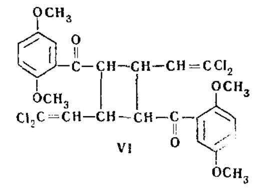
nyl)-2-pyrone (V). It is interesting that under the action of light I undergoes photodimerization being converted into a cyclobutane derivative with the structure VI. The structure of the conversion products has been confirmed by IR and UV spectra (see table).



EXPERIMENTAL

1, 1-Dichloro-5-(2', 5'-dimethoxyphenyl)-1, 3-pentadien-5-one (I) was obtained by method A, described previously, from 2, 5-dimethoxyacetophenone [1]. Compound II was obtained from the mother liquors from the recrystallization of I. It was also obtained from 2-hydroxy-5-methoxyacetophenone by method B [1].

6-(2', 5'-Dimethoxyphenyl)-2-pyrone (V) was obtained by the cyclization of I [2]. Under the same conditions, compound II forms III and IV.

Dimerization was carried out by irradiating I with sunlight. The properties of the compounds obtained are given in the table.

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SYNTHESIS OF SILACYCLOBUTANES FROM HALOALKYLMETHOXYSILANES

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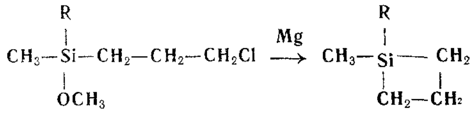
The possibility of synthesizing silacyclobutane derivatives from haloalkylalkoxysilanes has been studied (with γ-chloropropylmethyldimethoxysilane and γ-chloropropyldimethylmethoxysilane as examples). The intramolecular cyclization of these compounds takes place only when polar solvents are used.

Substituted 1-silacyclobutanes are of definite interest not only from the theoretical but also from the practical aspect as initial monomers for the production of silacarbane polymers [1].

The intramolecular organometallic ring closure of γ-chloropropyl derivatives of silicon in a polar solvent is usually used for the synthesis of the silacyclobutanes [2, 3]. We decided to transfer this reaction to γ-chloropropylmethyldimethoxysilane and γ-chloropropyldimethylmethoxysilane, since it appeared possible to carry out the ring-closure reaction in an excess of the initial methoxy derivatives, using them as the polar solvent.



$$\underset{\mathrm{OCH_3}}{\overset{\mathrm{R}}{CH_3-Si}}-CH_2-CH_2-CH_2Cl \xrightarrow{Mg} CH_3-\overset{\mathrm{R}}{Si}\underset{CH_2-CH_2}{-CH_2}$$

I II

$R=OCH_3$, CH_3

However, it was found that intramolecular cyclization does not take place under these conditions (see table).

Carrying out the reaction in an aromatic solvent (xylene) by the method used for synthesizing organometallic compounds proposed by Ashby [5] gave a very small yield of silacyclobutanes (II).

Only when polar solvents (diethyl and dibutyl ethers) were used were 1, 1-dimethylsilacyclobutane and 1-methyl-1-methoxysilacyclobutane, respectively, obtained in satisfactory yields. The latter has not been described in the literature (its structure was confirmed by independent synthesis by the direct methoxylation of 1-chloro-1-methylsilacyclobutane and also by spectral data). The IR spectrum of 1-methyl-1-methoxysilacyclobutane contains bands at 1187, 1123, and 909 cm^{-1}, which are characteristic for all silacyclobutane compounds [4], at 1098 cm^{-1}, which is characteristic for Si—O—C vibrations, and at 1253 and 790 cm^{-1} which are characteristic for the $Si—CH_3$ grouping.

EXPERIMENTAL

γ-Chloropropylmethyldichlorosilane and γ-chloropropyldimethylchlorosilane were synthesized by a published method [6]. γ-Chloropropylmethyldimethoxysilane and γ-chloropropyldimethylmethoxysilane were obtained by the methoxylation of the corresponding chlorosilanes in the presence of urea as hydrogen chloride acceptor. The γ-chloropropylmethyldimethoxysilane (yield 62%) had bp 70°–72° C (11 mm); n_D^{20} 1.4253, d_4^{20} 1.0250. Found: MR_D 45.60. Calculated for $SiC_6H_{15}ClO_2$: MR_D 45.90.

Yield of Silacyclobutanes as a Function of the Conditions of Their Synthesis

Solvent	Yield of 1,1-dimethyl-silacyclobutane	Yield of 1-methyl-1-methoxy-silacyclobutane
Without a solvent	No reaction	No reaction
Xylene	8	10
Dibutyl ether	38	45
Diethyl ether	60	62

Literature data [7]: bp 185° C (756 mm); n_D^{25} 1.4242; d_4^{25} 1.019.

The γ-chloropropyldimethylmethoxysilane (yield 65%) had mp 170°–171° C; n_D^{20} 1.4278; d_4^{20} 0.9413. Found: MR_D 45.17. Calculated for $SiC_6H_{15}ClO$: MR_D 45.12. Literature data [7]: bp 169° C (751 mm); n_D^{25} 1.4283; d_4^{25} 0.953.

Synthesis of 1-methyl-1-methoxysilacyclobutane from γ-chloropropylmethyldimethoxysilane. 127 g (0.7 mole) of γ-chloropropylmethyldimethoxysilane in 500 ml of absolute ethyl ether was added to 24 g (1 mole) of magnesium activated with iodine. The mixture was heated with stirring for 48 hr. Then the ethereal solution was separated from the precipitate that had deposited by filtration. Distillation through a column yielded 33 g (0.28 mole) of 1-methyl-1-methoxysilacyclobutane. Yield 40%, bp 115°–116° C; n_D^{20} 1.4221, d_4^{20} 0.8692. Found, %: C 51.44, 51.31; H 10.67, 10.82; MR_D 34.04. Calculated for $SiC_5H_{12}O$, %: C 51.66; H 10.41%; MR_D 33.98. IR spectrum: 1464 (m), 1455 (s), 1410 (s), 1394 (s), 1253 (s), 1187 (s), 1123 (v. s), 1089 (v. s), 1018 (w), 909 (s), 869 (s), 790 (v. s), 743 (s), 712 (s). Recorded on a UR-10 instrument with a layer thickness of 0.03 mm. The yield of 1-methyl-1-methoxysilacyclobutane rose to 62% if a mixture of magnesium and γ-chloropropylmethyldimethoxysilane was heated previously and the ether was added subsequently.

The experiments using other solvents and γ-chloropropyldimethylmethoxysilane were carried out similarly.

Synthesis of 1-methyl-1-methoxysilacyclobutane from 1-chloro-1-methylsilacyclobutane. With stirring and cooling, 48 g (0.04 mole) of 1-chloro-1-methylsilacyclobutane was added to a mixture of 48 g (0.8 mole) of urea and 50 g (1.6 mole) of methanol. The addition was carried out in such a way that the temperature of the reaction mixture did not rise above 10° C.

After the end of the addition, the mixture was stirred for an hour at room temperature and was then transferred to a separating funnel. The upper layer, containing the 1-methyl-1-methoxysilacyclobutane with a small amount of methanol, was separated off and distilled through a column. The yield of 1-methyl-1-methoxysilacyclobutane was 29 g (63%). The physical constants and IR spectrum were identical with the corresponding characteristics of the material obtained from γ-chloropropylmethyldimethoxysilane.

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CLEAVAGE OF THE AZIRIDINE RING

II. Reaction of N-Phenylethyleneimine with Isothiocyanates*

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On reaction with N-phenylethyleneimine in the presence of tetraethylammonium bromide, methyl and phenyl isothiocyanates form 2-methyl- and 2-phenyl-imino-3-phenylthiazolidines. In this reaction, methyl isothiocyanate partially trimerizes. Under the action of N-phenylethyleneimine phenylisocyanate trimerizes in high yield.

Ethyleneimimes possessing an active hydrogen atom react with isothiocyanates giving N,N'-ethylenethioureas [1,2].

We have shown that with methyl isothiocyanate and phenyl isothiocyanate in the presence of tetraethylammonium bromide (TEAB) or triethylamine at 120-150° C N-phenylethyleneimine (I) forms crystalline substances

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*For part I, see [9].