Journal of Organometallic Chemistry, 482 (1994) 183–185

Synthesis and reactions of silylcarbamates with bulky substituents

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(Received February 4, 1994)

Abstract

New silylcarbamates containing bulky substituents were synthesized in order to study their reactivity with nucleophilic agents as lactones and chloroformates. We suggest a mechanism for these reactions.

Key words: Silicon

1. Introduction

In a previous publication we reported the preparation and reactions of certain silylcarbamates [1]. Here, we report how the treatment of silylcarbamates with acid chlorides gives the corresponding acid amides. The reaction between silylcarbamates and acid anhydrides results in the corresponding silylesters and acid amides.

Recently some new silylcarbamates bearing bulky substituents on the silicon or on the nitrogen were prepared and their reactions with lactones and chloroformates were studied.

2. Experimental section

2.1. Preparation of silylcarbamates

All preparations were carried out in moisture free conditions. Silylcarbamates with bulky substituents on the nitrogen were synthesized by the method we reported earlier [1]. Silylcarbamates with bulky substituents on the silicon cannot be prepared this way, so we used the method of Sheludyakov *et al.* [2]. The reaction time and yield strongly depend on the bulk of the substituent. Physical and spectroscopical data of the products are summarized in Tables 1 and 2.

2.2. Reaction with chloroformates

To a solution of 16.5 g (0.103 mol) *N,N*-dimethyl-*O*-trimethylsilyl carbamate in 100 ml of abs. acetonitrile, 7.93 ml (0.103 mol) methyl chloroformate was added dropwise. The mixture was stirred for 3 days at 60°C. The reaction proceeds with evolution of carbon dioxide. The product, *N,N*-dimethyl-*O*-methyl carbamate, was purified by distillation (b.p. 98–100°C). The phenyl chloroformate reacts faster, the reaction taking only 30 min. The *N*-aryl-*O*-trimethylsilyl carbamates also react in a similar way. Data on the compounds obtained are summarized in Table 3. There was no reaction in the case of 1-pyrrolcarboxylic acid trimethylsilyl ester, *N,N*-diisopropyl-*O*-trimethylsilyl carbamate or the *N,N*-dimethyl-*O*-dimethylthexylsilyl carbamate.

2.3. Reaction with lactones

6.00 g (0.037 mol) of *N,N*-dimethyl-*O*-trimethylsilyl carbamate and 3.40 g (0.039 mol) β-butyrolactone (abs.) were stirred for four hours at 60°C. The product was distilled *in vacuo* (b.p. 66–68°C/3 mbar) and identified as 3-trimethylsiloxy-*N,N*-dimethylbutyramide. The *N,N*-dimethyl-*O*-trimethylsilyl carbamate also reacts with γ-butyrolactone and similarly the *N,N*-dimethyl-*O*-triphenylsilyl carbamate with β-butyro-lactone. Details of compounds formed in this reaction are listed in Table 4. There was no reaction in the cases of 1-pyrrolcarboxylic acid trimethylsilyl ester, *N*-methoxy-*N,O*-

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0022-328X/94/$7.00
SSDI 0022-328X(94)24624-R

bis-trimethylsilyl carbamate or the *N,N*-dimethyl-*O*-dimethylthexylsilyl carbamate.

We examined the effect of the steric hindrance on the reactivity of compounds **5–7** by treating them with β-butyrolactone under the same conditions. The reaction of β-butyrolactone with compound **5** went to completion. In the other cases low conversion (2% for **6**) or no conversion at all (**7**) were apparent.

TABLE 1. Physical and analytical data for $R^1R^2NC(O)OSiMe_3$ compounds

	R^1	R^2	Yield (%)	B.p. (°C/2mbar)	GC index	IR (cm^{-1}) ν (C=O)	MS M^+ m/e	MS I%	MS $(M-15)^+$ I%	NMR δ (ppm) $-Si(CH_3)_3$
1	Me	*c*-Hex	82	86–88	1420	1670	229	23	9	0.32
2	Et	*c*-Hex	95	88–90	1441	1671	243	28	12	0.31
3	*i*-Pr	*c*-Hex	75	93–94	1465	1669	257	21.5	14	0.31
4	*c*-Hex	*c*-Hex	87	– [a]	1797	1662	297	24.8	11	0.31
5	Me	Bz	95	96–98	1493	1676	237	12.5	28	0.33
6	*i*-Pr	Bz	92	106–108	1564	1670	265	9.4	31.5	0.32
7	*t*-Bu	Bz	86	108–110	1591	1674	279	11.6	23.5	0.33
8	2,6-diMe-piperidyl		89	96	1349	1668	227	29.2	31.7	0.32

[a] m.p. 85.0–85.3°C.

TABLE 2. Physical and analytical data for compounds $Me_2NC(O)OSiR^1_2R^2$

R^1	R^2	Yield (%)	Reaction time (h)	B.p. (°C/mbar)	GC index 150°C	IR (cm^{-1}) ν (C=O)	MS (M-15)	MS I%	NMR δ (ppm) $-SiR^1R^2$
t-Bu	H	93	80	120/3	1334	1690	216	66	1.01–1.06
Me	thex [a]	35	100	124/3	1391	1683	216	22	0.29
Ph	Ph	43	50	–	2115	1680	–	–	7.2 –7.8

[a] 2,3-dimethyl-2-butyl.

TABLE 3. Data for products of the reaction between $R^1R^2NC(O)OSiMe_3$ and chloroformate (ClC(O)OR *)

R^1	R^2	R *	Yield (%)	B.p. (°C/mbar)	GC index 130°C	IR (cm^{-1}) ν (C=O)	MS M^+ m/e	MS I%	MS $(M-15)^+$ I%	NMR δ (ppm)
										2.90s
CH_3	CH_3	CH_3	60	98–100	796	1702	103	60	62	3.66s
CH_3	CH_3	Ph	88	89–90/3	1352	1716	165	62	–	2.85s
										6.9–7.4m
H	*m*-tolyl	CH_3			1412		165	100		
H	*m*-tolyl	Ph			1976		227	82		

TABLE 4. Data for products of the reaction between $R^1R^2NC(O)OSiR_3$ * and lactones

Reagent	R^1	R^2	R *	Yield (%)	B.p. (°C/3 mbar)	GC index	IR (cm^{-1}) ν (C=O)	MS M^+ m/e	MS I%
A	CH_3	CH_3	CH_3	88	80–82	1354 [a]	1657	203	48
B	CH_3	CH_3	CH_3	95	70–72	1241 [a]	1650	203	54
B	CH_3	CH_3	Ph	41	–	2810 [b]	1650	–	–

A = with γ-butyro-lactone; B = with β-butyro-lactone.
[a] measured at 130°C; [b] measured at 200°C.

Scheme 1.

The *N*-aryl-*O*-trimethylsilyl carbamates also give the above reaction. The effect of *meta* and *para* substitution on reactivity was also examined. β-butyrolactone (less than the stochiometric amount) was added to a mixture of *meta* and *para* substituted *N*-aryl-*O*-trimethylsilyl carbamates (ratio 1:1). We found that the ratio of *meta* and *para* substituted products was less than 1; in the case of chlorine it was 0.30, and in the case of methyl 0.50.

2.4. Spectroscopic measurements

The electron impact mass spectra were recorded at 70 eV with an AEI-MS 902 instrument. The IR spectra were recorded with a Specord 75 spectrophotometer in 0.05 M CCl_4 solution. ^{1}H-NMR spectra were recorded by a Bruker WM-250 FT spectrophotometer (250 MHz) in $CDCl_3$ solution at RT containing TMS as internal standard. The chromatographic indices were determined by a Chrom 5 chromatograph with SPB-I capillary column.

3. Conclusion

Reactions of silylcarbamates with nucleophilic reactants are accompanied by evolution of carbon dioxide. Treatment of silylcarbamates with chloroformates gives trimethylchlorosilane and the corresponding *N*,*N*-dialkyl carbamate.

$$R^1R^2NC(O)OSiMe_3 + Cl{-}C(=O){-}OR^* \xrightarrow[\text{heating}]{CH_3CN} R^1R^2NC(O)OR^* + CO_2 + ClSiMe_3$$

The treatment of silylcarbamates with lactones yields the corresponding siloxybutyramides.

$$R^1R^2NC(O)OSiR_3 + \begin{array}{l} CH_2{-}C(=O) \\ | \quad\quad | \\ CH{-}O \\ | \\ CH_3 \end{array} \longrightarrow \begin{array}{l} R_3SiO \\ \diagdown \\ CH \\ \diagup \\ CH_3 \end{array} \begin{array}{l} {-}CH_2{-}C(=O) \\ \quad\quad\quad\quad \diagdown \\ \quad\quad\quad\quad NR^1R^2 \end{array} + CO_2$$

The products differ from that obtained by the reaction of silylamines with propiolactone which gives trimethylsilyl 3-aminopropionate [3].

The difference in the reactivity between the *meta* and *para* substituted *N*-aryl-*O*-trimethyl-silyl carbamates is in accordance with the results of a study of the solvolysis of these compounds with 2-propanol [4]. On the basis of these results we can conclude that nucleophilic attack on silicon plays an important role.

General conclusions are that there is no reaction if:

- a bulky substituent is bonded to the silicon;
- a bulky substituent is bonded to the nitrogen;
- the nitrogen is member of an aromatic ring.

On the basis of our experiments, we can suggest a six-member-ring transition state, in which a simultaneous nucleophilic attack takes place on the silicon and the carbonyl carbon atom (see Scheme 1).

Acknowledgment

We thank the National Science Foundation for financial support of this work (OTKA 2157).

References

1 D. Knausz, A. Meszticzky, L. Szakács, B. Csákvári and K. Újszászi, *J. Organomet. Chem., 256* (1983) 11.
2 V.D. Sheludyakov, A.D. Kirilin and V.F. Mironov, *Zsurnal Obsej Himii, 47* (1977) 1515.
3 Kenji Itoh, Shizuyoshi Sakai and Yoshio Ishii, *Tetrahedron Lett., 41* (1966) 4941.
4 Zs. Böcskei, D. Knausz, M. Gál, L. Szakács and B. Csákvári, *J. Organomet. Chem., 342* (1988) 159.