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TRIMETHYLSILYLATED *N*-ALKYL-SUBSTITUTED CARBAMATES

I. PREPARATION AND SOME REACTIONS

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Summary

Trimethylsilyl *N*-monoalkyl- and *N,N*-dialkyl-carbamates have been made in 85–95% yields by silylation of the corresponding ammonium carbamates with trimethylchlorosilane. Trimethylsilyl *N,N*-dimethylcarbamate can be used for silylation of alcohols, phenols, and carboxylic acids. The silylcarbamates react with carboxylic acid halides to give the corresponding acid amides. The reaction of trimethylsilyl carbamates with carboxylic anhydrides give the corresponding silyl carboxylate and acid amide, while the reaction with dicarboxylic anhydrides give the trimethylsilyl monoamide of the corresponding dicarboxylic acid, i.e. $Me_3SiO_2C{\sim\!\sim}CONR^1R^2$.

Introduction

Some reactions of silylcarbamates have been described [1–4], and they can be used as intermediates in various organosilicon and organic syntheses. In the present paper the preparation and the reactions of the silylated derivatives of some alkylcarbamates are reported.

Several methods are known for the preparation of silylcarbamates. Brederveld [5,6] and other authors [1–3,7–10] obtained silylated alkyl-substituted carbamates from silylated alkylamines by addition of carbon dioxide. Sheludyakov et al. [11,12] prepared silylcarbamates by treating amines or their salts with hexamethyldisilazane in the presence of carbon dioxide. Mironov et al. [13–15] prepared silylcarbamates by transamination with primary or secondary amines of high boiling points. Birkofer

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and Sommer [4,16] obtained trimethylsilyl *N*-trimethylsilylcarbamate by treatment of silver carbamate or ammonium carbamate with chlorosilane.

Results

A method was developed [17] for the preparation of silyl *N*-alkylcarbamates based on the reaction used by Birkofer and Sommer. In this method trimethylsilylated alkylcarbamates were prepared by silylation of alkylammonium salts of the *N*-alkylcarbamic acids which were obtained from aliphatic amines by treatment with carbon dioxide. The synthesis involves two steps. In the first the primary or secondary aliphatic amine is treated with carbon dioxide in a dichloromethane solution in an ice cooled bath to give the corresponding alkylammonium salt of *N*-alkylcarbamic acid:

$$2R^1R^2NH + CO_2 \xrightarrow[CH_2Cl_2]{-10\text{–}0^\circ C} [R^1R^2NC(O)O]R^1R^2NH_2$$

$(R^1 = \text{alkyl}, R^2 = \text{alkyl or H})$

In the second step, the carbamate is silylated with a stoichiometric amount of trimethylchlorosilane:

$$[R^1R^2NC(O)O]R^1R^2NH_2 + (CH_3)_3SiCl \xrightarrow[CH_2Cl_2]{0\text{–}20^\circ C} R^1R^2NC(O)OSi(CH_3)_3 + [R^1R^2NH_2]Cl$$

Trimethylsilylated *N*-alkylcarbamates can be prepared by this method in yields of 85 to 95% based on the trimethylchlorosilane used.

The above method is also suitable for the production of *N*,*O*-bis-silylated *N*-alkylcarbamic acid derivatives starting from a 1/2–2.5 molar mixture of the corresponding primary amine and triethylamine. This mixture is treated with carbon dioxide to give a carbamate, which is then treated with a stoichiometric amount of trimethylchlorosilane:

$$RNH_2 + Et_3N + CO_2 \xrightarrow[CH_2Cl_2]{-10\text{–}0^\circ C} [RHNC(O)O]Et_3NH$$

$$[RNHC(O)O]Et_3NH + Et_3N + 2(CH_3)_3SiCl \xrightarrow[CH_2Cl_2]{0\text{–}20^\circ C} R[(CH_3)_3Si]NC(O)OSi(CH_3)_3 + 2[Et_3NH]Cl$$

The *N*,*O*-bis-silylated carbamates can be obtained in yields of about 70% based on the chlorosilane used.

Tables 1 and 2 show the yields and physical parameters of the silylated *N*-alkylcarbamates obtained. The yields given in Table 1 refer to products of 99 to 99.5% gas chromatographic purity.

It is advisable to carry out the distillation of the product at as low a temperature as possible since decomposition occurs at higher temperatures, and this leads to contamination of the desired products and significantly lower yields. Thus trimethylsilyl *N*,*N*-dialkylcarbamates were found to decompose above 200°C in the con-

(Continued on p. 15)

TABLE 1

PHYSICAL CONSTANTS AND YIELDS OF $R^1R^2NC(O)OSi(CH_3)_3$ COMPOUNDS

	R^1	R^2	Yield (%)	B.p. (°C/mbar)	M.p. (°C)	GC retention index	n_D^{20} measured (lit.)	References
1.	CH_3	CH_3	95–96	28/1.5	–	944 ± 2	1.4197 (1.4157)	8
2.	C_2H_5	C_2H_5	91–93	36/1.5	–	1063 ± 2	1.4202 (1.4193)	8
3.	n-C_3H_7	n-C_3H_7	92–94	62.5–63/1.5	–	1206 ± 3	1.4253	–
4.	i-C_3H_7	i-C_3H_7	90–93	–	54–55	1128 ± 3	–	–
5.	n-C_4H_9	n-C_4H_9	92–94	90–92/1.5	–	1367 ± 3	1.4308	–
6.	i-C_4H_9	i-C_4H_9	86–89	87–89/2	–	1346 ± 3	1.4265	–
7.	$(CH_2)_5$		88–90	59–60/1.5	–	1254 ± 3	1.4527 (1.4501)	12
8.	$(CH_2)_2O(CH_2)_2$		84–88	–	41–42	1242 ± 4	–	–
9.	CH_3	H	86–89	36/1.5	–	955 ± 2	1.4244 (1.4241)	12
10.	C_2H_5	H	88–91	–	45.5–46	992 ± 2	–	–
11.	n-C_3H_7	H	84–87	58–59/1.5	–	1096 ± 2	1.4273	–
12.	i-C_3H_7	H	87–91	–	51–52	1008 ± 3	–	–
13.	n-C_4H_9	H	85–89	83/1.5	–	1170 ± 3	1.4305 (1.4303)	12
14.	i-C_4H_9	H	84–87	–	29–31	1145 ± 3	–	–
15.	s-C_4H_9	H	86–89	–	34–34.5	1124 ± 3	–	–
16.	t-C_4H_9	H	91–93	–	42.5–43	1025 ± 2	–	–
17.	CH_2CHCH_2	H	88–92	53–54/1.5	–	1045 ± 3	1.4386 (1.4380)	12
18.	c-C_6H_{11}	H	91–93	–	81–82 (dec)	1383	–	–
19.	$C_6H_5CH_2$	H	85–88	–	46–46.5	1520 ± 5	–	–
20.	CH_3	$(CH_3)_3Si$	67–70	44–45/1.5	–	1099 ± 2	1.4263	–
21.	n-C_4H_9	$(CH_3)_3Si$	69–71	88–89/1.5	–	1277 ± 3	1.4315 (1.4308)	2

TABLE 2

MASS SPECTRA, IR AND ^1H NMR DATA FOR $R^1R^2NC(O)OSi(CH_3)_3$ COMPOUNDS

	R^1	R^2	Mass spectra			IR (CCl_4 sol.)		^1H NMR τ, $CDCl_3$ sol., TMS standard	
			M^+		$M-15^+$				
			m/e	Int. (%)	Int. (%)	$\nu(N-H)$ (cm^{-1})	$\nu(C=O)$ (cm^{-1})	N–H	$OSi(CH_3)_3$ and $NSi(CH_3)_3$
1.	CH_3	CH_3	161	15	100	–	1682	–	9.71
2.	C_2H_5	C_2H_5	189	15	80	–	1676	–	9.71
3.	n-C_3H_7	n-C_3H_7	217	7	37	–	1675	–	9.71
4.	i-C_3H_7	i-C_3H_7	217	4	66	–	1671	–	9.71
5.	n-C_4H_9	n-C_4H_9	245	9	39	–	1675	–	9.72
6.	i-C_4H_9	i-C_4H_9	245	6	57	–	1675	–	9.72
7.	$(CH_2)_5$		201	32	100	–	1675	–	9.71
8.	$(CH_2)_2O(CH_2)_2$		203	15	90	–	1675	–	9.70
9.	CH_3	H	147	2	40	3345 [a]	1683 [a]	3.80	9.73
10.	C_2H_5	H	161	7	60	3332 [a]	1686 [a]	3.84	9.73
11.	n-C_3H_7	H	175	14	44	3320 [a]	1688 [a]	3.40	9.73
12.	i-C_3H_7	H	175	5	75	3335 [b]	1710 [b]	5.30	9.74
13.	n-C_4H_9	H	189	14	40	3340 [a]	1688 [a]	3.98	9.73
14.	i-C_4H_9	H	189	12	45	3336 [b]	1687 [b]	4.06	9.72
15.	s-C_4H_9	H	189	0.3	23	3338 [b]	1685 [b]	5.22	9.72
16.	t-C_4H_9	H	189	1	62	3345	1707	5.30	9.73
17.	$CH_2{=}CHCH_2$	H	173	6	57	3338	1684	3.92	9.72
18.	c-C_6H_{11}	H	215	5	52	3334 [a]	1685 [a]	4.33	9.72
19.	$C_6H_5CH_2$	H	223	4	48	3332 [a]	1686 [a]	4.02	9.73
20.	CH_3	$(CH_3)_3Si$	219	2	27	–	1693	–	9.73–9.80
21.	n-C_4H_9	$(CH_3)_3Si$	261	7	25	–	1690	–	9.72–9.78

[a] Capillary film. [b] Voltalef (fluorocarbon).

densed phase or in the gaseous phase with liberation of carbon dioxide, and formation of trimethylsilylamines:

$$R^1R^2NC(O)OSi(CH_3)_3 \xrightarrow{t > 200°C} R^1R^2NSi(CH_3)_3 + CO_2$$

The trimethylsilyl *N*-monoalkylcarbamates are converted into an *N,O*-bis-silylated derivative by autosilylation in the condensed phase at temperatures from 100–120°C:

$$2R(H)NC(O)OSi(CH_3)_3 \xrightarrow[\text{consensed phase}]{t > 100\text{–}120°C} R[(CH_3)_3Si]NC(O)OSi(CH_3)_3 + RNH_2 + CO_2$$

The *N,O*-bis-silylated derivatives are converted into aliphatic isocyanates with liberation of hexamethyldisiloxane:

$$R[(CH_3)_3Si]NC(O)OSi(CH_3)_3 \xrightarrow{t > 100\text{–}120°C} RNCO + [(CH_3)_3Si]_2O$$

The isocyanate reacts with the amine formed during the autosilylation to give the 1,3-dialkylurea:

$$RNCO + RNH_2 \rightarrow [R(H)N]_2CO$$

In our experience the appearance of dialkylurea in the reaction mixture is always preceded by the appearance of *N,O*-bis-silylated carbamate. We could not observe the reaction described by Mironov et al. [2] in which trimethylsilyl *N*-monoalkylcarbamates decompose to give isocyanate and silanol. *N*-Monoalkyl derivatives were found to liberate carbon dioxide above 220°C in the gas phase at reduced pressure to give silylamines:

$$R(H)NC(O)OSi(CH_3)_3 \xrightarrow[\text{gas phase}]{t > 220°C} R(H)NSi(CH_3)_3 + CO_2$$

Some characteristic reactions of silyl carbamate

Birkofer and Sommer [4] described the use of trimethylsilyl *N*-trimethylsilylcarbamate for the silylation of alcohols, phenols and carboxylic acids, but these are no reports of silylation by use of the trimethylsilylated derivatives of *N*-alkylcarbamic acid. Trimethylsilyl *N*-methylcarbamate, trimethylsilyl *N*-methyl-*N*-trimethylsilyl carbamate and trimethylsilyl *N,N*-dimethylcarbamate were found to be very efficient reagents for silylation of alcohols, phenols and carboxylic acids, the efficiency of silylation decreasing with the increasing length of the alkyl chain:

$$ROH + (CH_3)_2NC(O)OSi(CH_3)_3 \rightarrow ROSi(CH_3)_3 + (CH_3)_2NH + CO_2$$

$$(R = \text{alkyl, aryl, alkyl } C(O), \text{ aryl } C(O))$$

The above reaction gave silylated compounds in 75 to 95% yields. The reaction conditions, yields and physical properties of the products are summarized in Table 3.

N,N-Dialkylcarbamoyl chlorides were prepared by Birkofer and Krebs [1] by the reaction of trimethylsilyl *N,N*-dialkylcarbamates with phosphorus pentachloride or thionyl chloride. We examined the reactions of trimethylsilyl *N*-alkylcarbamates with carboxylic chlorides and with benzene sulphonylchloride. The corresponding

TABLE 3

$$\underset{(A)}{ROH} + \underset{(B)}{(CH_3)_2NC(O)OSi(CH_3)_3} \rightarrow ROSi(CH_3)_3 + (CH_3)_2NH + CO_2$$

REACTION CONDITIONS, YIELDS AND PHYSICAL PROPERTIES OF THE PRODUCTS

A compound	A/B	Conditions		Yield (%)	Ref.	m.p./b.p. [°C/mbar] measured (lit)	n_D^{20} measured (lit)
		temp. (°C)	time				
C_2H_5OH	1.1	room	5 m	77	18	75–75.2/1001 (74.6/982)	1.3743 (1.3742)
t-$C_5H_{11}OH$	1.1	50	24 h	64	19	122–123/1000 (121–122)	1.3940 (1.3934)
n-$C_7H_{15}OH$	1.1	room	10 m	78	18	192–193/1005 (189–190/984)	1.4115 (1.4108)
n-$C_{10}H_{21}OH$	1.1	50	10 m	91	20	98–100/4 (104/6.5)	1.4225 (1.4227)
cyclo-$C_6H_{11}OH$	1.1	50	20 m	72	20	168–169/994 (170)	1.4315 (1.4318)
$HO(CH_2)_2OH$	2.2	room	10 m	65	21	35–36/5 (65/26.5)	1.4049 (1.4052)
C_6H_5OH	1.1	room	10 m	56	18	182–183/996 (181.9–182.4/987)	1.4788 (1.4787)
m-$(CH_3)C_6H_4OH$	1.1	room	15 m	90	22	198–199.5/999 (198.5)	1.4800 (1.4796)
m-$C_6H_4(OH)_2$	2.2	60	1 h	62	18	241–243/1008 (237–240/984)	1.4752 (1.4748)
p-$C_6H_4(OH)_2$	2.2	60	1 h	94	22	49–49.5 (48.9–49.3)	–
CH_3COOH	1.1	room	10 m	87	23	104/1013 (105/1000)	1.3884 (1.3880)
C_6H_5COOH	1.1	room	10 m	78	23	59–60/3 (56/1)	1.4863 (1.4860)

acid amides were obtained in 85 to 95% yields:

$$R^{\star}Cl + R^1R^2NC(O)OSi(CH_3)_3 \rightarrow R^{\star}NR^1R^2 + CO_2 + (CH_3)_3SiCl$$

$$(R^{\star} = \text{alkyl } C(O), \text{ aryl } C(O), \text{ aryl } SO_2)$$

The reaction conditions, yields and the physical properties of the products are shown in Table 4.

The silylcarbamates were found to react with monocarboxylic anhydrides to give the corresponding trimethylsilyl carboxylate and carboxylic amide with evolution of carbon dioxide:

$$[RC(O)]_2O + R^1R^2NC(O)OSi(CH_3)_3 \rightarrow RC(O)OSi(CH_3)_3 + RC(O)NR^1R^2 + CO_2$$

The reactions between dicarboxylic anhydrides and silylcarbamates gave the trimeth-

(Continued on p. 19)

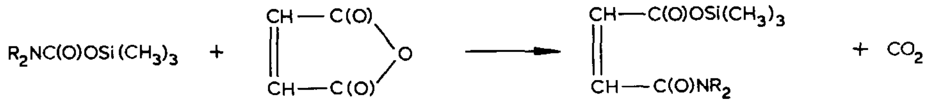
TABLE 4

$R^*Cl + R^1R^2NC(O)OSi(CH_3)_3 \rightarrow R^*NR^1R^2 + (CH_3)_3SiCl + CO_2$

REACTION CONDITIONS, YIELDS AND PHYSICAL PROPERTIES OF THE PRODUCTS

$R^1R^2NC(O)OSi(CH_3)_3$		R^*Cl	Conditions		B.p. (°C/mbar) measured (lit.)	M.p. measured (lit.)	n_D^{20} measured (lit.)	RNR^1R^2 Yield (%)	Ref.
R^1	R^2	R^*	Temp. (°C)	time					
CH_3	CH_3	$CH_3C(O)$	room	15 m	164–165/1000 (165/1008)	–	1.4382 (1.4380)	87	24
n-C_3H_7	n-C_3H_7	$CH_3C(O)$	room	15 m	95–97/17 (101/21)	–	1.4394 (1.4419)	92	25
C_2H_5	C_2H_5	$ClCH_2C(O)$	room	15 m	108–109/10 (112–113/13)	–	1.4611	89	26
CH_3	CH_3	$C_6H_5C(O)$	room	15 m	–	40.5–40.8 (41)	–	88	27
CH_3	CH_3	$C_6H_5SO_2$	80	2 h	–	47.2–47.5 (47)	–	92	27
$(CH_2)_2O(CH_2)_2$		$C_6H_5SO_2$	80	2 h	–	117.5–118 (118)	–	87	27

TABLE 5

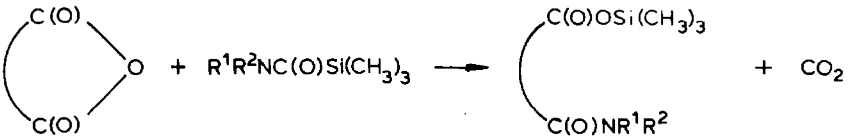


REACTION CONDITIONS, YIELDS AND PHYSICAL PROPERTIES OF THE PRODUCTS

R	Conditions		B.p. (°C/mbar)	Yield (%)	Mass spectra			IR (cm^{-1})		τ(CDCl$_3$) Si(CH$_3$)$_3$	N (%)	GC^a
	Temperature (°C)	time			m/e	M^+	$M-15^+$ (%)	ν(C=O) [OSi(CH$_3$)$_3$]	ν(C=O) [NR$_2$]		Found (calcd.)	
CH$_3$	room	30 m	111–112/4	83	215	0.7	56.7	1720	1652	9.74	6.38 (6.51)	1435
C$_2$H$_5$	room	60 m	132–132.5/5.5	91	243	1.6	56	1721	1648	9.73	5.88 (5.76)	1556
n-C$_3$H$_7$	80	60 m	158–160/2.5	93	271	3.0	30.4	1720	1647	9.74	5.02 (5.16)	1686
n-C$_4$H$_9$	80	60 m	182–184/1.5	87	299	6.1	50.8	1718	1648	9.74	4.52 (4.68)	1848

[a] 150°C, 5% OV-1/Gas Chrom Q 60–80.

ylsilyl monoamide of the corresponding dicarboxylic acid in 80–90% yields:



The results of reactions involving maleic anhydride are shown in Table 5.

Experimental

The mass spectroscopic data in the Tables were recorded at 70 eV. The ^{1}H NMR data were recorded on a 60 MHz Jeol type instrument, using $CDCl_3$ as the solvent. The IR spectra (of CCl_4 solutions) were obtained with a Specord 75 grid instrument. The GC retention index values [28] were determined with a Jeol 1100 type gas chromatograph on a glass spiral column of 3 m × 3 mm i.d., packed with 5% OV-1 on 60–80 Mesh Gas-Chrom Q and maintained at 130°C.

Trimethylsilyl N,N-dimethylcarbamate

Dimethylamine (54.2 g, 1.2 mol) was condensed into a 500 ml three-necked round-bottomed flask equipped with a stirrer, a drying tube, a reflux condenser and a gas inlet and anhydrous dichloromethane (100 ml) was added. The dimethylammonium salt of *N,N*-dimethylcarbamate was obtained by saturating the amine with dry carbon dioxide gas with cooling and stirring. The gas inlet tube was removed and a dropping funnel was inserted in its place and a solution of trimethylchlorosilane (65.3 g, 0.6 mol) in dichloromethane (50 ml) was added with cooling and stirring. The mixture was allowed to warm up to room temperature, and then stirred for a further 0.5 h. The aminehydrochloride was filtered off and the precipitate was washed with anhydrous dichloromethane. The solvent was distilled from the filtrate, and 100 ml of n-pentane was added to the residue to precipitate any aminehydrochloride still present, and the precipitate was filtered off. The pentane was distilled from the solution, and the product was purified by vacuum distillation. Yield: 91.8 to 92.7 g (95 to 96%), b.p. 28 to 29°C/1.5 mbar.

Trimethylsilyl N,N-di-n-butylcarbamate

Dry ice powder (140–150 g) was placed in the set-up described above but having a dropping funnel in place of the gas inlet tube. A solution of di-n-butylamine (129 g, 1 mol) in dichloromethane (150 ml) was added with stirring; the di-n-butylammonium salt of *N,N*-di-n-butylcarbamate was readily formed in an exothermic reaction. A solution of trimethylchlorosilane (54.2 g, 0.5 mol) in CH_2Cl_2(50 ml) was added to the stirred ice-cooled suspension of the carbamate in dichloromethane. Work-up as above gave the desired product (114 to 116.5 g; 93 to 95%), b.p. 92–93.5°C/2 mbar.

Trimethylsilyl N-n-butyl-N-trimethylsilyl carbamate

n-Butylamine (14.6 g; 0.2 mol), triethylamine (50.0 g, 0.5 mol), and anhydrous dichloromethane (100 ml) were placed in the apparatus described in the first experiment. The mixture was saturated with dry carbon dioxide gas with ice-cooling and stirring to give triethylammonium salt of n-butylcarbamate. A solution of trimethylchlorosilane (43.4 g, 0.4 mol) in anhydrous dichloromethane (50 ml) was added with cooling and stirring. The work-up was as described in the first experiment. It should be noted that owing to the presence of excess triethylamine, the solubility of triethylaminehydrochloride in the mixture was greater and thus repeated washing with pentane was necessary before the vacuum distillation of the product. Yield: 35.5 to 37.6 g (68 to 72%), b.p. 86 to 88°C/2 mbar.

The compounds listed in Tables 1 and 2 were obtained by the above procedure.

Preparation of silylated alcohols, phenols and carboxylic acids from trimethylsilyl N,N-dimethylcarbanate

The compound to be silylated placed in a three-necked round-bottom flask equipped with a stirrer, a reflux condenser, a drying tube, and a dropping funnel and trimethylsilyl *N,N*-dimethylcarbamate (10% excess) is added with stirring. The start of the reaction is indicated by evolution of carbon dioxide and reaction is generally complete within 3 to 5 minutes. However, longer times and/or higher temperatures were needed in the case of compounds containing bulky hindered groups. The products were purified by distillation. Table 3 shows that silylated compounds can be obtained in fairly good yields; the yields refer to compounds of 99.5 to 99.8% gas chromatographic purity. The silylation reactions take place quantitatively as indicated by GLC examination of the product mixtures. Thus the lower yields of isolated products are due to losses in the work-up.

Reaction of trimethylsilyl N,N-dialkylcarbamates with acid halides

In the type of equipment described above solution of 0.1 mol trimethylsilyl *N,N*-dialkylcarbamate in 30 ml dichloromethane was stirring with a solution of 0.1 mol acid halide in 20 ml dichloromethane. The beginning of the reaction was indicated by evolution of carbon dioxide. After completion of the reaction the solvent and the trimethylchlorosilane was distilled off, and the residue was purified by distillation and recrystallization. Table 4 shows that the acid amides can be prepared in fairly good yields.

Reaction of trimethylsilyl N,N-dimethylcarbamate with acetic anhydride

Acetic anhydride (15.1 g, 0.05 mol) and 20 ml anhydrous dichloromethane were placed in the usual apparatus and a solution of trimethylsilyl *N,N*-dimethylcarbamate (8.05 g, 0.05 mol) in 10 ml dichloromethane was added with stirring. Evolution of carbon dioxide was observed, but this ceased indicating that after 15 min the reaction was stopped complete. The solvent was distilled off at 38–40°C then the fraction of b.p. 101–105°C was trimethyl acetoxysilane (6.2 g, 94%); a fraction of b.p. 152–162°C was dimethyl acetamide (3.9 g, 90%).

Reaction of trimethylsilyl N,N-dialkylcarbamates with maleic anhydride

Maleic anhydride (9.8 g, 0.1 mol) and 25 ml dichloromethane were placed in the usual apparatus, then a solution of 0.1 mol trimethylsilyl *N,N*-dialkylcarbamate in 20 ml dichloromethane was added with stirring. Carbon dioxide was evolved. After completion of the reaction the solvent was distilled off and the product purified by vacuum distillation. The reaction conditions, the properties of the products and the yields are given in Table 5.

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