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Journal of Organometallic Chemistry 487 (1995) 267–271

Journal of Organometallic Chemistry

Preparation and solvolysis kinetics of trimethylsilyl *N*-alkyl-*N*-phenyl-carbamates

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Received 26 June 1994

Abstract

Some trimethylsilyl esters of *N*-phenyl-*N*-alkyl- (methyl-, ethyl-, ^{n}propyl-, ^{i}propyl-, ^{n}butyl-, ^{t}butyl-) carbamic acids were prepared by a novel method. Their solvolysis with isopropanol was studied. UV spectrophotometry was used to monitor the reaction and the pseudo first order rate constants were determined. A reaction mechanism is suggested on the basis of the dependence of rates on the ionic strength, on the temperature, on the isotope effect and on the concentration of various additives (sodium isopropoxide, sodium hydroxide, triethylamine and its hydrochloride, respectively).

Keywords: Silicon; Carbamate; Solvolysis; Kinetics; Mechanism

1. Introduction

Silylated carbamic acid derivatives are efficient for the silylation of various compounds containing mobile hydrogen [1–4]. Earlier the alcoholysis of trimethylsilyl *N,N*-dimethyl-carbamate [5] and the solvolysis of trimethylsilyl *N*-aryl-carbamates [6] were studied.

In this paper we report on the isopropanolysis kinetics of some trimethylsilylated *N*-alkyl-*N*-phenyl-carbamates. The solvolysis reaction is represented by the following equation:

$$\mathrm{PhN(R)COOSiMe_3} + {}^{i}\mathrm{PrOH} \longrightarrow {}^{i}\mathrm{PrOSiMe_3} + \mathrm{PhN(R)H} + \mathrm{CO_2}$$

2. Results

2.1. Preparation

Treatment of the corresponding *N*-alkyl-aniline with carbon dioxide and hexamethyl-disilazane to prepare trimethylsilyl *N*-alkyl-*N*-phenyl-carbamate gives no satisfactory yield. A three-step method was developed to obtain the products. In the first step the potassium salt of *N*-alkyl-anilides were prepared.

$$\mathrm{PhN(R)H} + \mathrm{KNH_2} \xrightarrow[\text{2. boiling xylene, } -\mathrm{NH_3}]{\text{1. liquid } \mathrm{NH_3}} \mathrm{PhN(R)K}$$

Insertion of carbon dioxide into the salt and the following silylation resulted in the formation of the trimethylsilyl-carbamate.

$$\mathrm{PhN(R)K} + \mathrm{CO_2} \xrightarrow{\text{xylene, } 0^{\circ}\mathrm{C}} \mathrm{PhN(R)COOK}$$

$$\mathrm{PhN(R)COOK} + \mathrm{Me_3SiCl} \xrightarrow[-\mathrm{KCl}]{\text{xylene, } 0^{\circ}\mathrm{C} \rightarrow 50^{\circ}\mathrm{C}} \mathrm{PhN(R)COOSiMe_3}$$

The physical and spectroscopic data of products are listed in Table 1.

2.2. Kinetic studies

The solvolysis of compounds were studied in isopropanol-dioxane mixtures. The reaction was followed by measurement of the extinction of the *N*-alkylaniline formed during the alcoholysis. The wavelength was selected so as to avoid interference by the extinction of carbamate (300 nm in all cases). The data were evaluated starting from $t_0 = 15$ min in most cases. The pseudo first order rate constants (k) were calculated from the equation

$$E = E_{inf} - (E_{inf} - E_0)\exp(-k(t - t_0))$$

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SSDI 0022-328X(94)05086-4

Table 1
Yields, physical constants and spectroscopic data of $RN(Ph)COOSiMe_3$ compounds

R:	Me	Et	^{n}Pr	^{n}Bu	^{i}Pr	^{t}Bu
yield(%)	85	77	70	80	70	65
b.p. (°C/mbar)	76/2	80–2/2	86–7/2	100–3/3	88–9/3	–
m.p. (°C)	–	–	–	–	42	53–4
GC ret. index	1375	1402	1479	1560	1424	1414
MS:						
M^+ (*m/e*)	223	237	251	265	251	265
(%)	100	33	76	23	37	3
$M-15^+$(%)	51	18	41	13	39	2
IR						
ν(C=O) (cm^{-1})	1684	1681	1684	1687	1681	1697
^{1}H NMR						
$\delta(SiMe_3)$ (ppm)	0.27	0.25	0.24	0.25	0.20	0.15
^{13}C NMR						
δ(NCO) (ppm)	154.3	153.7	153.9	154.1	153.9	154.0

matching its curve to the observed data by non-linear regression analysis (where E_0 is the measured extinction at $t = t_0$, both E_{inf} and k were considered as parameters).

Firstly, the effect of ionic strength on the rate of solvolysis was studied for some compounds in LiCl solutions of various concentrations (Table 2). As rates vary with the salt concentration, during further measurements the same concentration of LiCl was adjusted to maintain constant ionic strength.

Table 2
Rates of solvolysis of $RN(Ph)COOSiMe_3$ compounds depending on the concentration of LiCl (at 35°C)

R:	Me	^{n}Pr	^{i}Pr	^{t}Bu
conc. (mol dm^{-3})		$k \times 10^5$ (s^{-1})		
1×10^{-2}	12.7	8.7	6.2	2.6
2×10^{-2}	19.2	13.4	7.5	3.3
$dk/dc \times 10^3$				
(dm^3 mol^{-1} s^{-1})	6.5	4.7	1.3	0.7

Table 3
The pseudo first order rate constants and the activation free enthalpy values ($\Delta G^{\ddagger}$ at 25°C) of solvolysis of $RN(Ph)COOSiMe_3$ compounds with isopropanol (values for the deuterio analogue are in brackets). The kinetic isotope effect

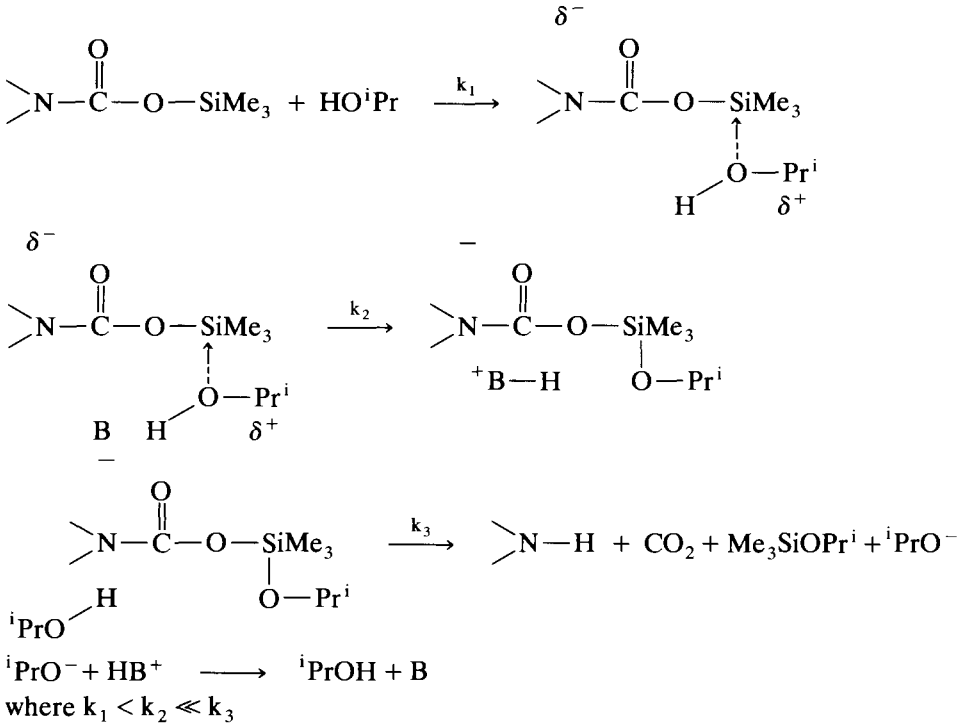
R:	Me	Et	^{n}Pr	^{n}Bu	^{i}Pr	^{t}Bu
			$k \times 10^5$ (s^{-1})			
25°C	7.4	5.5	4.9	4.1	3.5	1.7
	(5.4)	–	–	–	(2.5)	–
k(H)/k(D)	1.37	–	–	–	1.40	–
35°C	12.7	9.6	8.7	7.9	6.2	2.6
	(9.8)	(7.3)	–	–	(4.4)	–
k(H)/k(D)	1.30	1.32	–	–	1.41	–
45°C	20.7	16.3	15.1	14.2	10.7	4.7
	(15.9)	–	–	(10.7)	(7.8)	–
k(H)/k(D)	1.30	–	–	1.33	1.37	–
$\Delta G^{\ddagger}$ (kJ mol^{-1})	96.6	97.3	97.6	98.1	98.5	100.3
	(97.3)				(99.4)	

The solvolysis of compounds was also studied as a function of temperature (Table 3), and in order to study the isotope effect measurements were also carried out in *O*-deuterioisopropanol (Table 3).

To gain more details about mechanism, solvolysis of the *N*-methyl derivative was studied in presence of various additives including sodium isopropoxide, sodium hydroxide, triethylamine and its hydrochloride

Table 4
Rate constants of solvolysis of the $MeN(Ph)COOSiMe_3$ compound in the presence of some additives at 25°C

$c \times 10^3$ (mol dm^{-3})	$k \times 10^4$ (s^{-1})	$c \times 10^3$ (mol dm^{-3})	$k \times 10^4$ (s^{-1})
^{i}PrONa		*NaOH*	
0.03	1.1	0.15	2.3
0.13	1.9	0.31	3.7
0.27	3.1	0.46	5.4
0.47	5.0	0.61	7.7
TEA.HCl		*TEA*	
0.01	0.72	4.4	2.4
0.03	0.69	8.9	4.7
0.05	0.64	17.8	7.6
0.07	0.59	26.6	8.4
0.10	0.53	35.4	12.0
0.28	0.54		
1.6	0.55		
2.5	0.53		
BUFFERED MEDIA			
(values of the added concentration of TEA are shown)			
c(TEA.HCl)		c(TEA.HCl)	
$= 2 \times 10^{-4}$ mol dm^{-3}		$= 1 \times 10^{-3}$ mol dm^{-3}	
8.9	5.4	2.0	1.7
18	7.0	4.0	2.5
27	9.7	7.9	4.5
31	12.2	13.2	6.5
35	14.6	26	10.7
44	15.2		
c(TEA)/c(TEA.HCl) = 9.6		c(TEA)/c(TEA.HCl) = 4.8	
0.6	0.89	0.8	0.87
2.3	1.53	1.6	1.16
4.6	2.81	3.2	1.86
9.1	5.08	4.7	2.87



Scheme 1.

at different concentrations and ratios. During measurements the concentration of additives seemed to be constant in each run which was evidenced by the excellent fitting of the observed data to the first order kinetic model. The rates were plotted against the added concentration of additives and the k(add) values were determined from the slope of curves.

3. Discussion

From the data in Table 2, it is apparent that the rate, though to differing extents was increased by increasing LiCl concentration for all substrates. Thus, we can conclude that a polar intermediate was formed during the reaction. The salt effect gets less significant in the order Me > ^{n}Pr > ^{i}Pr > ^{t}Bu which can be attributed to the smaller difference in polarity between the transition state and the reactant.

From the data of Table 3 it seems that at fixed temperature the rate of solvolysis is decreasing with increasing length and branching of the alkyl chain. Similar tendency is valid for the increase of the activation free enthalpies ($\Delta G^{\ddagger}$) within the series.

The great difference in reactivity between the *N*-methyl and the *N*-^{t}butyl derivatives is noteworthy. The nucleophilic attack by alcohol on the silicon atom involves charge separation in the transition state where partial negative charge develops on the substrate. The bulky ^{t}butyl group destabilizes such a transition state because of steric hindrance resulting in its poorer solvation. The steric factor can also prevent the coplanarity between the amide bond and the phenyl ring which weakens the conjugation. Furthermore, the electron releasing effect of the alkyl groups increases the electron density on the silicon atom which doesn't favour the nucleophilic attack.

The rate constants were increased by a factor 1.3–1.4 when *O*-deuterioisopropanol was used in place of the protium analogue (Table 3). The weakness of the kinetic isotope effect indicates that the proton transfer does not seem to take place in the rate determining step but it plays role in the overall reaction.

Further discussion relates to the solvolysis study of the *N*-methyl derivative in presence of some additives (Table 4).

Both sodium isopropoxide and sodium hydroxide were found to act as catalysts, k(*i*-PrONa) = 0.9 dm^3 mol^{-1} s^{-1} and k(NaOH) = 1.0 dm^3 mol^{-1} s^{-1}, respectively. However, their use at higher concentrations ($> 10^{-3}$ mol dm^{-3}) was limited to their relatively poor solubility in the reaction medium (the possible formation of carbonates from the reaction between the base and the carbon dioxide evolved from substrate could be neglected.) Triethylamine proved to be less efficient catalyst than the oxides, k(TEA) = 0.035 dm^3 mol^{-1} s^{-1}. Addition of triethylammonium chloride caused the rate to fall rapidly to a smaller value which remained effectively constant with further increase of the salt concentration. The magnitude of the decrease of rate

could be compared to that of k(*i*-PrONa) (and of k(NaOH), respectively) so the base concentration in "non-added" medium could be in the range of 10^{-5}–10^{-4} mol dm^{-3}. This value is much higher than expected for the concentration of isopropoxide generated from the autoprotolysis of alcohol (in pure isopropanol $pK_s = 20.8$, ref [7]), however, traces of water or alkaline could result in this level of basicity. We could not show the catalysis of the isopropoxide generated from the proton transfer reaction between triethylamine and isopropanol since there were no significant differences between values of k(TEA) for the various types of buffered medium (0.035–0.045 dm^3 mol^{-1} s^{-1} in all cases).

Thus, from the foregoing, the mechanism of solvolysis of the trimethylsilyl *N*-alkyl-*N*-phenyl-carbamates can be best described as follows (Scheme). In the rate determining step nucleophilic attack of isopropanol (or isopropoxide in the catalyzed reaction) takes place on the silicon atom of substrate which is followed by a consecutive deprotonation of the intermediate. The nitrogen atom is protonated in a rapid step leading to the products.

4. Experimental details

4.1. Preparation of the trimethylsilyl N-methyl-N-phenyl-carbamate

Ammonia (passing through a drying tower filled with KOH pellets) was condensed into a 500 ml three-necked flask equipped with a stirrer, a Vigreux-condenser, and a dropping funnel under cooling with dry ice-acetone bath. Then freshly cut potassium (9.5 g, 0.24 mol) and a few crystals of ferric nitrate were added. After disappearing of the blue colour of the mixture, 26.2 ml (0.24 mol) of *N*-methylaniline in 100 ml of xylene was added dropwise while evaporating the ammonia. Some xylene (100 ml) was poured into the suspension and the flask was heated to reflux under slow stream of nitrogen. The formation of the anilide salt was followed by testing the outlet gas for ammonia (with indicator paper). The reaction was completed in three hours. Then carbon dioxide (dried with cc. sulfuric acid and phosphorus pentoxide) was introduced with vigorous stirring and ice-cooling for two hours. A solution of trimethylchlorosilane (32 ml, 0.25 mol) in 100 ml of xylene was added dropwise, the mixture was allowed to warm up to room temperature and then stirred for further two hours while gently heating. The precipitated potassium chloride was filtered off under nitrogen and washed with xylene. The solvent was evaporated at reduced pressure and the product was obtained by vacuum distillation.

The other compounds listed in Table 1 were prepared in a similar manner, however, depending upon the nature of the alkyl chain the formation of anilide salt was completed within a very wide range of time. The preparation of the potassium *N*-*t*-butylanilide, for example, took ten days to complete.

The ^{i}propyl and the ^{t}butyl derivatives were purified by both vacuum distillation and recrystallization from ^{n}hexane.

4.2. Rate measurements

1,4-Dioxane (Aldrich, spectr. grade) was refluxed on potassium metal and then distilled. Isopropanol (Aldrich, HPLC grade) was refluxed in the presence of calcium hydride and distilled. Then sodium (8 g l^{-1}) was added to it then redistilled. *O*-Deuterioisopropanol (Aldrich, 98 + atom% D) was refluxed on a little sodium and then distilled. All solvents were kept in well-closed flasks sealed with plastic tape (Parafilm) under argon. Lithium chloride (Fluka, anhydrous) was dried in an oven at 400°C for two hours before use, and then stored in a desiccator containing phosphorus pentoxide. Triethylamine was boiled on calcium hydride before distillation. Triethylamine hydrochloride was prepared by introducing HCl gas (evolved from NaCl and cc. sulfuric acid) into the solution of triethylamine in dichloromethane, then filtered off under nitrogen and dried in vacuum. Trimethylsilyl *N*-alkyl-*N*-phenyl-carbamates were distilled in vacuo then stored in glass ampoules.

Stock solutions containing substrate were made by diluting 60 μl of compound with 3 ml of dioxane in screw-capped vials. Solvolysing medium was an isopropanol-dioxane mixture of 1/1 (v/v) ratio containing LiCl of 1×10^{-2} mol dm^{-3} concentration. Stock solutions of additives were prepared by dissolving material in pure isopropanol.

In a typical run, 800 μl of solvolysing solution and the appropriate amount of additive were transferred to a 0.5 cm stoppered silica cell in a thermostatted cell holder. Then 8.0 μl of stock solution of substrate was injected by a hypodermic syringe (Hamilton) and the mixture was shaken well before starting measurement. Thus the concentration of substrate in the cell was approximately 9×10^{-4} mol dm^{-3} in all cases. The reference cell contained the same mixture without substrate. The reactions were generally followed up to 80–90% of conversion. The final extinction (E_{inf}) could not be determined accurately so its value was calculated from the observed data as described above.

Rate constants could be reproduced to within ±3%, but in the few cases in which the solvents were made up completely afresh, the reproducibility could be attained within ±10%. The rates for the "added" reactions listed in Table 4 were corrected to the same

"non-added" value, $k = 7.4 \times 10^{-5}$ s^{-1} because of the better comparing of data obtained from different stock solutions of solvolysing agent. In such cases the rate constant of the "non-added" reaction was measured again.

4.3. Instrumentation

Mass spectra were recorded with a Kratos MS 25 spectrometer at 70 eV (EI). IR spectra were obtained with a Specord 75 grid instrument using CCl_4 as solvent. ^1H and ^{13}C NMR spectra were measured on a Bruker AC 80 spectrometer in $CDCl_3$ solution with TMS as internal standard. The GC retention index values were determined with a CHROMPACK CP 9000 chromatograph on a CP-Sil 5CB col. (10m × 0.25mm × 0.2 μm); FID, He carrier gas, 120°C oven temperature.

The kinetical measurements were carried out with a Zeiss Specord M40 UV/Vis spectrophotometer.

Acknowledgment

We thank the OTKA (National Foundation for Science) No. T 4317 for financial support.

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