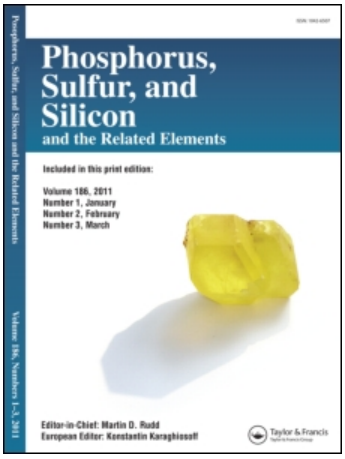


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

α-SUBSTITUTED PHOSPHONATES 68.[1] α-AMINOPHOSPHONATES AND PHOSPHONO-SUBSTITUTED HETEROCYCLES FROM DIETHYL [2,2,2-TRICHLORO-1-ISOCYANATO-ETHYL]PHOSPHONATE

Angela Köckritz[a]; Michael Schnell[a]
[a] Zentrum für Selektive Organische Synthese, Berlin

To cite this Article Köckritz, Angela and Schnell, Michael(1993) 'α-SUBSTITUTED PHOSPHONATES 68.[1] α-AMINOPHOSPHONATES AND PHOSPHONO-SUBSTITUTED HETEROCYCLES FROM DIETHYL [2,2,2-TRICHLORO-1-ISOCYANATO-ETHYL]PHOSPHONATE', Phosphorus, Sulfur, and Silicon and the Related Elements, 83: 1, 125 — 133
To link to this Article: DOI: 10.1080/10426509308034355
URL: http://dx.doi.org/10.1080/10426509308034355

Phosphorus, Sulfur, and Silicon, 1993, Vol. 83, pp. 125–133
Reprints available directly from the publisher
Photocopying permitted by license only

α-SUBSTITUTED PHOSPHONATES 68.[1] α-AMINOPHOSPHONATES AND PHOSPHONO-SUBSTITUTED HETEROCYCLES FROM DIETHYL [2,2,2-TRICHLORO-1-ISOCYANATO-ETHYL]PHOSPHONATE

ANGELA KÖCKRITZ and MICHAEL SCHNELL†
Zentrum für Selektive Organische Synthese, Rudower Chaussee 5, 12489 Berlin, Bundesrepublik Deutschland

(Received July 14, 1993)

Dedicated to Professor Hans Groß on the occasion of his 65th birthday

The easily accessible [2,2,2-trichloro-1-isocyanato-ethyl]phosphonate **1** reacts with aliphatic or aromatic amines to give the ureas **2,8**. The reaction of these ureas with morpholine has been studied. Quite different reaction products have been isolated or observed depending on reaction time and the amine used for the urea formation. Oxazoles **4,10** are obtained if the ureas **2,8** were prepared from **1** and aliphatic amines or secondary amines. Surprisingly, ureas derived from **1** and aromatic primary amines furnish mixtures of oxazoles **4**, guanidines **5**, and imidazoles **6** via ring opening—closure sequences which have not been known so far. However, the urea **2i** prepared from o-hydroxyaniline gives heterocyclic substituted α-aminophosphonate **7**. Under acidic conditions the oxazoles **4,10** are hydrolysed to α-aminophosphonates **11**.

Key words: Phosphonates; oxazoles; imidazoles; cyclization; NMR data.

INTRODUCTION

1-Aminosubstituted 2,2,2-trichloroethanephosphonates are easily accessible precursors for the synthesis of phosphono-substituted heterocycles as shown in previous communications.[2–6] Starting from diethyl [2,2,2-trichloro-1-isocyanato-ethyl]phosphonate **1**, Drach *et al.*[7] prepared some 2,2,2-trichloro-1-ureido-phosphonates, but they didn't report on reactions with amines or other nucleophiles. We expected that a reaction of these ureas with amines would provide a further route to phosphono-substituted oxazoles, analogously to other phosphonates.[2,3] So we prepared a variety of ureas **2,8** from **1** and aliphatic or aromatic amines to investigate the influence of the ureamoiety on cyclization reaction. We treated these ureas only with morpholine as nucleophile to simplify matters and to get a survey of this reaction.

RESULTS

Isocyanate **1** was obtained first by H. Ulrich *et al.*[8] by reaction of triethylphosphite with 1,2,2,2-tetrachloroethaneisocyanate which was prepared from trichloroacetaldehyde, urethane and phosphorus pentachloride.[10,11] Shokol *et al.*[9] reported on

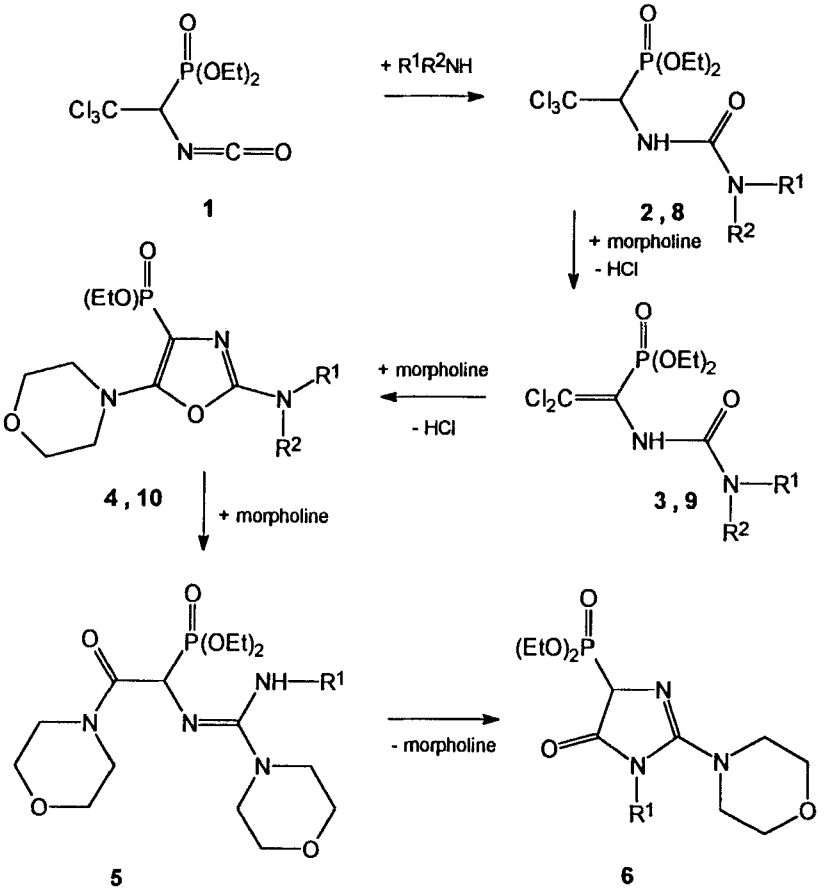
an improved synthesis of **1** in a similar procedure. Reproducing this work we can confirm the formation of **1**, but the yield of the distillable product was only average. We obtained **1** in 64% yield after distillation by reducing the reaction temperature to 20°C and using a slight excess of triethylphosphite (Scheme 1).

Addition of a variety of aliphatic and aromatic amines to the isocyanate **1** furnishes the desired ureas **2,8** (Scheme 2). In the case of aromatic amines a slight excess of amine does not cause any disadvantage, but with aliphatic amines the equivalent amounts of reactants have to be kept strictly, otherwise by-products occur on a remarkable scale. We isolated and characterised these ureas in some cases, however the reactions with morpholine were performed in a one-pot-synthesis without purifying them. After a period of two hours, morpholine was added to the reaction solutions and we monitored the formation of products with TLC or ^{31}P-NMR spectroscopy (Table 6). The first reaction observed in all examples is HCl elimination generating the vinyl compounds **3** and **9**. The elimination is completed within about one hour. As an example we isolated and characterised the vinyl compounds **3b,e** in full analytical details. In a second, slow reaction the desired oxazoles **4** and **10** are formed in 2 to 20 hours, except the oxazole **4d** which could not be observed. In the case of secondary and aliphatic primary amines, the oxazoles are final products (Scheme 2).

If primary aromatic amines were used, unexpected further conversions occurred. Depending on amine, reaction time, and concentration of products we observed signals in the range of 18.7–19.4 ppm in ^{31}P-NMR spectroscopy after 20 hours. In the cases of 2,4,6-trimethyl-aniline (urea **2d**) and p-NO_2-aniline (urea **2e**), these compounds were final products which could be isolated and identified as guanidine derivatives **5d,e**. With aniline (urea **2a**), p-toluidine (urea **2b**) and p-tert.butyl-aniline (urea **2c**) however the signals in the NMR spectrum at approx. 19 ppm disappeared after 2–3 days and new signals in the range of 14.4–14.8 ppm indicated the end of transformations. In two examples we separated the final products by column chromatography which proved to be imidazole derivatives **6b,c**. Table I presents the NMR spectra recorded during the reaction of urea **2b** with morpholine which shows the typical course of these conversions.

The structures of the imidazoles **6** were confirmed mainly by ^{1}H- and ^{13}C-NMR spectroscopy. Table II presents selected NMR data of the oxazole **4b** and imidazole **6b**. In the ^{13}C-NMR spectrum, the sp^3-hybridized C4 of **6b** shows a typical upfield shift with a smaller coupling constant and in the ^{1}H-NMR spectrum the proton on C4 of **6b** is detected at δ = 4.60 ppm; $^{2}J_{PCH}$ = 28.3 Hz in accordance to other aminophosphonates. A characteristic downfield shift in the ^{13}C-NMR of **6b** of the carbon in the ortho position of the aromatic moiety indicates that the nitrogen of the toluidine group is bound with two carbon atoms.

SCHEME 1 **1**



2,3,4,5,6	R^1	R^2
a	C_6H_5	H
b	4-Me-C_6H_4	H
c	4-tert.Bu-C_6H_4	H

2,3,4,5	R^1	R^2
d	2,4,6-Me-C_6H_2	H
e	4-NO_2-C_6H_4	H

2,3,4	R^1	R^2
f	Me	H
g	Et	H
h	nPr	H

8,9,10	R^1	R^2
a	Me	Me
b	$(CH_2)_2O(CH_2)_2$	
c	Me	C_2H_5
d	Et	C_2H_5

SCHEME 2

TABLE I

^{31}P-NMR spectra of the reaction of 0.21 g (0.5 mmol) of urea **2b** and 0.26 g (3 mmol) of morpholine in 3 ml of $CHCl_3$

time (min)	**3b** (%) δ_P=9.7-9.9	**4b** (%) δ_P=13.9[b)]	**5b** (%) δ_P=19.0-19.7	**6b** (%) δ_P14.8-15.0
50	82	16	2	0
100	66	21	13	0
300	43	16	41	0
1400	8	0	70	22
4300[a)]	0	0	7	70

a) Additional small signals at 17.9, 7.5, and -1.05 ppm; b)downfild shift due to basic medium. Because of the low concentration used in this experiment the times of transformations are extremely prolonged.

TABLE II

^{13}C-NMR data of oxazole **2b** and imidazole **6b**

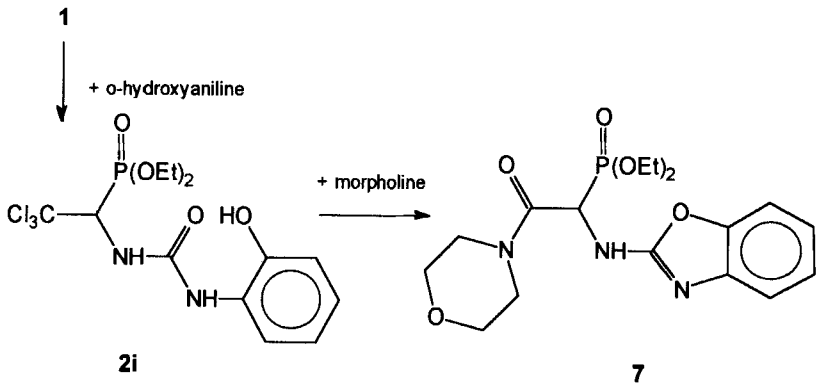
	C2[a)] δ ($^3J_{PC}$)	C4[a)] δ ($^1J_{PC}$)	C5[a)] δ ($^2J_{PC}$)	C1'[b)] δ	C2'[b)] δ	Me δ
2b	150.0(25.2)	103.9(251.4)	156.9(35.6)	136.4	117.0	20.6
6b	160.7(11.3)	65.9(151.0)	175.5(s)	138.5	125.9	21.3

a) Heterocyclic carbon atoms; b) aromatic carbon atoms.

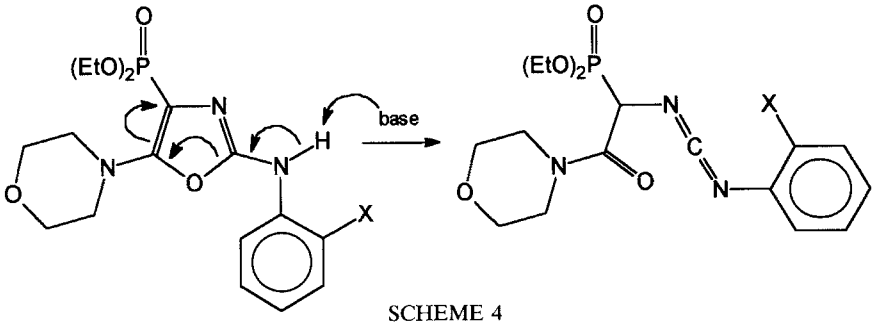
In contrast to the conversions described above the benzoxazole derivative **7** is formed if o-hydroxyaniline reacts with **1** and, subsequently, with morpholine (Scheme 3). **7** was obtained in 82% yield without formation of oxazole, guanidine or imidazole products. Obviously the OH-moiety is responsible for the dissimilar course of reaction.

A mechanism explaining all reactions mentioned above is given in Scheme 4. We assume that in all examples morpholine reacts with the urea **2** to give the oxazoles **4** via **3** (Scheme 2). A proton on the amino group in position C2 of the oxazoles **2a-e** and **2i** is responsible for the different products formed. It seems that the electron-withdrawing properties of aromatic amines are sufficient to remove this proton under basic reaction conditions. A concerted electron migration furnishes carbodiimide intermediates which react with excess morpholine to give guanidine derivatives **5**. If the aromatic ring possesses an OH-group in ortho position (X = OH), the intramolecular addition of this group predominates to yield benzoxazole **7**. In the ureas **2f–h**, the acidity of the NH-group is smaller and therefore ring-opening does not occur. There is no proton on a nitrogen in the oxazoles **10a–d** and, consequently, the products are stable under the reaction conditions. The guanidines **5a–c** undergo a cyclization reaction to form the imidazoles **6a–c**, whereas the guanidine **5d** does not react for sterical reasons and neither does the guanidine **5e** because of its low nucleophilicity.

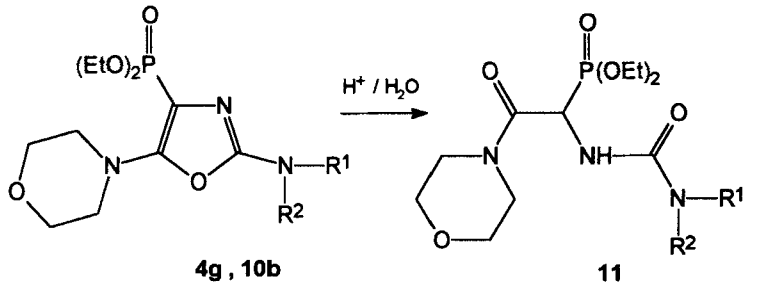
The oxazoles **4,10** are easily split under acidic conditions. Compared to 2-un-



SCHEME 3



SCHEME 4



11	R^1	R^2
a	Et	H
b	$(CH_2)O(CH_2)_2$	

SCHEME 5

substituted phosphonooxazoles described in a previous communication,[12] the new oxazoles **4,10** are more sensitive to acids. Actually, we have not been able to purify the oxazoles **4f** and **4g** by silica gel column chromatography (acetone/hexane) because they hydrolysed even under these mild conditions. On treatment with 2 n aqueous HCl the oxazoles **4g** and **10b** were smoothly cleaved into the ureas **11a,b** (Scheme 5).

EXPERIMENTAL

^{1}H-NMR spectra were recorded with a TESLA BS 587 A using $CDCl_3$ as solvent and HMDS as internal standard. ^{13}C-NMR (ref. internal TMS) and ^{31}P-NMR (ref. external 85% H_3PO_4) spectra were obtained on a Varian Gemini 300. The chemical shift are reported in ppm, with negative values being upfield of the standard, and positive downfield. The coupling constants are reported in Hz.

Column chromatography separations (pressure 4.7 kPa) were performed by using Merck silica gel 60 (0.040–0.063 mm). TLC analyses were done on Silufol^R (silica gel) precoated alumina plates and the spots were visualised with 1% ethanolic solution of molybdatophosphoric acid and 1% solution of ninhydrin and warming the plates.

Diethyl[2,2,2-trichloro-1-isocyanato-ethyl]phosphonates **1**. To a stirred solution of 20.88 g (10 mmol) tetrachloroisocyanate[10,11] in 30 ml CH_2Cl_2 16.81 g (10.5 mmol) triethylphosphite was added dropwise at r.t. After addition (approx. 1 hr) stirring was continued for 2 hr. Then the solution was evaporated and the residue purified by Kugelrohr distillation at 100–105°C at 30 Pa.

Yield: 18.1 g (64%); n_D^{25} = 1.4832. Lit.[9] n_D^{20} = 1.4817.

Diethyl[2,2,2-trichloro-1-(3-alkyl(aryl)-ureido)-ethyl]phosphonates **2a–i**; General Procedure: To a stirred solution of 1.55 g (5 mmol) phosphonoisocyanate **1** in 10 ml CH_2Cl_2 5 mmol of a primary amine was added at r.t. After standing for 2 hr the solution was evaporated at reduced pressure and the residue recrystallized from EtOH (**2a–e**) (Table III).

Diethyl[2-arylamino-5-morpholin-4-yl-oxazol-4-yl]phosphonate **4a–h** and Diethyl([2-dialkyl(alkylaryl)amino-5-morpholin-4-yl-oxazol-4-yl])phosphonate **10a–d**; General Procedure: 1.55 g (5 mmol) isocyanate **1** and 5 mmol of an amine were reacted as reported for **2** however in the case of **4a** and **4d** the solvent was dioxan. After 2 hr 2.61 g morpholine (30 mmol) was added to the stirred solution and stirring was continued; **4a–e** = 2 hr; **4f–h**, **10a–d** = 20 hr. The reaction mixture was dissolved in 30 ml CH_2Cl_2, washed with 10 ml H_2O, and the organic layer dried over Na_2SO_4. The solvent was evaporated at reduced pressure and the oily residue chromatographed on silica gel column (60 × 3 cm, acetone/hexane, 1:1) (Table IV–V).

Diethyl[2,2-dichloro-1-(3-p-tolyl-ureido)-vinyl]phosphonate **3b**. Obtained as by-product from the chromatographic separation of **4b**.

TABLE III

Diethyl[2,2,2-trichloro-1-(3-alkyl(aryl)-ureido)-ethyl]phosphonates **2a–i**

Product	Yield [%]	m.p. [°C]	^{31}P δ_P	^{13}C δ_{PC} ($^2J_{PC}$)	^{1}H δ_{CH} ($^2J_{PC}$)	Molecular Formula	Analysis calc. / found C	H [%]	N
2a[a]	76	162-64	15.3	61.5 (159.8)	5.01 (18.7)	$C_{13}H_{18}Cl_3N_2O_4P$ (403.6)	38.68 38.63	4.49 4.57	6.94 7.02
2b	71	152-55	15.3	61.7 (164.4)	5.30 (19.4)	$C_{14}H_{20}Cl_3N_2O_4P$ (417.7)	40.26 40.40	4.83 4.85	6.71 6.69
2c	32	162-64	15.5	61.7 (164.9)	5.27 (19.4)	$C_{17}H_{26}Cl_3N_2O_4P$ (459.8)	44.41 44.25	5.70 5.81	6.09 5.89
2d	42	124-27	14.9	61.9 (160.6)	5.20 -[b]	$C_{16}H_{24}Cl_3N_2O_4P$ (445.7)	43.11 43.35	5.43 5.77	6.29 5.98
2e	79	223-25	14.3	61.5 (159.6)	5.21 (19.1)	$C_{13}H_{17}Cl_3N_3O_6P$ (448.6)	34.80 34.72	3.82 3.82	9.37 9.28
2f[c]	-	-	15.9	-	-	-	-	-	-
2g[c]	-	-	15.7	-	-	-	-	-	-
2h[c]	-	-	15.7	-	-	-	-	-	-
2i[c]	-	-	15.4	-	-	-	-	-	-

[a] Lit.[7] m.p. 166-67 °C, [b] broad signal; [c] not isolated

TABLE IV

Diethyl[2-alkyl(aryl)amino-5-morpholin-4-yl-oxazol-4-yl]phosphonates **4**

Product[a]	Yield [%]	m.p. (n_D^{25})	^{31}P δ_P	^{13}C δ_{PC} ($^2J_{PC}$)	Molecular Formula	Analysis calc. / found C	H [%]	N
4a	24	-[c]	11.6	103.9 (250.8)	$C_{17}H_{24}N_3O_5P$ (381.4)	53.54 53.29	6.34 6.65	11.02 11.13
4b	42	141-44	11.7	103.9 (251.4)	$C_{18}H_{26}N_3O_5P$ (395.4)	54.68 54.60	6.63 6.68	10.63 10.46
4c	41	141-43	11.6	103.9 (251.4)	$C_{21}H_{32}N_3O_5P$ (437.5)	57.65 57.80	7.37 7.52	9.61 9.48
4e	39	195-98	11.1	103.4 (253.1)	$C_{17}H_{23}N_4O_7P$ (426.4)	47.89 47.80	5.44 5.43	13.14 13.11
4f[b]	-	-	12.5	105.5 (205.9)	-	-	-	-
4g[b]	-	-	12.3	105.2 (250.9)	-	-	-	-
4h	62	(1.5023)	12.4	105.1 (250.9)	$C_{14}H_{26}N_3O_5P$ (347.4)	48.41 48.15	7.54 7.68	12.10 11.97

[a] **4d** was not observed; [b] purification impossible due to hydrolysis during chromatographic separation; [c] pasty

TABLE V

Diethyl[2-dialkyl(alkylaryl)amino-5-morpholine-4-yl-oxazole-4-yl]-phosphonates **10**

Product	Yield [%]	n_D^{25}	^{31}P δ_P	^{13}C δ_{PC} ($^2J_{PC}$)	Molecular Formula	Analysis calc. / found C	H [%]	N
10a	24	1,5018	12,3	106,5 (250,3)	$C_{13}H_{24}N_3O_5P$ (333,3)	46,84 46,59	7,26 7,29	12,61 12,10
10b	79	1,5168	11,7	105,7 (251,1)	$C_{15}H_{26}N_3O_6P$ (375,4)	48,00 47,89	6,98 7,14	11,20 11,12
10c	81	1,5452	12,1	104,4 (252,0)	$C_{18}H_{26}N_3O_5P$ (395,4)	54,68 54,70	6,63 6,34	10,63 10,34
10d	73	1,5415	12,3	104,1 (251,2)	$C_{19}H_{28}N_3O_5P$ (409,4)	55,74 55,42	6,89 7,02	10,26 10,21

Yield 21; m.p. 143–46°C.

NMR: ^{31}P: δ 9.2; ^{13}C: δ_{PC} 124.7 (d), $^2J_{PC}$ 209.2 Hz.

$C_{14}H_{19}Cl_2N_2O_4P$ (381.2) calc. C 44.11 H 5.02 N 7.35%
found. C 44.14 H 5.10 N 7.38%

Diethyl[2,2-dichloro-1-(3-p-nitro-phenyl-ureido)-vinyl]phosphonate **3e**. Obtained as by-product from the chromatographic separation of **4e**.

Yield 25%; m.p. 203–5°C.

NMR: ^{31}P: δ 8.1; ^{13}C: δ_{PC} 126.7 (d), $^2J_{PC}$ 208.2 Hz.

$C_{13}H_{16}Cl_2N_3O_6P$ (412.2) calc. C 37.88 H 3.91 N 10.20%
found. C 37.67 H 3.90 N 10.11%

Diethyl[2-morpholin-4-yl-1-{morpholin-4-yl-(2,4,6-trimethyl-phenyl)-guanidino}-2-oxoethyl]phosphonate **5d**. 1.55 g (5 mmol) isocyanate **1**, 0.66 g (5 mmol) 2,4,6-trimethylaniline and 2.61 g morpholine were converted and worked-up as described for **4d** but the reaction time was 24 hr.

Yield 52%: n_D^{25} = 1.5363.

NMR: ^{31}P: δ 19.0; ^{13}C: broad signal at 51 ppm; ^1H: δ 5.15 (d), $^3J_{PCH}$ 18.4 Hz.

$C_{24}H_{39}N_4O_6P$ (510.6)	calc.	C 56.46	H 7.70	N 10.97%
	found.	C 56.12	H 7.57	N 10.52%

Diethyl[2-morpholin-4-yl-1-{morpholin-4-yl-(4-nitro-phenyl)-guanidino}-2-oxo-ethyl]phosphonate **5e**.

1.55 g (5 mmol) isocyanate **1**, 0.69 g (5 mmol) p-NO_2-aniline and 2.61 g morpholine were reacted and worked-up as described for **4e** but the reaction time was 24 hr.

Yield 31%; m.p. 52–54°C.

NMR: ^{31}P: δ 18.7; ^{13}C: δ_{PC} 48.9 (d), $^2J_{PC}$ 145.2 Hz; ^1H: δ 4.66 (d), $^3J_{PCH}$ 28.2 Hz.

$C_{21}H_{32}N_5O_8P$ (513.5)	calc.	C 49.12	H 6.28	N 13.64%
	found.	C 48.87	H 6.04	N 13.88%

Diethyl(2-morpholin-4-yl-5-oxo-1-p-tolyl-4,5-dihydro-1H-imidazol-4-yl)phosphonate **6b**. 1.55 g (5 mmol) isocyanate **1**, 0.54 g (5 mmol) toluidine and 2.61 g morpholine were converted and worked-up as described for **4b** but the reaction time was 3 days.

Yield 51%; m.p. 73–80°C.

NMR: ^{31}P: δ 14.7; ^{13}C: δ_{PC} 65.9 (d), $^2J_{PC}$ 151.0 Hz, ^1H: δ 4.60 (d), $^3J_{PCH}$ 28.3 Hz.

$C_{18}H_{26}N_3O_5P$ (395.4)	calc.	C 54.68	H 6.63	N 10.63%
	found.	C 54.88	H 6.73	N 10.34%

Diethyl[1-(4-tert-butyl-phenyl])-2-morpholin-4-yl-5-oxo-4,5-dihydro-1H-imidazol-4-yl])phosphonate **6c**. 1.55 g (5 mmol) isocyanate **1**, 0.75 g (5 mmol) p-tert.butylaniline and 2.61 g morpholine were reacted and worked-up as described for **4c** but the reaction time was 3 days.

Yield 39%; pasty.

^{31}P: δ 14.8; ^{13}C: δ_{PC} 65.9 (d), $^2J_{PC}$ 151.2 Hz, ^1H: δ 4.61 (d), $^3J_{PCH}$ 28.2 Hz.

$C_{21}H_{32}N_3O_5P$ (437.5)	calc.	C 57.65	H 7.37	N 9.61%
	found.	C 57.41	H 7.43	N 9.36%

Diethyl[1-(benzoxazol-2-yl-amino)-2-morpholin-4-yl-2-oxo-ethyl]phosphonate **7**. 1.55 g (5 mmol) isocyanate **1** and 0.55 g (5 mmol) o-aminophenol were converted as mentioned for **2**. Addition of 2.61 g morpholine (30 mmol) and worked-up as reported for **10**.

Yield 82%; m.p. 110–12°C.

NMR: ^{31}P: δ 16.1; ^{13}C: δ_{PC} 51.7 (d), $^2J_{PC}$ 149.1 Hz; ^1H: δ 5.33 (d), $^3J_{PCH}$ 16.94 Hz.

$C_{17}H_{24}N_3O_6P$ (397.4)	calc.	C 51.38	H 6.09	N 10.58%
	found.	C 51.18	H 6.17	N 10.50%

Diethyl[1-(3-alkyl-ureido)-2-morpholin-4-yl-2-oxo-ethyl]phosphonate **11**; General Procedure: 1 mmol oxazole **4g** or **10d**, respectively were dissolved in 10 ml HCl (10%) and stirred for 2 hr. Then the mixture was neutralised with K_2CO_3 and extracted with CH_2Cl_2 (2 × 20 ml). After drying of the combined organic layers (Na_2SO_4) the solvent was evaporated and the crude oily residue chromatographed on silica gel (acetone/hexane 1:1).

Diethyl[1-(3-ethyl-ureido)-2-morpholin-4-yl-2-oxo-ethyl]phosphonate **11a**. Yield 37%; n_D^{25} = 1.4971.

NMR: ^{31}P: δ 18.9; ^{13}C: δ_{PC} 48.3 (d), $^2J_{PC}$ 152.2 Hz; ^1H: δ 5.41 (d), $^3J_{PCH}$ 19.5 Hz.

$C_{13}H_{26}N_3O_6P$ (351.4)	calc.	C 44.44	H 7.46	N 11.96%
	found.	C 44.71	H 7.49	N 12.03%

TABLE VI

^{31}P-NMR data δ_P of compounds **3a–h**, **5a–e**, **8a–d**, and **9a–d**

	a	b	c	d	e	f	g	h
3	9.8	9.2	9.54	8.7	8.1	9.0	8.9	9.6
5	19.4	19.3	18,8	19.0	18.7			
8	14.4	14.7	14.7	14.8				
9	9.5	8.8	8.7	8.8				

Diethyl[1-(3-morpholin-4-yl-ureido)-2-morpholin-4-yl-2-oxo-ethyl]phosphonate **11b**. Yield 61%; m.p. 101–103°C.

NMR: ^{31}P: δ 18.5; ^{13}C: δ_{PC} 48.9 (d), $^2J_{PC}$ 151.0 Hz; ^{1}H: δ 5.24 (d), $^3J_{PCH}$ 19.7 Hz.

$C_{15}H_{28}N_3O_7P$ (393.4) calc. C 45.80 H 7.17 N 10.68%
found. C 45.17 H 7.11 N 10.42%

ACKNOWLEDGEMENT

Financial assistance from Bayer AG is gratefully acknowledged. We would like to thank Prof. H. Groß for supporting this work and Dr. E. Gründemann and Dr. B. Costisella for recording NMR spectra.

REFERENCES

1. 67th communication: H. Groß, B. Costisella, S. Ozegowski, I. Keitel and K. Forner, *Phosphorus, Sulfur, and Silicon*, in print.
2. S. Scheidecker, A. Köckritz and M. Schnell, *J. Prakt. Chem.*, **332,** 968 (1990).
3. G. Röhr, A. Köckritz and M. Schnell, *Phosphorus, Sulfur, and Silicon*, **71,** 157 (1992).
4. B. S. Drach and E. P. Sviridov, *Zh. Obshch. Khim.*, **43,** 1648 (1973).
5. B. S. Drach, E. P. Sviridov and Ya. P. Sharturshi, *Zh. Obshch. Khim.*, **44,** 1712 (1986).
6. B. S. Drach and O. P. Lobanov, *Zh. Obshch. Khim.*, **48,** 1994 (1978).
7. A. N. Martinjuk, B. S. Browarez, O. P. Lobanov and B. S. Drach, *Zh. Obshch. Khim.*, **51,** 2186 (1984).
8. H. Ulrich, B. Tucker and A. A. R. Sayigh, *J. Org. Chem.*, **33,** 2887 (1968).
9. N. K. Michailjushenko, B. N. Koshisko and B. A. Shokol, *Zh. Obshch. Khim.*, **53,** 548 (1983).
10. H. Zinner, U. Rosenthal, H.-P. Kruse, S. Rosenthal and M. Schnell, *J. Prakt. Chem.*, **320,** 625 (1978).
11. B. S. Drach, A. D. Sinica and A. W. Kirsanov, *Zh. Org. Khim.*, **5,** 2181 (1969).
12. G. Röhr, M. Schnell and A. Köckritz, *Synthesis*, **1992**, 1031.