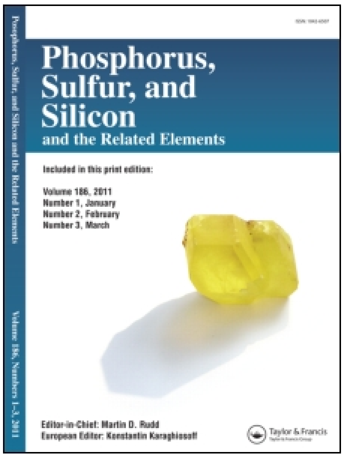


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Urea and Thiourea Derivatives of Bis(dimethyl-phosphinoylmethyl)-amine

Viktoria Lachkova[a]; Sabi Varbanov[b]; Gerhard Hägele[c]; Helmut Keck[c]; Tania Tosheva[b]
[a] Department of Ecology, Forestry University, Sofia, Bulgaria [b] Institute of Polymers, Bulgarian Academy of Sciences, Sofia, Bulgaria [c] Department of Inorganic Chemistry and Structural Chemistry, Heinrich-Heine University, Düsseldorf, Germany

To cite this Article Lachkova, Viktoria , Varbanov, Sabi , Hägele, Gerhard , Keck, Helmut and Tosheva, Tania(2002) 'Urea and Thiourea Derivatives of Bis(dimethyl-phosphinoylmethyl)-amine', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 5, 1303 — 1313

To link to this Article: DOI: 10.1080/10426500211707

URL: http://dx.doi.org/10.1080/10426500211707

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:1303–1313
Copyright © 2002 Taylor & Francis
1042-6507/02 $12.00 + .00
DOI: 10.1080/10426500290092587

UREA AND THIOUREA DERIVATIVES OF BIS(DIMETHYL-PHOSPHINOYLMETHYL)-AMINE

Viktoria Lachkova,[a] *Sabi Varbanov,*[b] *Gerhard Hägele,*[c]
Helmut Keck,[c] *and Tania Tosheva*[b]
Department of Ecology, Forestry University, Sofia, Bulgaria;[a]
Institute of Polymers, Bulgarian Academy of Sciences, Sofia, Bulgaria;[b] *and Department of Inorganic Chemistry and Structural Chemistry, Heinrich-Heine University, Düsseldorf, Germany*[c]

(Received December 13, 2001)

A group of hitherto unknown 1-aryl-3,3-bis(dimethyl-phosphinoylmethyl)-, 1-benzyl-3,3-bis(dimethyl-phosphinoylmethyl)- and 1-cyclohexyl-3,3-bis(dimethyl-phosphinoylmethyl) ureas and thioureas ***1–10*** *have been synthesized, characterized, and are reported in this article. The compounds were prepared via reaction of corresponding isocyanates or isothiocyanates with the secondary phosporus-containing amine: bis(dimethyl-phosphinoylmethyl)-amine. The composition of the novel compounds was proved by elemental analysis, corresponding structures were confirmed by IR, ^1H-, ^{31}P-, $^{31}P\{^1H\}$-NMR spectroscopy and by mass spectrometry.*

Keywords: Bis(dimethyl-phosphinoylmethyl)-amine; isocyanates; isothiocyanates; syntheses; tertiary phosphine oxides; thioureas; ureas

INTRODUCTION

The tertiary phosphine oxides functionalized with primary or secondary amino functions are a relatively small group of organophosphorus compounds.[1–10] Due to the high reactivity of the amino groups, these compounds could be used as phosphorylating agents of polymers,

The authors thank the National Science Foundation of Bulgaria and Deutsche Forschungsgemeinschaft-Germany (SV) for the financial support. They also thank the Fonds der Chemischen Industrie (Germany) for material support to G. H.

This article is dedicated to the memory of Professor Dr. L. M. Venanzi.

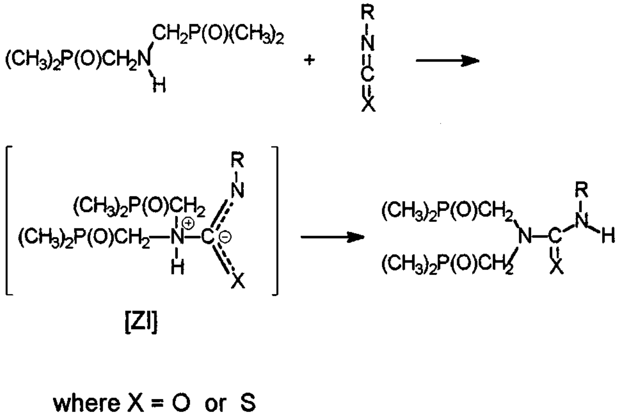
Address correspondence to S. Varbanov, Institute of Polymers, Bulgarian Academy of Sciences, BG 1113 Sofia, Bulgaria. E-mail: varbanov@polymer.bas.bg

for incorporation of tertiary phosphine oxide groups into organic molecules as well for preparation of new organophosphorus compounds.[11] For example L. Maier[12] and S. Varbanov et al.[13–17] have reported the synthesis of tertiary phosphine oxides containing primary amino groups: aminomethyl-dimethylphosphine oxide, bis(aminomethyl)methylphosphine oxide, several aminoalkyl-oxymethyl-dimethylphosphine oxides, and o-, m-, and p-dimethylphosphinoylmethyleneoxy-anilines. It has been shown that some of these compounds can be used to synthesize phosphorus-containing nitrosoureas,[18] bifunctional phosphorus containing monomers,[14] rigid polyurethane foams,[13] epoxide-amine polymers,[19] organometal complexes,[20,21] Schiff bases,[22] triazolo- and pyrazolopyrimidine derivatives.[23] The majority of those compounds exhibit biological activity, for example, the platinum complexes and the nitrosourea derivatives of aminomethyl-dimethyl-phosphine oxide and bis(aminomethyl)methyl-phosphine oxide possess antitumor activity being of low toxicity.[18,21] The phenoxyphenyl-aminoalkylphosphine oxides, reported by L. Maier,[24] triazolo- and pyrazolopyrimidine derivatives of aminomethyl-dimethyl-phosphine oxide[23] proved to be active herbicides.

The present work is a continuation of our previous investigations on the preparation of new nitrogen-containing tertiary phosphine oxides based on tertiary phosphine oxides containing amino groups[16,22,25,26] and reports on the synthesis and characterization of compounds **1–10**: urea and thiourea derivatives of bis(dimethyl-phosphinoylmethyl)-amine, which are expected to exhibit biological activity and complex-formation properties with metal ions.

RESULTS AND DISCUSSIONS

Urea and thiourea derivatives **1–10** (Table I) were synthesized by interaction of corresponding isocyanates or isothiocyanates with bis(dimethyl-phosphinoylmethyl)-amine in chloroform solution at room temperature. The method was chosen because it is known to be a route for the preparation of asymmetric N-substituted ureas and thioureas[27] including phosphorus-containing ureas and thioures[25,26] based on aminomethyl-dimethylphosphine oxide and dimethyl-phosphinoylmethyleneoxy-anilines. The reaction proceeds via a nucleophilic addition of the amine to the isocyanates or isothiocyanates according to the Scheme 1. A. Williams and W. P. Jenks[28] have shown that isocyanates react with amines according to a stepwise mechanism forming an intermediate zwitter ions [ZI].

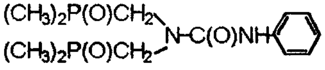
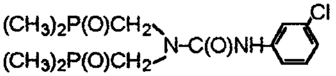
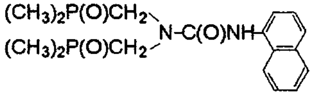
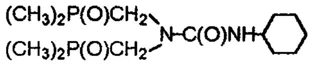
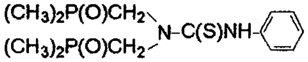
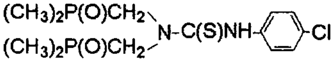
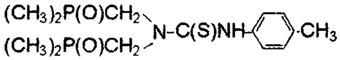
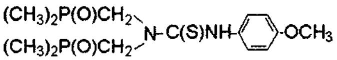
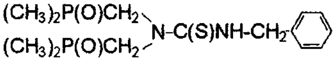
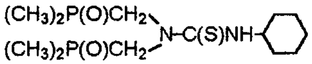


SCHEME 1

The same authors have also established that in the case of strong basic amines this reaction proceeds without any catalyst, while weak basic amines require a catalyst to transform the zwitter ion [ZI] into the corresponding urea derivative. It is known that electron withdrawing substituents attached to the amines decrease the basicity (respectively the nucleophilicity) and the rate of the reaction with isocyanates.[29,30] Because of having two electron withdrawing phosphoryl groups (P=O) in the molecule the pK_a value of bis(dimethyl-phosphinoylmethyl)-amine is as low as 2.52,[16] while the pK_a constants of secondary aliphatic amines are higher than 11.00, such as diethylamine 11.02, di-n-butylamine 11.25.[31] It means that bis(dimethyl-phosphinoylmethyl)-amine is considerably less basic. In spite of this fact the ureas and thioureas **1–10** were prepared in very high yields of about or above 80% (Table II). These results allow to conclude that the bis(dimethyl-phosphinoylmethyl)-amine has enough nucleophilicity to react very easily with high reactive isocyanates and isothiocyanates at 20–30°C without application of any catalyst to form the corresponding ureas and thioureas **1–10**. Furthermore the interactions proceed with slight exothermal effect. This effect is lower in case of isothiocyanates. The latter agrees with the lower reactivity of isothiocyanates. It was noted that the yields of the products **1–10** were insignificantly lower than the yields of the corresponding ureas and thioures of aminomethyl-dimethylphosphine oxide[25] prepared via the same route. This finding is explained with the higher basicity (pK_a 6.23[17]), respectively higher reactivity, of this phosphorus-containing primary amine.

Some preparative and analytical data of the compounds **1–10** are given in Table II. The compounds are colorless crystalline substances.

TABLE I Molecular Structure of Urea and Thiourea Derivatives of Bis(dimethyl-phosphinoylmethyl)-amine

No.	Compound
1	 1-Phenyl-3,3-bis(dimethyl-phosphinoylmethyl)urea
2	 1-(3-Chlorophenyl)-3,3-bis(dimethyl-phosphinoylmethyl)urea
3	 1-(Naphthalen-1-yl)-3,3-bis(dimethyl-phosphinoylmethyl)urea
4	 1-Cyclohexyl-3,3-bis(dimethyl-phosphinoylmethyl)urea
5	 1-Phenyl-3,3-bis(dimethyl-phosphinoylmethyl)thiourea
6	 1-(4-Chlorophenyl)-3,3-bis(dimethyl-phosphinoylmethyl)thiourea
7	 1-(4-Methylphenyl)-3,3-bis(dimethyl-phosphinoylmethyl)thiourea
8	 1-(4-Methoxyphenyl)-3,3-bis(dimethyl-phosphinoylmethyl)thiourea
9	 1-Benzyl-3,3-bis(dimethyl-phosphinoylmethyl)thiourea
10	 1-Cyclohexyl-3,3-bis(dimethyl-phosphinoylmethyl)thiourea

They are easily dissolved in DMSO and DMFA and are less soluble in methanol, ethanol, chloroform, dichloromethane, acetone or water. They are sparingly soluble in diethyl ether, tetrahydrofurane, dioxane while insoluble in aliphatic and aromatic hydrocarbons. The composition of **1–10** was established by elemental analysis for nitrogen

TABLE II Preparative and Analytical Data of Urea and Thiourea Derivatives of Bis(dimethyl-phosphinoylmethyl)-amine

No.	Yield (%)	m.p., °C (solvent for recr.)	General formula mol. mass	Nitrogen (%) Found	Nitrogen (%) Calcd.
1	92	164–165 (ethylacetat-ethanol)	$C_{13}H_{22}N_2O_3P_2$ 316.28	8.63	8.86
2	89	182–183.5 (ethanol)	$C_{13}H_{21}ClN_2O_3P_2$ 350.72	8.10	7.99
3	79	224–226 (ethylacetat-ethanol)	$C_{17}H_{24}N_2O_3P_2$ 366.34	7.48	7.65
4	93	166–167 (ethylacetat)	$C_{13}H_{28}N_2O_3P_2$ 322.32	8.53	8.69
5	82	86–87 (ethanol)	$C_{13}H_{22}N_2O_2P_2S$ 332.34	8.25	8.43
6	78	102–102.5 (ethanol)	$C_{13}H_{21}ClN_2O_2P_2S$ 366.78	7.76	7.64
7	95	99–100 (ethylacetat-ethanol)	$C_{14}H_{24}N_2O_2P_2S$ 346.36	8.21	8.09
8	97	93–94 (chloroform-ethanol)	$C_{14}H_{24}N_2O_3P_2S$ 362.36	7.49	7.73
9	85	134.5–135.5 (chloroform-ethylacetat)	$C_{14}H_{24}N_2O_2P_2S$ 346.36	7.86	8.09
10	97	179–181 (ethylacetat)	$C_{13}H_{28}N_2O_2P_2S$ 338.39	8.35	8.28

(Table II). Their structures were confirmed by IR, ^1H, ^{31}P and $^{31}P\{^1H\}$ NMR spectroscopy, and by mass spectrometry as well.

The infrared spectra of **1–10** (Table III and Table IV) showed characteristic bands assigned to the phosphoryl group (P=O) at 1126–1184 cm^{-1}, methyl group bonded to a phosphorus atom (CH_3—P) at 1296–1311 cm^{-1}, bands for the carbonyl group (C=O) involved in hydrogen bonds at 1644–1657 cm^{-1} (Amide I), and thiocarbonyl groups (C=S) at 936–941 cm^{-1}, 1059–1113 cm^{-1}, and 1292–1298 cm^{-1} (correspond to Amide I), bands for NH amide groups associated via hydrogen bonds at 1516–1572 cm^{-1} (Amide II) and several bands at 3045–3483 cm^{-1}, characteristic bands of C—N bonds at 1404–1448 cm^{-1} (Amide III). There were bands for aromatic rings at 1459–1513 cm^{-1} and 1588–1648 cm^{-1} respectively. The former were more intensive than the latter in all the cases. The bands of the phosphoryl groups (P=O) of **1–10** are shifted with 30–50 cm^{-1} to the lower frequencies as compared to non-substituted tertiary phosphine oxides, which is due to their association with N—H amide and thioamide protons via hydrogen bonds.[32] All the compounds **1–10** have shown two or three bands for the phosphoryl group. This phenomenon could be ascribed to different spatial isomers

TABLE III Characteristic Infrared Frequences (ν cm^{-1}) of Urea Derivatives of Bis(dimethyl-phosphinoylmethyl)-amine

No.	ν P=O	ν CH_3P	ν CH_2P	ν C=O (Amide I)	ν		ν C—N (Amide III)	ν C_6H_5
					Amide II	N—H		
1	1152(vs) 1156(vs)	1308(s)	755(s)	1651(vs)	1544(s)	3045(w) 3126(w) 3431(vs)	1448(s)	1597(s)
2	1156(m) 1173(vs)	1311(m)	747(w)	1657(s)	1544(m)	3088(w) 3118(w) 3221(w) 3274(w)	1421(w)	1486(m) 1595(m)
3	1150(vs) 1167(vs)	1296(m)	753(w)	1644(vs)	1525(vs)	2980(w) 3224(m)	1446(s)	1506(m) 1597(w)
4[a]	1132(vs) 1150(vs) 1180(s)	1305(m)	757(m)	1650(vs)	1516(vs)	3360(vs)	1422(m)	—

[a] The bands for CH_2 groups of this compound are at: 899(s) cm^{-1}, 2856(m) cm^{-1}, and 2935(s) cm^{-1}.

TABLE IV Characteristic Infrared Frequences (ν cm^{-1}) of Thiourea Derivatives of Bis(dimethyl-phosphinoylmethyl)-amine

No.	ν P=O	ν CH_3P	ν CH_2P	ν C=S	ν		ν C—N (Amide III)	ν C_6H_5
					Amide II	N—H		
5	1141(vs) 1175(s)	1308(s)	745(m)	941(vs) 1074(w) 1293(s)	1561(s)	3190(w) 3250(w) 3423(vs)	1415(w)	1498(m) 1598(s)
6	1139(vs) 1159(s)	1308(w)	756(w)	939(m) 1091(w) 1293(m)	1524(m)	3201(m) 3365(m)	1404(w)	1494(m) 1588(w)
7	1145(vs) 1162(vs)	1306(m)	754(w)	938(vs) 1113(w) 1292(m)	1524(vs)	3211(s) 3375(s)	1406(w)	1459(s) 1588(w)
8[a]	1126(vs) 1154(vs) 1182(m)	1306(m)	749(m)	937(vs) 1106(m) 1298(s)	1566(vs)	3201(w) 3254(w) 3452(vs)	1415(m)	1513(vs) 1612(m)
9[b]	1131(vs) 1146(vs)	1309(m)	755(w)	941(s) 1059(w) 1295(m)	1572(s)	3223(w) 3420(m) 3483(s)	1428(m)	1493(w) 1648(w)
10[c]	1137(vs) 1151(vs) 1184(m)	1310(m)	756(w)	936(w) 1081(w) 1298(m)	1539(s)	3303(vs) 3442(vs)	1408(w)	—

[a] The bands for CH_3—O—Ar are at 1034(m) cm^{-1} and 1245(vs) cm^{-1}.

[b] The band for CH_2Ar is at 733 cm^{-1}.

[c] The bands for CH_2 groups of this compounds are at 877(vs) cm^{-1}, 2855(s) cm^{-1}, and at 2925(vs) cm^{-1}.

TABLE V ^{1}H and $^{31}P\{^{1}H\}$ NMR Data of Urea and Thiourea Derivatives **1–10** of Bis(dimethyl-phosphinoylmethyl)-amine[a]

	^{1}H NMR data, protons							
	$CH_3P(O)$		$CH_2P(O)$		R—NH—C(X)		Ar—H	$^{31}P\{^{1}H\}$
No.	δ	$^{2}J_{HP}$	δ	$^{2}J_{HP}$	δ	$^{3}J_{HH}$	δ	δ
1	1.63(d)	12.69	3.99(bs)	—	9.91(s)	—	7.25–7.40(m)	+46.30
2	1.64(d)	12.27	3.99(bs)	—	10.11(s)	—	7.05–7.55(m)	+46.31
3	1.67(d)	12.56	4.11(bs)	—	9.79(s)	—	7.40–8.26(m)	+45.99
4[b]	1.57(d)	12.61	3.87(d)	3.47	7.25(bs)	—	—	+46.10
5	1.70(d)	12.82	4.58(d)	4.38	10.75(s)	—	7.13–7.44(m)	+47.45
6	1.70(d)	12.82	4.57(d)	4.33	10.83(s)	—	7.26–7.39(m)	+47.47
7	1.70(d)	12.88	4.57(d)	4.38	10.62(s)	—	7.10–7.30(m)	+47.39
8[c]	1.70(d)	12.82	4.57(d)	4.49	10.55(s)	—	6.80–7.50(m)	+47.33
9[d]	1.56(d)	12.82	4.39(d)	4.11	9.04(t)	4.49	7.16–7.32(m)	+46.72
10[e]	1.64(d)	12.88	4.41(d)	3.85	8.57(d)	6.62	—	+46.97

[a] Abbrevations: bs—broad singlet, d—doublet, m—multiplet, s—singlet, t—triplet.

[b] The signals of the methylene cyclohehane protons of the marked compound were at 1.15–1.95 ppm as four multiplets. The signal of cyclohexane CH—N—C(O) proton was as a multiplet at 3.45–3.60 ppm. After deuterium exchange with CD_3OD this signal transformed to a broad singlet at 3.50 ppm.

[c] The signal of methyl CH_3OAr proton of this compound was a sharp singlet at 3.79 ppm.

[d] The signal of methylene N—CH_2—Ph protons was at 4.74 (d) ppm with $^{2}J_{HH}$ 5.02 Hz. The signal transformed to a singlet at 4.75 ppm after deuterium exchange with CD_3OD.

[e] The signals of methylene cyclohexane protons of this compound were at 1.15–2.10 ppm as four multiplets. The signal of cyclohexane CH—N—C(S) proton was a multiplet at 4.1–4.2 ppm.

and to two kinds of phosphoryl groups: the first one is bonded with hydrogen bonds while the second one is not.[32]

^{1}H NMR spectra of **1–10** (Table V) showed resonance signals as doublets for the methyl group protons $CH_3P{=}O$ at 1.56–1.70 ppm and $^{2}J_{HP}$ 12.27–12.88 Hz. The resonance signals of the methylene protons $CH_2P{=}O$ were registered as broad singlets for ureas **1–3** and as doublets for urea **4** and thioureas **5–10** with $^{2}J_{PH}$ 3.47–4.57 Hz. These signals of ureas **1–3** were doublets in solution of CD_3OD or in a mixture of $CDCl_3$ and CD_3OD (5:1 by volume) with the expected $^{2}J_{HP}$ coupling constants of around 4 Hz. The signal of Ph—CH_2N protons in **9** was a doublet with $^{2}J_{HH}$ 5.02 Hz because of the coupling with NH—C(S) thioamide proton. That is why the signal transforms to a singlet after deuterium exchange of the thioamide proton. The resonance signal for NH—C(X) amide or thioamide protons of **1–3** and **5–8** were singlets at around 9.5–10.5 ppm, while the signals for the same kind of protons of **4**, **9**, and **10** were broad singlet, triplet, or doublet respectively, because of the coupling with cyclohexane CH—C(X) proton (**4** and **10**) or with

Ph—$CH_2NC(S)$ protons (**9**). The signals of NHC(X) amide or thioamide protons disappear after deuterium exchange, which is a relatively slow process even in homogeneous solution of $CDCl_3$ with CD_3OD at room temperature. In some cases this signal does not disappear even for 10 h, but its integral intensity is significantly reduced.

The $^{31}P\{^1H\}$ and ^{31}P NMR spectra of **1–10** were singlet or multiplet resonance signals, respectively in the range of +45.99–+47.47 ppm, typical of tertiary phosphine oxides containing two methyl and a methylene groups at the phosphorus atom.[13,16,22,26]

Mass spectrometric data (Table VI) confirm the proposed structures. In the EI mass spectra (70 eV) peaks for molecular ions $\mathbf{[M]}^{+\cdot}$ of **1–10** are detected though their intensity is very low in some of the cases because these multifunctional compounds have many possibilities of fragmentation. The most abundant signals that appear in the spectra are due to the even electron ions $[(CH_3)_2P(O)CH_2NHCH_2]^+$ (m/z 120), $[CH_3)_2PO]^+$ (m/z 77), and $[(CH_2)_2N]^+$ (m/z 42) and the distonic ion $[(CH_3)_2P^+(OH)(CH_2^{\cdot})]$ (m/z 92). The latter ion is an ylide ion with positive charge located on the phosphorus and the unpaired electron on the adjacent carbon atom.[22] Additionally FAB mass spectra have been measured with 3-nitrobenzyl alcohol as a matrix. Abundant signals for $[M + H]^+$ can be found in all the spectra with relative intensities of about 40%. The base peak in FAB mass spectra (with exception of **8**) is a signal at m/z 120 that is due to the ammonium ion $[(CH_3)_2P(O)CH_2N^+HCH_2]$ as observed in the EI mass spectra as well.

EXPERIMENTAL

Starting Materials

Bis(dimethyl-phosphinoylmethyl)-amine was prepared according to reference.[16] The used isocyanates and isothiocyanates were commercially available products from Fluka and Merck. The solvents were dried by standard procedures before usage.

Characterization of the Prepared Compounds 1–10

The elemental analysis for nitrogen content was performed according to the method of Duma. The melting points were measured on a Boetius microheating plate PHMK05 (Germany) and were uncorrected. Infrared spectra (400–4000 cm^{-1}) were recorded on a Bruker Vector-22 IR spectrometer as KBr pellets. The ^1H NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer operating at 500.13 MHz,

TABLE VI Significant Mass Spectrometric Data (m/z/rel.Int., %) of Ureas and Thioureas **1–10**

	EI-MS					FAB-MS	
Comp. no.	$[M + H]^{+\cdot}$	$[(CH_3)_2P(O)CH_2NHCH_2]^+$ m/z 120	$[(CH_3)_2P^+(OH)(CH_2^{\cdot})$ m/z 92	$[(CH_3)_2P(O)]^+$ m/z 77	$[(CH_2)_2N]^+$ m/z 42	$[M + H]^+$	$[(CH_3)_2P(O)CH_2NHCH_2]^+$ m/z 120
1	316/2	/10	/13	/13	/7	317/42	/100
2	350/11	/100	/54	/17	/93	351/40	/100
3	366/13	/100	/27	/11	/76	367/35	/100
4	322/8	/82	/17	/6	/37	323/43	/100
5	332/3	/67	/19	/93	/90	333/44	/100
6	366/1	/76	/20	/13	/84	367/35	/100
7	346/32	/100	/76	/27	/82	347/40	/100
8	362/1	/52	/17	/14	/100	363/25	/65
9	346/11	/59	/50	/29	/100	347/49	/100
10	338/6	/100	/32	/15	/99	339/22	/100

using $CDCl_3$ as a solvent. The chemical shifts are referenced versus int. TMS. The ^{31}P- and $^{31}P\{^1H\}$-NMR spectra were recorded on the same instrument at 202.45 MHz using the same samples as described above. The chemical shifts are referenced versus ext. 85% H_3PO_4. EI-mass spectra [EI-MS] (70 eV, source temperature 200°C, direct inlet system) as well as FAB mass spectra were recorded on a Finnigan MAT 8200 mass spectrometer.

General Procedure for the Preparation of Urea and Thiourea Derivatives 1–10

A solution of isocyanate or isothiocyanate (2.0 mmol) in chloroform (1.0 ml) was added dropwise at room temperature to a stirred solution of bis(dimethyl-phosphinoylmethyl)-amine (2.0 mmol) in dry chloroform (2.0 ml). A slightly exothermal reaction was observed. The reaction mixture was stirred at 30–40°C for 15 min, allowed to stay at room temperature for about 5–6 h, and cooled. A crystalline precipitate was formed. After addition of a few drops of dry diethyl ether to the reaction mixture, the precipitate was separated by filtration and washed with dry diethyl ether. The resulting crude product was recrystallized from a solvent until constant melting point. The preparative and analytical data of **1–10** are presented in Table II.

REFERENCES

[1] I. C. Popoff, L. K. Huber, B. P. Block, P. D. Morton, and R. P. Riordan, *J. Org. Chem.,* **28,** 2898 (1963).

[2] N. Kreutzkamp, K. Herberg, L. Lämerhirt, and E. Schmidt-Samoa, *Arch. Pharmaz.*, **304,** 896 (1971).

[3] N. Kreutzkamp, E. Schmidt-Samoa, and A. K. Herberg, *Angew. Chem.*, **77,** 1138 (1965).

[4] O. A. Mukhacheva, V. G. Nikolaeva, R. L. Yafarova, M. A. Shchelkunova, and A. I. Razumov, *Zh. Obshch. Khim.,* **35,** 526 (1975); CA **83,** 43438e (1975).

[5] W. Wegener and P. Scholz, *Z. Chem.*, **10,** 341 (1970).

[6] E. B. Trostyanskaya, E. S. Venkova, and Yu. A. Mikhailin, *Zh. Obshch. Khim.*, **37,** 1655 (1967); CA **68,** 13084j (1967).

[7] A. W. Frank, *Can. J. Chem.,* **59,** 27 (1981).

[8] G. Matolcsy, K. Bauer, A. Pal, I. Ujvary, I. Belai, A. Gerley, M. Kardos, P. Sohar, and I. Pelczer, *Acta Chimica Hungarica*, **123,** 145 (1986).

[9] H. J. Kleiner, *Liebigs Ann. Chem.*, **1974,** 751.

[10] J. Pellon and W. G. Karpenter, *J. Polymer. Sci.,* **1A,** 863 (1963).

[11] R. S. Edmundson, *The Chemistry of Organo-Phosphorus Compounds* (J Wiley, Chichester, 1992), vol. 2, pp. 287–407.

[12] L. Maier, *Phosphorus, Sulfur, and Silicon*, **53,** 43 (1990).

[13] S. Varbanov, G. Agopian, and G. Borisov, *Eur. Polym. J.*, **23,** 639 (1987).

[14] S. Varbanov, E. N. Tsvetkov, and G. Borisov, *Phosphorus and Sulfur*, **19,** 305 (1984).

[15] V. Vassileva, S. Varbanov, and E. Tashev, *Z. Naturforsch.,* **50b,** 1086 (1995).

[16] S. Varbanov, T. Tosheva, and E. Russeva, *Phosphorus, Sulfur, and Silicon*, **127,** 27 (1997).

[17] G. Hägele, S. Varbanov, J. Ollig, and H. W. Kropp, *Z. Anorg. Allg. Chem.*, **620,** 914 (1994).

[18] R. Gugova, S. Varbanov, Z. Raikov, G. Demirov, D. Todorov, and M. Ilarionova, *Parmazie*, **46,** 603 (1991).

[19] J. Klee, H. H. Hörhold, H. Schütz, S. Varbanov, and G. Borisov, *Angew. Makromol. Chem.*, **170,** 145 (1989).

[20] G. Borisov, S. Varbanov, L. M. Venanzi, A. Albinati, and F. Demartin, *Inorg. Chem.*, **33**(24), 5430 (1994).

[21] N. Dodoff, S. Varbanov, G. Borisov, and N. Spassovska, *J. Inorg. Biochem.,* **39,** 201 (1990).

[22] S. Varbanov, A .Georgieva, G. Hägele, H. Keck, and V. Lachkova, *Phosphorus, Sulfur, and Silicon*, **159,** 109 (2000).

[23] E. Stanoeva, S. Varbanov, V. Alexieva, I. Sergiev, V. Vasileva, M. Rashkova, and A. Georgieva, *Phosphorus, Sulfur, and Silicon*, **165,** 117 (2000).

[24] L. Maier, *Phosphorus, Sulfur, and Silicon*, **56,** 5 (1991).

[25] V. Lachkova, S. Varbanov, H. Keck, and T. Tosheva, *Phosphorus, Sulfur, and Silicon*, **152,** 53 (1999).

[26] S. Varbanov, V. Lachkova, G. Hägele, T. Tosheva, and R. Olschner, *Phosphorus, Sulfur, and Silicon*, **159,** 239 (2000).

[27] G. Matolcsy, N. Nadasy, and V. Andriska, *Pesticide Chemistry* (Elsevier, Amsterdam, 1988), pp. 652–692.

[28] A. Williams and W. P. Jencks, *J. Chem. Soc., Perkin Trans. II*, 1753 (1974).

[29] J. H. Saunders and K. C. Frish, *Polyurethanes—Chemistry and Technology, Part I—Chemistry* (Khimia, Moscow, 1988), pp. 227–233, Russian translation.

[30] A. V. Nikolaev, N. S. Blishchenko, Z. N. Mironova, Yu. A. Diadin, and I. I. Yakovlev, *Zh. Phiz. Khim.*, **44**(9), 2412 (1970); CA **74,** 12464v (1970).

[31] D. L. Lide (ed.), *CRC Handbook of Chemistry and Physics* (CRC Press, London-New York, 2001), 82nd ed., pp. 8.44–8.56.

[32] D. E. C. Corbridge, *Topics in Phosphorus Chemistry* (J Wiley, New York, 1969), vol. 6, pp. 235–265.