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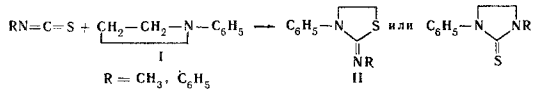
On reaction with N-phenylethyleneimine in the presence of tetraethylammonium bromide, methyl and phenyl isothiocyanates form 2-methyl- and 2-phenyl-imino-3-phenylthiazolidines. In this reaction, methyl isothiocyanate partially trimerizes. Under the action of N-phenylethyleneimine phenylisocyanate trimerizes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

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

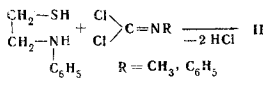
We have shown that with methyl isothiocyanate and phenyl isothiocyanate in the presence of tetraethylammonium bromide (TEAB) or triethylamine at 120-150° C N-phenylethyleneimine (I) forms crystalline substances

*For part I, see [9].

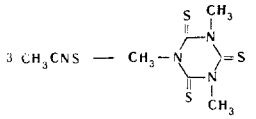
to which one of two possible structures may be ascribed, depending on the type of isothiocyanate bond opened:



The presence of a strong absorption band in the 1632 cm^{-1} region ascribed to the vibrations of a N=C bond confirms the correctness of formula II. In addition, the structure of the reaction products has been shown by independent synthesis—by the reaction of β-mercaptoethylaniline with the appropriate iminophosgenes. The IR spectra are identical (see figure).

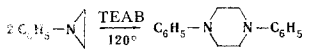


In the reaction of I with methyl isothiocyanate in the presence of TEAB or triethylamine, the formation of trimethyl trithioisocyanurate was observed:



A similar reaction takes place under the action of alkene oxides [3].

In the case of ethyl isothiocyanate we did not isolate the product of its interaction with I but obtained N, N'-diphenylpiperazine, the formation of which may be explained by the dimerization of the N-phenylethyleneimine under the action of the TEAB. Thus, when I was heated with TEAB at 120° C we obtained N, N'-diphenylpiperazine with a yield of 40%.



With a solution of I at room temperature the oxygen analog of phenyl isothiocyanate—phenyl isocyanate—is converted into triphenyl isocyanurate in 95% yield.

EXPERIMENTAL

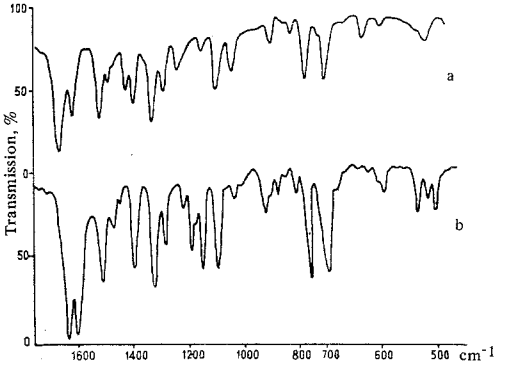
The N-phenylethyleneimine (I) was obtained by the dehydrochlorination of β-chloroethylaniline in analogy with Heine and Kapur's work [4].

3-Phenyl-2-phenyliminothiazolidine (III).

A. A mixture of 3.0 g (0.025 mole) of I, 3.4 g (0.025 mole) of phenyl isothiocyanate, and 0.02 g of TEAB was heated in a tube at 150° C for 15 hr. The contents of the tube crystallized: 5.5 g (86%) of III with mp 134° C (ethanol) was isolated. Found, %: C 70.87, 70.85; H 5.03, 5.29; N 11.34, 10.75; S 12.59, 12.49; mol. wt. 246. Calculated for $C_{15}H_{14}N_2S$, %: C 70.86; H 5.51; N 11.02; S 12.59; mol. wt. 254.

B. In drops, 17.4 g (0.1 mole) of N-phenyliminophosgene in 30 ml of ether was added to a solution of 15.3 g (0.1 mole) of β-mercaptoethylaniline and 20.2 g (0.2 mole) of triethylamine in 50 ml of dry ether at 5° C. The mixture was kept for a day at room temperature and treated with water, and the crystalline reaction product was filtered off. Yield 19 g (75%), mp 134° C (ethanol). The substance gave no depression of the melting point with the sample described above. Their IR spectra were identical.

Reaction of I with methyl isothiocyanate. A mixture of 1.5 g (0.013 mole) of I, 2.5 g (0.034 mole) of methyl isothiocyanate, and 0.02 g of TEAB was heated in a tube at 120° C for 20 hr. The contents were dissolved in ether and treated with 30% hydrochloric acid. The ethereal solution deposited 0.3 g (12.0%) of yellow crystals of trimethyl trithioisocyanurate, mp 165° C (heptane) [3]. The hydrochloric acid solution was neutralized with sodium carbonate solution and extracted with ether. The extract was dried. This yielded 0.7 g (32.5%) of 2-methylimino-3-phenylthiazolidine, mp 44° C (heptane). Found, %: C 62.40, 62.65; H 6.22, 6.26; N 14.54, 14.60; S 16.69, 16.66; mol. wt. 192, 191. Calculated for $C_{10}H_{12}N_2S$, %: C 62.50; H 6.25; N 14.58; S 16.66; mol. wt. 192.



IR spectra: a) 2-methylimino-3-phenylthiazolidine; b) 3-phenyl-2-phenyliminothiazolidine.

2-Methylimino-3-phenylthiazolidine. From β-mercaptoaniline and N-methyl-iminophosgene [6] by the method described above. The ethereal solution yielded 3.7 g (19%) of crystals, mp 44° C (heptane). The product gave no depression of the melting point with the product of the reaction of I with methyl isothiocyanate. The IR spectra of the two specimens were identical.

The IR spectra were obtained on a UR-10 spectrophotometer. Tablets of KBr (concentration 1%).

Trimerization of phenyl isocyanate. A mixture of 2.0 g (0.017 mole) of I and 2.0 g (0.015 mole) of phenyl isocyanate was kept at room temperature for 15 hr. The product crystallized, giving 1.9 g (95%) of crystals with mp 285° C (acetone [7]).

Dimerization of I. A mixture of 1.0 g (0.008 mole) of I and 0.02 g of TEAB was heated at 120° C for 15 hr. This yielded 0.4 g (40%) of crystals with mp 165° C (ethanol) [8]. They gave no depression with N, N'-diphenylpiperazine.

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