

# SYNTHESIS AND $^{29}\text{Si}$ -, $^{13}\text{C}$ -, AND $^{31}\text{P}$ -NMR SPECTRA OF ( $\omega$ -DIPHENYLPHOSPHINOALKYL)TRIMETHYLSILANES\*

Martin ČAPKA<sup>a</sup>, Jan SCHRAML<sup>a</sup> and Harold JANCKE<sup>b</sup>

<sup>a</sup>*Institute of Chemical Process Fundamentals,*

*Czechoslovak Academy of Sciences, 165 02 Prague-Suchdol and*

<sup>b</sup>*Central Institute of Physical Chemistry,*

*Academy of Sciences of GDR, 1199 Berlin-Adlershof, GDR*

Received February 2nd, 1978

Compounds of the type  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_m\text{P}(\text{C}_6\text{H}_5)_2$  with  $m = 1-4$  were prepared and their  $^{29}\text{Si}$ -,  $^{13}\text{C}$ -, and  $^{31}\text{P}$ -NMR spectra studied. The effects of the two terminal substituent groups on  $^{13}\text{C}$  chemical shifts of the methylene chain carbons are independent. The effect of the diphenylphosphino group on  $^{29}\text{Si}$  chemical shift and *vice versa* the effect of the trimethylsilyl group on  $^{31}\text{P}$  chemical shifts are smaller than the effects of the methylene chain length. What appears to be anomalous chemical shift in the compound with  $m = 2$  is in fact a general property of 1,2-disubstituted ethane derivatives. It is inferred from the spectra that the complexing power of the phosphino part of the molecule should not be adversely affected by the introduction of a silyl group into the alkylphosphine molecule.

Since the effects of substituents directly attached to the silicon atom were sufficiently documented (for reviews see<sup>1,2</sup>) we have undertaken an extensive programme of studying the effects of remote substituents on the silicon shielding. Under this programme we have investigated NMR spectra of the compounds of the type *I*



for the reasons discussed in detail earlier<sup>3-6</sup>. In brief, it has been hoped that multi-nuclear NMR studies of such compounds can elucidate both the factors contributing to the silicon shielding and some of the problems of the chemistry of these compounds, namely the question of  $\text{Si}\dots\text{Y}$  interactions. It has proved especially informative to study such compounds *I* that contain substituent groups *Y* which can be also studied by NMR techniques<sup>4,5</sup>. In the present paper, the results of such a study of compounds *I* with  $\text{Y} = \text{P}(\text{C}_6\text{H}_5)_2$  are presented.

Generally,  $\omega$ -(diphenylphosphino)alkyl substituted silanes are gaining technical importance since they are used for co-ordinative anchoring of transition metal

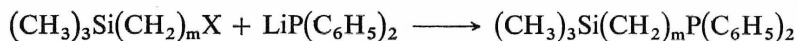
\* Part VI in the series NMR Study of Organosilicon Compounds; Part V: This Journal 42, 306 (1977).

complexes to inorganic supports. The heterogenized homogeneous catalysts obtained in this way have been proved to be very efficient catalysts for hydroformylation<sup>7</sup>, hydrogenation<sup>8</sup>, and hydrosilylation<sup>9</sup>. Since such anchoring agents bind to the inorganic support *via* the silicon atom while the phosphorus atom is entering the co-ordination sphere of a transition metal the knowledge of the electron distribution in these coupling agents is an essential prerequisite for catalyst tailoring.

## RESULTS AND DISCUSSION

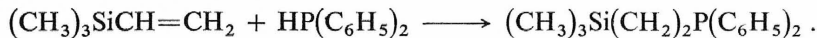
### *Methods of Preparation*

The silanes of the type *I* with  $n = 0$  and  $Y = P(C_6H_5)_2$  were, in the case of compounds with  $m = 1, 3$ , and  $4$ , prepared by the reaction analogous to that recently used<sup>10</sup> by us for the preparation of (3-triethoxysilylpropyl)diphenylphosphine, *i.e.* by the reaction



(where for  $m = 1$  and  $3$ ,  $X = Cl$  and for  $m = 4$ ,  $X = Br$ ). The advantage of this reaction is the relatively easy accessibility of both reactants. (The starting ( $\omega$ -halogenoalkyl)trimethylsilanes with  $m$  larger than  $2$  can be easily obtained by the hydrosilylation of  $\alpha$ ,  $\omega$ -halogenoalkenes by trichlorosilane followed by a methylation.) The reaction proceeds smoothly with high yields.

In the case of the compounds with  $m = 2$  the above reaction cannot be recommended because of  $\beta$ -elimination of halogenoethyl group<sup>11</sup>. Instead, it is more convenient to use radical hydrophosphination<sup>12</sup> of vinyltrimethylsilane:



The yields given in the Experimental are determined essentially by the available method of product isolation. According to GLC of the reaction mixture the desired products were obtained in almost quantitative yields.

### <sup>13</sup>C-NMR Spectra

*Assignment.* The aromatic carbon lines were assigned to different carbon atoms according to their spin-spin splitting due to the coupling with phosphorus nucleus using the assigned couplings in triphenylphosphine<sup>13</sup>. The methylene carbon lines could be assigned either according to their chemical shifts (decreasing  $\delta$ -values with increasing through-bond distances from the phosphorus atom) or according to their splitting by the <sup>31</sup>P-<sup>13</sup>C couplings (the spin-spin coupling constant decreasing with

the increasing distance). The two methods gave identical assignments in all cases except for (3-diphenylphosphinopropyl)trimethylsilane. Since several exceptions of the rule of increasing attenuation of the coupling constants by intermediate atoms were reported<sup>14</sup> the assignment based on the chemical shift was accepted here for the last mentioned compound. With this assignment the two-bond coupling  $^2J(\text{P-C})$  is larger than one-bond coupling  $^1J(\text{P-C})$  similarly as found by Mann<sup>15</sup> in several tertiary alkyl phosphines.

*Aromatic carbon chemical shifts and coupling constants.* As it is apparent from Table I these NMR parameters are almost independent of the alkyl chain length. The observed chemical shifts and coupling constants are remarkably close to the values reported for other alkylphenylphosphines<sup>15</sup> and some (dialkylphosphinoethyl)-diphenylphosphines<sup>18</sup>.

Since these parameters are related to the electron density<sup>19</sup> the above observations mean that the electron density distribution in the aromatic ring is not affected by the substitution of methyldiphenylphosphine with  $(\text{CH}_2)_{m-1}\text{Si}(\text{CH}_3)_3$  groups. Such behaviour is in agreement with the small differences between electronegativity values of all the involved (C, H, Si, and P) atoms<sup>20</sup> and with the length of the chain transmitting the substituent effect. Also, along the arguments put forward by Mann<sup>15</sup> the chemical shifts indicate negligible phosphorus-carbon  $\pi$ -bonding in the (trimethylsilyl)alkyl substituted diphenylphosphines similarly as in other tertiary phosphines<sup>15</sup> and the one-bond  $^1J(\text{C-P})$  coupling constants can be interpreted as indicating the same C-P-C angle as in  $\text{P}(\text{C}_6\text{H}_5)_3$  (*i.e.*  $102.1-103.6^\circ$  as found by Dally<sup>21</sup>).

*Methyl carbon chemical shifts.* The data in Table I show regular increase in the methyl carbon shielding with the  $\text{P}(\text{C}_6\text{H}_5)_2$  group getting closer to the  $\text{Si}(\text{CH}_3)_3$  group except when the two groups get so close as in the compound with  $m = 1$ . Comparison of the studied compounds with the compounds of the type *I* having  $\text{Y} = \text{H}^{16}$  shows that the chemical shifts are almost the same in the corresponding compounds with  $m = 1, 3,$  and  $4$ , but the shielding is by about  $1.6$  ppm larger in trimethylethylsilane than in (2-diphenylphosphinoethyl)trimethylsilane. As the observed chemical shifts reflect a combination of electronic and steric effects, the similarity of the chemical shifts in the compounds with  $m = 1, 3,$  and  $4$  can be taken as indicating that the polar effects of  $\text{P}(\text{C}_6\text{H}_5)_2$  group and hydrogen atom are very similar. The high field shift in trimethylethylsilane is almost certainly due to the steric  $\gamma$ -effect of the  $\gamma$  methyl group. The substitution of one hydrogen atom of this methyl group with the diphenylphosphino group removes the steric effect similarly as does the substitution with an alkyl group in higher alkyltrimethylsilanes.

*Methylene carbon chemical shifts and coupling constants.* In other derivatives of the type *I* the  $^{13}\text{C}$  chemical shifts correlate well with the total charges  $Q_{\text{C}}$  on the

carbon atom as calculated by the Del Re method<sup>4,5</sup>. The shifts determined in the present paper follow the dependence described earlier<sup>4,5</sup> but appreciable deviations occur for the carbon atoms attached directly to the phosphorus atom.

Using the data on <sup>13</sup>C chemical shifts in alkyltrimethylsilanes<sup>16</sup> the following values of substituent effects of P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> group can be derived from the present results for α, β, γ, and δ carbons 15, 3, -1, and 0 ppm, resp. The α and β values are in agreement with those (15 and 4 ppm, resp.) which can be derived from the results of Mann<sup>15</sup> and the shifts in alkanes<sup>22</sup>. On the other hand comparison with the shifts in alkyl-diphenylphosphines<sup>15</sup> leads to α and β substituent effects of the trimethylsilyl group (1.7 and 0.1 ppm) which are similar to the values found in alkyltrimethylsilanes<sup>16</sup>. Therefore, the two substituents of the methylene chain, the trimethylsilyl and diphenylphosphino groups, appear to exercise their effects independently.

### <sup>31</sup>P-NMR Spectra

As it is obvious from Table I, the chemical shift does not vary monotonously with *m*. While the shifts in the compounds with *m* = 1, 3, and 4 suggest increasing shielding with decreasing *m* value, the shielding in the ethane derivative is the lowest in the studied compounds (similarly as is the silicon-29 shielding). Such a trend is reminiscent of the trends well known for <sup>13</sup>C chemical shifts in alkanes<sup>22</sup> and <sup>31</sup>P chemical shifts in alkyl-diphenylphosphines<sup>15,17</sup> and found recently<sup>4</sup> also in <sup>14</sup>N chemical shifts in aminoalkylsilanes. Indeed, the chemical shifts in (CH<sub>3</sub>)<sub>3</sub>Si(CH<sub>2</sub>)<sub>*m*</sub> · P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> compounds correlate linearly with the shifts in H(CH<sub>2</sub>)<sub>*m*</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> compounds<sup>17</sup> of the same *m* as illustrated in Fig. 1. Obviously, the ω-trimethylsilyl

TABLE I  
<sup>13</sup>C, <sup>29</sup>Si, and <sup>31</sup>P Chemical Shifts δ and <sup>31</sup>P Coupling Constants *J*<sup>a</sup>

Group <i>m</i>	CH <sub>3</sub>		SiCH <sub>2</sub>		(SiC)CH <sub>2</sub>		CH <sub>2</sub> (CP)		CH <sub>2</sub> P			
	<i>J</i>	δ	<i>J</i>	δ	<i>J</i>	δ	<i>J</i>	δ	<i>J</i>	δ	<i>J</i>	δ(C <sub>3</sub> )
	<sup>13</sup> C-NMR <sup>b</sup>											
1	3.7	-0.2	29.3	14.5							14.6	141.0
2	0	-1.9	11.0	12.0	14.6	21.6					14.6	138.9
3	0	-1.7	11.0	18.4	17.1	20.3	13.5	32.1			14.6	139.0
4	0	-1.6	0	16.3	12.2	25.5	12.2	27.8	15.9	29.6	13.4	139.1

<sup>a</sup> Absolute values of coupling constants in Hz, <sup>13</sup>C and <sup>29</sup>Si chemical shifts in δ scale. <sup>b</sup> Estimated errors: coupling constants ±1 Hz, chemical shifts ±0.05 ppm. <sup>c</sup> Estimated errors: coupling constants ±0.4 Hz, chemical shifts ±0.02 ppm. <sup>d</sup> Chemical shifts relative to external H<sub>3</sub>PO<sub>4</sub>, paramagnetic shifts positive, estimated error ±0.05 ppm. <sup>e</sup> Substituent (P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>) chemical

substitution of the alkyl group attached to the phosphorus atom has little effect on the pattern of the shift dependence. Hence the interpretation of the  $^{31}\text{P}$  chemical shift trend in the studied compounds can be carried in two steps: interpretation of the trend found in alkyldiphenyl phosphines and interpretation of the substituent effect of the omega trimethylsilyl group on the phosphorus shielding.

In the attempts to interpret the trend in the shielding in alkylphosphines both McFarlane with coworkers<sup>17</sup> and Mann<sup>15</sup> considered the effects of substituent electronegativity, bond angles and phosphorus-carbon  $\pi$ -bonding<sup>15</sup> or hyperconjugation<sup>17</sup>. According to the earlier work<sup>17</sup> the observed trend is an outcome of two effects: inductive effect of the methyl group (an upfield shift) and hyperconjugation of the  $\alpha$  protons (the loss of which by a substitution with a methyl group leads to a downfield shift). Mann<sup>15</sup>, however, concluded on the basis of Letcher-Van Wazer theory<sup>23</sup> that the shifts are dominated by bond-angle changes and on the basis of the relationship shown in Fig. 2 claimed the same for  $^{13}\text{C}$  NMR shifts. Since such effects in  $^{13}\text{C}$  chemical shifts are now generally accepted to be due to steric effects<sup>22</sup> (the mechanism of which remains not clear), the relationship in Fig. 2 means that the  $^{31}\text{P}$  shifts are also affected by steric effects. Similar suggestion that  $^{31}\text{P}$  shielding by  $\gamma$ -carbons is of steric origin was put forward earlier by Quin and Breen<sup>25</sup>. Since electronegativity, steric bulkiness, and bond angles are closely interrelated, it is not possible to discard any of these interpretations by a simple argument and all of them are applicable to the compounds studied here (though some assumptions, not verifiable at present, are required).

TABLE I  
(Continued)

$\text{C}_6\text{H}_5$									
$J$	$\delta(\text{C}_{ortho})$	$J$	$\delta(\text{C}_{meta})$	$\delta(\text{C}_{para})$	$J$	$\delta$	SCS <sup>e</sup>	$\delta$	SCS <sup>f</sup>
						$^{29}\text{Si-NMR}^c$	$^{31}\text{P-NMR}^d$		
19.5	132.2	4.9	127.9	128.0	15.03	1.31	1.31	-30.7	-4
18.3	132.5	6.1	128.1	128.1	20.89	2.54	0.9	-18.6	-6
18.3	132.4	7.3	128.0	128.0	0	1.13	0.4	-26.1	-9
18.3	132.5	6.1	128.1	128.1	0	1.46	0.9	-24.9	-9

shift  $\text{SCS} = \delta(\text{Si}(\text{CH}_2)_m\text{P}(\text{C}_6\text{H}_5)_2) - \delta(\text{Si}(\text{CH}_2)_m\text{H})$  data for trimethylalkylsilanes taken from ref.<sup>16</sup>, error  $\pm 0.3$  ppm. <sup>f</sup> Substituent  $((\text{CH}_3)_3\text{Si})$  chemical shift  $\text{SCS} = \delta(\text{Si}(\text{CH}_2)_m\text{P}(\text{C}_6\text{H}_5)_2) - \delta(\text{H}(\text{CH}_2)_m\text{P}(\text{C}_6\text{H}_5)_2)$ , data for alkyldiphenylphosphines taken from ref.<sup>17</sup>.

Though some (constant) part of the negative trimethylsilyl group SCS values of  $^{31}\text{P}$  might be due to different experimental conditions used here and in refs<sup>16,17</sup> the trend in these values is hard to understand. These SCS can be seen in Fig. 2 as the horizontal deviations (dashed lines) of our experimental points from the corresponding points in Mann's plot<sup>15</sup>. The  $^{31}\text{P}$  chemical shifts are known to be insensitive to substitution beyond  $\gamma$  position<sup>15,17</sup> and yet the largest SCS values are found for  $\delta$  and  $\varepsilon$  trimethylsilyl groups.

If the chemical shifts can be interpreted straightforwardly in the terms of electron density, then the  $^{31}\text{P}$  NMR results indicate that the introduction of the trimethylsilyl group into the molecule of alkyldiphenylphosphine changes the electron density on the phosphorus atom less than the carbon chain length does. The change is to a higher electron density.

### $^{29}\text{Si}$ -NMR Spectra

The silicon chemical shift varies only little in the series of the studied compounds and as the SCS values (Table I) indicate, the effect of the diphenylphosphino group is small. Actually, the SCS values of  $^{29}\text{Si}$  were found so small also in other trimethyl-

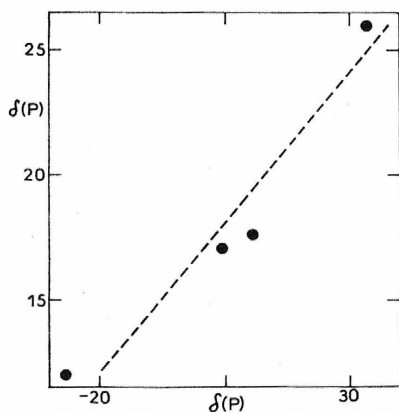


FIG. 1

A Plot of the  $^{31}\text{P}$  Chemical Shifts  $\delta(\text{P})$  in  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_m\text{P}(\text{C}_6\text{H}_5)_2$  (y-axis) Against that in  $\text{H}(\text{CH}_2)_m\text{P}(\text{C}_6\text{H}_5)_2$  (x-axis)

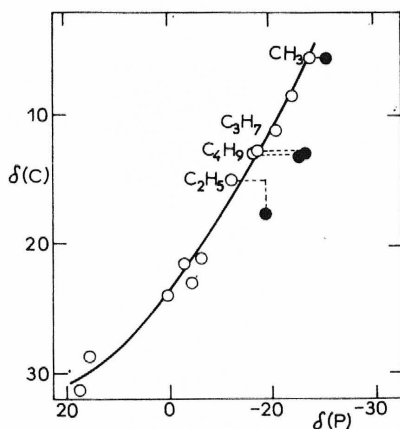


FIG. 2

A Plot of the  $^{13}\text{C}$  Chemical Shift  $\delta(\text{C})$  in  $\text{R}^{13}\text{CH}_3$  Against the  $^{31}\text{P}$  Chemical Shift  $\delta(\text{P})$  in  $\text{RP}(\text{C}_6\text{H}_5)_2$

Open circles adopted from Mann's plot<sup>15</sup> using more recent data<sup>22,24</sup>. Solid circles based on the present results and the data of ref.<sup>16</sup>.

silyl derivatives<sup>2,3-6</sup>. They become, however, larger if the methyl groups on the silicon atom are substituted by oxygenous groups or halogens. Since in the region of small silicon chemical shifts an increased charge causes a diamagnetic shift, the positive SCS values might be taken as an indication of decreased electronic charge on the silicon atom. But the effects are rather small and other factors (*e.g.* steric effects) might also contribute. It is interesting to note that the phosphorus – silicon coupling constant over three bonds (compound with  $m = 2$ ) is larger than that over two bonds ( $m = 1$ ) which is similar to the above discussed case of phosphorus–carbon couplings in the compound with  $m = 3$ .

### Structural Conclusions

The above discussion has shown that the effects of both trimethylsilyl and diphenylphosphino groups on <sup>13</sup>C chemical shifts are independent and about the same as they are in alkylsilanes or alkylphosphines, resp. The mutual influences of one group upon the other are small, the two groups in  $\alpha$ ,  $\omega$ -disubstituted alkanes retain their properties; only the electron density on the phosphorus atom might be slightly increased by the presence of the trimethylsilyl group in ( $\omega$ -diphenylphosphinoalkyl)trimethylsilanes relatively to that in alkyl-diphenylphosphines.

Since the introduction of a silyl group into the molecule of alkylphosphine is necessary in order to provide a binding site for the heterogenization of the homogeneous catalyst, the present results indicate that such groups should not have an adverse effect on the catalytic activity. Indeed, the increased electron density on the phosphorus atom should lead to its higher complexing power and thus perhaps to enhance the catalytic activity. If this NMR based prognosis is verified by catalytic experiments, the NMR technique would prove itself useful for catalyst tailoring. Besides these catalytic experiments it is also necessary to study the spectra of the coupling agents containing other silyl groups than the trimethylsilyl one. Such studies as well as the studies of mobility by relaxation measurements are in progress in our laboratories.

## EXPERIMENTAL

### Chemicals

Chloromethyltrichlorosilane and vinyltrichlorosilane were commercial products (Synthesia, Kolín). Chloromethyltrimethylsilane<sup>27</sup>, vinyltrimethylsilane<sup>28</sup>, (3-chloropropyl)trichlorosilane<sup>29</sup>, (3-chloropropyl)trimethylsilane<sup>27</sup>, and diphenylphosphine<sup>30</sup> were prepared by the reported procedures as indicated.

(4-Bromobutyl)trichlorosilane was prepared by the hydrosilylation of 46.2 g (0.34 mol) of 4-bromo-1-butene by 71.1 g (0.525 mol) of trichlorosilane in the presence of 7 ml of 0.01M solution of chloroplatinic acid in tetrahydrofuran. The reaction mixture was refluxed for 7 hours. The subsequent vacuum rectification afforded 77.5 g (84%) of (4-bromobutyl)trichlorosilane

boiling at 89°C/20 Torr. For C<sub>4</sub>H<sub>8</sub>BrSi (270.6) calculated: 17.79% C, 2.98% H; found: 18.01% C 3.11% H.

(4-Bromobutyl)trimethylsilane. Solution of methylmagnesiumbromide (90 ml) 1.1<sub>M</sub> solution in diethyl ether was added dropwise to 100 ml of diethyl ether solution of 7.5 g (0.028 mol) of (4-bromobutyl)trichlorosilane while stirring. After one hour reflux, the reaction mixture was poured onto ice acidified with hydrochloric acid. The water layer was separated and washed twice by the ether. The organic portions were washed with 5% NaHCO<sub>3</sub> and twice with water, then dried with sodium sulphate and rectified. (4-Bromobutyl)trimethylsilane was obtained in 76% yield (4.4 g); b.p. 80°C/20 Torr,  $n_D^{20}$  1.4547 (lit.<sup>31</sup> b.p. 85°C/26 Torr and  $n_D^{20}$  1.4551).

(2-Diphenylphosphinoethyl)trimethylsilane was prepared according to Niebergall<sup>12</sup>. Vinyltrimethylsilane (7.5 g, 0.075 mol) and diphenylphosphine (10 g, 0.54 mol) were irradiated for 30 hours with mercury discharge tube (250 W). Vacuum distillation gave the product with properties recorded in Table II.

General procedure for preparation of the silanes of the type I with Y = P(C<sub>6</sub>H<sub>5</sub>)<sub>a</sub> and m = 1, 3, and 4. A solution of 50 mmol of ω-halogenoalkyltrimethylsilane in 50 ml of dry tetrahydrofuran was stirred while 45 ml of 1M lithium diphenylphosphide (prepared by the reaction of chlorodiphenylphosphine with lithium metal) solution in tetrahydrofuran was added dropwise. The reaction mixture was kept boiling for two additional hours. After cooling, tetrahydrofuran was distilled off and the product was separated from the starting halogenoalkyltrimethylsilane by fractional distillation. The yields and physical properties of the products are presented in Table II. All the experiments with phosphinosubstituted alkyltrimethylsilane were carried under dry argon atmosphere<sup>34</sup>.

### Spectra

NMR spectra (<sup>29</sup>Si and <sup>13</sup>C) were recorded as described earlier<sup>5</sup>. <sup>31</sup>P-NMR spectra were measured on the same spectrometer at the frequency of 40.5 MHz. The spectra were referenced to the line of external 85% H<sub>3</sub>PO<sub>4</sub>.

TABLE II

Yields and Properties of Phosphinated Silanes of the Type (CH<sub>3</sub>)<sub>3</sub>Si(CH<sub>2</sub>)<sub>m</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>

m	Formula (m.wt.)	Calculated/Found		Yield %	$n_D^{20}$	B.p. °C/Torr
		% C	% H			
1	SiC <sub>16</sub> H <sub>21</sub> P (272.4)	70.54	7.77	61	1.5773 <sup>a</sup>	100/0.1 <sup>a,b</sup>
		70.29	7.75			
2	SiCl <sub>17</sub> H <sub>23</sub> P (286.6)	71.24	8.09	62	1.5732	110/0.1
		71.37	8.08			
3	SiC <sub>18</sub> H <sub>25</sub> P (300.7)	71.89	8.38	54	1.5648	127/0.1
		71.59	8.55			
4	SiC <sub>19</sub> H <sub>27</sub> P (314.7)	72.51	8.65	57	1.5611	160/0.5
		72.63	8.67			

<sup>a</sup> Ref.<sup>32</sup>:  $n_D^{20}$  1.5810, b.p. 124–125°C/1.5 Torr; <sup>b</sup> ref.<sup>33</sup>: b.p. 110°C/0.3 Torr.



## REFERENCES

1. Wells P. R. in the book: *Determination of Organic Structure by Physical Methods* (F. C. Nachod, J. J. Zuckerman, Eds), Vol. 4, p. 233. Academic Press, New York 1971.
2. Schraml J., Bellama J. M. in the book: *Determination of Organic Structures by Physical Methods* (F. C. Nachod, J. J. Zuckerman, E. W. Randall, Eds), Vol. 6, p. 203. Academic Press, New York 1976.
3. Nguyen-Duc-Chuy, Chvalovský V., Schraml J., Mägi M., Lippmaa E.: This Journal 40, 875 (1975).
4. Schraml J., Nguyen-Duc-Chuy, Chvalovský V., Mägi M., Lippmaa E.: Org. Magn. Resonance 7, 379 (1975).
5. Schraml J., Včelák J., Engelhardt G., Chvalovský V.: This Journal 41, 3758 (1976).
6. Schraml J., Chvalovský V., Mägi M., Lippmaa E.: This Journal 42, 306 (1977).
7. Allum K. G., Hancock R. D., Howell I. V., Pitkethly R. C., Robinson P. J.: J. Catal. 43, 322 (1976).
8. Kochloeff K., Liebelt W. W., Knözinger H.: J. Chem. Soc. Chem. Commun. 1977, 510.
9. Čapka M., Hetflejš J.: This Journal 39, 154 (1974).
10. Čapka M.: Syn. Inorg. Metal-Org. Chem. 7, 347 (1977).
11. Venc J., Hetflejš J., Čermák J., Chvalovský V.: This Journal 38, 1256 (1973).
12. Niebergall H.: Makromol. Chem. 52, 218 (1962).
13. Weigert F. J., Roberts J. D.: J. Amer. Chem. Soc. 91, 4940 (1969).
14. Van Wazer J. R. in the book: *Determination of Organic Structures by Physical Methods* (F. C. Nachod, J. J. Zuckerman, Eds), Vol. 4, p. 323. Academic Press, New York 1971.
15. Mann B. E.: J. Chem. Soc., Perkin Trans. 2 1972, 30.
16. Mägi M., Lippmaa E., Chvalovský V., Schraml J.: This Journal, in press.
17. Grim S. O., McFarlane W., Davidoff E. F.: J. Org. Chem. 32, 781 (1967).
18. King R. B., Cloyd jr J. C.: J. Chem. Soc., Perkin Trans. 2 1975, 938.
19. Nelson G. L., Williams E. A. in the book: *Progress in Physical Organic Chemistry* (R. W. Taft, Ed.) Vol. 12, p. 229. Wiley, New York 1976.
20. Bacanov S. S.: *Elektrootricatelnost Elementov i Khimicheskaya Svaz*, p. 14. Izd. Sibir. Otd. Akad. Nauk SSSR, Novosibirsk 1962.
21. Dally J. J.: J. Chem. Soc. 1964, 3799.
22. Stothers J. B.: *Carbon-13 NMR Spectroscopy*, p. 56. Academic Press, New York 1972.
23. Letcher J. H., Van Wazer J. R. in the book: *Topics in Phosphorus Chemistry* (M. Grayson, E. J. Griffith, Eds) Vol. 5, p. 75. Interscience, New York 1967.
24. Lindeman L. P., Adams J. Q.: Anal. Chem. 43, 1245 (1971).
25. Quin L. D., Breen J. J.: Org. Magn. Resonance 5, 17 (1973).
26. Engelhardt G., Radeglia R., Jancke H., Lippmaa E., Mägi M.: Org. Magn. Resonance 5, 561 (1973).
27. Petrov A. D., Šokolova E. B., Bakuchik G. P.: Dokl. Akad. Nauk SSSR 148, 598 (1963).
28. Sommer L. H., Bailey D. L., Goldberg G. M., Buck C. E., Bye T. S., Evans F. J., Whitmore F. C.: J. Amer. Chem. Soc. 76, 1613 (1954).
29. Ryan J. W., Menzie G. K., Speier J. L.: J. Amer. Chem. Soc. 82, 3601 (1960).
30. Kaufman K. B., Teter L. A.: Inorg. Syn. 9, 20 (1967).
31. Sommer L. H., English W. D., Ansul G. R., Vivona D. N.: J. Amer. Chem. Soc. 77, 2485 (1955).
32. Buzerenko E. F., Chernyshev E. A., Petrov A. D.: Izv. Akad. Nauk SSSR 1965, 286.
33. Cooper B. E., Owen W. J.: J. Organometal. Chem. 21, 329 (1970).
34. Shriver D. F.: *The Manipulation of Air Sensitive Compounds*. McGraw Hill, New York 1969.

Translated by the author (J. S.).