ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 7, pp. 1069–1080. © Pleiades Publishing, Inc., 2006.
Original Russian Text © A.V. Lebedev, A.B. Lebedeva, V.D. Sheludyakov, S.N. Ovcharuk, E.A. Kovaleva, O.L. Ustinova, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 7, pp. 1118–1128.

Organosilicon Synthesis of Isocyanates: III.[1] Synthesis of Aliphatic, Carbocyclic, Aromatic, and Alkylaromatic Isocyanatocatboxylic Acid Esters

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Received May 30, 2005

Abstract — A series of aminoacid esters was prepared by treating the aminoacid suspensions in ethanol with thionyl chloride. Best conversion of aminoacid esters to corresponding isocyanates was achieved in the case of aromatic and carbocyclic aminoesters by phosgeneation of their N-silyl derivatives, and in the case of aliphatic and alkylaromatic aminoesters by phosgeneation of O-silyl or N,O-bissilylurethanes on their basis. In the last case additional step of esterification of the by-products isocyanatoalkylcarboxylic acid chlorides is reqired after phosgeneation. Unusual generation of cynnamates and intramolecular N→O-migration of trimethylsilyl group in the solutions of silylated alkylaromatic β-aminoacid esters were found.
DOI: 10.1134/S1070363206070115

We have reported on the involvement of organosilicon derivatives to the synthesis of isocyanates of the furan, thiophene, and polyfluorophenyl series [2], and also for preparing aliphatic, carbocyclic, and alkylaromatic isocyanates [1]. Developing these studies of the isocyanate organosilicon synthesis we investigated transformations of the aminoacid ester silicon derivatives to corresponding isocyanates.

Aminoacids for a long time attracted intently attention as the compounds having at least two reactive functional groups and often as natural compounds. Variety of these compounds increases continuously. We have reported recently on the development of convenient method for preparing a broad range of previously unknown and hardly available β-aminoacids [3]. It seemed interesting to prepare new isocyanates on the basis of β-aminoacid esters. Synthesis of the latter compounds is also actual because the majority of β-aminoacids exist as betaine form and therefore they are poorly soluble in organic solvents. The low solubility decreases significantly synthetic performance of aminoacids. In this connection it seemed interesting to convert the aminoacids into esters having no betaine structure and therefore more convenient for further synthetic purposes, in part, as the precursors of new isocyanates.

We found that such transformation of β-aminoacids can be easily carried out, in accordance with expectation, by treating them with 50–70% excess of thionyl chloride in anhydrous ethanol [4]. This method is more convenient and gives better results as compared to the known aminoacid esterification with diazomethane, dialkyl sulfates, alcohols saturated with dry hydrogen chloride [5], or alcohols and hydrogen chloride in the presence of orthoformate [6]. Reaction proceeds according to the following scheme.

$$R^1C(R^2)CH_2COOH + SOCl_2 + C_2H_5OH \xrightarrow[-HCl]{-SO_2,} R^1C(R^2)CH_2COOC_2H_5,$$
$$\quad\quad NH_2 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NH_2\cdot HCl$$

Ia–**Io** **IIa**–**IIo**

R^2 = H, R^1 = C_6H_5 (**a**), 4-$CH_3OC_6H_4$ (**b**), 4-$(CH_3)_2CHOC_6H_4$ (**c**), 4-C_2H_5O-3-$CH_3OC_6H_3$ (**d**), 4-$(CH_3)_2CHO$-$_3$-$CH_3OC_6H_3$ (**e**), 4-$(CH_3)_2CHCH_2O$-3-$CH_3OC_6H_3$ (**f**), 4-$CH_3C_6H_4$ (**g**), 2-ClC_6H_4 (**h**), 2-thenyl (**i**), $(CH_3)_2CH$ (**j**), $CH_3(CH_2)_2$ (**k**), $(CH_3)_2CHCH_2$ (**l**), $CH_3(CH_2)_3$ (**m**), 3-pyridyl (**n**); $R^1 + R^2 = (CH_2)_5$ (**o**).

The corresponding ethyl ester hydrochlorides were prepared similarly from 4'-aminophenylacetic acid **III** and 4-(aminomethyl)cyclohexanecarboxylic acid **IV**. Treating these compounds with concentrated NaOH

[1] For communication II, see [1].

solution at 0–5°C gave free aminoesters **Va** and **Vb**. Yields, spectral characteristics and elemental analysis data of free aminoesters and their hydrochlorides are listed in Table 1.

The β-aminoacid ester hydrochlorides prepared are viscous oil **IIk** or slightly hygroscopic solids **IIa**–**IIj, III**–**IIo** with the broad (up to 40°C) range of melting points, easily isolating in 97–99% purity. They are well soluble in water, ethanol, chloroform, DMF, DMSO, acetone, acetonitrile, and insoluble in ether and toluene.

From Table 1 it follows that the yields of amino esters **IIa**–**IIm, IIo** reach 90–95%. In the case of aminoacid **In the aminoester IIn** · HCl is also formed, but competingly obtained aminoacid hydrochloride **In** · 2HCl is so poorly soluble in ethanol that its esterification results in formation of unseparable mixture of salts **In 2HCl** and **IIn HCl** in 1 : 1 ratio. Pure aminoester salt **IIn** · HCl can be isolated only when the reaction is performed in semimicro scale.

Esterification of aromatic aminoacids proceeds analogously to the above described. Using methanol or ethanol as the alcohol component and neutralizing hydrochlorides with aqueous solution of sodium hydroxide at low temperature we prepared esters **Vc**–**Vj** from the corresponding aminoacids. In the case of anthranylic acid and its derivatives a significant dilution of reaction mixture with ethanol and using of not less than double excess of thionyl chloride is needed for preparation of the aminoesters **Vc, Vd, Vi**, and **Vl**, due to low solubility of these aminoacids in alcohols.

Silylation of aminoesters by treating with 20% excess of hexamethyldisilazane at elevated temperature proceeds in high yields only in the case of aromatic aminoesters **Va, Vc**–**Vj** and compound **Vb**. Under these conditions the monosilylated derivatives **VIa** to **VIj** are formed. At the action of phosgene 10% excess used as 25% solution in toluene at 0–5°C and subsequent distilling toluene off they form corresponding isocyanates **VIIa**–**VIIj** in high yields. The formed compounds are easily isolated by vacuum distillation.

$$\underset{\textbf{Va–Vj}}{RNH_2} \xrightarrow[-NH_3]{(Me_3Si)_2NH} \underset{\textbf{VIa–VIj}}{RNHSiMe_3} \xrightarrow[-Me_3SiCl,\ -HCl]{COCl_2} \underset{\textbf{VIIa–VIIj}}{RN{=}C{=}O},$$

R = 4-$C_2H_5OC(O)CH_2C_6H_4$ (**a**), (4-ethoxycarbonylcyclohexyl)methyl (**b**), 2-$C_2H_5OC(O)C_6H_4$ (**c**), 2-$CH_3OC(O)C_6H_4$ (**d**), 3-$C_2H_5OC(O)C_6H_4$ (**e**), 3-$CH_3OC(O)C_6H_4$ (**f**), 4-$C_2H_5OC(O)C_6H_4$ (**g**), 4-$CH_3OC(O)C_6H_4$ (**h**), 2-$CH_3OC(O)$–5-ClC_6H_3 (**i**), 2,5-$[CH_3OC(O)]_2C_6H_3$ (**j**).

Silylation of the aliphatic, carbocyclic, and alkylaromatic α- and β-aminoacid ester hydrochlorides proceeds markedly more difficultly. Treating the hydrochlorides **VIIIa**–**VIIIe** and **IIj** with 5% molar excess of the equimolar mixture of hexamethyldisilazane and triethylamine in boiling benzene (method *a*) permits to prepare corresponding *N*-silyl derivatives **IXa**–**IXe** and **IXl** in 40–57% yield only. The

Table 1. Yields, ^{1}H NMR spectral and elemental analysis data of hydrochlorides **II** and free aminoesters **V**

Comp. no.	Yield, %	^{1}H NMR spectrum in DMSO-d_6, δ, ppm	Found, %		Formula	Calculated, %	
			C	H		C	H
IIa	90	1.1 t (3H, CH_3), 3.0 q (1H, CH_2), 3.20 q (1H, CH_2), 3.98 m (2H, OCH_2), 4.56 q (1H, CHN), 7.4 m (3H$_{arom}$), 7.56 d (2H$_{arom}$), 8.75 s (3H, NH_3)	–	–	$C_{11}H_{16}ClNO_2$	–	–
IIb	93	1.2 t (3H, CH_3), 3.05 q (1H, CH_2), 3.20 q (1H, CH_2), 3.77 s (3H, OCH_3), 4.02 q (2H, OCH_2), 4.50 m (1H, CHN), 7.03 d (2H$_{arom}$), 7.50 d (2H$_{arom}$), 8.41 s (3H, NH_3)	55.43	6.96	$C_{12}H_{18}ClNO_3$	55.49	6.98
IIc	95	1.2 t (3H, CH_3), 1.32 d (6H, $2CH_3$), 3.05 q (1H, CH_2), 3.20 q (1H, CH_2), 4.02 q (2H, OCH_2), 4.52 m (1H, CHN), 4.70 m (1H, OCH), 7.04 d (2H$_{arom}$), 7.51 d (2H$_{arom}$), 8.40 s (3H, NH_3)	58.37	7.66	$C_{14}H_{22}ClNO_3$	58.43	7.70

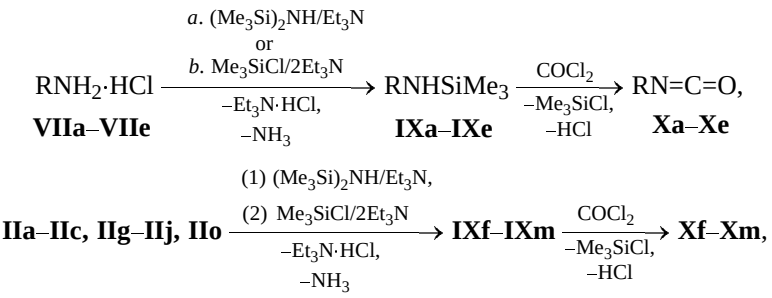
Table 1. (Contd.)

Comp. no.	Yield, %	^{1}H NMR spectrum in DMSO-d_6, δ, ppm	Found, %		Formula	Calculated, %	
			C	H		C	H
IId	95	1.2 t (3H, CH_3), 1.33 t (3H, CH_3), 2.87 q (1H, CH_2), 3.01 q (1H, CH_2), 3.77 s (3H, OCH_3), 4.05 m (4H, $2OCH_2$), 4.49 m (1H, CHN), 6.97 s ($2H_{arom}$), 7.21 s ($1H_{arom}$), 8.45 s (3H, NH_3)	55.30	7.26	$C_{14}H_{22}ClNO_4$	55.35	7.30
IIe	95	1.2 t (3H, CH_3), 1.29 d (6H, $2CH_3$), 2.88 q (1H, CH_2), 2.99 q (1H, CH_2), 3.77 s (3H, OCH_3), 4.05 q (2H, OCH_2), 4.50 m (1H, CHN), 4.71 m (1H, OCH), 6.97 d ($2H_{arom}$), 7.22 s ($1H_{arom}$), 8.43 s (3H, NH_3)	56.63	7.62	$C_{15}H_{24}ClNO_4$	56.69	7.61
IIf	95	1.01 d (6H, $2CH_3$), 1.21 t (3H, CH_3), 2.00 m (1H, CH), 2.85 q (1H, CH_2), 3.00 q (1H, CH_2), 3.71 d (2H, OCH_2), 3.76 s (3H, OCH_3), 4.07 q (2H, OCH_2), 4.48 m (1H, CHN), 6.97 s ($2H_{arom}$), 7.23 s ($1H_{arom}$), 8.43 s (3H, NH_3)	57.84	7.87	$C_{16}H_{26}ClNO_4$	57.91	7.90
IIg	93	1.10 t (3H, CH_3), 2.30 s (3H, CH_3), 2.94 q (1H, CH_2), 3.16 q (1H, CH_2), 4.00 q (2H, OCH_2), 4.51 q (1H, CHN), 7.21 d ($2H_{arom}$), 7.41 d ($2H_{arom}$), 8.67 s (3H, NH_3)	59.20	7.47	$C_{12}H_{18}ClNO_2$	59.14	7.44
IIh	95	1.08 t (3H, CH_3), 3.08 q (1H, CH_2), 3.25 q (1H, CH_2), 4.02 q (2H, OCH_2), 4.99 t (1H, CHN), 7.41 m ($2H_{arom}$), 7.51 d ($1H_{arom}$), 7.83 d ($1H_{arom}$), 8.89 s (3H, NH_3)	50.00	5.70	$C_{11}H_{15}ClNO_2$	50.02	5.72
IIi	90	1.12 t (3H, CH_3), 3.01 q (1H, CH_2), 3.16 q (1H, CH_2), 4.03 q (2H, OCH_2), 4.89 q (1H, CHN), 7.06 q ($1H_{arom}$), 7.24 d ($1H_{arom}$), 7.57 d ($1H_{arom}$), 8.60 br (3H, NH_3)	45.86	6.02	$C_9H_{14}ClNO_2S$	45.86	5.99
IIj	92	0.88 d (6H, $2CH_3$), 1.20 t (3H, CH_3), 1.95 m (1H, CH), 2.63 d (2H, CH_2), 3.42 q (1H, CHN), 4.08 q (2H, OCH_2), 8.30 s (3H, NH_3)	49.08	9.29	$C_8H_{18}ClNO_2$	49.10	9.27
IIk	95	0.98 t (3H, CH_3), 1.32 t (3H, CH_3), 1.45 m (2H, CH_2), 1.72 m (2H, CH_2), 2.77 q (1H, CH_2), 2.89 q (1H, CH_2), 3.71 m (1H, CHN), 4.26 q (2H, OCH_2)	49.06	9.30	$C_8H_{18}ClNO_2$	49.10	9.27
IIl	95	0.88 q (6H, $2CH_3$), 1.21 t (3H, CH_3), 1.37 m (1H, CH_2), 1.57 m (1H, CH_2), 1.74 m (1H, CH), 2.62 q (1H, CH_2), 2.79 q (1H, CH_2), 3.43 m (1H, CHN), 4.12 q (2H, OCH_2), 8.30 s (3H, NH_3)	51.51	9.64	$C_9H_{20}ClNO_2$	51.55	9.61
IIm	95	0.86 t (3H, CH_3), 1.19 t (3H, CH_3), 1.28 m (4H, $2CH_2$), 1.60 m (2H, CH_2), 2.68 q (1H, CH_2), 2.75 q (1H, CH_2), 3.37 m (1H, CHN), 4.09 q (2H, OCH_2), 8.26 s (3H, NH_3)	51.54	9.64	$C_9H_{20}ClNO_2$	51.55	9.61
IIn·HCl[a]	50	1.24 t (3H, CH_3), 3.38 m (2H, CH_2), 4.21 q (2H, OCH_2), 5.21 m (1H, CHN), 8.28 t ($1H_{arom}$), 8.87 d ($1H_{arom}$), 8.99 d ($1H_{arom}$), 9.10 s ($1H_{arom}$)	44.93	6.05	$C_{10}H_{16}Cl_2N_2O_2$	44.96	6.04
IIo	90	1.20 t (3H, CH_3), 1.32 m (1H, C_6H_{11}), 1.44 m (3H, C_6H_{11}), 1.66 m (2H, C_6H_{11}), 1.72 m (4H, C_6H_{11}), 2.74 s (2H, CH_2), 4.10 q (2H, OCH_2), 8.20 s (3H, NH_3)	54·14	9.11	$C_{10}H_{20}ClNO_2$	54.17	9.09
Va	95	1.16 t (3H, CH_3), 3.4 s (2H, NH_2), 4.04 q (2H, OCH_2), 4.92 s (2H, CH_2), 6.5 d ($2H_{arom}$), 6.87 d ($2H_{arom}$)	–	–	$C_{10}H_{13}NO_2$	–	–

[a] ^{1}H NMR spectrum was measured in D_2O.

yield can not be improved when trimethylchlorosilane is used instead of hexamethyldisilazane because in this case (procedure *b*) double amount of triethylamine and solvent is needed. Besides, triethylamine hydrochloride amorphous precipitate obtained includes reacting substances in its structure and hence prevents their interaction. Using methylene chloride instead of benzene favors crystallization of the ammonium salt precipitate [7], but no increase in the yield of silyl derivatives is observed. Combination of

silylating systems with the initial treating with hexamethyldiailazane-triethylamine mixture, filtering precipitate off and subsequent treating it with trimethylchlorosilane-triethylamine mixture does not increase yield of *N*-silyl derivatives **IXa**–**IXe, IXl**, and only for the alkylaromatic aminoester hydrochlorides **IIa**–**IIc, IIg**–**IIi** and compound **IIo** 70–75% yield of corresponding silylated aminoesters **IXf**–**IXk, IXm** may be achieved by using this combination. Phosgeneation of silicon derivatives **IXa**–**IXm** with 10% excess of phosgene used as 25% toluene solution at 0–5°C and subsequent distilling toluene off generates isocyanates **Xa**–**Xm** in 55–60% yield.



$RNH_2 \cdot HCl$ (**VIIa**–**VIIe**) → $RNHSiMe_3$ (**IXa**–**IXe**) → RN=C=O, (**Xa**–**Xe**)

IIa–**IIc, IIg**–**IIj, IIo** → **IXf**–**IXm** → **Xf**–**Xm**,

VIII–**X, XIV**–**XVI**, R = $CH_3OC(O)CH_2$ (**a**), $CH_3OC(O)(CH_2)_2$ (**b**), $CH_3OC(O)CH(CH_3)$ (**c**), $C_2H_5OC(O)CH_2$ (**d**), $C_2H_5OC(O)(CH_2)_2$ (**e**), $C_2H_5OC(O)CH_2CH(C_6H_5)$ (**f**), 4-$CH_3OC_6H_4CHCH_2COOC_2H_5$ (**g**), 4-$(CH_3)_2CHOC_6H_4CHCH_2 \cdot COOC_2H_5$ (**h**), 4-$CH_3C_6H_4CHCH_2COOC_2H_5$ (**i**), 2-$ClC_6H_4CHCH_2COOC_2H_5$ (**j**); R = $XCHCH_2COOC_2H_5$, X = 2-thenyl (**k**); R = $(CH_3)_2CHCHCH_2COOC_2H_5$ (**l**), 1-[(ethoxycarbonyl)methyl]cyclohexyl (**m**).

Yields and physicochemical characteristics of prepared compounds **IX** and **X** are listed in Table 2.

Analysis of ^1H, ^{13}C, and ^{29}Si NMR spectral data of trimethylsilyl derivatives **IXa**–**IXl** (Table 2) showed that they contain doubled resonance signals of all hydrogen, carbon, and silicon atoms and that for these compounds is characteristic the intramolecular transannular interaction of Si with the carboxylic group O atom. This interaction increases on dilution

Table 2. Yields, melting or boiling points, ^1H NMR spectra and mass spectra of compounds[a] **VI, VII, IX**–**XV, XVII, XVIII, XXI**, and **XXII**

Comp. no.	Yield, %	mp, °C or bp, °C (*p*, mm)	$M^{+\cdot}$ (*m/z*)	^1H NMR spectrum ($CDCl_3$), δ, ppm
VIa	98	142–145 (3)	–	0.10 s (9H, $3CH_3$), 1.18 t (3H, CH_3), 4.10 q (2H, OCH_2), 4.85 br (1H, NH), 5.02 s (2H, CH_2), 6.62 d ($2H_{arom}$), 7.08 d ($2H_{arom}$)
VIb	97	118–120 (1)	–	0.05 s, 0.14 s (9H, $3CH_3$), 0.85–1.0 m (2H, CH_2), 1.24 t (3H, CH_3), 1.30 m (2H, CH + NH), 1.35–1.48 m (2H, CH_2), 1.85 d.d (2H, CH_2), 2.0 m (2H, CH_2), 2.21 t.t (1H, CH), 2.53 d (2H, CH_2N), 4.10 q (2H, OCH_2)
VIc	97	118–120 (3)	237	–
VId	97	100–103 (2)	223	–
VIe	97	120–122 (3)	237	–
VIf	96	125–130 (4)	223	–
VIg	97	45–47	237	–
VIh	96	125–130 (4)	223	–
VIi	95	16–18	257	–
VIj	95	101–103	281	–
VIIa	98	115–118 (3)	205	1.27 t (3H, CH_3), 3.57 s (2H, CH_2), 4.17 q (2H, OCH_2), 7.03 d ($2H_{arom}$), 7.24 d ($2H_{arom}$)

Table 2. (Contd.)

Comp. no.	Yield, %	mp, °C or bp, °C (*p*, mm)	$M^{+\cdot}$ (*m*/*z*)	^{1}H NMR spectrum ($CDCl_3$), δ, ppm
VIIb	93	119–121(3)	211	0.88–1.02 m (2H, CH_2), 1.15 t (3H, CH_3), 1.27–1.41 m (2H, CH_2), 1.45 m (1H, CH), 1.77 m (2H, CH_2), 1.93 m (2H, CH_2), 2.13 t.t (1H, CH), 3.09 d (2H, CH_2N), 4.02 q (2H, OCH_2)
VIIc	95	29–31	191	1.41 t (3H, CH_3), 4.42 q (2H, OCH_2), 7.10 d ($1H_{arom}$), 7.24 t ($1H_{arom}$), 7.46 t ($1H_{arom}$), 8.00 d ($1H_{arom}$)
VIId	95	47–50	177	3.95 s (3H, OCH_3), 7.11 d ($1H_{arom}$), 7.24 t ($1H_{arom}$), 7.46 t ($1H_{arom}$), 8.00 d ($1H_{arom}$)
VIIe	95	112–115 (3)	191	1.37 t (3H, CH_3), 4.37 q (2H, OCH_2), 7.23 d ($1H_{arom}$), 7.38 t ($1H_{arom}$), 7.75 s ($1H_{arom}$), 7.86 d ($1H_{arom}$)
VIIf	94	35–38	177	3.94 s (3H, OCH_3), 7.23 d ($1H_{arom}$), 7.37 t ($1H_{arom}$), 7.74 s ($1H_{arom}$), 7.85 d ($1H_{arom}$)
VIIg	94	27–29	191	1.38 t (3H, CH_3), 4.36 q (2H, OCH_2), 7.12 d ($2H_{arom}$), 7.99 d ($2H_{arom}$)
VIIh	94	50–52	177	3.90 s (3H, OCH_3), 7.12 d ($2H_{arom}$), 7.99 d ($2H_{arom}$)
VIIi	88	160–163 (3)	211	–
VIIj	84	115–117	235	3.91 s (3H, OCH_3), 3.95 s (3H, OCH_3), 7.71 s ($1H_{arom}$), 7.82 d ($1H_{arom}$), 8.02 d ($1H_{arom}$)
IXa	51	60–64 (50)	161	0.044 s (9H, $3CH_3$), 1.40 br (1H, NH), 3.51 s (2H, CH_2), 3.68 s (3H, OCH_3)
IXc	57	50–53 (7)	175	0.046 s (9H, $3CH_3$), 1.34 d (3H, CH_3), 1.44 br (1H, NH), 3.64 q (1H, CH), 3.74 s (3H, OCH_3)
IXd	44	65–70 (50)	175	0.045 s (9H, $3CH_3$), 1.24 t (3H, CH_3), 1.38 br (1H, NH), 3.48 s (2H, CH_2), 4.17 q (2H, OCH_2)
IXe	40	58–60 (9)	189	0.047 s (9H, $3CH_3$), 1.24 t (3H, CH_3), 1.40 br (1H, NH), 2.47 t (2H, CH_2), 3.08 t (2H, CH_2), 4.07 q (2H, OCH_2)
IXf[b]	70	119–120 (1.5)	265	–0.04 s (9H, $3CH_3$), 1.15 br (1H, NH), 1.18 t (3H, CH_3), 2.51–2.58 q (1H, CH_2), 2.64–2.73 q (1H, CH_2), 4.10 q (2H, OCH_2), 4.38 br (1H, CH), 7.17–7.38 ($5H_{arom}$)
IXg	72	133–135 (1)	295	–0.04 s (9H, $3CH_3$), 1.13 br (1H, NH), 1.19 t (3H, CH_3), 2.50–2.58 q (1H, CH_2), 2.68–2.75 q (1H, CH_2), 3.88 s (3H, OCH_3), 4.08 q (2H, OCH_2), 4.40 br (1H, CH), 6.83 d ($2H_{arom}$), 7.36 d ($2H_{arom}$)
IXh	72	149–151 (1)	323	–0.04 s (9H, $3CH_3$), 1.14 br (1H, NH), 1.20 t (3H, CH_3), 1.32 d (6H, $2CH_3$), 2.52–2.60 q (1H, CH_2), 2.69–2.76 q (1H, CH_2), 3.88 s (3H, OCH_3), 4.08 q (2H, OCH_2), 4.38 br (1H, CH), 4.80 m (1H, OCH), 6.85 d ($2H_{arom}$), 7.38 d ($2H_{arom}$)
IXi	68	122–125 (1)	279	–0.04 s (9H, $3CH_3$), 1.10 t (3H, CH_3), 1.13 br (1H, NH), 2.28 s (3H, CH_3), 2.47–2.54 q (1H, CH_2), 2.63–2.69 q (1H, CH_2), 4.08 q (2H, OCH_2), 4.34 br (1H, CH), 7.00 d ($2H_{arom}$), 7.29 d ($2H_{arom}$)
IXj	67	140–142 (1)	299	–0.03 s (9H, $3CH_3$), 1.08 t (3H, CH_3), 1.14 br (1H, NH), 2.60–2.67 q (1H, CH_2), 2.71–2.78 q (1H, CH_2), 4.10 q (2H, OCH_2), 4.81 br (1H, CH), 7.18 d ($2H_{arom}$), 7.29 d ($1H_{arom}$), 7.70 d ($1H_{arom}$)
IXk	70	128–130 (1)	271	–0.03 s (9H, $3CH_3$), 1.14 br (1H, NH), 1.20 t (3H, CH_3), 2.52–2.59 q (1H, CH_2), 2.64–2.71 q (1H, CH_2), 4.12 q (2H, OCH_2), 4.71 br (1H, CH), 6.88 q ($1H_{arom}$), 7.06 d ($1H_{arom}$), 7.38 d ($1H_{arom}$)
IXl	60	85–90 (7)	231	0.048 s (9H, $3CH_3$), 0.98 d (6H, $2CH_3$), 1.22 t (3H, CH_3), 1.41 br (1H, NH), 1.98 m (1H, CH), 2.65 d (2H, CH_2), 3.44 q (1H, CHN), 4.08 q (2H, OCH_2)
IXm	75	105–110 (1.5)	257	0.05 s (9H, $3CH_3$), 0.98 br (1H, NH), 1.23 t (3H, CH_3), 1.30–1.62 m (10H, $5CH_2$), 2.40 s (2H, CH_2), 4.09 q (2H, OCH_2)
Xa	85	60 (12)	115	3.70 s (3H, OCH_3), 3.95 s (2H, CH_2)
Xb	78	68 (3)	129	2.56 t (2H, CH_2), 3.55 t (2H, CH_2N), 3.74 s (3H, OCH_3)
Xc	80	63–65 (3)	129	1.42 d (3H, CH_3), 3.77 s (3H, OCH_3), 4.07 q (1H, CH)

Table 2. (Contd.)

Comp. no.	Yield, %	mp, °C or bp, °C (*p*, mm)	$M^{+\cdot}$ (*m*/*z*)	^{1}H NMR spectrum ($CDCl_3$), δ, ppm
Xd	80	60 (9)	129	1.30 t (3H, CH_3), 3.91 s (2H, CH_2), 4.27 q (2H, OCH_2)
Xe	77	80 (5)	143	1.27 t (3H, CH_3), 2.57 t (2H, CH_2), 3.56 t (2H, CH_2N), 4.17 q (2H, OCH_2)
Xf	82	113–117 (2)	219	1.27 t (3H, CH_3), 2.73 q (1H, CH_2), 2.83 q (1H, CH_2), 4.19 q (2H, OCH_2), 5.13 q (1H, CH), 7.35 m ($5H_{arom}$)
Xg	77	126–128 (1)	249	1.27 t (3H, CH_3), 2.72 q (1H, CH_2), 2.82 q (1H, CH_2), 3.90 s (3H, OCH_3), 4.16 q (2H, OCH_2), 5.08 q (1H, CHN), 7.16 d ($2H_{arom}$), 7.38 d ($2H_{arom}$)
Xh	75	136–139 (1)	277	1.27 t (3H, CH_3), 1.34 d (6H, $2CH_3$), 2.72 q (1H, CH_2), 2.82 q (1H, CH_2), 4.16 q (2H, OCH_2), 4.82 m (1H, OCH), 5.08 q (1H, CHN), 7.16 d ($2H_{arom}$), 7.38 d ($2H_{arom}$)
Xi	79	117–119 (1)	233	1.18 t (3H, CH_3), 2.32 s (3H, CH_3), 2.67 q (1H, CH_2), 2.77 q (1H, CH_2), 4.17 q (2H, OCH_2), 5.04 q (1H, CHN), 7.14 d ($2H_{arom}$), 7.20 d ($2H_{arom}$)
Xj	68	132–134 (1)	253	1.17 t (3H, CH_3), 2.80 q (1H, CH_2), 2.89 q (1H, CH_2), 4.19 q (2H, OCH_2), 5.41 q (1H, CHN), 7.35 m ($3H_{arom}$), 7.60 d ($1H_{arom}$)
Xk	72	123–125 (1)	225	1.28 t (3H, CH_3), 2.73 q (1H, CH_2), 2.84 q (1H, CH_2), 4.20 q (2H, OCH_2), 5.32 q (1H, CHN), 6.96 t ($1H_{arom}$), 7.12 d ($1H_{arom}$), 7.28 d ($1H_{arom}$)
Xl	55	82–84 (9)	185	1.00 d (6H, $2CH_3$), 1.26 t (3H, CH_3), 2.00 m (1H, CH), 2.73 d (2H, CH_2), 4.08 q (2H, OCH_2), 4.14 t (1H, CHN)
Xm	96	110–115 (3)	211	1.17 m (1H, CH_2), 1.25 t (3H, CH_3), 1.35–1.67 m (7H, $4CH_2$), 1.82 d (2H, CH_2), 2.49 s (2H, CH_2), 4.14 q (2H, OCH_2)
XIa	–	–	161	0.053 s (9H, $3CH_3$), 1.40 br (1H, NH), 3.45 s (2H, CH_2), 3.64 s (3H, OCH_3)
XIb	–	–	175	0.056 s (9H, $3CH_3$), 1.28 d (3H, CH_3), 1.44 br (1H, NH), 3.58 q (1H, CH), 3.70 s (3H, OCH_3)
XId	–	–	175	0.055 s (9H, $3CH_3$), 1.27 t (3H, CH_3), 1.38 br (1H, NH), 3.41 s (2H, CH_2), 4.14 q (2H, OCH_2)
XIe	–	–	189	0.057 s (9H, $3CH_3$), 1.22 t (3H, CH_3), 1.40 br (1H, NH), 2.43 t (2H, CH_2), 3.03 t (2H, CH_2), 4.12 q (2H, OCH_2)
XIf[b]	–	–	265	0.05 s (9H, $3CH_3$), 1.22 t (3H, CH_3), 1.70 br (1H, NH), 2.65 d (2H, CH_2), 4.08 q (2H, OCH_2), 4.43 t (1H, CH), 7.17–7.38 ($5H_{arom}$)
XIg	–	–	295	0.05 s (9H, $3CH_3$), 1.23 t (3H, CH_3), 1.68 br (1H, NH), 2.70 d (2H, CH_2), 3.88 s (3H, OCH_3), 4.12 q (2H, OCH_2), 4.45 t (1H, CHN), 6.86 d ($2H_{arom}$), 7.40 d ($2H_{arom}$)
XIh	–	–	323	0.05 s (9H, $3CH_3$), 1.24 t (3H, CH_3), 1.34 d (6H, $2CH_3$), 1.72 br (1H, NH), 2.70 d (2H, CH_2), 4.11 q (2H, OCH_2), 4.43 t (1H, CHN), 4.76 m (1H, OCH), 6.88 d ($2H_{arom}$), 7.41 d ($2H_{arom}$)
XIi	–	–	279	0.05 s (9H, $3CH_3$), 1.08 t (3H, CH_3), 1.64 br (1H, NH), 2.24 s (3H, CH_3), 2.64 d (1H, CH_2), 4.06 q (2H, OCH_2), 4.39 t (1H, CH), 7.04 d ($2H_{arom}$), 7.32 d ($2H_{arom}$)
XIj	–	–	299	0.05 s (9H, $3CH_3$), 1.08 t (3H, CH_3), 1.70 br (1H, NH), 2.73 d (2H, CH_2), 4.08 q (2H, OCH_2), 4.85 t (1H, CH), 7.20 m ($2H_{arom}$), 7.32 d ($1H_{arom}$), 7.73 d ($1H_{arom}$)
XIk	–	–	271	0.05 s (9H, $3CH_3$), 1.17 t (3H, CH_3), 1.66 br (1H, NH), 2.66 d (2H, CH_2), 4.10 q (2H, OCH_2), 4.76 t (1H, CH), 6.94 t ($1H_{arom}$), 7.10 d ($1H_{arom}$), 7.41 d ($1H_{arom}$)
XIl	–	–	231	0.058 s (9H, $3CH_3$), 1.0 d (6H, $2CH_3$), 1.19 t (3H, CH_3), 1.41 br (1H, NH), 2.0 m (1H, CH), 2.68 d (2H, CH_2), 3.47 q (1H, CHN), 4.10 q (2H, OCH_2)
XIIf	5	–	176	1.34 t (3H, CH_3), 4.27 q (2H, OCH_2), 6.45 d (1H, CH=), 7.35 m ($3H_{arom}$), 7.54 t ($2H_{arom}$), 7.70 d (1H, CH=)

Table 2. (Contd.)

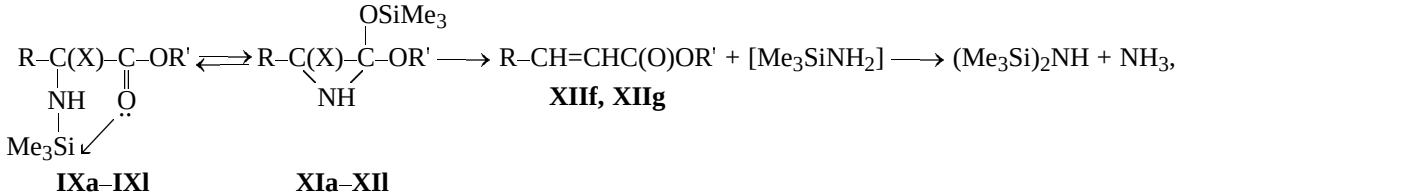
Comp. no.	Yield, %	mp, °C or bp, °C (*p*, mm)	$M^{+\cdot}$ (*m*/*z*)	^{1}H NMR spectrum ($CDCl_3$), δ, ppm
XIIg	8	–	206	1.34 t (3H, CH_3), 3.88 s (3H, OCH_3), 4.27 q (2H, OCH_2), 6.34 d (1H, CH=), 6.96 d ($2H_{arom}$), 7.49 d ($2H_{arom}$), 7.77 d (1H, CH=)
XIII	–	80–82	205	–
XIVa	35	–	205	0.23 s (9H, $3CH_3$), 3.75 s (3H, OCH_3), 3.96 d (2H, CH_2), 5.18 br (1H, NH)
XIVb	88	–	219	0.25 s (9H, $3CH_3$), 2.50 t (2H, CH_2), 3.40 q (2H, CH_2N), 3.70 s (3H, OCH_3), 5.20 br (1H, NH)
XIVc	42	–	219	0.24 s (9H, $3CH_3$), 1.32 d (3H, CH_3), 3.72 s (3H, OCH_3), 3.92 q (1H, CH), 5.20 br (1H, NH)
XIVd	37	–	219	0.23 s (9H, $3CH_3$), 1.27 t (3H, CH_3), 3.89 d (2H, CH_2), 4.20 q (2H, OCH_2), 5.20 br (1H, NH)
XIVe	88	–	233	0.25 s (9H, $3CH_3$), 1.25 t (3H, CH_3), 2.50 t (2H, CH_2), 3.40 q (2H, CH_2N), 4.14 q (2H, OCH_2) 5.19 br (1H, NH)
XIVf	92	–	309	0.26 s (9H, $3CH_3$), 1.16 t (3H, CH_3), 2.85 m (2H, CH_2), 4.06 q (2H, OCH_2), 5.11 q (1H, CH), 5.67 br (1H, NH), 7.24–7.36 m ($5H_{arom}$)
XIVg	90	–	339	0.26 s (9H, $3CH_3$), 1.17 t (3H, CH_3), 2.87 m (2H, CH_2), 3.88 s (3H, OCH_3), 4.08 q (2H, OCH_2), 5.10 q (1H, CH), 5.70 br (1H, NH), 6.86 d ($2H_{arom}$), 7.34 d ($2H_{arom}$)
XIVh	90	–	367	0.26 s (9H, $3CH_3$), 1.17 t (3H, CH_3), 1.30 d (6H, $2CH_3$), 2.88 m (2H, CH_2), 4.07 q (2H, OCH_2), 4.80 m (1H, OCH), 5.10 q (1H, CH), 5.70 br (1H, NH), 6.86 d ($2H_{arom}$), 7.34 d ($2H_{arom}$)
XIVi	88	–	323	0.25 s (9H, $3CH_3$), 1.17 t (3H, CH_3), 2.30 s (3H, CH_3), 2.86 m (2H, CH_2), 4.08 q (2H, OCH_2), 5.11 q (1H, CH), 5.72 br (1H, NH), 6.95 d ($2H_{arom}$), 7.30 d ($2H_{arom}$)
XIVj	92	–	343	0.28 s (9H, $3CH_3$), 1.18 t (3H, CH_3), 2.94 m (2H, CH_2), 4.08 q (2H, OCH_2), 5.15 q (1H, CH), 5.80 br (1H, NH), 7.31 m ($3H_{arom}$), 7.58 d ($1H_{arom}$)
XIVk	90	–	315	0.25 s (9H, $3CH_3$), 1.18 t (3H, CH_3), 2.86 m (2H, CH_2), 4.10 q (2H, OCH_2), 5.06 q (1H, CH), 5.70 br (1H, NH), 6.91 t ($1H_{arom}$), 7.10 d ($1H_{arom}$), 7.26 d ($1H_{arom}$)
XVa	65	–	277	0.28 s (9H, $3CH_3$), 0.30 s (9H, $3CH_3$), 3.72 s (3H, OCH_3), 3.90 s (2H, CH_2)
XVb	12	–	291	0.29 s (9H, $3CH_3$), 0.31 s (9H, $3CH_3$), 2.46 t (2H, CH_2), 3.34 t (2H, CH_2N), 3.68 s (3H, OCH_3)
XVc	58	–	291	0.28 s (9H, $3CH_3$), 0.30 s (9H, $3CH_3$), 1.30 d (3H, CH_3), 3.70 s (3H, OCH_3), 3.82 t (1H, CH)
XVd	63	–	291	0.27 s (9H, $3CH_3$), 0.29 s (9H, $3CH_3$), 1.24 t (3H, CH_3), 3.86 s (2H, CH_2), 4.15 q (2H, OCH_2)
XVe	12	–	305	0.26 s (9H, $3CH_3$), 0.28 s (9H, $3CH_3$), 1.25 t (3H, CH_3), 2.47 t (2H, CH_2), 3.37 t (2H, CH_2N), 4.12 q (2H, OCH_2)
XVf	8	–	381	0.20 s (9H, $3CH_3$), 0.28 s (9H, $3CH_3$), 2.85 m (2H, CH_2), 4.11 q (2H, OCH_2), 4.98 t (1H, CHN), 7.24–7.36 m ($5H_{arom}$)
XVg	10	–	411	0.20 s (9H, $3CH_3$), 0.28 s (9H, $3CH_3$), 1.20 t (3H, CH_3), 2.88 m (2H, CH_2), 3.88 s (3H, OCH_3), 4.13 q (2H, OCH_2), 4.97 t (1H, CHN), 6.87 d ($2H_{arom}$), 7.36 d ($2H_{arom}$)
XVh	10	–	439	0.20 s (9H, $3CH_3$), 0.28 s (9H, $3CH_3$), 1.20 t (3H, CH_3), 1.32 d (6H, $2CH_3$), 2.89 m (2H, CH_2), 4.11 q (2H, OCH_2), 4.78 m (1H, OCH), 4.98 t (1H, CHN), 6.87 d ($2H_{arom}$), 7.36 d ($2H_{arom}$)
XVi	12	–	395	0.20 s (9H, $3CH_3$), 0.28 s (9H, $3CH_3$), 1.20 t (3H, CH_3), 2.32 s (3H, CH_3), 2.88 m (2H, CH_2), 4.10 q (2H, OCH_2), 4.98 t (1H, CHN), 6.93 d ($2H_{arom}$), 7.33 d ($2H_{arom}$)

Table 2. (Contd.)

Comp. no.	Yield, %	mp, °C or bp, °C (*p*, mm)	$M^{+\cdot}$ (*m*/*z*)	^{1}H NMR spectrum ($CDCl_3$), δ, ppm
XVj	8	–	415	0.22 s (9H, $3CH_3$), 0.29 s (9H, $3CH_3$), 1.22 t (3H, CH_3), 2.96 m (2H, CH_2), 4.12 q (2H, OCH_2), 5.04 t (1H, CHN), 7.30 m ($3H_{arom}$), 7.56 d ($1H_{arom}$)
XVk	10	–	387	0.20 s (9H, $3CH_3$), 0.28 s (9H, $3CH_3$), 1.21 t (3H, CH_3), 2.90 m (2H, CH_2), 4.12 q (2H, OCH_2), 4.98 t (1H, CH), 6.89 t ($1H_{arom}$), 7.08 d ($1H_{arom}$), 7.24 d ($1H_{arom}$)
XVII	30	68–70 (15)	119	3.81 s (2H, CH_2)
XVIIIa	35	68–70 (15)	119	3.93 s (2H, CH_2)
XVIIIb	20	75–80 (5)	133	3.14 t (2H, CH_2), 3.64 t (2H, CH_2N)
XVIIIc	15	63–65 (3)	133	1.48 d (3H, CH_3), 4.57 q (1H, CHN)
XXI	12	130–133 (750)	137	3.37 s (3H, OCH_3), 3.44 t (2H, CH_2N), 3.49 t (2H, OCH_2), 5.88 br (1H, NH)
XXII	80	115–117 (735)	101	3.40 t (2H, CH_2N), 3.41 s (3H, OCH_3), 3.52 t (2H, OCH_2)

[a] Elemental analysis data (C and H content) of all the individual compounds prepared were in good agreement with their empirical formula. [b] ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 0.27 (3C, $SiMe_3$), 14.22 (1C, CH_3), 46.61 (1C, CH_2), 53.39 (1C, CH), 60.26 (1C, OCH_2), 126.05 ($2C_{arom}$), 126.72 ($1C_{arom}$), 128.30 ($1C_{arom}$), 146.40 ($1C_{arom}$), 171.54 (1C, C=O). ^{29}Si ($CDCl_3$) δ_{Si}, ppm: 3.70 (NSi). [c] ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 1.97 (3C, $SiMe_3$), 14.22 (1C, CH_3), 44.30 (1C, CH_2), 52.71 (1C, CH), 60.27 (1C, OCH_2), 126.10 ($2C_{arom}$), 127.20 ($1C_{arom}$), 128.61 ($2C_{arom}$), 146.42 (1Csa_r$4do$_m$), 171.96 (1C, NCO_2). ^{29}Si NMR spectrum ($CDCl_3$), δ_{Si}, ppm: 7.38 (OSi).

by $CDCl_3$, and in 5–10% solutions in polar solvents these compounds exist in an equlibrium with their cyclic *O*-silyl tautomers **XIa-m**. The difference in the frequency of proton resonance signals of CH or CH_2 groups at the nitrogen atom in compounds **IX** and **XI** is over 30 Hz that excludes absolutely a possibility of appearing additional signals in ^{1}H NMR spectra due to spin coupling. Besides, in ^{1}H NMR spectra of alkylaromatic derivatives **IXf**–**IXk** the CH_2 group resonance signal at the chiral center is observed as two characteristic quartets, and in their rigidly fixed tautomers **XIf**–**XIk** degeneration of fine structure leads to pseudoequivalence of the protons of CH_2 group bound with asymmetric center, thus the usual doublet of signals is observed in this group spectra. At the same time the resonance signal of the chiral center protons due to the decrease in dipole moment of the rigid structure **XIf**–**XIk** is observed as a characteristic triplet, while the higher dipole moment of the structure **IXf**–**IXk** leads to revealing resonance of the CH group proton as a broad signal. A polar solvent favors the tautomeric transformation while in concentrated solutions prevails structure **IX** (up to 90%). Tautomerism and ring strain in the isomers **XI** are probably responsible for a gradual decomposition of compounds **IXe** and **IXj** in diluted toluene solutions upon handling so that cynnamates **XIIf** and **XIIg** obtained in 5–8% amount according to NMR data, remain intacted even after completing the phosgeneation.



IXa–**IXl** **XIa**–**XIl**

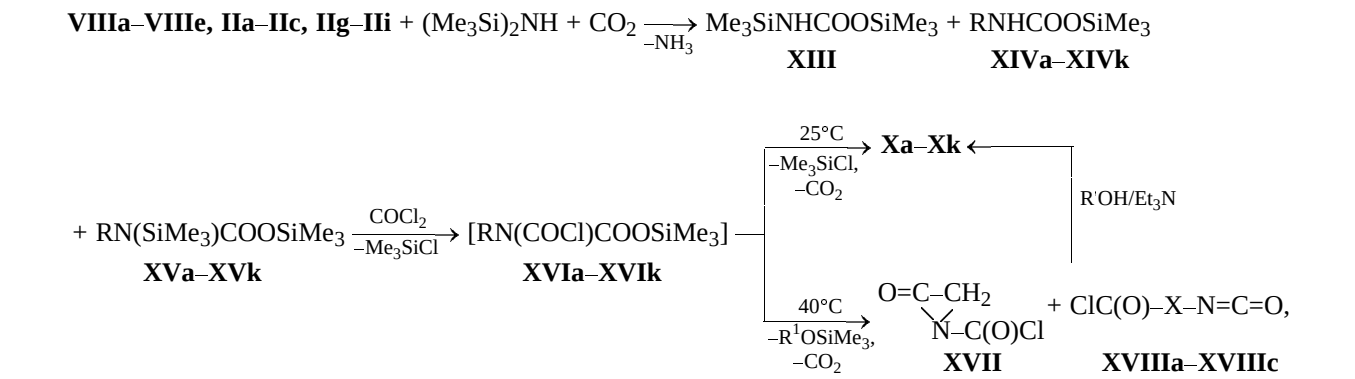
R = H (**a**–**e**), C_6H_5 (**f**), 4-$CH_3OC_6H_4$ (**g**), 4-$(CH_3)_2CHOC_6H_4$ (**h**), 4-$CH_3C_6H_4$ (**i**), 2-ClC_6H_4 (**j**), 2-thenyl (**k**), $(CH_3)_2CH$ (**l**); R^1 = CH_3 (**a**–**c**), C_2H_5 (**d**–**l**); X = H (**a, d**), CH_2 (**b, e**–**l**), CH_3 (**c**).

It is known [8–16] that 1,3-(*N*,*O*)-migration of silyl substituent is characteristic of silylamides, acetic and trifluoroacetic acid hydrazide silicon derivatives, some *N*-silylurethanes, *N*-trimethylsilylnitrocarbamates, and also of the silicon-containing carbazic acid derivatives. The 1,4- and 1,5-(*N*,*O*)-silatropic transformations of

silylated aminoesters found by us can be regarded as an example of far intramolecular donor-acceptor interaction of silicon and oxygen atoms.

It has been reported previously [17–19] that silylation of aminoesters and their hydrochlorides proceeds in high yield under the action of diethylaminotrimethylsilane. But yield of isocyanates **Xa**–**Xl** in the reaction of *N*-trimethylsilylaminoesters **IXa**–**IXl** with phosgene does not exceed 60% that can be probably explained by side formation of insoluble amino esters arising from the evolution of hydrogen chloride in the reaction course [18]. Due to that the total yield of isocyanates on an account of starting compounds **II** and **VIII** even in the case of silylation with Et_2NSiMe_3 is far below 50%. Considering this situation we studied the alternative two-stage approach to isocyanates **X** which includes *N*-siloxycarbonylation of amino ester hydrochlorides with the subsequent phosgeneation of the urethanes obtained.

In the preceeding report [1] we have established that amine hydrochlorides react with hexamethyldisilazane and CO_2 to form a mixture of mono- and bisilylurethanes. Under the analogous conditions, aliphatic **VIIIa**–**VIIIe** and alkylaromatic **IIa**–**IIc, IIg**–**IIi** aminoester hydrochlorides react with hexamethyldisilazane–CO_2 system to generate quantitatively a mixture of mono- (**XIVa**–**XIVk**) and bi- (**XVa**–**XVk**) silylurethanes. The ratio of these compounds depends on the electronic structure of starting aminoesters. Thus, in the case of glycine and alanine derivatives the bisilylated carbamates **XVa, XVc**, and **XVd** prevail. Their content in the reaction mixture falls to the range of 58–65 mol%. In the case of β-aminoesters, mono-*O*-silyl urethanes **XIVb, XIVe-XIVk** prevail: the content is 88–92 mol% that is caused evidently by the increase in the basicity of their nitrogen atom as compared to the compounds **XIVa, XIVc, and XIVd** because here the ester group is located remotely and aromatic substituent is conjugated with $NHCOOSiMe_3$ group. Probably by the same reason *N*-siloxycarbonylation of β-alanine ester hydrochlorides and its aromatic derivatives results in formation of known bis-trimethylsilylcarbamate **XIII** [20] as a by-product. Because of high boiling points of alkylaromatic isocyanatoesters **Xf**–**Xk** their preparation by means of the corresponding urethane pyrolysis in the presence of phenyltrichlorosilane is impossible. Transformation of the obtained mixtures of urerthans **XIVa**–**XIVk** and **XVa**–**XVk** to isocyanates **Xa**–**Xk** was carried out by treating with 10% excess of phosgene used as 25% toluene solution at 0°C. Under these conditions in the case of aliphatic aminoesters the corresponding isocyanatocarboxylic acid ester chlorides **XVIIIa**–**XVIIIc** are formed as byproducts. In the case of glycine the substituted aziridine **XVII** is additionally formed. Structures of all these compounds were established on the basis of ^1H NMR and mass spectral data of isolated phosgeneation products. Treating the byproducts **XVIIIa**–**XVIIIc** with methanol or ethanol in the presence of triethylamine at 0°C lead to quantitative formation of isocyanates **Xa**–**Xd** in total yield reaching 85%.



XIV–**XVI**, R = $CH_3OC(O)CH_2$ (**a**), $CH_3OC(O)(CH_2)_2$ (**b**), $CH_3OC(O)CH(CH_3)$ (**c**), $C_2H_5OC(O)CH_2$ (**d**), $C_2H_5OC(O)\cdot(CH_2)_2$ (**e**), $C_2H_5OC(O)CH_2CH(C_6H_5)$ (**f**), 4-$CH_3OC_6H_4CHCH_2COOC_2H_5$ (**g**), 4-$(CH_3)_2CHOC_6H_4CHCH_2COOC_2H_5$ (**h**), 4-$CH_3C_6H_4CHCH_2COOC_2H_5$ (**i**), 2-$ClC_6H_4CHCH_2COOC_2H_5$ (**j**); R = $XCHCH_2COOC_2H_5$, X = 2-thenyl (**k**). **XVIII, X** = CH_2 (**a**), $(CH_2)_2$ (**b**), $CHCH_3$ (**c**). R' = Me, Et.

Spectral characteristics and yields of compounds **X, XIV, XV, XVII**, and **XVIII** are listed in the Table 2. It is evident that phosgeneation of a mixture of urethanes **XIV** and **XV** proceeds through the intermediate generation of carbaminoyl chlorides **XVI**. Investigation of temperature effect on the phosgena-

tion products yield showed that careful slow increase in temperature to 25°C and starting distillation of volatile compounds only after the complete elimination of carbon dioxide leads to predominate formation of isocyanates **Xa**–**Xk** through elimination of trimethylchlorosilane and CO_2 from the intermediates **XVIa**–**XVIk**. When the temperature growths fastly, the carbamoyl chlorides **XVIa**–**XVIe** decomposition proceeds vigorously. In this case together with the trimethylchlorosilane elimination leading to formation of isocyanates **Xa**–**Xe**, elimination of methoxy- or ethoxytrimethylsilane takes place which affords compounds **XVII** and **XVIIIa**–**XVIIIc**. In the case of glycine derivatives their yield at 60°C reached 30% and 35% respectively. Note that formation of isocyanatocarboxylic acid chlorides of the type **XVIII** was previously observed in the course of phosgeneation of *N*-siloxycarbonylaminoacids trimethylsilyl esters [21]. In our case their generation is the first example of alkoxytrimethylsilane elimination with the participation of ester group. Thus, *N*-siloxycarbonylation of aminoester hydrochlorides with the subsequent phosgeneation of the formed *O*-silyl and *N*,*O*-bis-silylurethanes is an effective method for preparing isocyanatocarboxylic acid esters. It may be extended on the synthesis of the other hardly available isocyanates. We have reported [1] on the formation of 2-methoxyethylisocyanate in 60% yield by pyrolysis of 3 : 7 mixture of urethanes **XIX/XX** in the presence of $PhSiCl_3$. Phosgeneation of the same mixture in methylene chloride permitted to increase the isocyanate **XXII** yield to 80%.

$$\underset{\textbf{XIX}}{MeO(CH_2)_2NHCOOSiMe_3} + \underset{\textbf{XX}}{MeO(CH_2)_2N(SiMe_3)COOSiMe_3}$$

$$\xrightarrow[-HCl,\ -CO_2\ -Me_3SiCl]{COCl_2} \underset{\textbf{XXI}}{MeO(CH_2)_2NHC(O)Cl} + \underset{\textbf{XXII}, 80\%}{MeO(CH_2)_2N{=}C{=}O}.$$

Formation in small amount (8–12%) of carbamoyl chloride **XXI** in the above reaction was unexpected. Formally this substance may be regarded as the product of urethane **XIX** transacylation. But elucidation of real mechanism of its formation needs additional studies.

EXPERIMENTAL

The ^1H NMR spectra were taken in $CDCl_3$ on a Bruker AM-360 spectrometer (360.14 MHz). Mass spectra were obtained on a MAT-311A spectrometer at the electron ionization energy 70 eV with direct injection in the ion source.

Synthesis of β-aminoacids ester hydrochlorides. To a solution of 1 mol of aminoacid **Ia**–**Io, III** or **IV**, 3- or 4-aminobenzoic acid in 750 ml of corresponding absolute alcohol (methanol or ethanol) or to the suspension of 1 mol of antranylic, 2-amino-4-chlorobenzoic or aminoterephthalic acid in 1.7 l of alcohol 178.5 g (or 240 g in the case of aromatic *ortho*-aminoacid) of freshly distilled thionyl chloride was added at the initial temperature 50°C with the addition rate providing slight boiling of reaction mixture. After the addition was complete the resulting mixture was refluxed for 2 h. A sample (about 0.5 ml) was taken, solvent was evaporated from it and the aminoacid content in the residue was evaluated by means of ^1H NMR spectroscopy. If it still contained in the reaction mixture, an additional amount of thionyl chloride (1.5 mol per 1 mol of aminoacid) was added dropwise and reaction mixture was refluxed additionally for 1 h. When no free aminoacid could be detected in the analyzed sample, solvent was distilled off, 50 ml of corresponding alcohol was added and aminoacid hydrochloride obtained was precipitated by addition of 350–450 ml of dry ether. The precipitate formed was filtered off, washed with 150 ml of anhydrous ether and dried at 50°C. Compounds **IIa**–**IIo** were obtained by this procedure. In the case of other aminoacids the obtained hydrochloride was suspended in 400 ml of toluene and treated at 0°C under vigorous stirring with 100 ml of 38% aqueous sodium hydroxide. Filtration of insoluble aminoesters or evaporation of organic phase gave compounds **Va**–**Vj** in 90–92% yield. Aminoesters **Va, Vb** were additionally distilled in a vacuum. Boiling points 120–122°C (2 mm Hg) and 102–105°C (1 mm Hg), respectively.

Silylation of aromatic aminoacid esters. A mixture of 1 mol of aminoester **Va**–**Vj**, 96 g of hexamethyldisilazane and 2–3 drops of concentrated sulfuric acid was gradually heated to 170–180°C, kept for 30 min and distilled in a vacuum to give compounds **VIa**–**VIj**. For the ester **VIb**, n_D^{20} 1.4572.

Silylation of aminoester hydrochlorides. To a suspension of 1 mol of hydrochloride **VIIIa**–**VIIIe, IIj**in 400 ml of anhydrous benzene a mixture of 88 g

of hexamethyldisilazane and 111 g of triethylamine (method *a*) or a mixture of 119 g of trimethylchlorosilane, 222 g of triethylamine and 400 ml of benzene (method *b*) was added dropwise. After complete addition the reaction mixture was refluxed with stirring for 2 h, then cooled, filtered from the salt precipitate, and distilled in a vacuum to obtain compounds **IXa**–**IXe**, and **IXl** in 40–57% yield. The n_D^{20} values of compounds are: **IXa** 1.4210, **IXc** 1.4230, **IXd** 1.2193, **IXe** 1.4240.

Two-stage silylation of aminoester hydrochlorides. To a suspension of 1 mol of hydrochlorides **IIa**–**IIc, IIg**–**IIj, IIo** in 400 ml of anhydrous benzene a mixture of 88 g of hexamethyldisilazane and 111 g of triethylamine was added dropwise with stirring. After complete addition the reaction mixture was refluxed with stirring for 2 h, then cooled, and the salt precipitate was filtered off. Filtrate was treated dropwise with a mixture of 72 g of trimethylchlorosilane, 67 g of triethylamine, and 100 ml of benzene. Resulting mixture was refluxed for 1 h, cooled, and the salt precipitate was filtered off. Filtrate was distilled in a vacuum to give compounds **IXf**–**IXk, IXm** in 70–75% yield and silyl derivative **IXl** in 60% yield. The n_D^{20} values for the compounds are: **IXf** 1.4860, **IXm** 1.4614.

Phosgeneation of the aminoester *N*-rimethylsilyl derivatives. A solution of 0.2 mol of silylamine **Va**–**Vj, IXa-IXm** in 40 ml of toluene was added dropwise with stirring at 0°C to a solution of 2.18 g of $COCl_2$ in 80 ml of toluene. Complete dissolution of phosgeneated compounds was if necessary achieved by the addition of diethylene glycol dimethyl ether. When the addition of reagent was complete, trimethylchlorosilane and toluene were distiled off from the reaction mixture until the temperature of the vapor achieved 105°C. The residue was distilled in a vacuum to remove toluene, diglime, and obtained isocyanate. The last fraction was distilled again to remove toluene and diglime. In the case of isocyanates **Xa**–**Xe** a rectification column was used. Compounds **VIIa**–**VIIj, Xa**–**Xm** were obtained analogously. The n_D^{20} values for the compounds: **VIIa** 1.5189, **VIIb** 1.4647, **Xa** 1.4230, **Xf** 1.5070, Xm 1.4643.

***N*-Siloxylcarbonylation of aminoester hydrochlorides**. A suspension of 2 mol of a compound **VIIIa**–**VIIIe, IIa**–**IIc, IIg**–**IIi** in a mixture of 200 g of hexamethyldisilazane and 200 g of anhydrous benzene or toluene was heated under CO_2 flow for 5 h at 80–90°C. After the completing the gas bubbling the reaction mixture was cooled and the precipitate formed was filtered off. The hexamethyldisilazane excess and solvent were removed to give a mixture of urethanes **XIVa**–**k, XVa**–**XVk** in 99–100% yield on the starting aminoester hydrochloride. In the case of compounds **XIVb, XVe**–**XVk** after volatile solvent removing the residue was kept at 10°C for 120 h. Liquid mixture of urethanes was separated by filtration from the crystals of carbamate **XIII**. The latter was washed with cold hexane and distilled in a vacuum.

Phosgeneation of aminoester based *O*-silyl and *N,O*-bis-silylurethane mixture. A solution of a mixture of urethanes **XIVa**–**XIVk, XVa**–**XVk** in 40 ml of toluene or a solution of 3 : 7 mixture of urethanes **XIX, XX** in 40 ml of methylene chloride (1 mol on per 1 mole of unsubstituted aminoester) was added dropwise with stirring at 0°C to a solution of 21.8 g of $COCl_2$ in 80 ml of toluene or methylene chloride (for a mixture of compounds **XIX and XX**). After the addition was complete the reaction mixture was slowly heated to 25°C, and kept to the end of of CO_2 evolution. Trimethylchlorosilane and solvent were distilled off in a 50 mm Hg vacuum. Solvent was removed from the residue, and the isocyanates obtained were distilled in a 3 mm Hg vacuum. The distillate was distilled once again to remove the solvent admixture. In the case of isocyanates **Xa**–**Xe, XXII** a rectification column was used. Compounds **Xa**–**Xk, XXI,** and **XXII** were obtained by this procedure. In the case of isocyanates **Xa**–**Xe** the isocyanates obtained contained 8–12% of by-products **XVII** and **XVIIIa**–**XVIIIc**. In some experiments after the complete addition of a mixture of urethanes reaction mixture was quickly heated to 40°C not allowing its overburst, and the distillation of volatile products was begun immediately. In these cases a significant increase in the yield of by-products, compounds **XVII** and **XVIIIa**–**XVIIIc** was observed. These substances were distilled in a vacuum together with the target isocyanates **Xa**–**d**. For the transformation of the by-products to the target isocyanates their content in the mixture was evaluated from ^{1}H NMR spectral data. A mixture of compounds **Xa**–**Xe, XVII**, and **XVIIIa**–**XVIIIc** twice diluted with toluene was cooled to 0°C, and cool alcohol (ethanol or methanol)–triethylamine mixture (equimolar to compound **XVII** and **XVIIIa**–**XVIIIc** content) was added to it. After the addition was complete the resulting mixture was stirred for 30 min, filtered from the ammonium salt precipitate and distilled in a vacuum to give pure isocyanate **Xa**–**Xe**.

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