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A METHOD FOR FUNCTIONAL ANALYSIS OF ORGANOSILICON COMPOUNDS CONTAINING SILACYCLOBUTANE GROUPS

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A method of determining quantitatively silacyclobutane rings in organosilicon compounds is worked out. It is based on addition of bromine or iodine to a Si—C bond in the ring, followed by determination of those elements in the resultant Si—Br or Si—I group. The error in determining bromine or iodine numbers by the method is 0.5-2.0%; the error in determining percentage bromine (iodine) is 0.5-2.0%. A determination takes 3-4 hr. The silacyclobutane group does not react with thiocyanogen, so that it is possible to determine separately multiple bonds and silacyclobutane groups present in one and the same molecule.

1-Silacyclobutane derivatives are now being intensively studied. Considerable theoretical interest attaches to this type of organosilicon compound, since it is able to undergo a number of specific reactions, partly due to the ring Si—C bond (cleavage of the $>\overline{\mathrm{Si}(\mathrm{CH}_2)_2\mathrm{CH}_2}$ group by organic and inorganic acids, alcohols, water, etc) [1, 2], and partly to functional substituents at the silicon (e.g., alcoholysis and addition of olefins involving the Si—H bond in $\overline{\mathrm{CH}_2(\mathrm{CH}_2)_2\mathrm{Si}}\mathrm{HCH}_3$, reaction of $\overline{\mathrm{CH}_2(\mathrm{CH}_2)_2\mathrm{Si}}\mathrm{ClCH}_3$ with disilazanes, etc) [2-4]. These reactions are due to structural peculiarities of the strained organoelement heterocyclic ring, and either do not take place, or proceed considerably more slowly with structurally similar organic compounds. On the other hand, silacyclobutanes have potentialities as a new type of organosilicon monomers, since, due to the Si—C bond, they very readily polymerize with ring opening. In particular, it has proved possible to obtain hitherto unknown high-molecular polymers with carbon-silicon basic chains [5, 6]. As we have shown [7, 8] polysiloxane or carbon chain oligomers, containing a certain quantity of silacyclobutane groups, can be crosslinked in the absence of catalysts.

Although a large number of silacyclobutane compounds are already known, so far no paper has been published dealing with devising convenient chemical methods for functional analysis of them.*

It was recently stated in the literature [10] that $(\mathrm{C}_6\mathrm{H}_5)_2\overline{\mathrm{SiCH}(\mathrm{C}_6\mathrm{H}_5)\mathrm{CH}_2\mathrm{CH}_2}$ decolorizes a CCl_4 solution of bromine. Probably this is due to addition of bromine at a Si—C bond in the ring.

The present paper gives a method which makes it possible to determine quantitatively silacyclobutane groups, and which is identical with the method used for determining bromine and iodine numbers; it is based on addition of halogen at a ring Si—C bond.

The analytical results are readily checked by titrating the $>\mathrm{Si}-\mathrm{X}$ groups formed (X = Br or I).

Silacyclobutane groups can also be determined if double bonds are also present in the organosilicon molecule. First of all, the bromine number is used to determine the sum of the silacyclobutane groups and double bonds, and then the double bonds are found from the thiocyanogen number (unlike the double bond, the silacyclobutane groups do not react with thiocyanogen). The difference gives the silacyclobutane groups.

If the silacyclobutane compound contains Si—H bonds, they do not interfere with determination of silacyclo-

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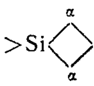
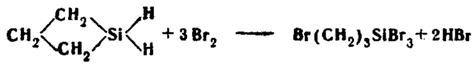
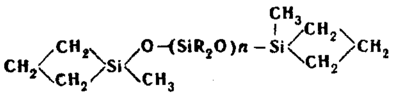
*Up to the present, only physical methods of analysis, based on IR and PMR spectra, have been used. Due to the "stiffness" of the silacyclobutane ring, the characteristic frequencies (1186, 1125, and 926 cm^{-1}) in the IR spectra of these compounds depend very little on the nature of the substituents at the silicon atom. In their PMR spectra, the chemical shifts of the α and β protons of the silacyclobutane ring  (in tetramethyl silane solution τ_α = 8.9; τ_β = 7.8) differ considerably from the chemical shifts of protons in the silacycloalkanes $\mathrm{R}_2\overline{\mathrm{Si}(\mathrm{CH}_2)_n\mathrm{CH}_2}$ with n ≥ 3, or in the open-chain alkylchlorosilanes $\mathrm{R}_3\mathrm{Si}(\mathrm{CH}_2)\,n\,\mathrm{CH}_3$ (n ≥ 3). However, it is difficult to determine silacyclobutane groups quantitatively by these convenient qualitative methods.

butane groups. However, addition of bromine at the ring Si–C link is accompanied by substitution of the hydride hydrogen by bromine, e.g.:

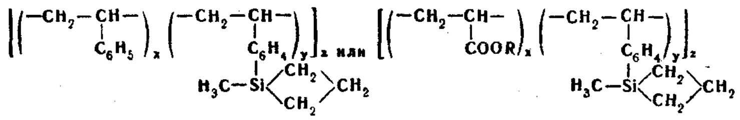


The table gives some examples of analytical results.

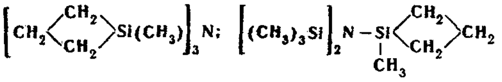
We have successfully used the method offered for determining silacyclobutane groups in polysiloxane oligomers of the type [8]:



and in carbon chain oligomers of the type [7]:



Satisfactory results in determining the silacyclobutane group are also obtained in the analysis of a number of silylamines which we have synthesized [3]:



etc.

However, further experimental evidence is necessary before the bromine number method can legitimately be extended to all types of silamines and polysilazanes containing silacyclobutane groups, since under the conditions used for determining the bromine numbers side reactions can be expected.

Experimental

The following silacyclobutane derivatives were used for analysis: 1,1-dimethyl- and 1-methyl-1-ethylsilacyclobutane [11], 1-(p-styryl)-1-methyl-1-silacyclobutane [7], tris(1-methyl-1-silacyclobutyl) amine [3].

1,1-(Trimethylene)-1,3,3,3-tetramethyldisiloxane [12]. Prepared by cohydrolyzing 180 g trimethylchlorosilane and 28.5 g 1-chloro-1-methyl-1-silacyclobutane. Yield 21.4 g (52%), bp 63-65°C (44 mm); n_D^{20} 1.4161; d_4^{20} 0.8431; MR_D 51.91; calculated MR_D 51.92 [11]. 1,1-(Trimethylene)-1,3,3,-trimethyl-1-phenyldisolaxane was prepared by heterofunctional condensation of 30.9 g 1-chloro-1-methylsilacyclobutane and Na dimethylphenylsilanolate prepared from 39 g dimethylphenylsilanol bp 76°C (2.5 mm), n_D^{20} 1.5145 and 5.9 Na. After the chloride had been added to a benzene solution of the silanolate, the mixture was refluxed and vigorously stirred for 10 hr. Then the precipitate was filtered off, the benzene distilled off from the filtrate, and the residue vacuum-distilled to give 30 g (50%) disoloxane, 65–68°C (3.10^{-2} mm); n_D^{20} 1.4905; d_4^{20} 0.9548. Found: Si 23.74; C 60.96; H 8.53%. MR_D 71.64; M 236. Calculated for Si 23.96; C 60.64; H 8.61%; MR_D 71.74; M 236.4.

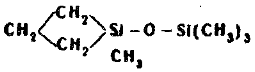
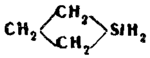
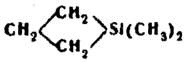
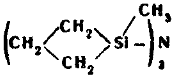
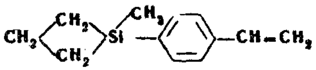
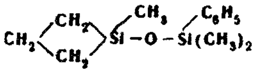
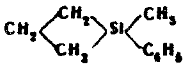
1-Silacyclobutane. a) 75 g 1,1-dichloro-1-silacyclobutane was added to 13.8 g $LiAlH_4$ in 200 ml Bu_2O, and the mixture warmed for 3 hr at 55-60° C. Readily volatile products were blown off in a current of argon, and distilled through a column, yield 20.6 g (55%), bp 43°C; n_D^{20} 1.4422; d_4^{20} 0.7791. Found: Si 38.62; C 49.98; H 11.15%. M 71.6; 72.0; MR_D 24.52. Calculated for C_3H_8Si: Si 38.79; C 49.93; H 11.17%; M 72.54; MR_D 24.54.

b) Reduction was effected as described in [13]. 10 g LiH and 40 g 1,1-dichloro-1-silacyclobutane gave 6.5 g (25%) 1-silacyclobutane. Its physical constants were identical with those given above. Reaction proceeded considerably slower, than with $LiAlH_4$.

Analytical method

The following were used for analysis: 0.1 N bromine in dry MeOH saturated with NaBr (Kaufman solution), 10% KI, 0.1 N $Na_2S_2O_3$, and 0.1 N KOH.

Functional Analytical Data for Silacyclobutane and its Derivatives

Compound analyzed	*M*	Bromine number		Absolute error, %	Br, %		Absolute error, %	Iodine number		Absolute error, %	I, %		Absolute error, %
		Calculated	Found		Calculated	Found		Calculated	Found		Calculated	Found	
	174	92	91.10	−0.98	23.96	23.86	−0.42	146	145.05	−0.65	29.78	30.60	+2.7
	72	666.5	663	−0.52	61.5	61.0	−0.81						
	100	160	157.2	−1.75	30.79	31.0	+0.68	254	250	−1.57	35.9	35.75	−0.42
	269	178.4	179	−0.44	32.16	32.7	+1.68						
	187	171	168	−1.75	15.75	16.0	+1.59				62**	63**	−1.6
	236	67.7	67.10	−0.81									
	114	140.2	138.4*	−1.28				222.1	221.4	−0.31	34.5	34.0	−0.43

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* Determined in AcOH

** Thiocyanogen number.

Determination. A sample (about 0.1 g) was weighed out into a 250 ml conical flask, 5 ml CCl_4 (distilled over P_2O_5)added, and after the sample had dissolved, 25 ml bromide solution added, the contents shaken, left 3-4 hr, and 25 ml KI solution added in the dark; the iodine liberated was titrated with thiosulfate. A blank was run simultaneously. The result was calculated using a known formula [14]. After titrating the iodine, 20 ml dry MeOH and 15 ml ether were added to completely dissolve and effect hydrolysis of the bromides formed. The contents of the flask were vigorously shaken and titrated with 0.1 N KOH using phenolphthalein as the indicator. The bromine content (Si—Br was calculated from the formula:

$$\mathrm{Br}=\frac{V\cdot 0{,}00799\cdot 100}{a\cdot K},\ \%.$$

V = volume of 0.1 N KOH solution consumed, 0.00799 = weight of bromine corresponding to 1 ml 0.1 N KOH, α = sample weight, g, K = factor for converting from molecular weight of starting material to that of the bromide.

The iodine number was determined similarly, using a solution of 25 g iodine in 100 ml dry EtOH, followed by titration of the iodine present as Si—I.

A 0.1 N solution of bromine in glacial AcOH can be used for determining the bromine number, in which case it is unnecessary to use a blank when determining bromine in Si—Br.

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