	$C_{14}H_{26}NO_2P$ 271.34	C: 61.97 H: 9.66 N: 5.16	C: 62.07 H: 9.60 N:5.17
2b	55	146-147	$C_{15}H_{28}NO_2P$ 285.37	C: 63.13 H: 9.89 N: 4.91	C: 63.81 H: 10.11 N: 4.89
3	38	130-131	$C_{16}H_{29}F_3NO_5PS$ 435.44	C: 44.13 H: 6.71 N: 3.22 F: 13.09	C: 44.05 H: 6.76 N: 3.13 F: 13.60
4	70	139-140	$C_{16}H_{31}INO_2P$ 427.31	C: 44.97 H: 7.31 N: 3.28	C: 44.74 H: 7.34 N: 2.92
8	80	187-188	$C_{17}H_{28}NO_3PS$ 357.45	C: 57.12 H: 7.90 N: 3.92	C: 56.82 H: 7.78 N: 3.87
9a	37	139-140	$C_{21}H_{35}N_2O_4PS$ 442.55	C: 56.99 H: 7.97 N: 6.33	C: 56.98 H: 8.08 N: 6.16
9b	43	141	$C_{22}H_{37}N_2O_4PS$ 456.58	C: 57.87 H: 8.17 N: 6.14	C: 57.49 H: 8.05 N: 6.31
12a	51	163-164	$C_{16}H_{29}N_2O_3P$ 328.39	C: 58.52 H: 8.90 N: 8.53	C: 58.33 H: 8.84 N: 8.52
12b	47	167-168	$C_{17}H_{31}N_2O_3P$ 342.42	C: 59.63 H: 9.13 N: 8.18	C: 58.99 H: 9.08 N: 8.07

P,P,P-Triisopropyl-P-(2-methyl-2-cyano-2-ethoxycarbonyl)ethylphosphonium iodide **4**

A mixture of a solution of **2b** (2.8 g, 10 mmol) and MeI (4.26 g, 30 mmol) in 10 ml of acetone was stirred for 48 h at room temperature. The solvent was then removed i.v. and the product was obtained as colorless crystals by recrystallization from acetone. For ^{31}P-NMR and IR data see Table I, for ^{1}H- and ^{13}C-NMR data see Table II.

The Zwitterionic Product **8** *and the Molecular Complexes* **9a** *and* **9b**

Route A.[3] To a solution of triisopropylphosphine (1.6 g, 10 mmol) in diethyl ether (10 ml) a solution of tosyl isocyanate (1.97 g, 10 mmol) in diethyl ether (10 ml) was added dropwise during 1 min at 0°C. The colorless precipitate of **8** was filtered off and purified by recrystallization from acetone.

Route B (Equation (7) and (8)). A solution of tosyl isocyanate (0.48 g, 2 mmol) in 10 ml of acetonitrile was added dropwise to a solution of **2b** (0.6 g, 2 mmol) in 15 ml of acetonitrile at room temperature.

After 24 h the solvent was removed i.v., and the colorless crystalline residue was purified by recrystallization from hot acetone (2 ml). The product was separated as colorless crystals, and the solvent from the filtrate was removed i.v. The residue was dissolved in $CDCl_3$ and studied by ^1H NMR spectroscopy. A multiplet in the region of 2.5–3.0 ppm (methylene groups of the polymeric chain), a triplet at 1.2 ppm (CH_3), and a quartet at 4.2 ppm (OCH_2) were observed.

Route C (Equation (9)). To a solution of **2a** (**2b**) (5 mmol) in 5 ml of acetone containing traces of water a solution of tosyl isocyanate (0.98 g, 5 mmol) in 5 ml of diethyl ether was added dropwise at 0°C during 2 minutes with stirring. The white precipitate of **8** formed in the course of the reaction, was filtered off and was purified by recrystallization from acetone. The solvent was removed from the filtrate i.v. and the crystalline residue was purified by recrystallization from a mixture of chloroform and diethyl ether, resulting in the crystalline product **9a** (**9b**).

8: ^1H NMR ($CDCl_3$): 1.28–1.40 (m, 18H, $(CH_3)_2CHP$), 2.34 (s, 3H, $C_6H_4CH_3$), 2.52–2.85 (m, 3H, $(CH_3)_2CHP$), 7.16–7.90 (m, 4H, C_6H_4); ^{13}C NMR ($CDCl_3$): 16.9 (d, $^2J(CP)$ = 3.0 Hz, $(CH_3)_2CHP$), 21.28 (d, $^1J(CP)$ = 34.86 Hz, $(CH_3)_2CHP$), 21.41 (s, $C_6H_4CH_3$), 126.29–141.66 (m, C_6H_4), 160.0 (d, $^1J(CP)$ = 95.2 Hz, C(:O)).

9a: ^1H NMR ($CDCl_3$): 1.23–1.48 (m, 18H, $(CH_3)_2CHP$), 2.37 (s, 3H, $C_6H_4CH_3$), 2.34–2.61 (m, 3H, $(CH_3)_2CH$), 3.17 (d, 2H, $^2J(HP)$ = 6.44 Hz, CH_2P), 3.51 (s, 3H, CH_3O), 5.54 (broad s, 2H, NH_2), 7.15–7.75 (m, 4H, C_6H_4); ^{13}C NMR ($CDCl_3$): 16.12 (d, $^2J(CP)$ = 3.44 Hz $(CH_3)_2CHP$), 17.6 (d, $^1J(CP)$ = 43.9 Hz, CH_2P), 20.12 (d, $^1J(CP)$ = 40.64 Hz, $(CH_3)_2CH$), 20.05 (s, $C_6H_4CH_3$) 31.67 (s, C^-), 51.2 (s, CH_3O), 126.29–141.66 (m, C_6H_4), 129.6 (s, CN), 172.1 (s, C(:O)).

9b: ^1H NMR ($CDCl_3$): 1.14 (t, 3H, $^3J(HH)$ = 7.1 Hz, CH_3CH_2O), 1.23–1.54 (m, 18H, $(CH_3)_2CHP$), 2.36 (s, 3H, $C_6H_4CH_3$), 2.45–2.77 (m, 3H, $(CH_3)_2CH$), 3.17 (d, 2H, $^2J(HP)$ = 6.2 Hz, CH_2P), 4.0 (q, 2H, $^3J(HH)$ = 7.1 Hz, CH_3CH_2O), 5.63 (broad s, 2H, NH_2), 7.20–7.77 (m, 4H, C_6H_4).

The Zwitterionic Species **12a**, **12b**

To a solution of **2a** (**2b**) (10 mmol) in 15 ml of acetonitrile a solution of MeNCO (30 mmol) in 5 ml of acetonitrile was added. The mixture was stirred for one week at room temperature. To the reaction mixture a mixture of diethyl ether (20 ml) and hexane (5 ml) was added, and the resulting solution was cooled to −20°C. The product was formed as colorless crystals, which were collected by filtration and purified by recrystallization from a mixture of dichloromethane and diethyl ether (1:1, 10 ml).

12a: ^1H NMR ($CDCl_3$): 1.20–1.31 (m, 18H, $(CH_3)_2CHP$), 2.46–2.69 (m, 3H, $(CH_3)_2CHP$), 3.01 (s, 3H, CH_3N), 3.1 (d, 2H, $^2J(HP)$ = 8.10 Hz, CH_2P), 3.43 (s, 3H, CH_3O); ^{13}C NMR ($CDCl_3$): 16.57 (d, $^2J(CP)$ = 3.32 Hz $(CH_3)_2CHP$), 17.10 (d, $^1J(CP)$ = 44.5 Hz, CH_2P), 20.25 (d, $^1J(CP)$ = 39.90 Hz, $(CH_3)_2CHP$), 33.86 (s, C^-), 46.12 (s, CH_3N), 50.8 (s, CH_3O), 127.0 (s, CN), 152.9, 169.5 (s, C(:O)).

12b: ^1H NMR ($CDCl_3$): 1.21 (t, 3H, $^3J(HH)$ = 7.1 Hz, CH_3CH_2O), 1.40–1.51 (m, 18H, $(CH_3)_2CHP$), 2.65–2.75 (m, 3H, $(CH_3)_2CHP$), 3.03 (s, 3H, CH_3N), 3.17 (d, 2H, $^2J(HP)$ = 8.20 Hz, CH_2P), 4.12 (q, 2H, $^3J(HH)$ = 7.1 Hz, CH_3CH_2O); ^{13}C NMR ($CDCl_3$): 14.65 (s, CH_3CH_2O), 16.71 (d, $^2J(CP)$ = 3.40 Hz, $(CH_3)_2CHP$), 17.10 (d, $^1J(CP)$ = 44.0 Hz, CH_2P), 18.9 (d, $^1J(CP)$ = 39.80 Hz, $(CH_3)_2CHP$), 34.4 (s, C^-), 48.2 (s, CH_3N), 57.7 (s, CH_3CH_2O), 126.7 (s, CN), 154.7, 169.7 (s, C(:O)).

X-Ray Structure Determinations

Summary of crystal data: see Table III

Data collection and reduction: Crystals were mounted on glass fibres in inert oil and transferred to the cold gas stream of the diffractometer (Siemens P4 with LT-2 low temperature attachment). The orientation matrix was refined from setting angles of ca. 50 reflections in the 2θ range 6–25° (monochromated Mo K_α radiation).

Structure solution and refinement: The structures were solved by direct methods and refined anisotropically on F^2 (program system: SHELXL-93, G.M. Sheldrick, University of Göttingen). H atoms were included using a riding model or rigid methyl groups. The weighting schemes were of the form $w^1 = [\sigma^2(F_o^2) + (aP)^2 + bP]$, with $P = (F_o^2 + 2F_o^2)/3$. Full details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, from where this material may be obtained on quoting the full literature citation and the reference number CSD 404773–404776 for compounds **2b**, **8**, **9a**, and **12b**.

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