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AMINOLYSIS OF DIPHENYLDICHLOROSILANE AND HETEROCYCLIC CHLOROSILANES

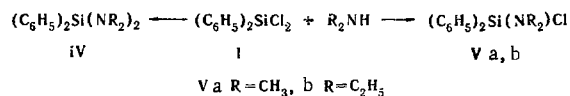
D. Ya. Zhinkin, M. M. Morgunova,
T. M. Antonova, Yu. M. Varezhkin,
T. L. Krasnova, and E. A. Chernyshev

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Reaction of diphenyldichlorosilane, dichlorosilafluorene, and dichlorosiloxarophenanthrene with amines in mono- or disubstituted organoaminosilanes gave mono- or disubstituted organoaminosilanes.

In the present paper we report the results of aminolysis of diphenyldichlorosilane, dichlorosilafluorene, and dichlorosiloxarophenanthrene in connection with the possibility of transformation of organosilicon heterocyclic derivatives. Diorganodichlorosilanes react with amines to give chlorine-substitution products [1]: thus diphenyldichlorosilane reacts with primary amines to give the corresponding disubstituted derivatives [2].

The reaction of diphenyldichlorosilane (I) with secondary amines differs from its reaction with primary amines: the degree of substitution of the chlorine atoms depends not only on the component ratio but also on the structure of the amine. One or both chlorine atoms can be replaced by an amine residue in the case of dimethylamine; the formation of a total substitution product occurs only as a result of prolonged contact of the incomplete substitution product with excess amine. In the case of diethylamine, only N,N'-diethylaminodiphenylchlorosilane (IV) is obtained, regardless of the reaction conditions.



Heterocyclic chlorosilanes - dichlorosilafluorene (II) and dichlorosiloxarophenanthrene (III) - react readily with primary and secondary amines to give the corresponding organoaminosilanes (VI, VII).

The difference in the amination reactions of I, II and III can be explained by shielding of the chlorine atom in the partially aminated product (V) by phenyl groups as compared with II and III, which have a planar orientation of the fluorene and phenanthrene fragments.

The isolated organoaminosilanes are readily hydrolyzed. After 30-min contact of VIa with moist air, the absorption bands at 1000, 1290 cm^{-1} (Si-N), and 2800 cm^{-1} (methylamino group) vanish completely, and a band appears at 1050 cm^{-1} ; this indicates hydrolysis of N,N'-bis(dimethylamino)silafluorene (VIa) at the Si-N bond to give an Si-O-Si bond.

EXPERIMENTAL

The purity of the chlorosilanes used in this research was no less than 99.9% according to gas-liquid chromatography; the organic amines (chemically pure grade) were additionally purified by fractionation over sodium metal.

Reaction of Diphenyldichlorosilane with Dimethylamine. Dimethylamine [90 g (2 moles)] was added with vigorous stirring at 15-20° to a solution of 25.3 g (0.1 mole) of diphenyldichlorosilane in 200 ml of toluene.

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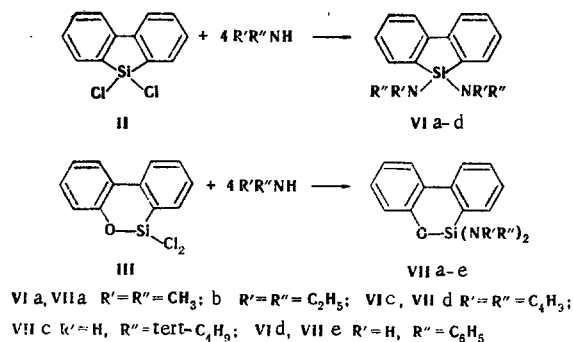
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TABLE 1. Reaction of Diphenylchlorosilane and Heterocyclic Chlorosilanes with Organic Amines

Compound	bp, °C (mm)	mp, °C	n_D^{20}	Empirical formula	Found			Calculated			Yield, %		
					C, %	H, %	N, %	C, %	H, %	N, %		Si, %	M
IV	139 (4)	---	1.5558	$C_{12}H_{20}N_2Si$	71.1	8.2	10.3	71.1	8.2	10.4	10.4	270.5	71
V b	119-120 (3)	---	---	$C_{12}H_{20}N_2Si(Cl)$	66.3	7.0	4.8	66.3	7.0	4.8	9.7	280.9	80
VI a	156 (5-6)	94-95	---	$C_{12}H_{20}N_2Si$	71.6	7.5	9.8	71.6	7.5	10.4	10.5	268.5	70
VI b	177 (5-6)	68-69	---	$C_{20}H_{30}N_2Si$	73.8	9.2	8.8	73.6	9.3	8.6	8.6	326.6	90
VI c	212 (5-6)	70-71	---	$C_{20}H_{30}N_2Si$	77.2	9.9	6.2	77.4	9.7	6.4	6.5	334.8	55
VI d	---	38-39	---	$C_{24}H_{36}N_2Si$	79.0	5.5	7.6	79.1	5.5	7.7	7.7	364.5	96
VII a	171-172 (3-4)	78-80	---	$C_{16}H_{24}N_2SiO$	67.6	7.0	9.9	67.6	7.1	9.9	9.9	284.4	60
VII b	188-189 (4)	---	1.5662	$C_{20}H_{30}N_2SiO$	70.2	8.9	8.0	70.1	8.8	8.2	8.2	342.6	87
VII c	183-184 (4)	---	1.5611	$C_{20}H_{30}N_2SiO$	70.4	8.8	8.3	70.1	8.8	8.2	8.2	342.6	69
VII d	207 (1.5-2)	---	1.5380	$C_{24}H_{36}N_2SiO$	74.4	9.5	6.1	74.6	9.4	6.2	6.2	450.3	69
VII e	---	134-135	---	$C_{24}H_{36}N_2SiO$	75.5	5.4	7.4	75.3	5.3	7.4	7.4	380.3	99

after which the mixture was allowed to stand at room temperature for 20 h. Workup gave 17.85 g (71%) of N,N'-bis(dimethylamino)diphenylsilane (IV).

Reaction of Diphenyldichlorosilane with Diethylamine. Diphenyldichlorosilane [25.32 g (0.1 mole)] was added slowly dropwise with stirring at 20-25° to 146.46 g (2 moles) of diethylamine. after which the mixture was allowed to stand at the same temperature for 20 h. Workup gave 23.21 g (80%) of diethylaminochlorodiphenylsilane (Vb). Found:



Reaction of Dichlorosilafluorene and Dichlorosiloxarophenanthrene with Organic Amines. The reaction was carried out as in the first experiment above by reaction of 0.1 mole of dichlorosilafluorene and 0.5 mole of the appropriate amine. At the end of the addition of the amine, the mixture was stirred at room temperature for 5 h. The physicochemical characteristics of IV-VII are presented in Table 1.

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TRANSFORMATIONS OF HETARYLIDENEOXAZOLONES

S. V. Krivun*

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Hetarylideneoxazolones are converted to hetarylideneamino acid esters by methanolysis in the presence of sodium. Alkaline hydrolysis in aqueous alcohol gives the corresponding amino acids. Hydrazinolysis of pyranlydeneoxazolone gives pyranlydeneamino acid hydrazide. Complete hydrolysis of oxazolone gives formylpyran, the methylation of which gives the methoxymethylpyrylium salt. Benzamidomethyl-substituted pyrylium salts were obtained by treatment of the hetarylideneamino acids with perchloric acid.

Like arylideneoxazolone [1], hetarylideneoxazolones undergo methanolysis on refluxing in absolute methanol in the presence of catalytic amounts of sodium to give the corresponding amino acid esters (type II). The hydrolysis of such oxazolones with an equimolar amount of aqueous alcoholic alkali gives the sodium salts of the hetarylideneamino acids, from which it is easy to arrive at the corresponding amino acids (III). The latter are high-melting crystalline substances that are insoluble in benzene and ether. This fact and the IR spectral data provide a basis for the assumption that the acids exist in the form of inner salts (III \rightleftharpoons IIIa).

* Deceased.

Donetsk Physical Organic Chemistry Branch, Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR. Translated from *Khimiya Geterotsiklicheskih Soedinenii*, No. 6, pp. 757-763, June, 1976. Original article submitted June 5, 1975.

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