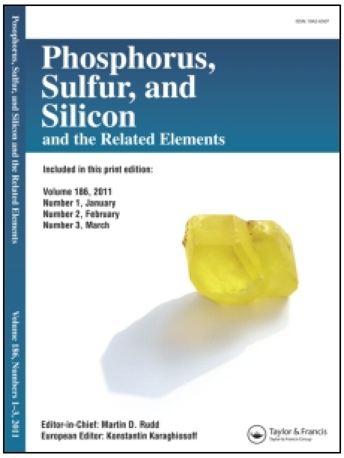

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THE INTERACTION OF PHOSPHENIMIDOUS AMIDES AND PHOSPHENODIIMIDIC AMIDES WITH AMINES

L. N. Markovski[a]; V. D. Romanenko[a]; A. V. Ruban[a]
[a] Institute of Organic Chemistry Academy of Sciences of the Ukrainian SSR, Kiev, U.S.S.R.

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THE INTERACTION OF PHOSPHENIMIDOUS AMIDES AND PHOSPHENODIIMIDIC AMIDES WITH AMINES

L. N. MARKOVSKI, V. D. ROMANENKO, and A. V. RUBAN

Institute of Organic Chemistry Academy of Sciences of the Ukrainian SSR, 252660, Kiev, U.S.S.R.

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Phosphenimidous amides **1** react with amines to give phosphonimidic diamides **3**a-b or phosphorous triamides **3**d-f respectively. The nature of the product depends on the substituent R (Me_3Si or t-Bu) attached to the imidic nitrogen. The amide and imide forms of the compounds **3** are relatively stable and incapable of interconvertion under the conditions investigated. The reaction between phosphenodiimidic amides **2** and amines leads to phosphorimidic triamide **4**. The influence of different factors on the reactions is described. The spectroscopic data of the compounds are discussed in relation to their structure.

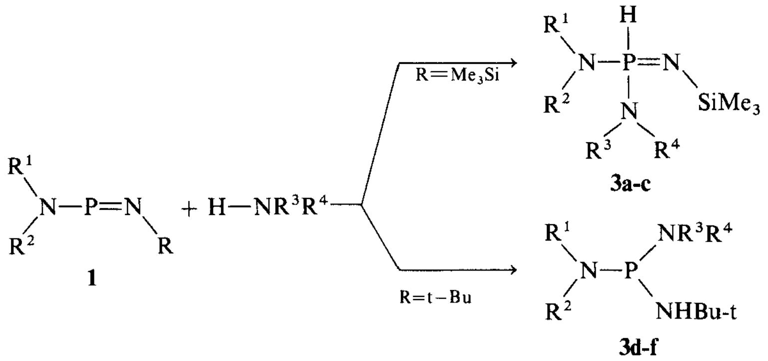
INTRODUCTION

The attachment of nucleophilic reagents to the phosphorus-nitrogen double bond of phosphenimidous amides and phosphenodiimidic amides has been very little studied in spite of great interest in the chemistry of two-coordinate trivalent and three-coordinate pentavalent phosphorus compounds.[1] The examples cited in the literature are limited to the reactions of phosphenimidous amides[2–4] and tetrakis(trimethylsilyl)-phosphenodiimidic amide (2, $R = R^1 = R^2 = Me_3Si$) with alcohols.[5]

In the present paper we report the results concerning the reactions of amines with phosphenimidous amides and phosphenodiimidic amides. We have described the synthesis of phosphenodiimidic amides in our previous paper.[6]

RESULTS AND DISCUSSION

Phosphenimidous amides and phosphenodiimidic amides react smoothly and exothermically with equimolar amounts of the primary and non-bulky secondary aliphatic amines according to the Eqs. (1) and (2).



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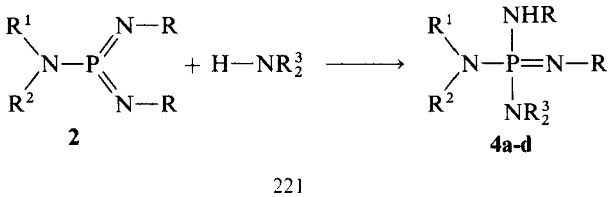

(2)

TABLE I

Physical properties and analytical data

Reaction product No.	R	R^1	R^2	R^3	R^4	Reaction condition	Yield[a] %	B.p., M.p. °C (torr)	Formula	C %		H %		P %		Si %	
										Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
3a	Me_3Si	Me_3Si	Me_3Si	Et	Et	0°, 2h, ether	78	78–79(0.02)	$C_{13}H_{38}N_3PSi_3$	44.39	44.56	10.89	11.00	8.81	8.72	23.96	23.75
3b	Me_3Si	Me_3Si	Me_3Si	$—(CH_2)_5—$		0°, 2h, ether	54[b]	95–96(0.02)	$C_{14}H_{38}N_3PSi_3$	46.23	46.03	10.53	10.62	8.51	8.53	23.17	23.11
3c	Me_3Si	Me_3Si	Me_3Si	H	t-Bu	20°, 1h, ether	79	64–65(0.02)	$C_{13}H_{38}N_3PSi_3$	44.39	44.36	10.89	11.24	8.81	8.86	23.96	24.01
3d	t-Bu	Me_3Si	Me_3Si	Et	Et	20°, 3h, ether	73	77–80(0.02)	$C_{14}H_{38}N_3PSi_2$	50.10	50.12	11.41	11.43	9.22	9.23	16.74	16.78
3e	t-Bu	Me_3Si	Me_3Si	$—(CH_2)_2O(CH_2)_2—$		20°, 3h, ether	61	106–108(0.02)	$C_{14}H_{36}N_3OPSi_2$	48.10	48.35	10.38	10.63	8.86	8.85	16.07	16.09
3f	t-Bu	t-Bu	Me_3Si	Et	Et	20°, 3h, ether	87	79–79.5(0.02)	$C_{15}H_{38}N_3PSi$	56.38	56.26	11.98	12.01	9.69	9.73	8.79	8.78
4a	Me_3Si	Me_3Si	Me_3Si	Et	Et	0°, 2h, benzene	80	105–108[c]	$C_{16}H_{47}N_4PSi_4$	43.78	43.95	10.79	10.66	7.05	7.05	25.60	25.55
4b	Me_3Si	Me_3Si	Me_3Si	i-Pr	i-Pr	20°, 5h, ether	75	154–156 (from ether)	$C_{18}H_{51}N_4PSi_4$	46.30	46.43	11.01	11.35	6.63	6.62	24.06	24.00
4c	t-Bu	t-Bu	Me_3Si	Me	Me	20°, 3h, benzene	78	55–58(0.02)	$C_{17}H_{43}N_4PSi$	56.31	56.42	11.95	11.91	8.54	8.53	7.74	7.71
4d	t-Bu	$—(H_3C)_2C(CH_2)_3C(CH_3)_2—$		Et	Et	20°, 3h, ether	100	oil[e]	$C_{19}H_{47}N_4PSi_2$	54.49	54.85	11.31	11.18	7.39	7.44	13.41	13.44

[a] Yield of product isolated by distillation or recrystallization except for **4d**.

[b] Yield of product isolated by double distillation.

[c] After sublimation at 105°/0.02 torr.

[d] Measured by bulb-to-bulb distillation.

[e] Decomposes during distillation under high vacuum at the bath temperature of 150–200°. Sample kept 1h at 20°/0.02 torr prior to analysis.

The reactions are completed in 1–2 hours at room temperature. The formation of the addition products is conveniently monitored by ^{31}P nmr spectroscopy. Large upfield shifts (in some case up to 300 ppm) were observed for the phosphorus nuclei. The order in which the reactants are mixed is unimportant and the products formed are practically pure. Reaction conditions and yields are presented in the Table I along with analytical data and some physical properties of the compounds.

2,2,6,6-Tetramethylpiperidin, N-trimethylsilyl-t-butylamine, bis(trimethylsilyl) amine and other branched amines do not combine with phosphenimidous amines and phosphenodiimidic amides. In these cases only the starting materials were recovered, even if the reaction mixture was refluxed for many hours. These results suggest that steric effects have a significant influence on the course of the reactions.

It is interesting to compare the effect of the steric and electronic factors on the reactivity of phosphenimidous amides and phosphenodiimidic amides toward amines.

Tris(trimethylsilyl)-phosphenimidous amide (**1**; $R = R^1 = R^2 = Me_3Si$), N,N-bis(trimethylsilyl)-N′-(t-butyl)-phosphenimidous amide (**1**; R = t-Bu, $R^1 = R^2 = Me_3Si$) and N,N′-bis(t-butyl)-N-(trimethylsilyl)-phosphenimidous amide (**1**; $R = R^1$ = t-Bu, $R^2 = Me_3Si$) readily combine with diethylamine, but do not react with di-isopropylamine. No change was observed in their ^{31}P nmr spectra even after (in the last instance) 7 days at room temperature. This failure is almost certainly due to steric repulsions. Unlike tris(trimethylsilyl)-phosphenimidous amide (1; $R = R^1 = R^2 = Me_3Si$), tetrakis (trimethylsilyl)-phosphenodiimidic amide (2, $R = R^1 = R^2 = Me_3Si$ smoothly adds di-isopropylamine under similar conditions. In as much as steric hindrance evidently plays a more important part in addition reactions of amines to phosphenodiimidic amides than to phosphenimidous amide,[7] this fact indicates that the electrophility of the phosphorus atom in tetrakis(trimethylsilyl)-phosphenodiimidic amide (2; $R = R^1 = R^2 = Me_3Si$) is greater than that in tris-trimethylsilyl)-phosphenimidous amide (1; $R = R^1 = R^2 = Me_3Si$).

On the other hand, exchange of a trimethylsilyl group (linked to the imidic nitrogen atoms) by a t-butyl group leads to a decrease of the reactivity of phosphenodiimidic amides toward amines. Thus, unlike tetrakis(trimethylsilyl)-phosphenodiimidic amide (**2**; $R = R^1 = R^2 = Me_3Si$), N,N′,N″-tris(t-butyl) - N - (trimethylsilyl) - phosphenodiimidic amide (**2**; $R = R^1$ = t-Bu, $R^2 = Me_3Si$) reacts neither with diethylamine nor with t-butylamine. The ability of N,N′,N″-tris(t-butyl)-N-(trimethylsilyl)-phosphenodiimidic amide to combine with dialkylamines is so low that only the most reactive amines (e.g. dimethylamine) are able to do so under the conditions investigated. This may be due to electronic effects, as well as to the increase in steric hindrance. Probably, both factors play a part. However the high reactivity of N,N′-bis(t-butyl)-N-(trimethylsilyl)-phosphenimidous amide (**1**; $R = R^1$ = t-Bu, $R^2 = Me_3Si$), exceeding that one of N,N′,N″-tris(t-butyl) - N - (trimethylsilyl) - phosphenodiimidic amide (**2**; $R = R^1$ = t-Bu, $R^2 = Me_3Si$), shows that electronic factors can play only a subordinate part in decreasing the reactivity of the phosphorus-nitrogen double bond on passing from phosphenimidous amides **1** to phosphenodiimidic amides **2**. The facts given above illustrate the complex interrelationships of the polar and steric factors which influence the reactivity of the compounds **1** and **2**.

The structures of the products formed in the reactions of phosphenimidous amides **1** and phosphenodiimidic amides **2** with amines are noteworthy. The ir, ^{1}H and ^{31}P nmr spectra of the addition products of amines with phosphenodiimidic amides **2** are consistent with their formulation as phosphorimidic triamides. *Table II* lists the spectrascopic parameters of the new imidophosphoric derivatives **4a–d**. The assignments were made by analogy with related compounds.[8] Each compound shows a single peak in the ^{31}P spectrum in the region 3.1 to −15.9 ppm this being characteristic of four-coordinate phosphorus centers.[9] The $^3J(PH)$ values are in the same range as observed for numerous compounds of this type.[10] The infrared spectra of the products 4a-d show a sharp band (at 1310–1350 cm^{-1}) characteristic of the P═N bond and a band (at 3385–3410 cm^{-1}) characteristic of the NH group.[11]

The infrared and nmr spectroscopic studies of the addition products of diethylamine, piperidine, morpholine and t-butylamine to phosphenimidous amides (1) show that the products exist either in the PH-imide or the amide forms depending on the nature of the substituent R (Me_3Si or t-Bu, respectively). The reaction between tris(trimethylsilyl)-phosphenimidous amide (1; $R = R^1 = R^2 = Me_3Si$) and amines leads only to phosphonimidic diamides (3a–c). These products exhibit in their

TABLE II

Spectroscopic data

	^{31}P n.m.r.[a]	^{1}H n.m.r.[c]		i.r. (film), ν_{max}cm^{-1}		
Compd.	(ppm)[b], J(Hz)	(ppm), J(Hz)	Assignment	P═N	P—H	N—H
3a	-11.7(d)	0.22(s)	27, $Si(CH_3)_3$	1310	2290	
	$^{1}J_{PH}511$	0.90(t), $^{3}J_{HH}7.0$	6, CH_3			
		2.85(m), $^{3}J_{PH}13.5$	4, CH_2			
		7.78(d), $^{1}J_{PH}511$	1, PH			
3b	-8.9(d)	0.20(s)	27, $Si(CH_3)_3$	1325	2285	
	$^{1}J_{PH}$ 521	1.25(m)	4, NCH_2			
		2.75(m)	6, CH_2			
		7.58(d), $^{1}J_{PH}521$	1, PH			
3c	-21.1(d)	0.22(s)	27, $Si(CH_3)_3$	1310	2290	3340
	$^{1}J_{PH}519$	1.14(s)	9, $C(CH_3)_3$			
		7.35(d), $^{1}J_{PH}519$				
3d	108.6	0.22(s)	18, $Si(CH_3)_3$			3240
		0.93(t), $^{3}J_{HH}7.5$	6, CH_3			
		1.10(s)	9, $C(CH_3)_3$			
		2.79(m), $^{3}J_{PH}7.0$	4, CH_2			
3e	104.3	0.09–0.29(m)	18, $Si(CH_3)_3$			3260
		1.02–1.32(m)	9, $C(CH_3)_3$			
		2.39–3.65(m)	8, CH_2			
3f	107.7	0.30(s)	9, $Si(CH_3)_3$			3240
		1.00(t), $^{3}J_{HH}7.5$	6, CH_3			
		1.25(s)	9, $C(CH_3)_3$			
		1.33(s)	9, $C(CH_3)_3$			
		2.85(m), $^{3}J_{PH}5.5$	4, CH_2			
4a	3.1[d]	0.17(s), 0.27(s)	36, $Si(CH_3)_3$	1310		3385
		0.87(t), $^{3}J_{HH}7.5$	6, CH_3			
		2.92(m), $^{3}J_{PH}13.5$	4, CH_2			
4b	-4.6[d]	0.22(s), 0.32(s)	36, $Si(CH_3)_3$		1335	3410
		1.12(m), $^{3}J_{HH}6.0$	12, CH_3			
		3.67(m), $^{3}J_{PH}14.0$	2, CH			
4c	15.9	0.23–0.40(m)	$36 \left\{ \begin{array}{l} Si(CH_3)_3 \\ C(CH_3)_3 \end{array} \right.$		1350	3390
		1.07–1.47(m)				
		2.44(d), $^{3}J_{PH}10.5$	6, NCH_3			
4d	-0.6	0.19–0.27(m)	18, $Si(CH_3)_3$		1310	3390
		0.87(t), $^{3}J_{HH}7.5$	6, CH_3			
		1.00–1.48(m)	18, $—(CH_3)_2C(CH_2)_3C(CH_3)_2—$			
		3.02(m)	4, CH_2			

[a] Phosphorus chemical shifts were measured at 30 MHz relative to 85% H_3PO_4 as external standard.

[b] All values refer to neat liquids except where stated.

[c] Proton chemical shift were measured at 60 MHz relative to tetramethylsilane as internal standard. Solvent: benzene.

[d] Spectrum run using a benzene solution (ca. 60%).

the phosphorus chemical shift (-8.9 to -21.2 ppm) corresponds to the phosphonate structure. Furthermore, the resonance peak is split into a doublet, which shows that one hydrogen atom is attached directly to the phosphorus. The value of ^{1}J(PH) for the doublet (about 520 Hz) is similar to that reported for the related compounds.[12,14] The ^{31}P spectra of the products 3a–c do not contain peaks in the region where resonance is observed for the phosphorus triamides.[8] Proton magnetic resonance measurements of the phosphonimidic diamides (3a–c) are in complete agreement with conclusion reached from the ^{31}P studies.

N,N-Bis(trimethylsilyl) - N′ - (t-butyl) - phosphenimidous amide (**1**; R = t-Bu, $R^1 = R^2 =$ Me_3Si) and N,N′-bis(t-butyl) - N - (trimethylsilyl)-phosphenimidous amide (**1**; $R = R^1 =$ t-Bu, $R^2 =$ Me_3Si) add amines to give phosphorous triamides (3d–f) which based on nmr evidence exist entirely in the amide. This fact is supported by the observainfrared spectra the characteristic P—H and P=N stretching bands (see Table II). The magnitude of tion of absorption at low fields in the ^{31}P nmr spectra, considered to be characteristic of phosphorus triamides. The other spectrascopic data (ir, ^{1}H nmr; see Table II) leave no doubt about their structures.

Physical measurements have failed to detect the existence of an "imide-amide" type of equilibrium in the products 3. These substances are relatively stable and show no tendency to form a mixture of the two tautomeric forms. Thus, the infrared spectra are virtually unaffected by changes in solvent or temperature. These data suggest that different tautomers are thermodynamically favoured if N-(t-butyl) were replaced by N-trimethylsilyl substituents.

The difference in the structure of the products **3a–c** and **3d–f** is probably primarily due to the specific nature of the interaction between the atoms of the P—N—Si system.

It is known that the properties of nitrogen-bridged silicon compounds can be rationalized in terms of conjugation of the lone-pair on the nitrogen atom with the 3d orbitals of silicon.[13] In the case discussed, substitution of the trimethylsilyl group by the t-butyl group (attached to the nitrogen of the P—NH—R system) probably, increases the NH acidity and as a result decreases the stability of the amide form. Other examples of this kind can be quoted.[13] However, the contribution of the steric factors to the thermodynamic stability of the tautomeric forms is unclear. Since the Me_3Si and t-Bu groups are very bulky and since these substituents seem to lead to greater molecular crowding of the structure with three-coordinate phosphorus atom when spacefilling molecular models are constructed, the phosphonimidic structure appears to be sterically most favoured but any conclusion at this stage is purely speculative. This point is of current interest and will be discussed with other structural problems in a study to be published soon.

EXPERIMENTAL

The amines were obtained from commercial sources and were distilled prior to use. Known methods were used for the preparation of tris(trimethylsilyl)-phosphenimidous amide,[2] N,N-bis(trimethylsilyl)-N′-(t-butyl)-phosphenimidous amide[3] and N,N′-bis(t-butyl)-N-(trimethylsilyl)-phosphenimidous amide.[4] Phosphenodimidic amides were prepared as described earlier.[6] Diethyl ether and benzene were purified by distillation from sodium. Solvents for nmr and ir studies were dried over molecular sieves. Standard vacuum and inert atmosphere techniques were used in all experiments. Proton and ^{31}P nmr spectra were recorded, on TESLA BS 467 and TESLA BS 487 B spectrometers respectively. Infrared spectra were obtained on a SPECORD 75 IR spectrophotometer (C. Zeiss).

Reaction of phosphenimidous amides (1) and phosphenodiimidc amides (2) with amines.

The reaction was carried out in a flask fitted with a magnetic stirrer, a dropping funnel, and a thermometer. 0.03 Mol of amine is addded dropwise, under a stream of argon at an appropriate temperature, to a stirred solution of 0.03 mol of **1** or **2** in 70 ml solvent (see Table I for conditions). After the addition is complete, stirring is continued for the time indicated in Table I. The solvent is then removed on a rotary evaporator at 20°/10–15 torr and the residue is distilled under reduced pressure or is recrystallized. Yields, physical constants and spectroscopic data of the products are compiled in Tables. The products **3** as well as **4c,d** are all colourless, air-sensitive liquids whilst **4a,b** are white crystalline solids.

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