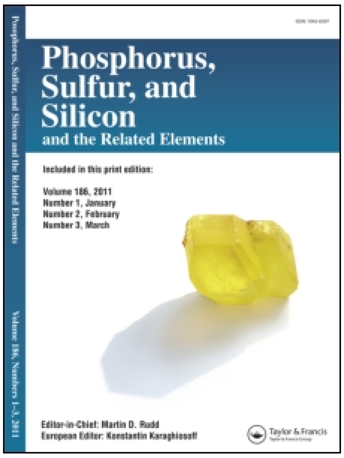

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AN NMR STUDY OF THE REACTIONS OF CHLOROPHOSPHINES WITH $AlC1_3$. PHOSPHENIUM CATIONS FEATURING A S-P-N LINKAGE

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AN NMR STUDY OF THE REACTIONS OF CHLOROPHOSPHINES WITH $AlCl_3$. PHOSPHENIUM CATIONS FEATURING A S-P-N LINKAGE

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The N-P^+-S phosphenium cations **1**, **2** and **3** have been prepared by treatment of the respective precursor chlorophosphines **4**, **5** and **6** with the stoichiometric quantity of $AlCl_3$ in CH_2Cl_2 solution. The cations **3** are noteworthy that they are the first aliphatic phosphenium cations featuring a P-S bond. That the values of ^{31}P chemical shifts of phosphenium cations **3** are larger than those of aliphatic N-P^+-N and N-P^+-Cl cations characterize a relative inferior π-donor ability of RS group to R_2N group and to Cl. The *exo* conformation of group at sulfur to dialkylamino group in **3** is proposed on the rare steric effect on ^{31}P chemical shifts of substitutes at sulfur.

Keywords: phosphenium ion; ^{31}P NMR; 1,3,4,2-thiadiazaphosphole; 1,3,2-thiazaphospholane; (dialkylamino)(alkylthio)cholorphosphine

INTRODUCTION

Phosphenium cations are six electron reactive intermediates with a lone electron pair and a vacant orbital. The first stable ones were reported independently in 1972 by Fleming[1] and by Maryanoff.[2] Their extensive chemistry were respectively reviewed by Cowley[3] in 1985 and by

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Sanchez[4] in 1990. Recent interest has focused on the role of complexation and functionallization of the phosphorus center in the stability and reactivity.[5–10] Phosphenium cations can be stabilized by strong π-donor substituents,[3,4] by a bulky substituent,[7,11] π-delocalization[12,13,14] and by a chelating ligand.[8,9,15] The principal objective of our work was to explore the possibility of the stabilization of phosphenium ions by using one RS- and one R_2N substituent in three different systems. We have reported the synthesis of two 1, 3, 4, 2-thiadiazaphosphenium cations.[17–19] Present approach results in the synthesis of another 29 novel persistent phosphenium cations featuring a S-P-N bond including 7 6π-heterocyclic phosphenium cations (**1**), 5 alicyclic ones (**2**) and 17 aliphatic examples (**3**).

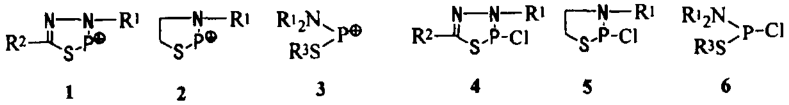
RESULTS AND DISSCUSION

Preparation of Precursor Chlorophosphines

The substituted 2-chloro-2,3–2(H)-1,3,4,2-thiadiazaphospholes (**4**) were synthesized according to a procedure by Huang et al.[20] 2-Chloro-3-N-phenyl-1,3,2-thiazaphospholanes (**5**) were prepared by the reactions of β-aminoethanethiol (7) with PCl_3 in the presence of Et_3N. (Dialkylamino)(alkylthio)chlorophosphines (**6**) were synthesized by the reaction of R_2NPCl_2 with RSH in the presence of triethylamine. ^{31}P chemical shifts of **4**,[20] **5** and **6** were shown in Table I, other data were listed in the experimental part. The β-(*p*-substituted)anilinoethanethiol (**7b-7e**) were prepared according to a reported procedure for β-anilinoethanethiol (**7a**),[23] whose structures were confirmed by the presence of somewhat strong signals at 2560 to 2580 cm^{-1} ($\nu_{S\text{-}H}$) in IR.

Reaction of Chlorophosphines with $AlCl_3$

The N-P^+-N phosphenium ions are the most numerous[3,4] and even one of them is aromatic in a favorable case.[12] Burford[16] reported that the dithiaphospholidinium cation accommodated *in situ* to tetracoordinate spirocyclic tetrathiaphosphonium cation at low temperature. These showed that sulfur is inferior to nitrogen in the ability of dative π-conjugating with the positive phosphorus center. This raised the question whether the N-P^+-S phosphenium cation is stable. Therefore, the solutions of the reaction of chlorophosphines (4,[20] 5, 6) with $AlCl_3$ are studied with NMR spectroscopy. The results show that the N-P^+-S phosphenium cations (**1**, **2**, **3**) are persistent and sensitive to structural alteration.



SCHEME 1

TABLE I ^{31}P NMR data for Phosphenium cation **1**, **2** and **3**and precursor **4**, **5** and **6**

Phosphenium Cation[a]			$\delta^{31}P$ (ppm)	Formula	Yield b (%)	Chlorophosphine[c]	
No.	R^1	R^2 or R^3				No.	$\delta^{31}P$ (ppm)
1a	Ph	Et	321.0	$C_9H_{10}N_2PS\bullet AlCl_4$	100	**4a**[20]	149.9[20]
1b	Ph	$PhCH_2$	322.7	$C_{14}H_{12}N_2PS\bullet AlCl_4$	100	**4b**[20]	151.4[20]
1c	Ph	Ph	318.9	$C_{13}H_{10}N_2PS\bullet AlCl_4$	100	**4c**[20]	148.5[20]
1d	Ph	p-$MeOC_6H_4$	320.1	$C_{14}H_{12}N_2OPS\bullet AlCl_4$	100	**4d**[20]	148.3[20]
1e	Ph	p-BrC_6H_4	331.9	$C_{13}H_9BrN_2PS\bullet AlCl_4$	95	**4e**[20]	148.7[20]
1f	Ph	2-furyl	312.0	$C_{11}H_8N_2OPS\bullet AlCl_4$	90	**4f**[20]	144.2[20]
1g	Ph	1-naphthyl	318.0	$C_{17}H_{12}N_2PS\bullet AlCl_4$	100	**4g**[20]	145.2[20]
2a	Ph		406.4	$C_8H_9NPS\bullet AlCl_4$	100	**5a**	161.7
2b	p-MeC_6H_4		402.6	$C_9H_{11}NPS\bullet AlCl_4$	90	**5b**	168.7
2c	p-$MeOC_6H_4$		411.75	$C_9H_{11}NOPS\bullet AlCl_4$	100	**5c**	164.8
2d	p-$EtOC_6H_4$		406.2	$C_{10}H_{13}NOPS\bullet AlCl_4$	95	**5d**	161.8
2e	p-BrC_6H_4		402.7.2	$C_8H_8ClNPS\bullet AlCl_4$	90	**5e**	160.3
3a	Et	Et	427.9	$C_6H_{15}NPS\bullet AlCl_4$	100	**6a**	171.7
3b	Et	n-Pr	426.3	$C_7H_{17}NPS\bullet AlCl_4$	100	**6b**	172.6
3c	Et	i-Pr	426.9	$C_7H_{17}NPS\bullet AlCl_4$	100	**6c**	171.0
3d	Et	n-hexyl	427.5	$C_{10}H_{23}NPS\bullet AlCl_4$	90	**6d**	172.5
3e	Et	n-octyl	427.5	$C_{12}H_{27}NPS\bullet AlCl_4$	90	**6e**	172.4
3f	Et	n-dodecyl	427.4	$C_{16}H_{35}NPS\bullet AlCl_4$	90	**6f**	172.3

Phosphenium Cation[a]			$\delta^{31}P$ *(ppm)*	*Formula*	*Yield b (%)*	*Chloro-phosphine*[c]	
No.	R^1	R^2 *or* R^3				*No.*	$\delta^{31}P$ *(ppm)*
3g	*i*-Pr	Et	437.9	$C_8H_{19}NPS \cdot AlCl_4$	100	**6g**	169.0
3h	*i*-Pr	*n*-Pr	437.8	$C_9H_{21}NPS \cdot AlCl_4$	100	**6h**	169.9
31	*i*-Pr	*i*-Pr	435.0	$C_9H_{21}NPS \cdot AlCl_4$	100	**61**	168.3
3j	*i*-Pr	*sec*-Bu	435.2	$C_{10}H_{23}NPS \cdot AlCl_4$	95	**6j**	169.8
3k	*i*-Pr	*n*-hexyl	438.0	$C_{12}H_{27}NPS \cdot AlCl_4$	90	**6k**	169.6
31	*i*-Pr	*n*-octyl	437.4	$C_{14}H_{31}NPS \cdot AlCl_4$	90	**61**	169.7
3m	*i*-Pr	*n*-dodecyl	437.15	$C_{18}H_{39}NPS \cdot AlCl_4$	90	**6m**	169.6
3n	$-(CH_2)_5-$	*n*-Pr	418.68	$C_8H_{17}NPS \cdot AlCl_4$	90	**6n**	166.9
3o	Me	*n*-Pr	430.6	$C_5H_{13}NPS \cdot AlCl_4$	95	**6o**	176.2
3p	*n*-Bu	*n*-Pr	428.1	$C_{11}H_{25}NPS \cdot AlCl_4$	90	**6p**	174.7
3q	*i*-Bu	*n*-Pr	431.5	$C_{11}H_{25}NPS \cdot AlCl_4$	90	**6q**	177.8

a. Since Cation products are very sensitive to moisture, elemental analyses are not measured.
b. From ^{31}P NMR integral.
c. The maximum analysis deviations of C and H for **5** and **6** are C ± 0.35, H ± 0.10.

^{31}P NMR spectroscopy is an ideal tool both for the characterization of phosphenium ions and for the elucidation of subsequent reaction. We allow a mixture of an appropriate chlorophosphine and a stoichiometric quantity of sublimed $AlCl_3$ in CH_2Cl_2 to stir in a dry evacuated dual compartment vessel at –20 °C for 6 to 12 hrs. The completion of reaction was indicated by the disappearance of granular $AlCl_3$. The clear filtrates were directly used for ^{31}P NMR analyses. The ^{31}P chemical shifts were listed in Table I. Inspection of the data of $\delta^{31}P$ in Table I reveals that phosphenium cations (**1**, **2** and **3**) have been formed. The ^{31}P chemical shifts of **1**, **2** and **3** respectively fall in the range +312 to +332 ppm, +402 to + 411 ppm and +418 to +438 ppm, and their phosphorus nuclei are respectively about 180 ppm, 250 ppm and 270 ppm downfield of those of **4**,[20] **5** and **6**. The ^{31}P NMR analyses of the reaction mixtures showed that half gave phosphenium cations as sole products, others gave >90% (by ^{31}P integral) cation products.

The cations $(R^1{}_2N)(R^3S)P^+$ (**3**) are particularly noteworthy because they are the first aliphatic phosphenium cations to feature a P-S bond. They are also significant in that the values of their ^{31}P chemical shifts are rather larger than those of known N-P^{+}-N and N-P^{+}-Cl phosphenium cations. This trend is a reflection of the relative inferior π-donor ability of RS group to R_2N group and to Cl.

^{27}Al, ^{1}H and ^{13}C Evidences for Cationic Character for 1a, 2a and 3c

Further evidence for cationic character **1a**, **2a** and **3c** is revealed upon examination of the ^{27}Al, ^{1}H and ^{13}C NMR spectra. Ten ^{27}Al NMR spectra of solutions where phosphenium cations were quantitatively formed gave sharp single peaks at 102.3 to 103.9 ppm. This indicated of the formation of $AlCl_4^-$ anions. Thus, the values of $\delta^{27}Al$ of **1a·AlCl$_4^-$, 2a·AlCl$_4^-$** and **3c·AlCl$_4^-$** are respectively 103.70, 103.38 and 102.60 ppm. CH_2Cl_2 and other volatile components in solutions were removed off under vacuum. The solutions of residues containing **1a**, **2a** and **3c** in CD_2Cl_2 were further examined on ^{1}H and ^{13}C NMR. Data of $\delta^{1}H$ and $\delta^{13}C$ listed in Experimental part showed that protons and carbon nuclei in **1a, 2a** and **3c** were significantly deshielded from those in neutral precursors. These can be ascribed to the presence of partial positive charge in **1a, 2a** and **3c.**

Steric effects of substituents at N and S on ^{31}P chemical shifts

Steric effects can play a role in determining the ^{31}P chemical shifts. For example, the ^{31}P chemical shifts of bis(amido)-substituted cations $((R^1R^2N)(R^3R^4N)P^+)$[3,4] increase with increasing ligand size. Two single-crystal X-ray structures of $[(i\text{-}Pr_2N)_2P]^+$ reveal that this cation possesses a near planar skeletal structure with approximately trigonal-planar geometries at the nitrogen and phosphorus.[21,24] In view of the structure, reducing the N(2p)-P(3p) overlap with increasing ligand bulk is responsible for raising the ^{31}P chemical shift. We now find, quantitatively, that the ^{31}P chemical shifts[3,4] of $(R^1R^2N)(R^3R^4N)P^+$ are correlative to total E_S[22] of substituents at both nitrogens:

$$\delta_{31P} = -54.39\sum E_S + 261$$
$$n = 7, \quad r = 0.999, \ S = 2.296.$$

For (*n*-propylthio)(amido)-substituted cation $(R^1_2N)(n\text{-PrS})P^+$($R^1$=Et for **3b**, R^1=*i*-Pr for **3h**, R^1=-(CH_2)-for **3n**, R^1=Me for **3o**, R^1=*n*-Bu for **3p** and R^1=*i*-Bu for **3q**), more bulky R^1 make the value of ^{31}P chemical shift increase too, but linear laest-squares analysis of the data shows a very poor correlation (r=0.80). Whereas the size of substituent (R^3) at sulfur hardly changes the value of ^{31}P chemical shifts, we associate this with the *exo* conformation of R^3S, i. e. the R^3 is bent away from $R^1{}_2N$ group.

Kinetic Stability-Life Time of phosphenium cation in solution

The cation **1a** can exit in a sealed tube in 0.15 M at room temperature for at least one month; **2a** was decomposed into PCl_3 and unidentified oil within several days; **3b** was changed into $PrSPCl_2$ and $(PrS)_2PCl$ and others within 12 to 24 hrs. Moreover, the compound 3-N-phenyl-5-methylthio-1,3,4,2-thiadiazaphosphenium ion ($\delta^{31}P = 261.9$ppm)[20] is definitely stable in CH_2Cl_2 at room temperature for at least three years. These examples show that the stability of N-P^+-S phosphenium cation seem to be roughly parallel to their ^{31}P values, the smaller the ^{31}P value of phosphenium cation is, the more stable it is.

Reaction not Resulting in Phosphenium Ions

There was one reaction not resulting in phosphenium cation. No signal of phosphenium cation to be found in ^{31}P NMR spectroscopy of the solution of the reaction of 2-chloro-3-N-acetyl-5-methylthio-1,3,4,2-thiadiazaphosphole with $AlCl_3$. Expected 3-N-acetyl-5-methylthio-1,3,4,2-thiadiazaphospholenium cation is unstable even if it may be a 6π-heterocyclic cation. These probably implied that N-acetyl group was a sensitive group for the phosphenium cation.

EXPERIMENTAL

Elemental analyses were obtained with a PE-2400 elementary analyzer. Mass spectra were recorded with a HP 5988A spectrometer at 70 ev ionization energy. The ^1H, ^{13}C, ^{31}P NMR were recorded with Varian XL-200 spectrometer. The chemical shifts were reported in ppm relative to the internal standard TMS or solvent CD_2Cl_2 for ^1H and ^{13}C NMR, and external standard 85% H_3PO_4 for ^{31}P NMR. IR were recorded on PE-983G spectrometer.

Ether was distilled from benzophenone ketyl; n-Hexane and benzene were dried with sodium. $AlCl_3$ was sublimed under vacuum. CH_2Cl_2, CD_2Cl_2 (Aldrich) and $CDCl_3$ were dried over P_2O_5 and stored over CaH_2. PCl_3, R_2NH, RSH, Et_3N, and ethylene sulfur were obtained commercially. The β-anilinoethanethiol (**7a**) was prepared by the reaction of ethylene sulfur with *p*-substituted-aniline according to the reported procedure.[23] R_2NPCl_2[25] was prepared from PCl_3 and R_2NH.

All manipulations were carried out under an atmosphere of dry nitrogen. Standard Schlenk technology was applied.

Reaction of chlorophosphine (4, 5 and 6) with Aluminum Chloride resulting 1, 2 and 3

These reactions were performed in dual compartment vessels, which were flame-dried before used. Typically, a mixture of equimolar quantities of respective chlorophosphine and $AlCl_3$ (ca. 3 mmol of each) in 20 ml of CH_2Cl_2 was stirred for 4 to 12 hrs at −20 °C. After granular $AlCl_3$ has disappeared, a transparent solution was formed with a little oil-like residue sticking on the wall. In the cases of **1** and **2**, the reaction solution is red. In the instances of **3**, they were nearly colorless. About 0.5 ml of each filtrate was measured on ^{31}P NMR at 80.984 MHz and ^{27}Al NMR at 52.115 MHz. After CH_2Cl_2 and other volatile components in filtrate were removed off under vacuum, the solutions of **1a**, **2a** and **3c** in CD_2Cl_2were examined on ^1H and ^{13}C NMR. For **1a**. δ^1H (ppm): 1.51 (t, 3H, 7Hz, CH_3), 2.97 (m, 2H, CH_2), 7.48–7.98 (m, 5H, Ph). For **2a**. δ^1H (ppm): 3.11 (m, 2H, SCH_2), 4.33 (m, 2H, NCH_2), 7.52–8.17 (m, 5H, Ph); $\delta^{13}C$: 39.27 (d, $^2J_{PSC}$=32 Hz), 64.78 (d, $^2J_{PNC}$=71 Hz), 122.5, 132.4, 138.99, 155.0 (Ph). For **3c**. δ^1H (ppm): 1.61 (t, 6H, 6.6Hz, 2Me), 1.74 (d, 6H, 6.8Hz, 2Me), 4.0 (m, 4h, $N(CH_2\text{-})_2$). $\delta^{13}C$: 15.65 (d, $^3J_{PSCC}$=10.8Hz), 25.28 (d, $^3J_{PNCC}$=6.2Hz), 44.25 (d, $^2J_{PSC}$=26.3 Hz), 46.05 (d, $^2J_{PNC}$=21.4 Hz), 52.65 (d, $^2J_{PNC}$=44.7 Hz). δ^{27} Al of **1a**: 103.70. δ^{27} Al of **1b**: 103.68. δ^{27} Al of **1c**: 103.79. δ^{27} Al of **1g**: 103.62. δ^{27} Al of **2a**: 103.38. δ^{27} Al of **3a**: 102.60. δ^{27} Al of **3b**: 102.36. δ^{27} Al of **3c**: 102.60. δ^{27} Al of **3g**: 102.55. δ^{27} Al of **3h**: 102.34. δ^{27}Al of **3i**: 102.79. Data of ^{31}P chemical shifts of **1**, **2** and **3** were shown in Table I.

Substituted 2-chloro-2,3–2(H)-1,3,4,2 -thiadiazaphospholes (4)

Were synthesized according to the reported procedure.[20]

2-Chloro-3-N-(p-substituted)phenyl-1,3,2-thiazaphospholanes (5)

To a stirring solution of β-(*p*-substituted)anilinoethanethiol (7, 10 mmol) and triethylamine (3 ml, 21.6 mmol) in benzene (15) and *n*-hexane (10 ml) is added dropwise a solution of PCl_3 (1 ml, 1 1 mmol) in *n*-hexane (15 ml) at room temperature during 30 min. The mixture is stirred continuously for 0.5 hr at rt and for 2.5 hrs at about 60 °C. Triethylamine hydrochloride is filtered off. The filtrate is evaporated and vacuum to remove the solvent. The residue is distilled under high vacuum. **5a**: colorless oil, 1.85 g (85.1%), bp 178 °C/0.1 mmHg. IR (film, cm^{-1}): 690, 755, 845, 920, 990, 1175, 1250, 1490,1585, 2950, 3050. δ^1H (ppm): 3.40 (m, 2H, SCH_2), 3.94 (m, 2H, NCH_2), 7.01~7.35 (m,5H, Ph). $\delta^{13}C$ (ppm): 33.37 (d, $^2J_{PSC}$=11.5 Hz), 54.63 (d, $^2J_{PNC}$=14. 1 Hz), 118.6, 123.0, 129.5, and 143.4 (Ph). **5b**: colorless oil, 2.05 g (88.6%), bp 164 °C/0.5 mmHg. IR (film, cm^{-1}): 810, 935, 1040, 1180, 1460, 1510,1610, 2950, 3030. δ^1H (ppm): 2.35 (s, 3H, Me), 3.40 (m, 2H, SCH_2), 3.73 (m, 2H, NCH_2), 7.25 (d, 2H, 7 Hz), 7.75 (d, 2H, 7 Hz). **5c**: colorless oil, 2.06 (83.4%), bp 190 °C/0.2 mmHg. δ^1H (ppm): 3.45 (m, 2H, SCH_2), 3.80 (s, 3H, MeO), 3.93 (m, 2H, NCH_2), 6.90 (d, 2H, 7.0 Hz), 7.15 (dd, 2H, 7.0 Hz, 2Hz). **5d**: colorless oil, 2.03 g (77.6%), bp 191 °C/0. 1 mmHg. δ^1H (ppm): 1.43 (t, 3H, 7.26 Hz Me), 3.45 (m, 2H, SCH_2), 3.86 (s, 3H, MeO), 3.93 (m, 2H, NCH_2), 4.05 (q, 2H, 7.26 Hz, OCH_2), 6.89 (d, 2H, 7.1 Hz), 7.17 (dd, 2H, 7.1 Hz, 2Hz). **5e**: colorless oil, 1.43 g (56.6%), bp 187 °C/0.2 mmHg. δ^1H (ppm): 3.65 (m, 2H, SCH_2), 3.96 (m, 2H, NCH_2), 7.09 (d, 2H, 7.16 Hz), 7.51 (dd, 2H, 7.16 Hz, 1.6 Hz). The data of ^{31}P chemical shifts were shown in Table I.

(Dialkylaminc)(alkylthio)chlorophosphines (6)

Stirred a mixture of R_2NPCl_2 (10 mmol), RSH (10.5 mmol) and triethylamine (11 mmol) in *n*-hexane (40 ml) at 0 °C to 20 °C for 1.5 hrs and at 70 °C for 2.5 Hrs. then treated with the same procedure as above to give pure product which all are colorless oil. The data of ^{31}P chemical shifts were listed in Table I. For **6a** (44%), bp 90 °C/1 mmHg. δ^1H (ppm): 1.19 (t, 7 Hz, 3H, Me), 1.38 (m, 6H, 2Me), 2.81 (m, 2H), 3.33 (m, 4H). IR (cm^{-1}):

671, 790, 945, 1020, 1140, 1205, 1258, 1380, 1455, 2950. For **6b** (50%), bp 140 °C/1.5 mmHg. δ^1H (ppm): 1.02 (t, 3H, 7.2 Hz, Me), 1.18 (t, 3h, 6.84 Hz, Me), 1.27 (t, 3H, 7.04 Hz, Me), 1.73 (m, 2H, CH_2), 2.80 (m, 2H, SCH_2), 3.30 (m, 2H, NCH_2).. IR (cm^{-1}): 668, 790, 940 (P-N), 1020, 1168,1204, 1290, 1380, 1460, 2950. For **6c** (44%), bp 110 °C/0.2 mmHg. δ^1H (ppm): 1.43 (t, 6H, 7.5Hz, Me), 1.16 (d, 6H, Me), 3.05 (m, 1H, SCH), 3.31 (m, 2H, NCH_2). $\delta^{13}C$: 14.72 (Me), 15.88 (Me), 38.07 (SCH), 44.4 (NCH_2). IR (cm^{-1}): 658, 790, 940, 1020, 1055, 1165, 1205, 1250, 1370, 1380, 1460, 1960. For **6d** (80%), bp 120 °C/0.05 mmHg. δ^1H (ppm): 0.89 (t, 6.8 Hz, Me), 1.17–1.45 (m, 6H, $3CH_2$), 1.70 (m, 2H, CH_2), 2.8 (m, 2H, SCH_2), 3.0 (m, 2H, NCH_2), 3.30 (m, 2H, NCH_2). IR (cm^{-1}): 658, 790, 940, 1020, 1168, 1205, 1380, 1460, 2950. For **6e** (32%), bp 140°C/0.01 mmHg. δ^1H (ppm): 0.88 (t, 6.6 Hz, Me), 1.17–1.47 (m, 10H, $5CH_2$), 1.70 (m, 2H, CH_2), 2.74 (m, 2H, SCH_2), 3.0 (m, 2H, NCH_2), 3.30 (m, 2H, NCH_2). IR (cm^{-1}): 658, 790, 940, 1020, 1165, 1203, 1284, 1380, 1460, 2950. For **6f** (36%), bp 168 °C/0.03 mmHg. δ^1H (ppm): 0.88 (t, 6.5 Hz, Me), 1.2–1.3 (br, 18H, $9CH_2$), 1.70 (m, 2H, CH_2), 2.70 (m, 2H, SCH_2), 3.0 (m, 2H, NCH_2), 3.30 (m, 2H, NCH_2). IR (cm^{-1}): 655, 789, 940, 1020, 1168, 1205, 1380, 1464, 2950. For **6g** (81%), bp 103 °C/2 mmHg. δ^1H (ppm): 1.30 (t, 7.0 Hz, Me), 1.35 (d, 6.9 Hz, 2Me), 2.90 (m, 2H, SCH_2), 3.40 (m, 1H, NCH), 3.90 (m, 1H, NCH). IR (cm^{-1}): 655, 665, 880, 960, 990, 1120, 1150, 1200, 1370, 1390. For **6h** (91.4%), bp 124 °C/4 mmHg. δ^1H (ppm): 1.01 (t, 7.2 Hz, Me), 1.32 (d, 6.4 Hz, Me), 1.49 (d, 6.5 Hz, Me), 1.80 (m, 2H, CH_2), 2.74 (m, 2H, SCH_2), 3.40 (m, 1H, NCH), 3.90 (m, 1H, NCH). IR (cm^{-1}): 630, 655, 785, 880, 960, 1020, 1120, 1150, 1170, 1200, 1376, 1392, 1460, 2980. For **6i** (85%), bp 108 °C/1.5 mmHg. δ^1H (ppm): 1.01 (d, 7. 1 Hz, Me), 1.31 (d, 6.2 Hz, Me), 1.42 (d, 7.0 Hz, Me), 3.15 (m, 1H, CH), 3.90 (m, 2H, 2CH). IR (cm^{-1}): 630, 650, 880, 975, 1020, 1050, 1120, 1154, 1170, 1200, 1240, 1378, 1385, 1390, 1460, 2980. For **6j** (74%), bp 124 °C/5 mmHg. δ^1H (ppm): 1.0 (t, 6.5 Hz, Me), 1.20 (d, 6.84 Hz, Me), 1.30 (d, 7.0 Hz, Me), 1.50 (m, 2H, CH_2), 2.95 (m, 1H, SCH), 3.90 (m, 2H, 2CH). IR (cm^{-1}): 630, 650, 730, 880, 975, 1025, 1125, 1154, 1170, 1200, 1378, 1385, 1390, 1450, 2980, For **6k** (67%), bp 154°C/2 mmHg. δ^1H (ppm): 0.89 (t, 6.4 Hz, Me), 1.10 (d, 7.0 Hz, Me), 1.21 (d, 7.0 Hz, Me), 1.3 (m, 6H, $3CH_2$), 1.70 (m, 2H, CH_2), 2.74 (m, 2H, SCH_2), 3.90 (m, 2H, 2CH). IR (cm^{-1}): 655, 665, 725, 880, 965, 1020, 1120, 1154, 1170, 1200, 1265, 1290, 1368, 1380, 1460, 2980. For **6l** (47.2%), bp 150 °C/0.02 mmHg. δ^1H (ppm): 0.88 (t, 6.7 Hz, Me), 1.10 (d, 6.70 Hz, Me), 1.21 (d, 6.40 Hz, Me), 1.1–1.4 (m, 10H, 5CH_2), 1.70 (m, 2H, CH_2), 2.70 (m, 2H, SCH_2), 3.0 (m, 2H, 2CH), 3.30 (m, 2H, NCH_2), IR (cm^{-1}): 630, 660, 770, 885, 970, 1030, 1120, 1160, 1200, 1250, 1370, 1395, 1460, 2950. For **6m** (31%), bp 190 °C/0.04 mmHg. δ^1H (ppm): 0.89 (t, 6.6 Hz, Me), 1.10 (d, 6.6 Hz, Me), 1.18 (d, 6.8 Hz, Me), 1.26–1.70 (br, 18H, 9CH_2), 1.70 (m, 2H, CH_2), 2.70 (m, 2H, SCH_2), 3.90 (m, 2H, 2CH). IR (cm^{-1}): 630, 660, 790, 855, 880, 970, 1030, 1120, 1160, 1200, 1280, 1370, 1395, 1460, 2950. For **6n** (49%), bp 139 °C/0.7 mmHg. δ^1H (ppm): 1.07 (t, 7 Hz, Me), 1.67 (m, CH_2), 1.92 (m, 3CH_2), 2.90 (m, SCH_2), 3.28 (m, 2CH_2). IR (cm^{-1}): 690, 775, 835, 855, 950, 1025, 1060, 1110, 1160, 1210, 1240, 1275, 1330, 1370, 1450, 2950. For **6o** (81%), bp 96°C/2 mmHg. δ^1H (ppm): 1.04 (t, 6.8 Hz, Me), 1.81 (m, CH_2), 2.80 (s, 2Me), 2.95 (m, CH_2). IR (cm^{-1}): 685, 785, 890, 960, 1030, 1060, 1170, 1240, 1270, 1380, 1455, 2950. For **6p** (77%), bp 152 °C/3 mmHg. δ^1H (ppm): 0.98 (t, 6.9 Hz, Me), 1.45 (m, CH_2), 1.60 (m, CH_2), 1.88 (m, CH_2), 2.99 (m, CH_2), 3.24 (m, 2CH_2). IR (cm^{-1}): 730, 785, 925, 990, 1030, 1090, 1160, 1240, 1295, 1345, 1380, 1460, 2950. For **6q** (73%), bp 144°C/2 mmHg. δ^1H (ppm): 0.93 (t, 7 Hz, Me), 1.10 (d, 7 Hz, 2Me), 1.88 (m, CH_2). 2.28 (m, CH), 2.83 (d, 6.6 Hz, CH_2), 2.99 (m, CH_2). IR (cm^{-1}): 640, 730, 770, 820, 880, 940, 960, 1020, 1100, 1160, 1195, 1240, 1275, 1320, 1370, 1390, 1460, 2950.

β-(p-substituted)anilinoethanethiol (7b-7e)

Taking similar method by Braz,[23] four new anilinoethanethiols were prepared. **7b**: colorless oil, 72%, bp 148–152 / 1 mmHg. IR (film, cm^{-1}) 810, 910, 1125, 1185, 1260, 1290, 1320, 1515, 1615, 2560 (S-H), 2950, 3030, 3400 (N-H). δ^1H (ppm): 2.22 (s, 3H, Me), 2.65 (t, 6.23 Hz, 2H, SCH_2), 3.22 (t, 6.26 Hz, 2H, NCH_2), 6.53 (d, 8.44 Hz, 2H), 6.95 (d, 8.44 Hz, 2H). **7c**: colorless oil, 11%, bp 180–182 / 1 mmHg. IR (film, cm^{-1}): 825, 1035, 1240, 1510, 1620, 2580 (S-H), 2950, 3030, 3350 (N-H). δ^1H (ppm): 2.67 (t, 6.45 Hz, 2H, SCH_2), 3.22 (t, 6.46 Hz, 2H, NCH_2), 3.69 (s, 3H, MeO), 6.59 (d, 7.84 Hz, 2H), 6.75 (d, 7.78 Hz, 2H). **7d**: colorless oil, 62.6%, bp 163 / 0.5 mmHg. IR (film, cm^{-1}): 825, 1035, 1240, 1510, 1620, 2580 (S-H), 2950, 3030, 3350 (N-H). **7e**: colorless oil, 19%, bp 183 / 1 mmHg. IR (film, cm^{-1}): 810, 1490, 1590, 2580 (S-H), 2950, 3030, 3400 (N-H).

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References

[1] S. Fleming, M. K. Lupton, K. Jekot, *Inorg. Chem.*, **11**, 2534 (1972).

[2] R. O. Hutchins, B. E. Maryanoff, *J. Org. Chem.*, **37**, 3475 (1972)

[3] A. H. Cowley, R. A. Kemp, *Chem. Rev.*, **85**, 367 (1985).

[4] M. Sanchez, M-R. Mazieres, L. Lamande and R.Wolf: *Phosphenium cation.* In *Multiple Bond and Low Coordination in phosphorus Chemistry;* edited by M. Regitz and O. J. Scherer, (Georg Thieme, Stuttgart, 1990), chapter **D. 1**, pp. 129–148.

[5] N. Burford, P. Losier, C. Macdonald, V. Kyrims, P. K. Bahshi, and T. S. Cameron, *Inorg. Chem.*, **33**, 1434 (1994).

[6] N. Burford, P. Losier, S. V. Sereda, and T. S. Cameron, *J. Am. Chem. Soc.*, **116**, 6474 (1994).

[7] R. W. Reed, Zuowei Xie, and C. A. Reed, *Organometallics*, **14**, 5002 (1995).

[8] W. Becker, D. Schomburg, P. G. Jones and R. Schmutzler, *Phos. Sulf. Silc.*, **49/50**, 109 (1990).

[9] J. P. Bezombes, F. Carre, C. Chuit, R. J. P. Corriu, A. Mehdi, and C. Reye, *J. of Organometallic Chemistry*, **535**, 81 (1997).

[10] V. A. Jones, M. Thornton-Pett and T. P. Kee, *Chem. Commun.*, 1317 (1997).

[11] A. H. Cowley, M. Lattman, and J. C. Wilburn, *Inorg. Chem.*, **20**, 2916 (1981).

[12] M. K. Denk, S. Gupta and R. Ramachandran, *Tetrahedron Letters*, **50**, 9025 (1996).

[13] J. Hogel, A. Schmidpeter, *Chem. Ber.*, **118**, 1621 (1985).

[14] N. Burford, A. I. Dipchand, B. W. Royan, and P. S. White, *Inorg. Chem.*, **29**, 4938 (1990).

[15] R. Reed, R. Reau, F. Dahan and G. Bertrand, *Angew. Chem. Int. Ed. Engl.*, **32**, 399 (1993).

[16] N. Burford, B. W. Royan, J. M. Whalen, J. F. Richardson, and R. Rogers, *Chem. Commun.*, 1273 (1990).

[17] T.-B. Huang, J.-L. Zhang, C.-G. Zhan, Y.-J. Zhang, *Science in China*, **36**, 641 (1993).

[18] T.-B. Huang, J.-L. Zhang, *Phos. Sulf. Silc.* **76**, 79 (1993).

[19] T.-B. Huang, J.-L. Zhang, X.-L. Xu, W.-F. Huang, *Zh. Obshch Khim*, **64**, 149 (1994).

[20] Tian-Bao Huang, Jing-Ling Zhang,, *Phos. Sulf. Silc.* **104**, 33 (1995).

[21] A. H. Cowley; M. C. Cushner; J. S. Szobota, *J. Am. Chem. Soc.*, **100**, 7784 (1978).

[22] T. H. Lowry, K. S. Richardson, *Mechanism and Theory in Organic Chemistry* (Harper & Row, New York, 1987), 3rd ed., chap. 2, pp. 152–154.

[23] G. I. Braz, Zh. Obshch. Khim. **21**, 688 (1951).

[24] N. Burford, P. Losier, P. K. Bakshi, and T. S. Cameron, *J. Chem. Soc., Dalton Trans.*, 201 (1993).

[25] H. Noth and H, J. Vetter, *Chem. Ber.*, **96**, 1109 (1963).