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Organosilicon Synthesis of Isocyanates: II.[1] Synthesis of Aliphatic, Carbocyclic, and Fatty–Aromatic Isocyanates

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Abstract—Silylation of a series of aliphatic, carbocyclic, and fatty–aromatic amines gave the corresponding silyl derivatives whose yield depended on the electronic and steric structure of the substrate and the nature of the silylating agent. The yield of isocyanates obtained by phosgenation of the silyl derivatives under mild conditions decreased in going from aliphatic amines to benzylamines and rose as the length of the alkyl chain in fatty–aromatic amines extended. The most convenient procedure for the synthesis of low-boiling alkyl isocyanates was found to be based on the transformation of amines or ammonium salts into silyl or silyl silylcarabamates, followed by pyrolysis of the latter in the presence of trichloro(phenyl)silane.

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Organic isocyanates have become demanded again in modern organic synthesis. Therefore, search for convenient laboratory methods of synthesis of these compounds is now an important problem. Undoubtedly, one of such methods is organosilicon synthesis of isocyanates. We previously reported [1] on the application of this metodoligy to the preparation of isocyanates of the furan, thiophene, and mono- and polyfluorinated benzene series. The present communication describes the results of our study on the use of silyl derivaives in the synthesis of both known and hitherto unknown aliphatic, carbocyclic, and fatty–aromatic isocyanates.

We found that heating of isopentylamine (**Ia**), 2-methoxyethylamine (**Ib**), 3-methoxypropylamine (**Ic**), or 3-ethoxypropylamine (**Id**) with excess (20 mol %) hexamethyldisilazane (HMDS) in the presence of concentrated sulfuric acid as catalyst leads to formation of mono- (**IIa**–**IId**) and bis-trimethylsilyl derivatives (**IIIa**–**IIId**) in quantitative yield and that the excess amount of HMDS is consumed completely for the synthesis of bis-silyl derivatives.

$$\underset{\mathbf{Ia–Im}}{\mathrm{RNH_2}} \xrightarrow[-\mathrm{NH_3}]{(\mathrm{Me_3Si})_2\mathrm{NH}} \underset{\mathbf{IIa–IIm}}{\mathrm{RNHSiMe_3}} + \underset{\mathbf{IIIa–IIId}}{\mathrm{RN(SiMe_3)_2}} \xrightarrow[-\mathrm{Me_3SiCl}]{\mathrm{COCl_2}} [\underset{\mathbf{IVa–IVm}}{\mathrm{RNHC(O)Cl}} + \underset{\mathbf{Va–Vd}}{\mathrm{RN(SiMe_3)C(O)Cl}}]$$

$$\xrightarrow[\substack{-\mathrm{Me_3SiCl},\\ -\mathrm{HCl}}]{} \underset{\mathbf{VIa–VIm}}{\mathrm{R–N{=}C{=}O}} + \underset{\mathbf{VIIe–VIIj}}{\mathrm{R–OCN}},$$

R = $(CH_3)_2CH(CH_2)_2$ (**a**), $CH_3O(CH_2)_2$ (**b**), $CH_3O(CH_2)_3$ (**c**), $C_2H_5O(CH_2)_3$ (**d**), $C_6H_5CH_2$ (**e**), 4-$CH_3OC_6H_4CH_2$ (**f**), 4-$CH_3C_6H_4CH_2$ (**g**), 4-$FC_6H_4CH_2$ (**h**), 3,4-$CH_2O_2C_6H_3CH_2$ (**i**), 3-$CH_3OC_6H_4CH_2$ (**j**), $C_6H_5(CH_2)_2$ (**k**), 4-$CH_3OC_6H_4 \cdot (CH_2)_2$ (**l**), 3,4-$(CH_3O)_2C_6H_3(CH_2)_2$ (**m**).

Under analogous conditions, fatty–aromatic amines **Ie**–**Im** give rise to 86–96% of the corresponding monosilyl derivatives **IIe**–**IIm** as the only products; presumably, the reason is the reduced basicity of the substrate due to the presence of an electron-acceptor aromatic substituent at the alkyl chain. Cyclopentylamine (**In**) and cyclohexylamine (**Io**) failed to react

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

with HMDS at all, which may be due to steric hindrances created by branching of the hydrocarbon skeleton at the amino group; moreover, the hydrocarbon skeleton in cyclohexylamine is not planar. We succeeded in effecting silylation of cycloalkylamines **In** and **Io** only with the use of chlorotrimethylsilane in the presence of triethylamine as hydrogen chloride acceptor.

$$\mathbf{In,\ Io}\ \xrightarrow[-Et_3N\cdot HCl]{Me_3SiCl/Et_3N}\ \mathbf{IIn,\ IIo}\ \xrightarrow[-Me_3SiCl,\ -HCl]{COCl_2}\ \mathbf{VIn,\ VIo},$$

R = cyclopentyl (**n**), cyclohexyl (**o**).

Treatment of *N*-trimethylsilylamines **IIa**–**IIo** or their mixtures with *N,N'*-bis-silyl derivatives **IIIa**–**IIId** with a 25% solution of phosgene (1.1 equiv with respect to monosilyl derivative **II**) in toluene at 0°C, followed by removal of chlorotrimethylsilane and toluene afforded the corresponding isocyanates **VIa**–**VIo**, which can readily be isolated by distillation (if necessary, through a rectification column). Obviously, isocyanates **VIa**–**VIo** are formed through intermediate carbamoyl chlorides **IVa**–**IVo** and **Va**–**Vd**. Compound **IVa** was isolated in a mixture with **VIa** (at a ratio of 7 : 13) by distillation. The complete transformation of **IVa** into isocyanate **VIa** requires additional heating of mixture **IVa/VIa** for 4 h at the boiling point.

The structure of silylamines **IIa**–**IIo** and **IIIa**–**IIId**, carbamoyl chloride **IVa**, and isocyanates **VIa**–**VIo** was confirmed by the data of elemental analysis, ^{1}H NMR spectroscopy, and mass spectrometry (see table). The yields of aliphatic isocyanates **VIa**, **VIc**, and **VId** ranged from 66 to 67%, while the yields of benzyl isocyanates **VIe**–**VIj** were lower (40–58%). Presumably, the isocyanato group in the latter is activated due to stronger polarization of the C–N bond, which favors oligo- and polymerization. The same factor is likely to be responsible for the presence of a small amount (5–6%) of isomeric cyanates **VIIe**–**VIIj** in the isolated products **VIe**–**VIj**. As an exception, the isomer ratio **VIi/VIIi** reached 76 : 24. Extension of the alkyl chain in fatty–aromatic amines weakens the effect of the aromatic substituent, so that the yield of isocyanates **VIk**–**VIm** attains 66–77%. The poor yield (30%) of isocyanate **VIb** may be rationalized in terms of possible generation and polymerization of aziridine during the process. Steric hindrances in carbocyclic amines **In** and **Io** may be responsible for not only their failure to react with HMDS but also poor yield (30%) of isocyanates **VIn** and **VIo** in the phosgenation of **IIn** and **IIo**.

Low-boiling aliphatic amines **Ip**–**It** did not undergo silylation by the action of HMDS. Therefore, these amines, as well as cycloalkylamines **In** and **Io**, were converted into isocyanates **VIn**–**VIt** according to a different procedure. The reaction of amines **In**–**It** with HMDS and carbon dioxide gave the corresponding silyl carbamates **VIIIn**–**VIIIt** which were subjected to pyrolysis at 150–200°C in the presence of trichloro(phenyl)silane. As a result, isocyanates **VIn**–**VIt** were obtained in 50–65% yield in most cases.

$$\underset{\mathbf{In–It}}{RNH_2}\ \xrightarrow[-NH_3]{(Me_3Si)_2NH/CO_2}\ \underset{\mathbf{VIIIn–VIIIt}}{RNHCOOSiMe_3}$$

$$\xrightarrow[-Me_3SiCl]{PhSiCl_3}\ \underset{\mathbf{VIn–VIt}}{RN{=}C{=}O},$$

R = $(CH_3)_2CH$ (**p**), $CH_3(CH_2)_2$ (**q**), $C_2H_5CH(CH_3)$ (**r**), $(CH_3)_2CHCH_2$ (**s**), $CH_2{=}CHCH_2$ (**t**).

The yields and physical properties of compounds **VIp**–**VIt** and **VIIIn**–**VIIIt** are collected in table. It should be noted that the above procedure is simple in operation, for removal of excess HMDS from the reaction mixture gives sufficiently pure carbamates **VIIIn**–**VIIIt** (no additional purification is necessary). Formally, the role of trichloro(phenyl)silane is limited to binding of the liberated water. However, in fact, transsilylation processes with subsequent formation of polymeric siloxanes and hydrogen chloride are essential in the pyrolysis mechanism. Transsilylation should occur exceptionally readily in the first step of the reaction of silyl carbamates **VIII** with trichloro(phenyl)silane.

$$\begin{aligned} &PhNCOOSiMe_3 + PhSiCl_3 \\ &\xrightarrow[-Me_3SiCl]{}\ [RNHCOOSiCl_2Ph] \\ &\longrightarrow RN{=}C{=}O + [PhCl_2SiOH]. \end{aligned}$$

Phenols are the strongest acids in the series alcohols–glycols–phenols, and they give rise to the least thermally stable phenyl carbamates. Like phenols, silanols also exhibit pronounced acidic properties which are enhanced in dichloro(phenyl)silanol due to the presence of electron-acceptor substituents on the silicon atom. Just that factor is responsible for easy formation of isocyanates with elimination of dichloro(phenyl)silanol molecule. The latter is quickly removed from the reaction zone via transformation into a mixture of oligosiloxanes, which is accompanied by liberation of HCl [2].

$$PhCl_2SiOH\ \xrightarrow[-HCl]{}\ PhCl_2Si\text{–}(OSiClPh)_n\ OSiCl_2Ph.$$

However, allyl isocyanate (**VIt**) was formed only in 3–5% yield under the above conditions. It is known

Melting or boiling points, ^{1}H NMR and mass spectra, and elemental analyses of compounds **II–IV** and **VI–XI**

Comp. no.	Yield, %	mp, °C or bp, °C (p, mm Hg)	$M^{+\cdot}$	^{1}H NMR spectrum, δ, ppm	Found, %		Formula	Calculated, %	
					C	H		C	H
IIa	100	143–145 (737)	–	0.01 s (9H, $3CH_3$), 0.65 br (1H, NH), 0.85 d (6H, $2CH_3$), 1.26 q (2H, CH_2), 1.60 m (1H, CH), 2.69 t (2H, CH_2)	–	–	$C_8H_{21}NSi$	–	–
IIb	100	133–135 (750)	–	0.01 s (9H, $3CH_3$), 0.95 br (1H, NH), 3.11 t (2H, CH_2N), 3.32 s (3H, OCH_3), 3.42 t (2H, OCH_2)	–	–	$C_6H_{17}NOSi$	–	–
IIc	100	143–145 (748)	–	0.01 s (9H, $3CH_3$), 1.0 br (1H, NH), 1.64 m (2H, CH_2), 2.75 t (2H, CH_2N), 3.28 s (3H, OCH_3), 3.40 t (2H, OCH_2)	–	–	$C_7H_{19}NOSi$	–	–
IId	100	162–164 (748)	–	0.01 s (9H, $3CH_3$), 1.0 br (1H, NH), 1.17 t (3H, CH_3), 1.64 m (2H, CH_2), 2.77 t (2H, CH_2N), 3.44 m (4H, $2OCH_2$)	–	–	$C_8H_{21}NOSi$	–	–
IIe	91.3	62–65 (2)	179	–	66.86	9.51	$C_{10}H_{17}NSi$	66.98	9.55
IIf	96.5	91–94 (2)	209	–	62.97	9.11	$C_{11}H_{19}NOSi$	63.11	9.15
IIg	92.8	98–100 (4)	193	–	68.20	9.83	$C_{11}H_{19}NSi$	68.33	9.90
IIh	96.3	93–95 (3)	197	–	60.63	8.12	$C_{10}H_{16}FNSi$	60.87	8.17
IIi	86.2	116–118 (3)	223	–	58.98	7.60	$C_{11}H_{17}NO_2Si$	59.16	7.67
IIj	96.5	93–94 (2)	209	–	63.01	9.11	$C_{11}H_{19}NOSi$	63.11	9.15
IIk	90.5	125–126 (6)	193	–	68.20	9.84	$C_{11}H_{19}NSi$	68.33	9.90
IIl	94.3	118–120 (3)	223	–	64.31	9.44	$C_{12}H_{21}NOSi$	64.52	9.48
IIm	93.6	140–145 (2)	253	–	61.40	9.10	$C_{13}H_{23}NO_2Si$	61.62	9.15
IIIa	20	165–168 (737)	–	0.03 s (18H, $6CH_3$), 0.88 d (6H, $2CH_3$), 1.32 q (2H, CH_2), 1.62 m (1H, CH), 2.72 t (2H, CH_2)	–	–	$C_{11}H_{29}NSi_2$	–	–
IIIb	20	158–160 (750)	–	0.03 s (18H, $6CH_3$), 3.10 t (2H, CH_2N), 3.33 s (3H, OCH_3), 3.41 t (2H, OCH_2)	–	–	$C_9H_{25}NOSi_2$	–	–
IIIc	20	170 (748)	–	0.03 s (18H, $6CH_3$), 1.72 m (2H, CH_2), 2.75 t (2H, CH_2N), 3.29 s (3H, OCH_3), 3.44 t (2H, OCH_2)	–	–	$C_{10}H_{27}NOSi_2$	–	–
IIId	18	180–182 (748)	–	0.03 s (18H, $6CH_3$), 1.17 t (3H, CH_3), 1.73 m (2H, CH_2), 2.79 t (2H, CH_2N), 3.44 m (4H, $2OCH_2$)	–	–	$C_{11}H_{29}NOSi_2$	–	–
IVa	–	–	149	0.94 d (6H, $2CH_3$), 1.47 q (2H, CH_2), 1.62 m (1H, CH), 3.27 t (2H, CH_2), 5.60 br (1H, NH)	–	–	$C_6H_{12}ClNO$	–	–
VIa	67.3	135–137 (747)	113	0.92 d (6H, $2CH_3$), 1.50 q (2H, CH_2), 1.72 m (1H, CH), 3.30 t (2H, CH_2)	63.65	9.75	$C_6H_{11}NO$	63.69	9.80
VIb	60	115–117 (750)	101	3.40 t (2H, CH_2N), 3.41 s (3H, OCH_3), 3.52 t (2H, OCH_2)	47.43	6.94	$C_4H_7NO_2$	47.52	6.98
VIc	66.6	140–143 (744)	115	1.83 m (2H, CH_2), 3.33 s (3H, OCH_3), 3.40 t (2H, CH_2N), 3.45 t (2H, OCH_2)	52.20	7.79	$C_5H_9NO_2$	52.16	7.88

Table (Contd.)

Comp. no.	Yield, %	mp, °C or bp, °C (p, mm Hg)	$M^{+\cdot}$	^{1}H NMR spectrum, δ, ppm	Found, %		Formula	Calculated, %	
					C	H		C	H
VId	67.5	157–159 (748)	129	1.19 t (3H, CH_3), 1.84 m (2H, CH_2), 3.42 t (2H, CH_2N), 3.50 m (4H, 2OCH_2)	55.75	8.55	$C_6H_{11}NO_2$	55.80	8.58
VIe	54.8	67–70 (3)	133	4.49 s (2H, CH_2), 7.31–7.44 m (5H_{arom})	72.21	5.28	C_8H_7NO	72.17	5.30
VIf	58.4	97–99 (3)	163	3.82 s (3H, OCH_3), 4.40 s (2H, CH_2), 6.93 d (2H_{arom}), 7.26 d (2H_{arom})	66.22	5.54	$C_9H_9NO_2$	66.25	5.56
VIg	40.8	85–90 (3)	147	2.36 s (3H, CH_3), 4.44 s (2H, CH_2), 7.20 m (4H_{arom})	73.50	6.13	C_9H_9NO	73.45	6.16
VIh	58.2	64 (2)	151	4.45 s (2H, CH_2), 7.06 m (2H_{arom}), 7.29 m (2H_{arom})	63.56	3.99	C_8H_6FNO	63.58	4.00
VIi	46.8	115–116 (3)	177	4.36 s (2H, CH_2), 5.95 s (2H, OCH_2), 6.78 m (3H_{arom})	60.98	3.95	$C_9H_7NO_3$	61.02	3.98
VIj	56.5	98–100 (3)	163	3.83 s (3H, OCH_3), 4.42 s (2H, CH_2), 6.90 m (2H_{arom}), 7.14 m (2H_{arom})	66.28	5.55	$C_9H_9NO_2$	66.25	5.56
VIk	65.7	73–75 (3)	147	2.95 t (2H, CH_2), 3.56 t (2H, CH_2N), 7.29 d (2H_{arom}), 7.39 t (1H_{arom}), 7.41 t (2H_{arom})	73.47	6.11	C_9H_9NO	73.45	6.16
VIl	76.1	110–114 (3)	177	2.86 t (2H, CH_2), 3.49 t (2H, CH_2N), 3.82 s (3H, OCH_3), 6.90 d (2H_{arom}), 7.16 d (2H_{arom})	67.70	6.26	$C_{10}H_{11}NO_2$	67.78	6.26
VIm	77.3	140–145 (2.5)	207	2.80 t (2H, CH_2), 3.45 t (2H, CH_2N), 3.82 s (3H, OCH_3), 3.84 s (3H, OCH_3), 6.72 d (2H_{arom}), 6.80 d (1H_{arom})	63.70	6.28	$C_{11}H_{13}NO_3$	63.76	6.32
VIn	55	145–147 (750)	111	1.62–1.78 m (8H, 4CH_2), 3.88 m (1H, CHN)	64.82	8.16	C_6H_9NO	64.84	8.16
VIo	55	169–170 (750)	125	1.32 m (3H, C_6H_{11}), 1.47 m (3H, C_6H_{11}), 1.69 m (2H, C_6H_{11}), 1.87 m (2H, C_6H_{11}), 3.42 m (1H, CHN)	–	–	$C_7H_{11}NO$	–	–
VIp	65.2	74–75 (749)	85	1.29 d (6H, 2CH_3), 3.71 m (1H, CHN)	56.50	8.27	C_4H_7NO	56.45	8.29
VIq	49.6	83–84 (755)	85	0.98 t (3H, CH_3), 1.64 m (2H, CH_2), 3.26 t (2H, CH_2N)	56.41	8.26	C_4H_7NO	56.45	8.29
VIr	56	100–101 (750)	99	0.97 t (3H, CH_3), 1.27 d (3H, CH_3), 1.50 m (2H, CH_2), 3.47 m (1H, CHN)	60.54	9.13	C_5H_9NO	60.58	9.15
VIs	60	104 (748)	99	0.96 d (6H, 2CH_3), 1.84 m (1H, CH), 3.12 d (2H, CH_2N)	60.51	9.11	C_5H_9NO	60.58	9.15
VIt	52	87–89 (755)	83	–	57.72	6.03	C_4H_5NO	57.82	6.07
VIu	50	39–40 (750)	57	3.02 s (3H, CH_3N)	–	–	C_2H_3NO	–	–
VIv	48	60–62 (750)	71	1.25 t (3H, CH_3), 3.22 q (2H, CH_2N)	–	–	C_3H_5NO	–	–
VIw	50	135 (750)	105	–	–	–	C_3H_4ClNO	–	–

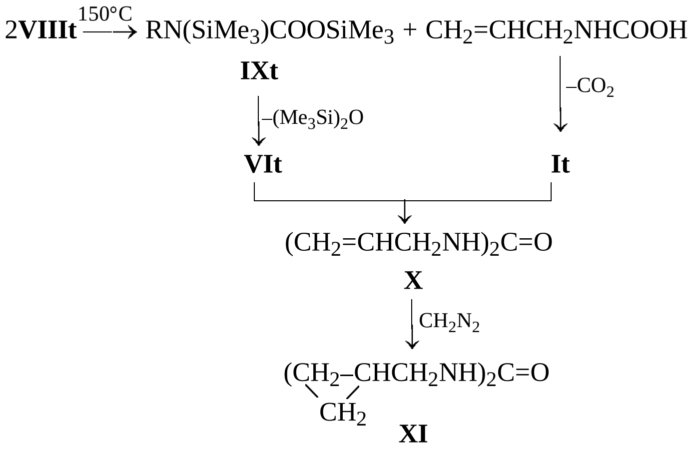
Table (Contd.)

Comp. no.	Yield, %	mp, °C or bp, °C (*p*, mm Hg)	$M^{+\cdot}$	^{1}H NMR spectrum, δ, ppm	Found, %		Formula	Calculated, %	
					C	H		C	H
VIIe	3	67–70 (3)	133	4.61 s (2H, CH$_2$), 7.31–7.44 m (5H$_{arom}$)	–	–	C_8H_7NO	–	–
VIIf	7	97–99 (3)	163	3.82 s (3H, OCH$_3$), 4.59 s (2H, CH$_2$), 6.91 d (2H$_{arom}$), 7.34 d (2H$_{arom}$)	–	–	$C_9H_9NO_2$	–	–
VIIg	5	85–90 (3)	147	2.36 s (3H, CH$_3$), 4.57 s (2H, CH$_2$), 7.21 m (4H$_{arom}$)	–	–	C_9H_9NO	–	–
VIIh	3.5	64 (2)	151	4.57 s (2H, CH$_2$), 7.06 m (2H$_{arom}$), 7.37 m (2H$_{arom}$)	–	–	C_8H_6FNO	–	–
VIIi	15	115–116 (3)	177	4.52 s (2H, CH$_2$), 5.95 s (2H, OCH$_2$), 6.85 m (3H$_{arom}$)	–	–	$C_9H_7NO_3$	–	–
VIIj	3.5	98–100 (3)	163	3.83 s (3H, OCH$_3$), 4.60 s (2H, CH$_2$), 6.92 m (2H$_{arom}$), 7.13 m (2H$_{arom}$)	–	–	$C_9H_9NO_2$	–	–
VIIIb	88.7	–	191	0.25 s (9H, 3CH$_3$), 3.30 t (2H, CH$_2$N), 3.33 s (3H, OCH$_3$), 3.43 t (2H, OCH$_2$), 5.08 br (1H, NH)	43.79	8.90	$C_7H_{17}NO_3Si$	43.95	8.96
VIIIn	96.2	45–47	201	0.24 s (9H, 3CH$_3$), 1.56–1.73 m (8H, 4CH$_2$), 3.66 m (1H, CHN), 4.80 br (1H, NH)	53.63	9.49	$C_9H_{19}NO_2Si$	53.69	9.51
VIIIo	95.5	63–65	215	0.23 s (9H, 3CH$_3$), 1.28 m (3H, C$_6$H$_{11}$), 1.45 m (3H, C$_6$H$_{11}$), 1.67 m (2H, C$_6$H$_{11}$), 1.85 m (2H, C6H11), 3.23 (1H, CHN), 4.82 br (1H, NH)	55.60	9.73	$C_{10}H_{21}NO_2Si$	55.77	9.83
VIIIp	98.3	53–54	175	0.25 s (9H, 3CH$_3$), 1.20 d (6H, 2CH$_3$), 3.50 m (1H, CHN), 4.70 br (1H, NH)	47.80	9.72	$C_7H_{17}NO_2Si$	47.96	9.77
VIIIq	97.1	51 (1.5)	175	0.26 s (9H, 3CH$_3$), 0.94 t (3H, CH$_3$), 1.60 m (2H, CH$_2$), 3.08 t (2H, CH$_2$N), 4.60 br (1H, NH)	47.84	9.74	$C_7H_{17}NO_2Si$	47.96	9.77
VIIIr	97.8	43–45	189	0.28 s (9H, 3CH$_3$), 0.92 t (3H, CH$_3$), 1.13 d (3H, CH$_3$), 1.45 m (2H, CH$_2$), 3.58 m (1H, CHN), 4.52 br (1H, NH)	50.59	10.03	$C_8H_{19}NO_2Si$	50.75	10.11
VIIIs	92.4	40–42	189	0.27 s (9H, 3CH$_3$), 0.9 d (6H, 2CH$_3$), 1.74 m (1H, CH), 2.96 t (2H, CH$_2$N), 4.74 br (1H, NH)	50.65	10.07	$C_8H_{19}NO_2Si$	50.75	10.11
VIIIt	95	60–61 (2.5)	173	–	48.40	8.65	$C_7H_{15}NO_2Si$	48.52	8.72
VIIIu	50	58–59 (3)	147	0.31 s (9H, 3CH$_3$), 2.74 d (3H, CH$_3$), 4.50 br (1H, NH)	–	–	$C_5H_{13}NO_2Si$	–	–
VIIIv	50	–	161	0.3 s (9H, 3CH$_3$), 1.23 t (3H, CH$_3$), 3.12 q (2H, CH$_2$N), 4.53 br (1H, NH)	–	–	$C_6H_{15}NO_2Si$	–	–
VIIIw	41	–	195	0.30 s (9H, 3CH$_3$), 2.62 m (4H, ${}_2$CH$_2$)	–	–	$C_6H_{14}ClNO_2Si$	–	–

Table (Contd.)

Comp. no.	Yield, %	mp, °C or bp, °C (*p*, mm Hg)	$M^{+\cdot}$	^{1}H NMR spectrum, δ, ppm	Found, %		Formula	Calculated, %	
					C	H		C	H
IXb	70	–	263	0.21 s (9H, $3CH_3$), 0.28 s (9H, $3CH_3$), 3.27 t (2H, CH_2N), 3.31 s (3H, OCH_3), 3.38 t (2H, OCH_2)	–	–	$C_{10}H_{25}NO_3Si_2$	–	–
IXt	75	55–56 (1)	245	–	–	–	$C_{10}H_{23}NO_2Si_2$	–	–
IXu	50	63–67 (4)	219	0.26 s (9H, $3CH_3$), 0.32 s (9H, $3CH_3$), 2.63 s (3H, CH_3N)	–	–	$C_8H_{21}NO_2Si_2$	–	–
IXv	50	–	233	0.25 s (9H, $3CH_3$), 0.32 s (9H, $3CH_3$), 1.24 t (3H, CH_3), 3.04 q (2H, CH_2N)	–	–	$C_9H_{23}NO_2Si_2$	–	–
IXw	41	–	267	0.25 s (9H, $3CH_3$), 0.30 s (9H, $3CH_3$), 2.64 m (4H, $2CH_2$)	–	–	$C_9H_{22}ClNO_2Si_2$	–	–
X	55	92–93	140	–	59.90	8.60	$C_7H_{12}N_2O$	59.97	8.63
XI	85	133–135	168	0.18 q (4H, $2CH_2$), 0.49 q (4H, $2CH_2$), 0.96 m (2H, 2CH), 3.04 d (4H, $2CH_2N$), 4.42 br (2H, 2NH)	64.22	9.57	$C_9H_{16}N_2O$	64.25	9.59

that direct pyrolysis of carbamate **VIIIt** gives no isocyanate **VIt**. It was believed [3] that the pyrolysis process is terminated owing to intermediate formation of trimethylsilanol and then water, yielding *N*,*N'*-diallylurea (**X**). By GLC analysis we revealed an alternative mechanism of thermal decomposition of compound **VIIIt**. The pyrolysis begins with formation of silyl silylcarbamate **IXt** via disproportionation, and the scheme of thermal decomposition of **VIIIt** may be represented as follows.



The above mechanism of formation of urea **X** was proposed previously by Knaush *et al.* [4], but no experimental evidence was given by the authors. By treatment of **X** with diazomethane we obtained difficultly accessible *N,N'*-bis(cyclopropylmethyl)urea (**XI**).

Taking into account that the pyrolysis of silylcarbamate **IXt** occurs in a selective fashion, yielding isocyanate **VIt**, carbamate **VIIIt** was subjected to further silylation by the action of chlorotrimethylsilane–HMDS (3 : 1). Pyrolysis of carbamate mixture **VIIIt/IXt** (1 : 3) thus obtained in the presence of trichloro-

(phenyl)silane afforded allyl isocyanate (**VIIIt**) in a good yield (52%).

It is advisable to involve the corresponding hydrochlorides instead of low-boiling alkylamines in reaction with HMDS–CO_2. For example, 2-chloroethylamine is stable only as hydrochloride. According to [5], amine hydrochlorides react with HMDS–CO_2 to give silyl carbamates. We found that 2-methoxyethylamine hydrochloroide (**XIIb**), methylamine hydrochloride (**XIIu**), ethylamine hydrochloride (**XIIv**), and 2-chloroethylamine hydrochloride (**XIIw**) react with HMDS and carbon dioxide to give equimolar mixtures of *O*-silyl and *O*,*N*-bis-silyl derivatives **VIIIb/IXb** and **VIIIu/IXu**–**VIIIw/IXw**. Pyrolysis of these mixtures in the presence of trichloro(phenyl)silane (cf. **VIIIt/IXt**) yields 50% of isocyanates **VIb** and **VIu**–**VIw**.

$$\underset{\textbf{XIIb, XIIu–XIIw}}{RNH_2\cdot HCl} \xrightarrow[-NH_4Cl]{(Me_3Si)_2NH/CO_2} \textbf{VIIIb, VIIIu–VIIIw} + \textbf{IXb, IXu–IXw} \xrightarrow[-Me_3SiCl,\ -HCl]{PhSiCl_3} \textbf{VIb, VIu–VIw},$$

$$R = CH_3\ (\textbf{u}),\ C_2H_5\ (\textbf{v}),\ ClCH_2CH_2\ (\textbf{w}).$$

The subsequent silylation of silyl carbamate **VIIIb** with a 3 : 1 mixture of chlorotrimethylsilane and HMDS leads to silyl silylcarbamate **IXb** in 70% yield, and pyrolysis of mixture **VIIIb/IXb** (30 : 70) in the presence of trichloro(phenyl)silane gives up to 60% of isocyanate **VIb**.

The formation of persilylated carbamates from hydroxylamine and hydrazine salts was reported previously [6, 7]. We can state that generation of *N*,*O*-bis-silyl derivatives **IX** by the action of HMDS–CO_2 is a general reaction of ammonium salts. This may be interpreted in terms of NH acidity of quaternary ammonium cations: hydrogen atoms in ammonium salts are replaced more readily than in free amines. Therefore, the known catalytic activity of mineral acids in the silylation of amines [8] becomes obvious:

$$[RNH_3]^+X^- + (Me_3Si)_2NH + CO_2$$
$$\longrightarrow [RNH_2COOSiMe_3]^+X^- + [Me_3SiNH_2]$$
$$\longrightarrow [RNH(SiMe_3)COOSiMe_3]^+X^- + NH_3$$
$$\longrightarrow RN(SiMe_3)COOSiMe_3 + NH_4X,$$
$$R = Alk,\ OH,\ NH_2;\ X = Cl,\ 1/2SO_4.$$

On the other hand, easy N-silylation of ammonium salts may be determined by the following reaction:

$$RNH_2\cdot HX + (Me_3Si)_2NH$$
$$\rightleftarrows Me_3SiX + RNH_2 + [Me_3SiNH_2].$$

In this case, the silylating agents are silicon derivatives of mineral acids, which are characterized by enhanced reactivity. Replacement of a proton by Me_3Si group is accompanied by insertion of carbon dioxide molecule into the Si–N bond being formed. Initial exhaustive silylation of the nitrogen atom is ruled out, for persilylated nitrogen compounds do not react with CO_2 [9, 10]. The presence of persilylated carbamates as mixtures with monosilylcarbamates is likely to be responsible for 50% yield of isocyanates from carbamates **VIIIb**, **VIIIt**, and **VIIIw**; pyrolysis of the latter in the absence of carbamates **IXb**, **IXt**, and **IXw** gives almost no isocyanates.

EXPERIMENTAL

The ^1H NMR spectra were measured on a Bruker AM-360 spectrometer operating at 360.14 MHz; $CDCl_3$ was used as solvent. The mass spectra (electron impact, 70 eV) were obtained on an LKB-2091 mass spectrometer with direct sample admission into the ion source. The reaction mixtures were analyzed by GLC on an LKhM-80 chromatograph equipped with a thermal conductivity detector (SE-30 capillary column, 50 m; carrier gas helium; detector temperature 200°C, injector temperature 140°C, oven temperature programming at a rate of 8 deg min^{-1}). The products were identified by comparing with authentic samples.

Silylation of amines with hexamethyldisilazane *(general procedure).* Hexamethyldisilazane, 96.6 g, and 2 drops of concentrated sulfuric acid were added to 1 mol of amine **Ia**–**Im**. The mixture was heated for 2 h under reflux and distilled to isolated silylamine mixture **IIa/IIIa**–**IId/IIId** or compound **IIIe**–**IIIm**.

Silylation of amines with chlorotrimethylsilane *(general procedure).* Amine **In** or **Io**, 1 mol, was dissolved in 700 ml of anhydrous toluene, and a mixture of 113.9 g of chlorotrimethylsilane and 106 g of triethylamine was added dropwise. When the addition was complete, the mixture was stirred for 2 h at 100°C, cooled to 5°C, and filtered. The filtrate was distilled to isolate silylamine **IIn** or **IIo** (yield 92–93%) as the last fraction.

Phosgenation of silylamines *(general procedure).* A solution of silylamine mixture **IIa/IIIa**–**IId/IIId** (calculated per mole of amine **Ia**–**Id**) or 1 mol of compound **IIe**–**IIo** in 200 ml of toluene was added dropwise to a solution of 109 g of $COCl_2$ in 380 ml of toluene under stirring at 0°C. When the addition was complete, chlorotrimethylsilane and toluene were distilled off up to a vapor temperature of 105°C. Toluene and the resulting isocyanate were distilled off from the residue under reduced pressure, and the distillate was repeatedly distilled to remove toluene; in the synthesis of isocyanates **VIa**–**VId**, the distillation was performed using a rectification column. We thus isolated mixture **IVa/VIa** (7 : 13), isocyanates **VIb**–**VId** and **VIm**–**VIo** or inseparable mixtures **VIe/VIIe**–**VIj/VIIj** which contained 5–6% of cyanates **VIIe**–**VIIh** and **VIIj** or 35% of cyanate **VIIi**. By heating mixture **IVa/VIa** for 4 h at 140°C we obtained pure isocyanate **VIa**. Listed below are compound no., n_D^{20}: **VIa**, 1.4200; **VIb**, 1.4105; **VIc**, 1.4190; **VId**, 1.4180; **VIe**, 1.5260; **VIf**, 1.4328; **VIg**, 1.5224; **VIh**, 1.5052; **VIj**, 1.4300; **VIk**, 1.5222; **VIl**, 1.5270; **VIm**, 1.5350; **VIn**, 1.4470; **VIo**, 1.4552.

***N*-Siloxycarbonylation of free amines** *(general procedure).* A mixture of 2 mol of amine **Ib** or **In**–**It** and 200 g of HMDS was heated to 40°C, and dry carbon dioxide was bubbled through the solution over a period of 3 h, maintaining the temperature (the reaction was accompanied by heat evolution) at 55–60 (**Ib**, **Ip**–**It**), 63–65 (**In**), or 70–80°C (**Io**) to avoid clogging of the bubbler. The mixture was cooled, and excess HMDS was distilled off at 50°C (5 mm) to leave carbamate **VIIIb** or **VIIIn**–**VIIIt** containing 96–98% of the main substance.

***N*-Siloxycarbonylation of ammonium salts** *(general procedure).* A suspension of 2 mol of compound **XIIb** or **XIIu**–**XIIw** and 200 g of HMDS in 200 ml of anhydrous toluene was kept for 3 h at 80–90°C while bubbling carbon dioxide through the mixture. The mixture was cooled and filtered, and excess HMDS and the solvent were distilled from the filtrate to isolate carbamate mixture **VIIIb/IXb** or **VIIIu/IXu**–**VIIIw/IXw** at a ratio of 1 : 1. Yield 88–90%, calculated on the initial amine hydrochloride.

***N*-Silylation of silylcarbamates VIIIb and VIIIt.** Chlorotrimethylsilane, 163 g, and HMDS, 80 g, were added to 1 mol of compound **VIIIb** or **VIIIt**, and the mixture was kept for 3 days with occasional stirring. The mixture was filtered, and excess chlorotrimethylsilane and HMDS were distilled off from the filtrate under reduced pressure to obtain carbamate mixture **VIIIb/IXb** (3 : 7) or **VIIIt/IXt** (1 : 3).

Pyrolysis of silyl carbamates in the presence of trichloro(phenyl)silane *(general procedure).* Silyl carbamate **VIIIn**–**VIIIs**, 1 mol, or carbamate mixture **VIIIb/IXb** (3 : 7), **VIIIt/IXt** (1 : 3), or **VIIIu/IXu**–**VIIIw/IXw** (1 : 1) equivalent to 1 mol of initial amine was added dropwise to 1 mol of trichloro(phenyl)silane. An additional 1 mol of trichloro(phenyl)silane was added to the mixture, and it was gradually heated under stirring to 200°C with simultaneous removal of volatile substances by distillation into a receiver cooled to –5°C. The distillate was subjected to rectification until 96–99% purity (according to the GLC and ^{1}H NMR data) of the isolated product. Yield of isocyanates **VIn**–**VIs** 50–65%, of **VIb**, 60%, of **VIt**, 52%, and of **VIu**–**VIw**, 50%. Compound **VIv** was isolated as a mixture with chlorotrimethylsilane. To remove the latter, mixture Me_3SiCl/**VIv** was diluted with a double volume of toluene and cooled to –2°C, and an equimolar mixture of 1-butanol and triethylamine (equivalent to the chlorotrimethylsilane) in an equal volume of toluene, cooled to 0°C, was added dropwise. The mixture was stirred for 1 h and filtered, and the filtrate was distilled through a rectification column to isolate 48% of isocyanate **VIv** with a purity higher than 96%. Below are listed compound no., n_D^{20}: **VIp**, 1.3820; **VIq**, 1.3940; **VIr**, 1.4000; **VIs**, 1.4110; **VIt**), 1.4170; **VIv**, 1.3803; **VIw**, 1.4492.

Pyrolysis of carbamate VIIIt. Compound **VIIIt**, 0.2 mol, was heated for 3 h at 150–160°C. GLC analysis showed formation and accumulation of carbamate **IXt** in the temperature range from 120 to 150°C. The mixture was cooled, 30 ml of hexane was added, and the precipitate was filtered off and washed with hexane to isolate 7.7 g (55%) of *N,N'*-diallylurea (**X**).

***N,N'*-Bis(cyclopropylmethyl)urea (XI).** *N*-Methyl-*N*-nitrosourea, 16.48 g, was added to a mixture of 60 ml of 40% aqueous potassium hydroxide and 300 ml of diethyl ether. The ether layer solution was separated by decanting, dried for 2 h over solid KON, and mixed with 30 ml of methanol, the mixture was added to 5.6 g of urea **X**, and the resulting mixture was stirred. When gaseous products no longer evolved (~1 h), 10 ml of acetic acid was added, the solvent was distilled off, and the residue was recrystallized from ethanol. Yield 5.7 g (85%).

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