Heteroorganic betaines

1. Synthesis of betaines containing the $^+P—C—Si—S^-$ and $^+P—C—C—S^-$ fragments and their characterization by multinuclear NMR spectroscopy

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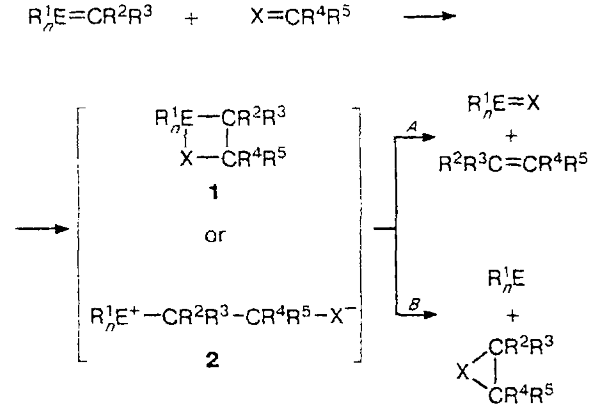
A method for the synthesis of a new class of betaines, *viz.*, $R^1{}_3P^+CR^2R^3SiR^4R^5S^-$, was developed. The experimental evidence for the intermediate formation of betaines $R^1{}_3P^+—CR^2R^3—CR^4R^5—S^-$ in the Wittig reaction for a series of thiocarbonyl compounds was obtained. A comparative analysis of the NMR spectra of betaines containing the $^+P—C—Si—S^-$ and $^+P—C—C—S^-$ fragments was performed.

Key words: Wittig and Corey—Chaykovsky reactions, organocyclosilathianes, phosphorus ylides, betaines, NMR spectroscopy.

The Wittig and Corey—Chaykovsky reactions (Scheme 1) are fundamental reactions in organic chemistry. The literature on different aspects of these reactions is quite voluminous.[1]

Scheme 1

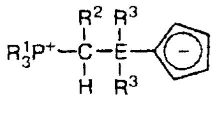


E = P, As, Sb, Bi, S, Se, Si;
X = C, O, S, Se, NR;
A is Wittig-type olefination;
B is Corey—Chaykovsky-type cyclization.

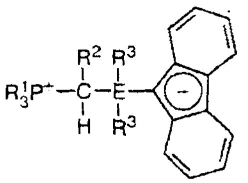
The structures of intermediates formed in these reactions are being studied intensively. Originally, it was suggested[2a] that these intermediates have zwitterionic structures 2 (X = O or S).[2b] This view gained broad acceptance and the term "betaine" was commonly used over many years in spite of the lack of evidence for the formation of these intermediates.[3a] The more recent demonstration of the oxaphosphetane nature of these intermediates and "the lack of evidence for uncomplexed betaines revolutionized impressions about the Wittig reaction mechanism for most organic chemists".[1a] Oxaphosphetanes and related compounds in which the phosphorus atom is replaced by the four-coordinate boron, sulfur, or selenium atom or by the five-coordinate silicon, germanium, or tin atom were independently prepared by Japanese researchers and were further converted into olefins or heterocyclopropanes.[4]

The results of quantum-chemical calculations demonstrated that both a synchronous mechanism of the Wittig reaction through phosphetanes **1** and a stepwise mechanism through intermediate betaines **2** followed by their conversions into phosphetanes are possible.[5] However, only adducts of betaines with LiX were experimentally detected.[6a] These adducts were formed as a result of decomposition of oxaphosphetanes under the action of lithium salts, which were present in the reaction mixture.[6b]

The first organophosphorus betaines **3** with carbanionic centers and their heteroorganic analogs **4—6** have been prepared by us in the reactions of fulvenes or transient sila- and germafulvenes with phosphorus ylides.[7]



3, 4



5, 6

E = C (**3**), Si (**4**, **5**), Ge (**6**)

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Scheme 2

$$n\,R^1_3P{=}CR^2R^3 + \underset{(n = 2,\ 3)}{(R^4R^5SiS)_n} \longrightarrow \underset{\textbf{7a—n}}{n\,R^1_3P^+{-}CR^2R^3{-}SiR^4R^5{-}S^-}$$

	a	b	c	d	e	f	g	h	i	j	k	l	m	n
R^1	Ph	Me	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Et	Et	Me_2N	Ph
R^2	Me	H	Me	Me	Me	Me	Me	H	H	H	H	H	Me	Me
R^3	Me	H	Me	Me	Me	Me	Me	Me	H	H	Me	Me	Me	Me
R^4	Me	Ph	Me	Me	Ph	H	H	Me	Me	Me	Me	Ph	Me	Me
R^5	Me	Ph	CH_2Ph	Ph	Ph	Ph	Et	Me	Me	Ph	Me	Ph	Me	OEt

It was postulated that betaines of this type were formed in a number of cyclopropanation reactions of polar olefins[1] or stable silaolefin[8] with phosphorus ylides.

The available data gave impetus to a search for procedures for the synthesis of heteroorganic betaines containing heteroanionic centers, *viz.*, analogs of the assumed intermediates of the Wittig and Corey—Chaykovsky reactions.

Taking into account the high strength of the Si—O bond and the growing interest in the Wittig reaction for a series of thiocarbonyl compounds,[9] we believed that studies of betaines of types **3—6** containing the thiolate center held promise. When studying the reactions of phosphorus ylides with [8-(dimethylamino)methyl-1-naphthyl]phenylsilanethione, which is stable under usual conditions,[10a] we have demonstrated that the above-mentioned betaines can, in principle, exist.*

In the present work, we developed a preparative procedure for the synthesis of betaines $R^1{}_3P^+CR^2R^3SiR^4R^5S^-$ (**7**) and obtained experimental evidence for the intermediate formation of betaines in the Wittig reaction (using thiocarbonyl compounds as examples). A comparative analysis of the NMR spectra of betaines **7** and their carbon analogs was performed. Selected results have been reported previously in preliminary communications.[10b—e]

Results and Discussion

Synthesis of heteroorganic betaines. We found that organocyclodisilathianes and trisilathianes, being formally silicon analogs of cyclooligomers of thiocarbonyl compounds, reacted with nonstabilized phosphorus ylides to form betaines **7a—n** (Scheme 2). Under the same conditions, the thioacetone cyclotrimer did not react even with such strong nucleophile as $Et_3P{=}CHMe$.

When stoichiometric quantities of organocyclosilathiane and phosphorus ylide were mixed in inert organic solvents, the specific color of the phosphorus ylide disappeared and crystalline betaine **7** precipitated. Ether is the best solvent for such reactions. The yields of betaines **7** were somewhat lower when benzene or THF were used as solvents. Betaines **7** are colorless or light-yellow crystalline compounds whose melting points or decomposition temperatures are higher than 80 °C. In the solid state, these compounds can be stored in the absence of atmospheric oxygen and moisture over a long period. These compounds are virtually insoluble in saturated hydrocarbons, slightly soluble in benzene and ether, moderately soluble in THF and MeCN, and more readily soluble in pyridine. The higher the nucleophilicity of the phosphorus ylides, the faster the reaction with organocyclosilathianes (see Scheme 2) and the greater the stability of the resulting betaines **7** in solutions. Trialkylalkylidene- and tris(dialkylamino)alkylidenephosphoranes are the most active compounds. Charge delocalization in the ylide fragment leads to a decrease in the reactivity. Semistabilized phosphorus ylides, for example, $Ph_3P{=}CHPh$, did not react with $(Me_2SiS)_3$ in the conditions under study.

The nature of the radicals at the silicon atom in cyclosilathianes affects substantially the course of the reaction under consideration due, apparently, to steric factors. This fact is exemplified by the reactions of $Ph_3P{=}CMe_2$ with different organocyclosilathianes. When a mixture of oligomers $(Me_2SiS)_n$ (n = 2 or 3) was used, the reaction was completed in several hours giving betaine **7a** in ~90% yield. In the case of $(Ph_2SiS)_n$ (n = 2 or 3), betaine **7e** was obtained in approximately 25% yield, whereas $(Pr^i{}_2SiS)_n$ (n = 2 or 3) did not react with the above-mentioned phosphorus ylide under the same conditions.

When the reagents were taken in a stoichiometric ratio, betaines **7** were always obtained as the final products of the reactions under consideration. Apparently, the reaction proceeds according to a stepwise mechanism as exemplified by the reaction of $Ph_3P{=}CHMe$ with $(Me_2SiS)_3$ (the reagent ratio was 3 : 2). The resulting betaine **8** is stable in the crystalline state, but it undergoes reversible disproportionation to betaine **7h** and $(Me_2SiS)_n$ in a pyridine solution (Scheme 3). The equilibrium concentration of betaine **8** in solutions was no more than 28%.

When studing the reaction of $(Me_2SiS)_n$ with $Ph_3P{=}CMe_2$ in the presence of LiBr, we demonstrated that the NMR spectral characteristics of the resulting compound in pyridine-d_5 are identical to those of betaine **7a**. Therefore, there is no need to use individual phosphorus ylides (under salt-free conditions) for the preparation of betaines **7**. These compounds can be generated *in situ* according to a standard procedure, which extends the possibilities of the further synthetic use of betaines **7** in preparative chemistry. As mentioned above, lithium salts change the nature of intermediates of the classical Wittig reaction in the series of carbonyl compounds.[1a,b]

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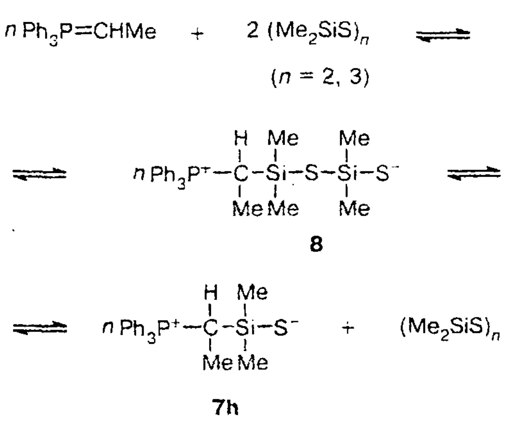
* Unlike the carbon analogs, most compounds with E=X multiple bonds (E = Si, Ge, or Sn; X = O, S, or NR) are kinetically unstable under usual temperature conditions.[11]

Scheme 3



NMR spectra of heteroorganic betaines. Betaines **7** contain five NMR-active nuclei four of which make it possible to use multinuclear NMR spectroscopy as the basic technique for the identification of these compounds in solutions. The NMR spectral parameters of the synthesized betaines are given in Tables 1—4.

The characteristics of these compounds agree closely with those of the parent phosphonium cations $R^1_3P^+CHR^2R^3$. The ^{31}P NMR signals of the betaines fall within the spectrum region characteristic of four-coordinate phosphorus,[12a,b] but these signals are slightly shifted downfield (by 3—8 ppm) relative to those for the parent phosphonium cations[12a—c] in the $R^1_3P^+CHR^2R^3Hal^-$ salts (see Tables 3 and 4).

The ^1H and ^{13}C NMR spectra of the betaines have an obvious resemblance to the spectra of the silylated

Table 1. ^1H and ^{29}Si NMR spectra of betaines $Ph_3P^+—CR^2R^3—SiR^4R^5—S^-$ (**7a,c—j,n**, **8**, and **11**) in pyridine-d_5

Compound	δ_H (J_{HP}/Hz; J_{HH}/Hz)						δ_{Si} (J_{SiP}/Hz)
	R^2R^3		Ph_3P^+, R^4R^5				
	CH_3CP^+	CH_nP^+	AlkSi		H—Si	PhP^+ and ArSi (or C)	
			CH_3	CH_2			
7c	1.76 d (20.7); 1.83 d (20.7)		0.10 s	δ_A 2.14, δ_B 2.42 (J_{AB} = 12.7)		6.98—8.47	13.6 (1.5)
7d	1.69 d (20.8); 1.72 d (20.8)		0.49 d (1.0)			7.18—8.34	8.0 (2.9)
7e	1.90 d (21.0)					7.27—8.53	1.3 (3.6)
7f	1.55 d (19.9); 1.80 d (19.9)				5.71 br.s	7.19—8.11	
7g	1.64 d (20.6); 1.87 d (20.6)		1.31 dt. (7.8, 3.3^a)	0.65—0.82 m	5.27 t (3.3^a)	7.56—8.20	9.5 (1.3)
7h	1.65 dd (21.1; 7.2)	3.17 dq (18.3; 7.2)	0.29 s; 0.34 s			7.55—8.24	6.7 (2.4)
7i		2.90 d (17.9)	0.44 s			8.08—8.19; 7.54—7.64; 7.64—7.73	0.2 (6.3)
7j		δ_A 2.85, δ_M 2.72 ($J_{AX} = J_{MX}$ = 17.5; J_{AM} = 14.5)	0.62 s			7.28—8.27	−4.3 (5.6)
7n	1.66 (20.5); 1.92 (20.5)		0.4 s; 1.06^b t (7.0)	δ_A 4.01^c m δ_B 3.86 m (J_{AB} = 10.3; J_{HH} = 7.0)		7.40—8.25	
8	~1.65 (19.6)^d	~3.10^d	−0.21 s; 0.57 s; 1.05 s; 1.07 s				16.1^e; 17.2 br ($\nu_{1/2}$ = 5.35 Hz)
11	1.63 m, br	2.26 m, br	2.73^f s			—^{f}	

[a] $^3J_{HSiCH}$. [b] $OCH_2C\underline{H}_3$.

[c] The complicated multiplet, the AB part of the ABX_3 spectrum of $OC\underline{H}_2CH_3$.

[d] The spin-spin coupling constants $^2J_{PH}$ and $^3J_{HH}$ and the signals in the aromatic region were not identified because they overlap with the signals of betaine **7h**. [e] SSiS.

[f] The second signal for the nonequivalent Me_2N groups and the signals in the aromatic region were not identified due to overlapping with the signals of decomposition products of betaine **11** and the low relative concentration of the latter.

Table 2. ^{13}C and ^{31}P NMR spectra of betaines $Ph_3P^+—CR^2R^3—SiR^4R^5—S^-$ (**7a,c—j,n**, **8**, and **11**) in pyridine-d_5

Compound	δ_C (J_{CP}/Hz)												δ_P
	Ph_3P^+				R^2R^3	P^+CSi	R^4R^5						
							AlkSi		ArSi (or C)				
	C_i	C_o	C_m	C_p			CH_3	CH_2	C_i	C_o	C_m	C_p	
7a	122.1 (80.4)	136.7 (9.1)	129.2 (11.7)	133.7 (2.4)	23.8 (2.7)	27.7 (22.9)	6.7 (1.9)						39.7
7c	122.1 (80.0)	136.8 (9.0)	129.2 (11.7)	133.9 (2.8)	23.6 (3.0); 24.0 (3.0)	28.7 (23.2)	3.5	32.0	143.4	127.8 or 130.0	130.0 or 127.8	123.7	38.8
7d	122.3 (80.1)	136.7 (8.9)	129.1 (11.5)	133.6 (2.5)	24.6 (2.5); 24.8 (2.5)	28.9 (21.7)	4.9 (2.0)		144.4 (3.8)	136.8	127.1	128.0	40.4
7e	122.0 (80.5)	136.6 (8.9)	128.9 (11.8)	133.5 (2.8)	26.1 (3.0)	30.9 (23.3)			142.1 (2.7)	137.6	127.2	128.1	40.4
7f	121.2 (80.7)	136.1 (8.9)	129.5 (11.8)	133.9 br	23.2 (2.1); 25.4 (2.1)	25.2 (22.9)			142.3 br	136.6	127.5	129.0	39.8
7g	121.3 (80.8)	136.0 (9.1)	129.6 (11.7)	134.1 (2.8)	23.5 (2.8); 24.1 (2.6)	24.7 (23.8)	9.7	11.0 (2.9)					39.2
7h	122.4 (84.3)	135.0 (9.5)	129.7 (11.9)	133.9 (2.8)	12.7 (4.4)	17.8 (32.1)	7.7 (3.1); 8.5 (3.1)						32.9
7i	123.6 (86.9)	134.5 (10.4)	129.8 (12.0)	134.1 (2.5)		15.2 (38.1)	10.3 (4.8)						26.7
7j	123.4 (87.7)	134.5 (10.8)	129.6 (12.6)	134.0 (2.6)		15.1 (39.5)	8.5 (3.6)		146.8 (6.2)	134.9	127.1	128.1	26.5
7n	122.3 (80.8)	136.2 (8.7)	129.3 (11.7)	133.7 (2.6)	23.9 (2.7); 25.1 (2.7)	26.7 (20.7)	6.37	18.7[a]; 57.7[b]					40.1
8	121.3 (83.9)	134.4 (9.9)	130.4 (12.2)	134.2 br	12.2 br	15.9 (23.4)	0.6; 6.2; 6.5 (2.4); 10.4 (3.7)						31.7
11[c]	119.5 (85.3)	134.4 (10.1)	130.5 (12.4)	—[d]	14.4 br	—[d]			—[d]	—[d]	110.8 br; 110.8 br	145.7; 148.4	27.3

[a] $OCH_2\underline{C}H_3$.

[b] $O\underline{C}H_2CH_3$.

[c] For $Ar_2\underline{C}$, δ 51.46 (br).

[d] Signals were not observed due to overlapping with signals of the final fragmentation products of betaine **11** and the relatively low concentration of the latter.

phosphonium cations $R^1{}_3P^+—CHR^2—SiR^3{}_3$ [13] and the parent phosphonium cations $R^1{}_3P^+—CHR^2R^3$.[12b—d] In all cases, the ^1H and ^{13}C resonance signals for the R^2 and R^3 substituents at the carbon atom of the betaine fragment $^+P—C—Si—S^-$ are observed at lower field (they are shifted downfield by 0.3—0.6 and 5.3—5.9 ppm, respectively) than the analogous signals for the substituents in the $R^1{}_3P^+—CHR^2R^3$ cation. The vicinal and geminal spin-spin coupling constants ($^3J_{PH}$ and $^2J_{PH}$) of all betaines **7** are higher by 0.5—2 and ~4—6 Hz, respectively, than those in the spectra of silylated phosphonium cations[13c,d] and siliconorganophosphorus betaines **4** and **5** containing the cyclopentadienylide or fluorenylide anionic centers.[7]

Betaines containing the thiolate center are characterized by a downfield shift (by 1—9.5 ppm) of the ^{13}C signal of the $^+P—C—Si—S^-$ fragment with respect to that of the parent phosphonium cation. The values of all

Table 3. ^{1}H and ^{29}Si NMR spectra of betaines $Alk_3P^+{-}CR^2R^3{-}SiR^4R^5{-}S^-$ (**7b,k—m**, and **10**) in pyridine-d_5

Compound	δ_H (J_{HP}/Hz; J_{HH}/Hz)						δ_{Si} ($J_{Si,P}$/Hz)
	Alk_3P^+		R^2R^3		R^4R^5		
	CH_3	CH_2	$CH_3{-}C{-}P^+$	$CH_n{-}P^+$	CH_3	ArSi (or C)	
7b	1.97 d (14.3)			2.09 d (17.6)		7.14—8.59	−9.6 (4.4)
7k	1.11 dt (18.1; 7.7)	2.67 m[a]	1.26 dd (18.6; 7.5)	1.54 dq (18.1; 7.5)	0.54 s; 0.58 s		4.4 (2.2)
7l	0.95 dt (17.3; 7.8)	2.42—2.51 m[a]	1.35 dd (18.3; 7.4)	2.32—2.51 m[b]		7.33—7.43; 8.40—8.43	−3.2 (1.0)
7m	2.79 d[c] (8.9)		1.40 d (19.5)		0.46 s		14.1 (1.8)
10	1.02 dt (16.8; 7.7)	2.43—2.67 m[a]	1.59 dd (19.2; 7.7)	2.20 dq (12.3; 7.7)	2.69 s[c]; 2.73 s[c]	6.70, 6.78 (both m, H_m); 8.34, 8.55 (both m, H_o)	

[a] The complex multiplet, the AB part of the $ABMX_3$ spectrum.

[b] The complex multiplet, the superposition of the AB part of the $ABMX_3$ spectrum and the A part of the A_3MX spectrum.

[c] Me_2N groups.

Table 4. ^{13}C and ^{31}P NMR spectra of betaines $Alk_3P^+{-}CR^2R^3{-}SiR^4R^5{-}S^-$ (**7b,k—m**, and **10**) in pyridine-d_5

Compound	δ_C (J_{CP}/Hz)									δ_P
	Alk_3P^+		P^+CSi	R^2R^3	R^4R^5					
	CH_3	CH_2			AlkSi	PhSi (or C)				
						C_i	C_o	C_m	C_p	
7b	11.8 (56.0)		14.2 (45.5)			144.9 (br)	135.3	127.7	128.4	26.1
7k	6.3 (5.2)	13.2 (49.4)	14.9 (35.9)	10.6 (5.1)	6.8; 8.7 (5.1)					43.7
7l	6.3 (5.3)	13.1 (48.8)	13.4 (35.1)	11.5 (5.3)		142.7 (5.1); 144.6 (1.6)	135.7 136.3	127.3 127.8	128.5 128.6	44.7
7m	39.4 (3.1)		30.2 (83.9)	24.1 (3.9)	8.2 (1.7)					74.1
10[a]	7.7 (5.4)	17.1 (51.6)	49.0[b] (67.6)	14.7 (3.9)	40.5[c] 40.7[c]	140.7 (13.0); 143.8 (br)	129.7 130.7	111.9 112.0	148.3 148.5	25.5

[a] For $Ar_2\underline{C}$, δ 57.14 (br).

[b] $P^+\underline{C}HMeCAr_2$.

[c] Me_2N groups.

direct couplings $^1J_{PC}$ decrease by Δ = 10—25 Hz, which characterizes a change in the degree of the *s* character of the central P—C bond. The Δ value correlates with the stability of the betaines in solutions, *viz.*, the higher this value in magnitude, the lower the stability of the betaine to decomposition.[14] Thermostable betaines containing either carbanionic (**3—6**)[7] or thiolate centers (**7b,k,l**) are characterized by close Δ values (8.7—10.7 and 9.6—12.9 Hz, respectively).

The ^{1}H and ^{13}C chemical shifts for the $R^1{}_3P^+$ fragment of the betaines are observed in the regions characteristic of phosphonium salts.[12b,c,e—g] The ^{13}C resonance signals are noticeably shifted downfield, *viz.*, by 1—2.5 ppm when R = Alk and by 2.6—3.8 (C_i) and 0.2—2.2 ppm (C_o) when R = Ph, the chemical shifts of the C_m and C_p atoms being observed at higher field (are shifted upfield by 1—2 and 1—1.5 ppm, respectively) than those in the spectra of the corresponding $Ph_3P^+CHR^2R^3$ cations.

Unlike betaines based on trialkyl(alkylidene)phosphoranes for which the $^1J_{PC}$ value for the Alk_3P^+ fragment increases by approximately 0.8—1.4 Hz, the $^1J_{PC}$ value for betaines containing the phenyl substituents at the phosphorus atom (Ph_3P^+) decreases by 1.8—2.5 Hz. Other spin-spin coupling constants ($^2J_{PC}$,

$^3J_{PC}$, and $^4J_{PC}$) have values typical of the corresponding phosphonium cations $R^1{}_3P^+—CHR^2R^3$.[12a,b,f,g]

The ^{29}Si resonance signals of the betaines (see Tables 1 and 2) are shifted upfield by 5—22 ppm compared to the signals of the initial organocyclosilathianes.[12d] The geminal spin-spin coupling constant $^2J_{SiP}$ has the typical value (1—6 Hz). Previously, we have observed[7] analogous constants for silicon-containing organophosphorus betaines **4** and **5**. The presence of this constant as well as of $^3J_{PCSiC}$ for the R^2 and R^3 substituents in the spectra of compounds **7** serves as a reliable criterion for the validity of their structures.

Betaines **7h,k,l** and **8** and betaines **7c,d,f,g,j,n** contain the chiral carbon and silicon atoms, respectively. This is manifested in the diastereotopic doubling of the ^{1}H and ^{13}C NMR signals for the R^4 and R^5 groups (in the first case) and for the R^2 and R^3 groups (in the second case).

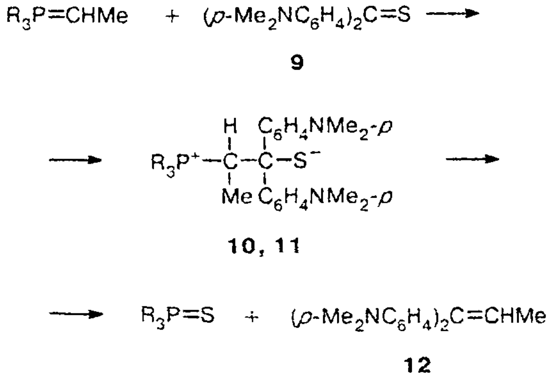
The CP-MAS ^{13}C and ^{31}P NMR spectra of solid betaine **7a** demonstrated an insignificant difference in the chemical shifts of ^{31}P and ^{13}C compared to that observed in solutions. The nonequivalence of all methyl groups in the CP-MAS ^{13}C NMR spectrum is attributed to the absence of free rotation around the P—C and C—Si bonds in the solid state. Apparently, betaine **7a** has identical structures in solutions and in the crystalline state.

The above-considered results make it possible to experimentally prove the general nature of silicon-containing organophosphorus betaines **7** and intermediates of the classical Wittig reaction for the series of thiocarbonyl compounds.

Studies by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy showed that the reactions of Michler thioketone **9** with $Et_3P=CHMe$ and $Ph_3P=CHMe$ afforded betaines **10** and **11**, respectively. Betaine **10** is rather stable in the solid state and in solutions at room temperature. When heated (125 °C), betaine **10** decomposed to form $Et_3P=S$ and 1,1-diarylpropene **12** (Scheme 4).

In solutions, Et_3P was identified along with $Et_3P=S$, which indicates that the Corey—Chaykovsky-type fragmentation of betaine **10** probably occurred, which was followed by desulfurization of intermediate thiirane. It is known that the reactions of phosphorus ylides with adamantanethione[15a] or thiopivalaldehyde[15b] afforded thiiranes as the major products.

Scheme 4



R = Et (**10**), Ph (**11**)

The NMR spectra of betaine **10** are characterized by the diastereotopism of the C and H atoms of two aromatic rings due to the presence of the chiral center in the molecule. Because of this, the ^{1}H NMR spectra have two singlets of the Me_2N groups and two AA'XX' patterns from the protons of the benzene rings (see Table 2). The ^{13}C NMR spectra have two signals for the *ipso*-carbon atoms of the aromatic rings at δ 140.66 and 143.78 (see Table 4). A pronounced splitting on the ^{31}P nucleus (13 Hz) is observed for the first signal, whereas the second signal is only slightly broadened because the corresponding spin-spin coupling constant with the ^{31}P nucleus is small. This region in the spectrum of organosilicon betaine $Et_3P^+—CHMe—SiPh_2—S^-$ (**7l**) is analogous to that described above. In this spectrum, the ^{13}C—^{31}P spin-spin splitting (5.1 Hz) is also observed only for one of the *ipso*-carbon atoms of the Ph rings. These data unambiguously confirmed the structure of compound **10**.

The reaction of Michler thioketone **9** with $Ph_3P=CHMe$ proceeded much more slowly, but the resulting betaine **11** rapidly decomposed to form 1,1-bis(4-*N,N*-dimethylaminophenyl)propene (**12**) and $Ph_3P=S$. According to the NMR spectral data (see Tables 1 and 3), the content of betaine **11** in the reaction mixture obtained within ~3 h after the preparation of a solution in pyridine-d$_5$ was 9.4%. Betaine **11** was completely converted into alkene **12** and $Ph_3P=S$ upon slight heating. Note that, unlike the silicon analogs (see above), betaine **11**, which is unstable in solutions, is characterized by a high negative Δ value.

More recently, similar results were obtained[16] in the study of the reaction of 4,4'-dimethoxythiobenzophenone with $Et_3P=CHMe$ by NMR spectroscopy. The spectral characteristics of the intermediate that formed are very similar to those reported above (in THF, δ_P 20.7, $^1J_{PC}$ = 70.8 Hz, and $^3J_{PC(ipso\text{-}Ar)}$ = 0 and 14.1 Hz). According to the data of X-ray diffraction analysis, this intermediate in the crystal adopts a *gauche* conformation analogous to that observed in silicon-containing organophosphorus betaines studied by us previously.[10c] It is suggested that this betaine exists as a superposition of the zwitterionic and thiaphosphetane structures.

To summarize, we developed a procedure for the synthesis of a new class of silicon-containing organophosphorus betaines and proved for the first time that their carbon analogs are formed as intermediates in the Wittig reactions for the series of thiocarbonyl compounds. We found criteria for the identification of these betaines in solutions by multinuclear NMR spectroscopy. The detailed X-ray diffraction analysis of silicon-containing organophosphorus betaines, the results of investigation of their chemical properties, studies of decomposition under different conditions resulting in the intermediate formation of compounds with the multiple Si=X bond (X = O, S, or NR) and three-membered thiasilaheterocycles, and the data on the synthesis, properties, and fragmentation of organogermanium-, organotinphosphorus-, and organoarsenicbetaines containing the thiolate centers will be published elsewhere.

Experimental

The ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra were recorded on a Bruker AM-360 instrument in C_6D_6, THF-d_8, and C_5D_5N. The chemical shifts in the ^{1}H and ^{13}C NMR spectra were measured in ppm relative to signals of the solvent and were converted to the δ scale using standard formulas. The chemical shifts in the ^{29}Si and ^{31}P NMR spectra were measured in ppm relative to Me_4Si and a 85% H_3PO_4 solution in D_2O, respectively, as the external standard. The accuracy of measurements of the ^{1}H, ^{13}C, ^{31}P, and ^{29}Si chemical shifts was ±0.01, ±0.05, ±0.1, and ±0.2 ppm, respectively. The accuracy of measurements of the spin-spin coupling constants (J_{HH}, J_{HP}, J_{CP}, J_{SiP}, J_{HSi}, and J_{CSi}) was ±0.1 Hz. The assignment of the signals in the ^{13}C NMR spectra was made with the use of the INEPT and DEPT procedures and off-resonance experiments. The NMR spectral parameters for betaines **7** are given in Tables 1—4. The ^{13}C and ^{31}P MAS-NMR spectra (rotation speed 2.7—3.4 kHz) with cross-polarization were recorded on a Bruker MSL-300 spectrometer at –20 °C (adamantane and a 85% H_3PO_4 solution in D_2O, respectively, as the external standards).

All operations were carried out under an atmosphere of dry oxygen-free argon using the standard Schlenk technique or in a dry box under an inert atmosphere. Some syntheses were carried out *in vacuo* (10^{-3} Torr) in seamless-soldered apparatus with the use of techniques of broken walls and tubes. The solvents THF, Et_2O, and C_6H_6 were distilled from Na or $LiAlH_4$, stored over sodium benzophenone ketyl, and distilled from the latter into reaction vessels immediately before use. Pyridine was distilled and stored over CaH_2. The hydrocarbon solvents were distilled from sodium or $LiAlH_4$. All solvent used in NMR spectroscopy were purified as described for the corresponding nondeuterated solvents. Organochlorosilanes of reagent grade purity were purchased from the Redkinskii pilot-production plant.

Elemental analysis was performed on an automated CHN-microanalyzer (Klinlaborpribor, Klin, Russian Federation). The melting points were determined in tubes sealed *in vacuo* without correction for a rising column.

Michler thioketone (**9**),[17] diisopropyldichlorosilane,[18] hexamethyldisilathiane,[19] mixtures of organocyclosilathianes $(R^4R^5SiS)_n$ (n = 2 or 3)[12d,20] (except for the compound with $R^4 = R^5 = Pr^i$, phosphonium salts[21]), and phosphorus ylides[12e,13c,22] were prepared according to procedures reported previously. The quantitative calculations were carried out in mmol per R^4R^5SiS monomer unit.

Isopropyl(hexamethyltriamido)phosphonium iodide was prepared according to a modified procedure[23] described for the synthesis of $(Me_2N)_3P^+EtBr^-$. A mixture of $(Me_2N)_3P$ (23.24 g, 142.5 mmol) and Pr^iI (30.2 g, 177.9 mmol) was refluxed for 24 h and kept at –20 °C. K for one month. Hexane (100 mL) was added to the resulting mixture and the precipitate was filtered off and dried *in vacuo*. The yield was 69.5%, m.p. >300 °C. Found (%): C, 32.63; H, 7.47; I, 38.47; N, 12.45. $C_9H_{25}IN_3P$. Calculated (%): C, 32.44; H, 7.56; I, 38.09; N, 12.61. ^{1}H NMR (C_5D_5N), δ: 1.12 (dd, 6 H, Me_2C-P^+, $^3J_{HP}$ = 18.2 Hz, $^3J_{HH}$ = 7.1 Hz); 2.71 (d, 18 H, Me_2N, $^3J_{HP}$ = 9.6 Hz); 3.66 (d.sept, 1 H, CHP^+, $^2J_{HP}$ = 9.7 Hz, $^3J_{HH}$ = 7.1 Hz). ^{13}C NMR (C_5D_5N), δ: 16.4 (d, Me_2C-P^+, $^2J_{CP}$ = 3.3 Hz); 24.7 (d, CHP^+, $^1J_{CP}$ = 101.9 Hz); 37.6 (d, Me_2N, $^2J_{CP}$ = 2.7 Hz). ^{31}P NMR (C_5D_5N), δ: 66.6.

Isopropylidene(hexamethyltriamido)phosphorane was prepared according to a modified procedure reported previously[23] for the synthesis of $(Me_2N)_3P{=}CHMe$. A 1.62 *N* solution of Bu^nLi (14.6 mL, 23.65 mmol) was added dropwise to a suspension of $(Me_2N)_3P^+(Pr^i)I^-$ (7.22 g, 21.67 mmol) in ether (150 mL) at a temperature from –60 to –56 °C. The reaction mixture was stirred for 4 h with a gradual increase in the temperature to –20 °C and kept overnight. The precipitate was filtered off. The solvent was removed from the filtrate *in vacuo* with the use of an oil pump and the residue was fractionated. The yield was 53.4%, b.p. 70—72 °C (0.1 Torr). Because of the high sensitivity of the compound under study with respect to atmospheric oxygen and moisture, elemental analysis was not carried out and the melting point was not determined. ^{1}H NMR (C_5D_5N), δ: 1.74 (br.d, 6 H, $P{=}CMe_2$, $^3J_{HP}$ = 15.3 Hz); 2.56 (d, 18 H, Me_2N, $^3J_{HP}$ = 8.7 Hz). ^{13}C NMR (C_5D_5N), δ: 11.7 (br.d, P=C, $^1J_{CP}$ = 217.8 Hz); 19.3 (br.d, $P{=}C\underline{Me_2}$, $^2J_{CP}$ = 16.3 Hz); 38.1 (d, Me_2N, $^2J_{CP}$ = 3.2 Hz). ^{31}P NMR (C_5D_5N), δ: 56.6.

A mixture of tetraisopropylcyclodi- and hexaisopropylcyclotrisilathiane was prepared by mixing hexamethyldisilathiane (5.23 g, 29.38 mmol) with diisopropyldichlorosilane (5.27 g, 28.48 mmol). The reaction mixture was kept at –20 °C for 45 days. Trimethylchlorosilane was distilled off at the temperature of the bath (180 °C) and the residue was fractionated *in vacuo*. The product was obtained in a yield of 2.6 g (72.5%), b.p. 114—115 °C (0.1 Torr). Found (%): C, 49.01; H, 9.73; S, 21.56. $(C_6H_{14}SSi)_n$. Calculated (%): C, 49.25; H, 9.64; S, 21.91.

Synthesis of heteroorganic betaines under an argon atmosphere (general procedure). 2,3-Dimethyl-3-triphenylphosphonio-2-silabutane-2-thiolate, $Ph_3P^+CMe_2SiMe_2S^-$ (7a). A dark-red solution of $Ph_3P{=}CMe_2$ (8.28 g, 27.24 mmol) in diethyl ether (70 mL) was added to a solution of $(Me_2SiS)_n$ (n = 2 or 3) (2.45 g, 27.21 mmol) in ether (15 mL). The reaction mixture was stirred at –20 °C for 1 h and kept overnight. The precipitate that formed was filtered off, washed with ether until the filtrate became colorless, and dried *in vacuo*. Compound **7a** was obtained in a yield of 9.8 g (91.4 %) as light-pink crystals. After additional purification by crystallization from MeOH or EtOH or by washing with a 50 : 1 pentane—acetone mixture, product **7a** was characterized by the m.p. 152—153 °C (with decomp.).

Analogously, betaine **7a** was prepared by mixing $Ph_3P{=}CMe_2$ (12.99 g, 42.73 mmol) with $(Me_2SiS)_n$ (3.75 g, 38.97 mmol) in THF (60 mL) (the yield was 12.68 g (77.2%)) or by mixing $Ph_3P{=}CMe_2$ (4.18 g, 13.75 mmol) with $(Me_2SiS)_n$ (1.24 g, 13.78 mmol) in benzene (65 mL) (the yield was 3.2 g (79.7%)). Found (%): C, 70.53; H, 6.96; S, 8.82. $C_{23}H_{27}PSSi$. Calculated (%): C, 70.01; H, 6.89; S, 8.13. ^{13}C CP-MAS NMR, δ: 5.6 and 6.4 (both s, Me_2Si); 23.1 and 25.8 (both s, $\underline{Me_2}C$); 27.6 (s, $Me_2\underline{C}$, $\nu_{1/2}$ = 40 Hz). ^{31}P CP-MAS NMR, δ: 39.6.

Synthesis of heteroorganic betaines *in vacuo* (general procedure). 1,1-Diphenyl-2-trimethylphosphonio-1-silaethane-1-thiolate, $Me_3P^+CH_2SiPh_2S^-$ (7b). $Me_3P{=}CH_2$ (0.11 g, 1.18 mmol) was added to a solution of $(Ph_2SiS)_n$ (0.25 g, 1.17 mmol) in THF-d_8 (3.5 mL), which was cooled with liquid nitrogen, by condensation *in vacuo*. When heated to –20 °C, the mixture turned blue for a short period and then turned dark-blue after which the solution rapidly turned greenish-yellow. The colorless precipitate that formed during 0.5 h was washed with the cold solvent by recondensing onto the precipitate. Then the precipitate was dissolved in pyridine-d_5 at –20 °C and transferred into a NMR tube. According to the ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra, the solution contained betaine **7b**; the yield was 70%.

2,3-Dimethyl-1-phenyl-3-triphenylphosphonio-2-silabutane-2-thiolate, $Ph_3P^+CMe_2SiMe(CH_2C_6H_5)S^-$ (7c), was prepared analogously to betaine **7a** by mixing $Ph_3P=CMe_2$ (2.44 g, 8.03 mmol) with $[MeSi(CH_2C_6H_5)S]_n$ (1.33 g, 8.01 mmol) in diethyl ether (50 mL). Compound **7c** was obtained in a yield of 1.52 g (40.2%) as light-yellow crystals, decomp. temp. 80—130 °C.

3-Methyl-2-phenyl-3-triphenylphosphonio-2-silabutane-2-thiolate, $Ph_3P^+CMe_2SiMe(Ph)S^-$ (7d), was prepared analogously to betaine **7a** by mixing $Ph_3P=CMe_2$ (9.33 g, 30.70 mmol) with $(MePhSiS)_n$ (4.71 g, 30.99 mmol) in ether (110 mL). Compound **7d** was obtained in a yield of 11.91 g (85.1%) as light-pink crystals, decomp. temp. 150—164 °C.

2-Methyl-1,1-diphenyl-2-triphenylphosphonio-1-silapropane-1-thiolate, $Ph_3P^+CMe_2SiPh_2S^-$ (7e), was prepared analogously to betaine **7a** by mixing $Ph_3P=CMe_2$ (3.36 g, 11.05 mmol) with $(Ph_2SiS)_n$ (2.34 g, 10.92 mmol) in ether (110 mL). Compound **7e** was obtained in a yield of 1.42 g (25.1%) as white crystals, decomp. temp. 140—150 °C.

2-Methyl-1-phenyl-2-triphenylphosphonio-1-silapropane-1-thiolate, $Ph_3P^+CMe_2SiPh(H)S^-$ (7f), was prepared analogously to betaine **7a** by mixing $Ph_3P=CMe_2$ (5.78 g, 19.01 mmol) with $[Ph(H)SiS]_n$ (2.70 g, 19.56 mmol) in diethyl ether (125 mL). Compound **7f** was obtained in a yield of 4.96 g (59%) as white crystals, decomp. temp. 145—150 °C.

1-Ethyl-2-methyl-2-triphenylphosphonio-1-silapropane-1-thiolate, $Ph_3P^+CMe_2SiEt(H)S^-$ (7g), was prepared analogously to betaine **7a** by mixing $Ph_3P=CMe_2$ (3.55 g, 11.68 mmol) with $[Et(H)SiS]_n$ (6.89 g, 20.67 mmol) in diethyl ether (55 mL). Compound **7g** was obtained in a yield of 4.64 g (100%) as colorless crystals, decomp. temp. 90—140 °C.

2-Methyl-3-triphenylphosphonio-2-silabutane-2-thiolate, $Ph_3P^+CHMeSiMe_2S^-$ (7h), was prepared analogously to betaine **7a** by mixing $Ph_3P=CHMe$ (7.04 g, 24.28 mmol) with $(Me_2SiS)_n$ (2.18 g, 24.21 mmol) in diethyl ether (130 mL). Compound **7h** was obtained in a yield of 6.64 g (72.0%) as yellow crystals, decomp. temp. 80—100 °C.

2-Methyl-1-triphenylphosphonio-2-silapropane-2-thiolate, $Ph_3P^+CH_2SiMe_2S^-$ (7i), was prepared analogously to betaine **7a** by mixing $Ph_3P=CH_2$ (7.63 g, 25.10 mmol) with $(Me_2SiS)_n$ (2.57 g, 28.56 mmol) in diethyl ether (130 mL). Compound **7i** was obtained in a yield of 6.81 g (74.1%) as white crystals, decomp. temp. 94—115 °C.

2-Phenyl-1-triphenylphosphonio-2-silapropane-2-thiolate, $Ph_3P^+CH_2SiMe(Ph)S^-$ (7j), was prepared by mixing $Ph_3P=CH_2$ (0.49 g, 2.07 mmol) with $(MePhSiS)_n$ (0.26 g, 1.71 mmol) in THF-d_8 (2 mL) as described above for betaine **7b**. According to the NMR spectra, the yield was 59%.

2-Methyl-3-triethylphosphonio-2-silabutane-2-thiolate, $Et_3P^+CHMeSiMe_2S^-$ (7k), was prepared analogously to betaine **7a** by mixing $Et_3P=CHMe$ (3.94 g, 26.99 mmol) with $(Me_2SiS)_n$ (2.45 g, 27.21 mmol) in diethyl ether (130 mL) or by mixing $Et_3P=CHMe$ (0.41 g, 2.81 mmol) with $(Me_2SiS)_n$ (0.26 g, 2.88 mmol) in THF (10 mL). Compound **7k** was obtained in yields of 5.83 g (91.5%) and 0.46 g (69.4%), respectively, m.p. 135—136 °C.

1,1-Diphenyl-2-triethylphosphonio-1-silapropane-1-thiolate, $Et_3P^-CHMeSiPh_2S^-$ (7l), was prepared analogously to betaine **7a** by mixing $Et_3P=CHMe$ (1.35 g, 9.25 mmol) with $(Ph_2SiS)_n$ (2.04 g, 9.54 mmol) in diethyl ether (100 mL). Compound **7l** was obtained in a yield of 2.83 g (81.4%) as a white solid, m.p. 139—140 °C.

2,3-Dimethyl-3-tris(dimethylamino)phosphonio-2-silabutane-2-thiolate, $(Me_2N)_3P^+CMe_2SiMe_2S^-$ (7m), was prepared analogously to betaine **7a** by mixing $(Me_2N)_3P=CMe_2$ (0.89 g, 4.2 mmol) with $(Me_2SiS)_n$ (0.35 g, 3.9 mmol) in diethyl ether (25 mL). Compound **7m** was obtained in a yield of 0.85 g (74.0%) as a white solid, m.p. 130—131 °C.

2-Ethoxy-3-methyl-3-triphenylphosphonio-2-silabutane-2-thiolate, $Ph_3P^+CMe_2SiMe(OEt)S^-$ (7n), was prepared analogously to betaine **7a** by mixing $Ph_3P=CMe_2$ (15.79 g, 51.9 mmol) with $[Me(EtO)SiS]_n$ (5.83 g, 48.6 mmol) in diethyl ether (110 mL). Compound **7n** was obtained in a yield of 1.72 g (56.9 %) as white crystals, decomp. temp. 130—150 °C.

2,4-Dimethyl-5-triphenylphosphonio-2,4-disila-3-thiahexane-2-thiolate, $Ph_3P^+CHMeSiMe_2SSiMe_2S^-$ (8), was prepared analogously to betaine **7a** by mixing $Ph_3P=CHMe$ (1.54 g, 5.31 mmol) with $(Me_2SiS)_n$ (0.96 g, 10.68 mmol) in diethyl ether (50 mL). Compound **8** was obtained in a yield of 2.17 g (87.0%) as white crystals, m.p. 100—100.2 °C (with decomp.).

Synthesis of betaine 7a in the presence of LiBr. A dark-red solution of $Ph_3P=CMe_2$, which was prepared from $[Ph_3P^+CHMe_2]Br^-$ (20 g, 51.95 mmol) and PhLi (51.5 mL of a 1.1 *N* solution in diethyl ether, 56.7 mmol), was added to a solution of $(Me_2SiS)_n$ (4.96 g, 18.37 mmol) in ether (150 mL), and the reaction mixture was kept at ~20 °C for ~48 h. The precipitate that formed was filtered off, washed with ether (2×100 mL), and dried at 20—50 °C *in vacuo* (10^{-3} Torr). A solid compound was obtained in a yield of 14.49 g. The data of elemental analysis for this compound correspond to the formula $2[Ph_3P^+CMe_2SiMe_2S^-] \cdot LiBr$. Found (%): C, 62.92; H, 6.32; S, 7.24; Br, 9.02. $C_{46}H_{54}BrLiP_2S_2Si_2$. Calculated (%): C, 63.07; H, 6.21; S, 7.32; Br, 9.12. The ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra of the compound are identical to those of betaine **7a**.

1,1-Bis(*p*-dimethylaminophenyl)-2-(triethylphosphonio)propane-1-thiolate (10) and 1,1-bis(*p*-dimethylaminophenyl)-2-(triphenylphosphonio)propane-1-thiolate (11). The reaction of Michler thioketone (9) with $Et_3P=CHMe$ and $Ph_3P=CHMe$. When a solution of compound **9** (0.52 g, 1.83 mmol) in THF (20 mL) was mixed with $Et_3P=CHMe$ (0.26 g, 1.83 mmol), its color changed from violet-red to red-green. After ~3 min, a finely crystalline red-brown precipitate formed. After ~30 min, the precipitate was filtered off and washed on a filter with THF. Then the solvent was removed. Pyridine-d_5 (1.2 mL) was condensed onto the light-yellowish precipitate and the resulting red-green solution was transferred into a NMR tube, which was sealed off. According to the ^1H, ^{13}C, and ^{31}P NMR spectra, the solution contained betaine **10** (68%) and products of its decomposition, *viz.*, $Et_3P=S$ (28%), Et_3P (4%), and alkene **12**. The NMR spectral parameters of betaine **10** are given in Tables 3 and 4. Thioketone 9. ^1H NMR (C_6D_6), δ: 2.44 (s, 12 H, Me_2N); 6.44 (m, 4 H_m); 8.22 (m, 4 H, H_o). ^{13}C NMR (C_6D_6), δ: 39.5 (Me_2N); 110.7 (C_m); 133.0 (C_o); 137.66 (C_i); 152.90 (C_p—N); 229.56 (C=S). Alkene 12. ^1H NMR (C_6D_6), δ: 1.85 (d, 3 H, $\underline{CH_3}CH=$, $^3J_{HH} = 7.0$ Hz); 2.77 and 2.81 (both s, 6 H each, Me_2N); 6.09 (q, 1 H, $CH_3\underline{CH}=$, $^3J_{HH} = 7.0$ Hz); 6.74 and 6.82 (both m, 2 H each, H_m); 7.22 and 7.38 (both m, 2 H each, H_o). ^{13}C NMR (C_6D_6), δ: 15.95 ($\underline{Me}CH=$); 40.3 and 40.3 (Me_2N); 112.6 and 112.65 (C_m); 119.6 (CH=); 128.7 and 131.3 (C_o); 128.8 and 132.8 (C_i); 143.0 (C=); 149.9 and 150.1 (C_p—N). According to the NMR spectra measured after heating of the solution (125 °C, 4 h), the mixture contained $Et_3P=S$ and alkene **12** (the quantitative yield).

The reaction of thioketone **9** with $Ph_3P=CHMe$ was carried out analogously. The characteristics of the NMR spectra of betaine **11** are given in Tables 1 and 2.

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