

RESEARCH ON THE MOLECULAR STRUCTURE OF PHENYL-HALOSILANES I

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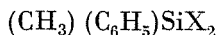
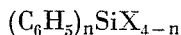
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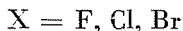
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Introduction

The phenyl-halo-silanes showed a sharp increase in their importance during the last years. Their growing industrial utilization argued theoretical research to explain the relationships between molecular structure and chemical and physical properties. This research work consisted in the preparation of some phenyl-halo-silanes, different spectroscopic analyses and qualitative evaluation of the spectra. Quantum-chemical calculations on the molecular structures will be described in a subsequent paper. Our research concerned the compounds:



where $n = 1, 2, 3$

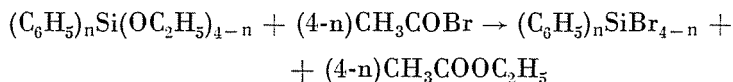


Preparation

The phenyl-fluoro-silanes were produced by the method of SPIALTER [1] starting from the corresponding chloro-silanes dissolved in pentane by using an aqueous solution of hydrogen fluoride at 0 °C in polyethylene vessel.

Phenyl-chloro-silanes were commercially available only when purification by distillation was necessary.

Phenyl-bromo-silanes were prepared by a new method not yet known in the literature according to the equation:



The product was purified by vacuum fractionation. The compounds were controlled for purity and identified by confrontation of calculated and

measured molar refraction, molecular weight determination by cryoscopic method and, with the bromine derivatives, by bromine content analysis. Physical and chemical data of the produced compounds are compiled in Table I.

Table I

Physical and Chemical Data of the phenyl-halo-silanes

	Bp. °C/Hgmm	d_4^{20} g/ml	n_D^{20}	MR _D ml calculated	MR _D ml observed
C ₆ H ₅ SiF ₂	66/210	1.1841	1.4104	32.54	33.95
(C ₆ H ₅) ₂ SiF ₂	106/12	1.1566	1.5240	58.28	58.30
(CH ₃)(C ₆ H ₅)SiF ₂	69/53	1.0898	1.4469	38.39	38.77
C ₆ H ₅ SiBr ₃	130/12	2.0218	1.5961	58.16	58.05
(C ₆ H ₅) ₂ SiBr ₂	191/1	1.5860	1.6173	75.36	75.49
(CH ₃)(C ₆ H ₅)SiBr ₂	140/60	1.6060	1.5548	55.47	55.94
(C ₆ H ₅) ₃ SiBr	209/1	—	—	—	—

Ultraviolet spectra

The ultraviolet absorption spectra of the phenyl-halo-silanes were determined using a Spektromom 201 spectrophotometer. Solvent was n-hexane, the concentration varied in the range 10^{-2} to 10^{-5} mol/l. Tests were carried out using quartz cuvettes with liquid layers of 1 cm and 0.2 cm width. The ultraviolet spectra are shown in Figs 1 to 4, while Table II presents absorption maxima.

λ in the Table represents the wave-length corresponding to the maximum absorption, while ϵ is the extinction coefficient. The sign + shows that no local maximum exists about the given wave-length.

Infrared spectra

The infrared spectra of the phenyl-halo-silanes were taken by a Perkin-Elmer-457 spectrometer. The test was carried out under cooling in order to avoid the decomposition of the compounds. Tables III, IV and V show the assignation of the absorption maxima in the infrared spectra. To characterize the absorption band intensity, the following representation is used: vs = very strong; s = strong; m = medium; w = weak.

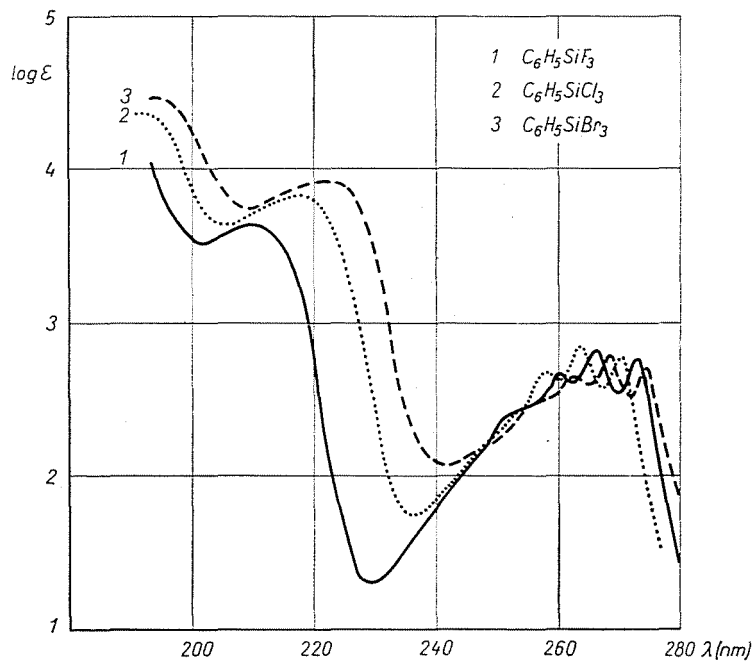


Fig. 1. Ultraviolet spectra of the phenyl-trihalo-silanes

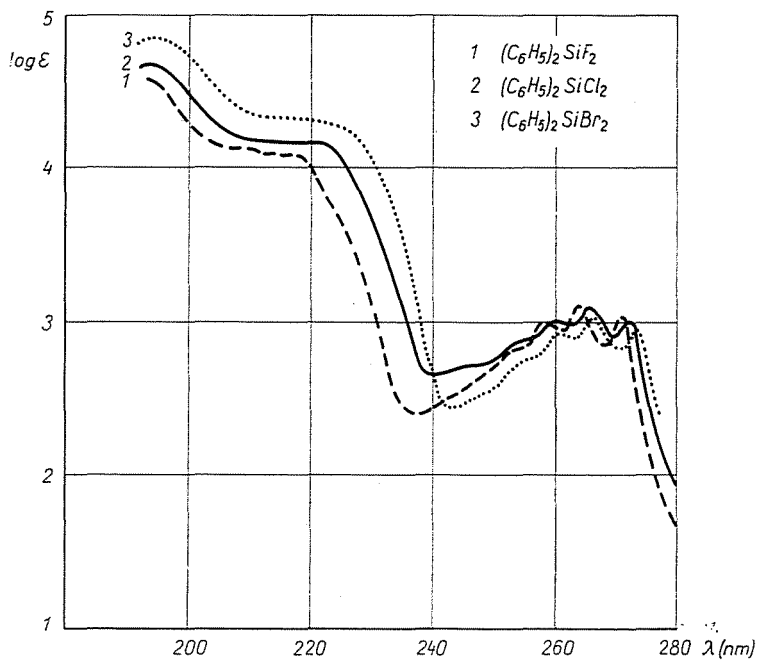


Fig. 2. Ultraviolet spectra of the diphenyl-dihalo-silanes

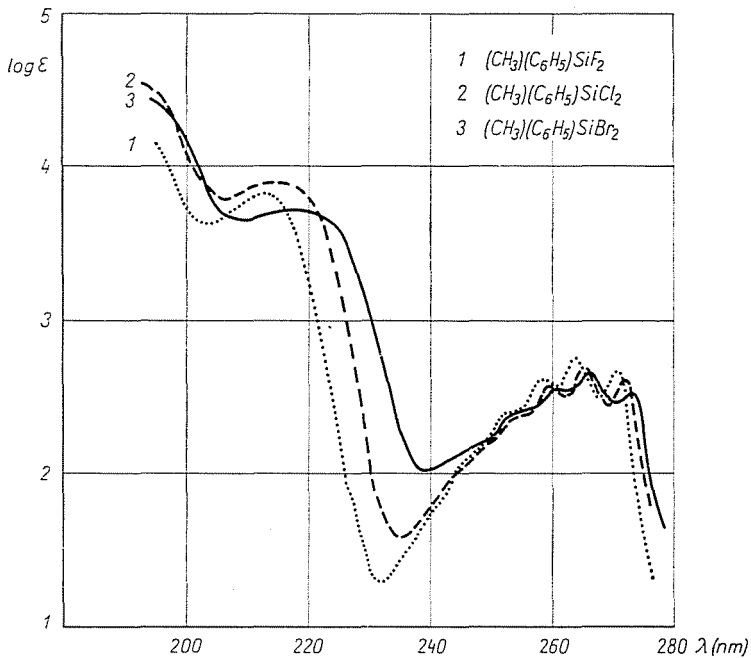


Fig. 3. Ultraviolet spectra of the methyl-phenyl-dihalo-silanes

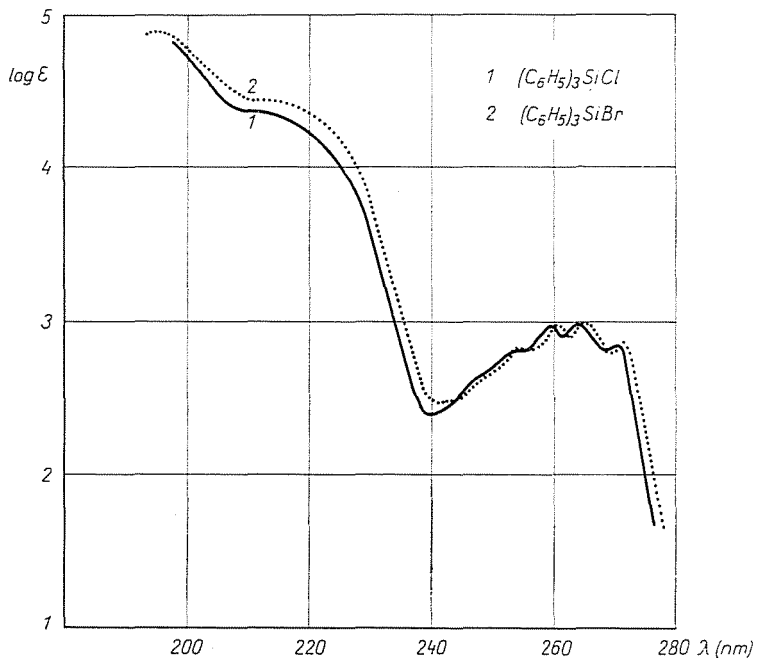


Fig. 4. Ultraviolet spectra of the triphenyl-halo-silanes

Table II

Ultraviolet absorption data of phenyl-halo-silanes

	$C_6H_5SiF_3$		$C_6H_5SiCl_2$		$C_6H_5SiBr_2$	
	λ (nm)	ϵ	λ (nm)	ϵ	λ (nm)	ϵ
α -band	271	620	273	590	275	580
	264	700	266	670	269	620
	258	500	260	480	263	470
	252 ⁺	270	254 ⁺	290	256 ⁺	310
p-band	210	4790	218	7650	223	8980
	$(C_6H_5)_2SiF_2$		$(C_6H_5)_2SiCl_2$		$(C_6H_5)_2SiBr_2$	
	λ (nm)	ϵ	λ (nm)	ϵ	λ (nm)	ϵ
α -band	271	1080	273	1110	274	850
	265	1300	266	1310	267	1050
	259	980	260	1030	261	830
	254 ⁺	670	255 ⁺	760	256 ⁺	600
p-band	210 ⁺	14560	219	16910	222 ⁺	21430
	$(CH_3)(C_6H_5)SiF_2$		$(CH_3)(C_6H_5)SiCl_2$		$(CH_3)(C_6H_5)SiBr_2$	
	λ (nm)	ϵ	λ (nm)	ϵ	λ (nm)	ϵ
α -band	270	460	272	400	273	340
	264	550	265	480	266	440
	258	400	259	370	260	360
	253 ⁺	240	254 ⁺	240	255 ⁺	250
p-band	211	6820	216	7610	218	5420
			$(C_6H_5)_3SiCl$		$(C_6H_5)_3SiBr$	
			λ (nm)	ϵ	λ (nm)	ϵ
α -band			270	700	271	740
			263	950	265	980
			260	920	261	940
			253	670	254	680
p-band			210	25400	213	27800

NMR spectra

The nuclear magnetic resonance spectra of the diphenyl-dihalo-silanes and of the methyl-phenyl-dihalo-silanes were taken on a VARIAN A-60 D instrument at 60 MHz frequency by using TMS as reference material and carbontetrachloride as solvent. Data of NMR spectra are compiled in Table VI.

Table III

Evaluation of infrared spectra for the phenyl-fluoro-silanes

Compound	$C_6H_5SiF_2$	$(C_6H_5)_2SiF_2$	$(CH_3)(C_6H_5)SiF_2$
Assignment	cm^{-1}	cm^{-1}	cm^{-1}
	3108 w	3101 w	3102 w
	3088 m	3082 m	3081 m
$\nu_{C_{Ar}H}$	3063 m	3064 m	3060 m
	3030 m	3029 m	3036 m
	3019 w	3013 w	3014 w
$\nu_{as}CH_3$	—	—	2982 m
ν_sCH_3	—	—	2931 w
	1610 s	1606 s	1600 s
$\nu_{C_{Ar}C_{Ar}}$	1506 w	1498 w	1495 w
	1442 s	1438 vs	1439 m
$\delta_{as}CH_3$	—	—	1412 m
δ_sCH_3	—	—	1275 vs
$\nu_{SiC_{Ar}}$	1150 s	1142 vs	1135 vs
$\nu_{as}SiF$	960 s	910 s	913 vs
ν_sSiF	856 vs	858 vs	880 vs
$\nu_{SiC(H_3)}$	—	—	800 vs
	760 m	744 vs	740 vs
$\gamma(=CH)$	741 s	730 vs	731 vs
$\gamma_{C_{Ar}C_{Ar}}$	698 s	698 s	699 vs
$\beta_{as}SiF$	490 m	515 s	478 vs
β_sSiF	468 s	483 s	425 vs

Evaluation

Studying the ultraviolet spectra it appears that all the investigated compounds show a benzene-like structure in their spectra; the α -band with a vibration fine structure and the p-band are clearly visible. The figures exhibit spectra of identical general run with maxima nearly at the same place. It can be concluded that the spectra of the phenyl-halo-silanes indicate a bathochromic shift relative to the benzene spectrum. This can be explained by the $+I$ and $-M$ effect of the silicon lowering the π^* level of the benzene that results in an absorption maximum shifted towards the higher wavelengths. Among the compounds of identical type a slight bathochromic shift can be observed in the order: fluor, chlorine, bromine with values of 1–3 nm in the α -band, but higher in the p-band. The values of the maxima are practically the same for the identical halogen compounds. At the same time, the

Table IV
Evaluation of infrared spectra for the phenyl-chloro-silanes

Compound	$C_6H_5SiCl_3$	$(C_6H_5)_2SiCl_2$	$(CH_3)(C_6H_5)SiCl_2$	$(C_6H_5)_3SiCl$
Assignment	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
$\nu_{C_{Ar}H}$	3105 w	3103 m	3105 w	3103 w
	3088 m	3084 m	3088 m	3084 m
	3062 m	3066 s	3069 s	3066 m
	3032 m	3039 m	3030 m	3040 m
	3018 w	3021 m	3017 m	3022 m
$\nu_{as}CH_3$	—	—	2982 m	—
ν_sCH_3	—	—	2918 w	—
$\nu_{C_{Ar}C_{Ar}}$	1610 m	1610 m	1612 m	1590 m
	1505 w	1503 w	1446 s	1486 m
	1447 s	1442 s		1430 vs
$\delta_{as}CH_3$	—	—	1419 m	—
δ_sCH_3	—	—	1274 s	—
$\nu_{SiC_{Ar}}$	1128 vs	1128 vs	1128 vs	1128 vs
$\nu_{SiC(H_3)}$	—	—	800 vs	—
$\gamma(=CH)$	742 vs	747 vs	740 vs	745 m
	722 vs	724 vs	732 m	721 vs
$\gamma_{C_{Ar}C_{Ar}}$	696 vs	700 vs	698 vs	700 vs
$\nu_{as}SiCl$	587 vs	575 vs	551 vs	518 vs
ν_sSiCl	519 vs	515 vs	507 vs	482 vs
$\beta_{as}SiCl$	465 m	475 vs	470 s	438 vs
β_sSiCl	390 w	405 m	390 m	375 w

methyl-phenyl-derivates present a small hypsochromic deviation relative to the diphenyl derivates. In the investigated compounds the silicon atom has a +I (inductive) and —M (mesomere) effect.

These two effects act oppositely on the electron shifting, thus the resulting phenomenon will depend on the relative value of the two effects. If only +I effect would exist a hypsochromic shift would result from the raising π^* level of benzene. The influence of the —M effect acts in the opposite direction, it is generally higher, so it offsets the +I effect and lowers the π^* level, that is a bathochromic shift appears. At the same time, the halogen atoms connected to the silicon present a +M effect. The bathochromic shift observed in the order: fluor-chlorine-bromine, is produced originally by these added effects.

It had been concluded [2] from the coincidence of the maxima of the identical halogen compounds that the central silicon atom produced conju-

Table V
Evaluation of infrared spectra for the phenyl-bromo-silanes

Compound	$C_6H_5SiBr_2$	$(C_6H_5)_2SiBr_2$	$(CH_3)(C_6H_5)_2SiBr_2$	$(C_6H_5)_3SiBr$
Assignment	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
$\nu_{C_{Ar}H}$	3102 m	3098 m	3100 w	3105 w
	3088 m	3082 m	3084 m	3086 m
	3068 m	3065 m	3065 m	3058 m
	3030 w	3036 m	3027 w	3031 w
	3010 m	3020 m	3012 w	3016 m
$\nu_{as}CH_3$	—	—	2989 w	—
ν_sCH_3	—	—	2912 w	—
$\nu_{C_{Ar}C_{Ar}}$	1610 m	1606 m	1606 m	1610 m
	1497 w	1498 m	1502 w	1505 w
	1448 vs	1441 s	1442 s	1442 s
$\delta_{as}CH_3$	—	—	1410 m	—
δ_sCH_3	—	—	1266 vs	—
$\nu_{SiC_{Ar}}$	1110 vs	1120 vs	1118 vs	1130 vs
$\nu_{SiC(H_3)}$	—	—	803 vs	—
$\gamma(=CH)$	742 vs	744 vs	736 vs	742 m
	712 vs	723 vs	—	718 vs
$\gamma_{C_{Ar}C_{Ar}}$	698 vs	698 vs	696 vs	702 vs
$\nu_{as}SiBr$	498 vs	502 vs	480 vs	518 s
ν_sSiBr	463 vs	473 vs	445 vs	485 s

gative connection with each phenyl group by separate free d orbitals and this $d\pi - d\pi$ bond did not extend to the whole molecule. Quantum-chemical calculations demonstrated this supposition to be wrong in closer approximation. In our subsequent publication this problem will also be treated, viz. for the case of phenyl-halo-silanes. The hypsochromic shift of the methyl-phenyl derivatives can be explained, among others, by the fact that the methyl group reduces delocalisation.

Data in Tables III and IV led to the conclusion that the symmetric and asymmetric stretching frequencies did not show significant differences within one halo-compound group. β_{as} and β_s plain deformation vibrations for fluor and chlorine have been determined. With the bromine derivatives these vibrations probably exhibit such a low wave number beyond our means of observation. Comparing the wave number differences of the asymmetric and symmetric deformation vibration frequencies for methyl-phenyl derivatives to those for diphenyl derivatives, the former exhibit a greater split attributed to the change in the F—Si—F bond angle. Thus, for methyl-phenyl compounds

Table VI

Data of NMR spectra of the phenyl-halo-silanes

Compound	δCH_3	δArH
$(\text{CH}_3)(\text{C}_6\text{H}_5)\text{SiF}_2$	0.49 triplette ($J_{\text{HF}} = 6 \text{ Hz}$)	430—470 Hz AB_2C_2 multiplette
$(\text{CH}_3)(\text{C}_6\text{H}_5)\text{SiCl}_2$	0.95	430—475 Hz AB_2C_2 multiplette
$(\text{CH}_3)(\text{C}_6\text{H}_5)\text{SiBr}$	1.23	430—475 Hz AB_2C_2 multiplette
$(\text{C}_6\text{H}_5)_2\text{SiF}_2$		415—470 Hz AB_2C_2 multiplette
$(\text{C}_6\text{H}_5)_2\text{SiCl}_2$		425—475 Hz AB_2C_2 multiplette
$(\text{C}_6\text{H}_5)_2\text{SiBr}_2$		430—480 Hz AB_2C_2 multiplette

this angle exceeds that for the diphenyl ones. A similar, although fainter phenomenon is manifest for the corresponding chlorine compounds. In the wave number of the $\nu\text{SiC}_{\text{AR}}$ group vibration a slight decrease appears when going from the fluor to the bromine. The tendency is similar for the methyl-phenyl derivatives for the $\nu\text{SiC}_{\text{methyl}}$ vibrations. For the methyl-phenyl compounds the $\nu_{\text{as}}\text{CH}_3$, $\nu_{\text{s}}\text{CH}_3$, $\delta_{\text{as}}\text{CH}_3$, the methyl sweeping $\delta_{\text{s}}\text{CH}_3$ and the $\nu\text{SiC}(\text{H}_3)$ vibration have been identified.

The $\nu\text{C}_{\text{Ar}}\text{C}_{\text{Ar}}$ deformation skeletal vibrations perpendicular to the plan — in accordance with the monosubstituted phenyl group — show up with high intensity for all compounds. No doublette split can be found, and this points to the equivalence of the phenyl groups. As expected, the hybrid band $\nu\text{SiC}_{\text{Ar}}$ appears at a very high intensity for all compounds. The position of the $\nu(=\text{CH})$ bands perpendicular to the plan points to the presence of five hydrogen atoms connected to aromatic rings each. Three bands of the aromatic skeleton valence vibrations have been identified the fourth being uncertain. The valence vibration frequencies $\nu\text{C}_{\text{Ar}}\text{H}$ presented themselves at an adequate intensity in the range 3110 to 3010 cm^{-1} .

The NMR spectra exhibit the characteristic chemical shift of the hydrogen atoms in the phenyl group and for methyl derivatives, the τ sign of the hydrogens from the methyl group is visible, too. The δCH_3 values for the methyl-phenyl derivatives are growing in the order: fluor, chlorine, bromine. This

deviation implies that the shading is the deepest for the fluor compounds and here the hydrogen atoms in the methyl group are the most negative. If the fluor had $-I$ effect only it would withdraw the electrons from the silicon atom and the carbon and hydrogen atoms of the methyl group. The $+M$ effect of fluor atom on the other hand pushes back the electrons, so the partial charge of the hydrogen atoms in the methyl group will be more negative. In the chlorine and bromine compounds the mesomeric effect of the halogen atoms is slighter and therefore hydrogens of the methyl groups will be more positive. The separation for the hydrogens of the phenyl group can be explained by the same effect. The C_2 part of the AB_2C_2 multiplette in the spectrum resulting from the aromatic protons doesn't separate distinctly from the AB_2 part for the fluor compounds while this separation is clearly established for the chlorine and bromine compounds. Shifting of the C_2 part towards the smaller τ values can be attributed to the modification of partial charge of the ortho protons in the same direction as for the methyl-protons. The effect on the protons in meta and para position is but slight, the AB_2 part of the spectrum appears practically at the same place. In the spectra of the diphenyl compounds only the AB_2C_2 multiplette resulting from the aromatic protons appears, where the C_2 part (due to the $-I$ effect of the second phenyl group) separates even more as for the methyl-phenyl compounds. The AB_2 part of the spectrum is shifted towards smaller δ values due to the mutual shading effect of the two phenyl rings.

Experimental part

Phenyl trifluoro-silane

In a polyethylene vessel ice-cooled 52.8 g (0.25 mole) phenyl trichloro-silane dissolved in 200 ml pentane was reacted with 96 g solution of hydrogen fluoride in water at 40% concentration. The reaction time was 2 hours under continuous stirring. The two phases were separated, the organic one dried by Na_2SO_4 and the excess hydrogen fluoride absorbed by NaF. The crude product was purified by vacuum distillation. Yield: 70%.

Diphenyl-difluoro-silane

Synthesis was carried out as described above. Quantities: 200 ml pentane, 63.3 g (0.25 mole) diphenyl-dichloro-silane, 50 g H_2F_2 solution concentration 40%. Yield: 74%.

Methyl-phenyl-difluoro-silane

Synthesis was achieved as described above. Quantities: 200 ml pentane, 39.6 g (0.25 mole) methyl-phenyl-dichloro-silane, 50 g H_2F_2 solution concentration 40%. Yield: 65%.

Phenyl-tribromo-silane

In a glass vessel, equipped with a mercury-sealed stirrer, reflux cooler and gas introduction, 24 g (0.1 mole) phenyl-triethoxy-silane and about 1 g water-free FeCl_3 was weighed in. Under continuous stirring and nitrogen gas flux, 34 ml (55.4 g, 0.45 mole) acetyl bromide was added drop by drop to the mixture. After 8 hours of boiling, the product was separated by vacuum distillation. Yield: 15.8 g, 46%. Molecular weight: calculated 344.9, observed: 347.2. Br% calculated 69.5; observed: 67.1.

Diphenyl-dibromo-silane

Preparation was similar to the preceding one. Quantities: 27 g (0.1 mole) diphenyl-dioxy-silane, 1 g FeCl_3 , 37.1 g (0.3 mole) acetyl bromide. Yield: 21.5 g, 63%. Molecular weight: calculated: 342.1; observed: 342.0; Br% calculated: 46.7; observed: 46.8.

Methyl-phenyl-dibromo-silane

Production was carried out by the method described above. Quantities: 21 g (0.1 mole) methyl-phenyl-dioxy-silane; 1 g FeCl_3 ; 37.1 g (0.3 mole) acetyl-bromide. Yield: 21 g, 74%. Molecular weight: calculated: 280.0; observed: 283.7. Br% calculated: 57.1; observed: 56.2.

Triphenyl-bromo-silane

Production process is not sensitive to air, so nitrogen atmosphere is unnecessary, and so are catalyst and stirring. Quantities: 30 g (0.1 mole) triphenyl-etoxy-silane; 13 g (0.106 mole) acetyl-bromide. The crude product was purified by recrystallisation from ether. Yield: 27 g, 79.6%. Molecular weight: calculated: 339.3; observed: 336.1. Br% calculated: 23.6; observed: 22.1.

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Summary

This work concerned preparation and spectroscopic analysis of phenyl-halo-silanes. A new method for the production of phenyl-bromo-silanes was worked out using acetyl-bromide as reactant. The ultraviolet spectra pointed to a bathochromic shift in the order: fluor-chlorine-bromine in every compound series of identical type. The absorption maxima of identical halo-compounds are practically consistent. Evaluation of the infrared spectra resulted in the determination of frequencies corresponding to the most important vibrations. From the NMR spectra, the chemical shift of hydrogens in the phenyl and methyl group was identified.

References

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