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INTERACTION OF KETENE WITH SILYLATED AMINES OR AMIDES*

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SUMMARY

In a study of the interaction of ketene with mono- or dialkylaminosilanes a number of new rearrangements was observed. When acted upon by ketene, dialkylaminosilanes, depending on the conditions applied, produce either amides of β-siloxyvinylacetic acid (I) (route "a", scheme A) or amides of silylated acetic acid (II) (routes "b", "c"). In both cases an intermediate α-siloxyvinyldialkylamine (III) was isolated which may be rearranged to give amide (II).

N-Trialkylsilyl-*N*-alkylacetamides (IV) are obtained both through the interaction of ketene with *N*-alkylsilylamines (route "d", scheme B) and a thermal rearrangement of *N*-alkylamides of silylated acetic acid (VII) (route "e"). Further action of ketene on amides (IV) may lead to *N*-alkyl-α-siloxyvinylacetamides (V) (route "g"). Amides (IV) react with trialkylsilylacetyl chloride (VIII) yielding an acylated *N*-alkylamide of trialkylsilylacetic acid (VI), thermal isomerisation of the latter leading to the analogues of (V) (route "k"). This rearrangement is interesting in that its direction is the reverse of that of a reaction studied earlier—the isomerisation of *O*-methyl-*O*-silylketeneacetals to esters of silylated acetic acid—and it enables the factors that have a decisive influence on such rearrangements to be more closely studied.

INTRODUCTION

We have recently carried out a detailed investigation into the interaction of ketene with alkoxy- or amino-derivatives of tin[1] or germanium[2] and have shown that the reaction products depend both on the nature of the element and the functional group bonded to it, and on the experimental conditions. Alkoxystannanes, as well as dialkylaminostannanes or germanes, add one mole of ketene to yield *C*-derivatives: esters or amides of metalated acetic acid.

$$R_3SnOR' + CH_2{=}C{=}O \rightarrow R_3SnCH_2COOR' \quad (1)$$

$$R_3MNR'_2 + CH_2{=}C{=}O \rightarrow R_3MCH_2CONR'_2 \quad (2)$$

(R and R', alkyls; M = Ge, Sn)

The interaction of ketene with alkoxygermanes produces esters of β-germyloxyvinylacetic acid together with the acetic acid derivatives.

* Part of this work was reported by the senior author at the 2nd International Symposium on Organosilicon Chemistry held at Bordeaux, France, July 9–12, 1968.

$$R_3GeOR' + CH_2{=}C{=}O \begin{cases} \longrightarrow CH_2{=}C(OGeR_3)CH_2COOR' \\ \xrightarrow{HgI_2\ R'OH} R_3GeCH_2COOR' \end{cases} \quad (3)$$

Recent papers[3,4] deal with the interaction between ketenes and organosilicon derivatives, *e.g.*, the insertion of ketenes into the silicon–oxygen bond of *O*-silylated keteneacetals has been observed[3,4].

$$CH_2{=}C(OCH_3)OSi\lessgtr + \gtrless C{=}C{=}O \rightarrow \gtrless C{=}C(OSi\lessgtr)CH_2COOCH_3 \quad (4)$$

It was also found that hydrosilylation of perfluorodimethylketene[5], diphenylketene[6] or phenylalkylketene[6] led to the formation of *O*-silylated enoles (eqn. (5)) whereas the insertion of ketene into the P–Si bond gave a *C*-derivative (eqn.(6))[7].

$$R_3SiH + \gtrless C{=}C{=}O \rightarrow \gtrless C{=}C\begin{matrix} OSiR_3 \\ H \end{matrix} \quad (5)$$

$$Ph_2PSiMe_3 + CH_2{=}C{=}O \rightarrow Me_3SiCH_2COPPh_2 \quad (6)$$

Limburg and Post[8] assumed that ketene reacted with hexamethyldisilazane or trimethylsilylbutylamine giving bis(trimethylsilyl)acetamide or the *N*-butylamide of trimethylsilylacetic acid, respectively. Birkofer and Ritter[9] pointed out, however, that their bis(trimethylsilyl)acetamide obtained *via* an independent route had distinctly different physical properties. It will be shown below that the structure proposed by Limburg and Post for the product arising from the reaction of ketene with trimethylsilylbutylamine, (the product they believed to be the *N*-butylamide of trimethylsilylacetic acid) is also incorrect.

Our preliminary communication[10] dealt with the interaction between ketene and dialkylaminosilanes leading to the formation of amides of silylated acetic acid and β-siloxyvinylacetic acid. Subsequently, other authors[11] found amides of β-siloxyvinylacetic and β-siloxycrotonic acids among the products of the reaction.

DISCUSSION

This paper describes the conditions of ketene reactions with silylated amines or amides which are summarized in schemes A and B.

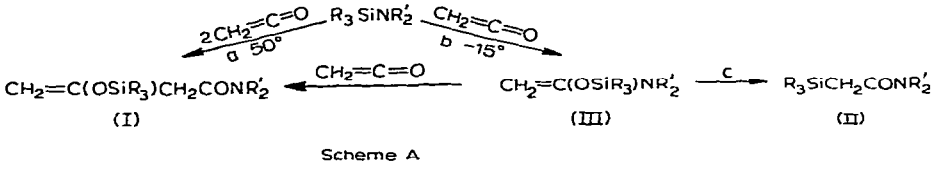
Reaction of ketene with dialkylaminosilanes (route "a")

Ketene readily reacts with dialkylaminosilanes at room temperature, the reaction mixture heating up spontaneously to 50–60°. Two moles of ketene are adsorbed under these conditions giving a high yield of the *O*-derivatives—dialkylamides of β-trialkylsiloxyvinylacetic acid (I).

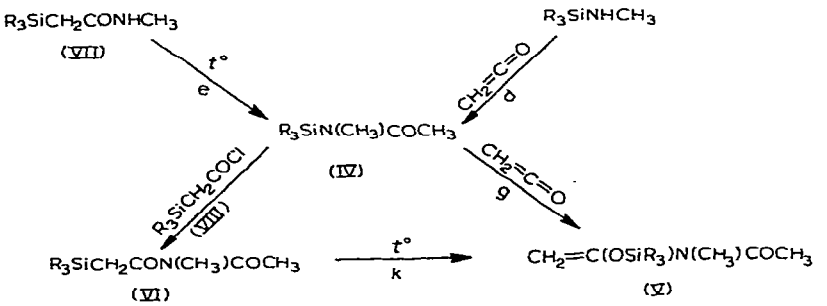
$$R_3SiNR'_2 + 2\,CH_2{=}C{=}O \rightarrow \underset{\text{Ia–e}}{CH_2{=}C(OSiR_3)CH_2CONR'_2} \quad (7)$$

(Ia, $R = R' = CH_3$; Ib, $R = CH_3$, $R' = C_2H_5$; Ic, $R = C_2H_5$, $R' = CH_3$;
Id, $R = R' = C_2H_5$; Ie, $R = OCH_3$, $R' = C_2H_5$;

If, $R = CH_3$, $R'_2 = \begin{matrix} CH_2{-}CH_2 \\ CH_2{-}CH_2 \end{matrix}O$)



Scheme A



Scheme B

Amides (I) could be considered as the products of a secondary reaction of ketene with α-siloxyvinyldialkylamines (III) formed initially. Evidence for such a scheme has already been given by the formation of esters of β-trialkylgermyloxyvinylacetic acid from trialkylalkoxygermanes and ketene[2]. Under milder conditions (at −10 to −15°), with NMR control of the reaction mixture, the reaction may be cut at the step of the formation of compounds (III), *e.g.*, α-trimethylsiloxyvinyldimethylamine* (IIIa).

$$Me_3SiNMe_2 + CH_2{=}C{=}O \xrightarrow{-10\text{ to }-15^\circ} \underset{\text{(IIIa)}}{CH_2{=}C(OSiMe_3)NMe_2} \qquad (8)$$

This compound, isolated by fractional distillation, is very labile: in several days it rearranges to the *C*-derivative, the dimethylamide of silylated acetic acid (IIa).

$$\underset{\text{(IIIa)}}{CH_2{=}C(OSiMe_3)NMe_2} \rightarrow \underset{\text{(IIa)}}{Me_3SiCH_2CONMe_2} \qquad (9)$$

The isomerisation is complete after 15 min in the presence of catalytic amounts of trimethylbromosilane. It should be noted that the rearrangement is a second example of silicon migration from oxygen to carbon**.

α-Siloxyvinyldimethylamine (IIIa) readily undergoes an exothermal reaction with ketene to give the dimethylamide of β-trimethylsiloxyvinylacetic acid (Ia).

$$\underset{\text{(IIIa)}}{CH_2{=}C(OSiMe_3)NMe_2} + CH_2{=}C{=}O \rightarrow \underset{\text{(Ia)}}{CH_2{=}C(OSiMe_3)CH_2CONMe_2} \qquad (10)$$

The prolonged interaction of ketene with dimethylaminosilanes at low temperatures (−15°) results in reactions (8), (9) and (10) taking place simultaneously to give

* The syntheses of other compounds (III) will be published elsewhere (*Zh. Obshch. Khim.*).

** Earlier we reported[12] the first example of such a migration, the rearrangement of *O*-silyl-*O*-methylketeneacetals to esters of silylated acetic acid.

a mixture of the three compounds, (Ia), (IIa) and (IIIa). With the preliminarily addition of trimethylbromosilane to the reaction mixture, (already mentioned as a catalyst of the isomerisation (9)) the formation of *C*-derivatives (IIa) is predominant.

Structure and spectra of compounds of type (I), (II) or (III), the products of the interaction of ketene with dialkylaminosilanes

The structures of the compounds isolated from reactions (7)–(10) were confirmed by the elemental analyses (Table 1) and ^{1}H NMR data (Table 2); examples of the spectra are given in Fig. 1. The spectra of the *C*-derivatives, amides of silylated acetic acid (II), contain the signals of the CH_2-group attached directly to the silicon atom, $\delta = 1.8$–1.95* (chemical shifts, δ, are given in ppm). ^{1}H NMR spectra of the vinylacetic acid derivatives (I) contain the signals of CH_2 protons, chemical shift $\delta = 2.95$–3.07, as well as those of the protons of the terminal CH_2=-group, $\delta = 3.97$–4.30**. Usually, CH_2=-protons form a clear *AB* spin system in ^{1}H NMR spectra and

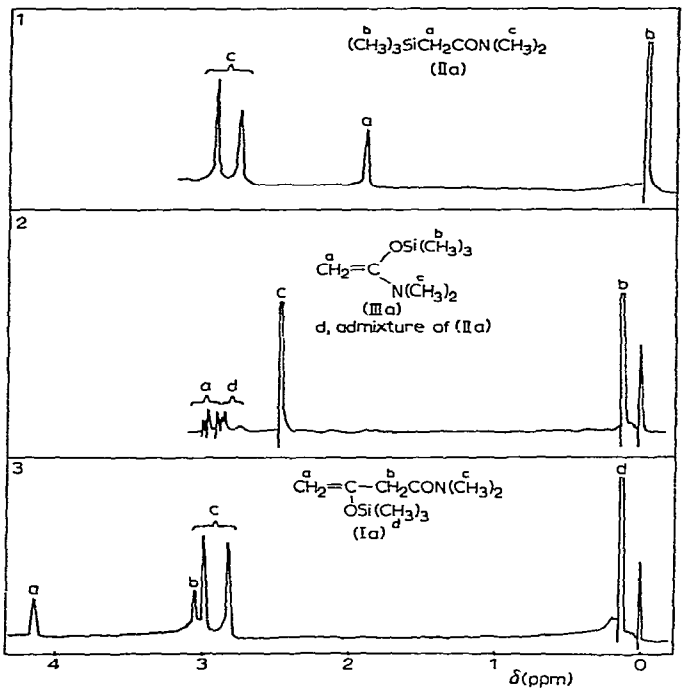


Fig. 1. ^{1}H NMR spectra (without a solvent): (1) dimethylamide of trimethylsilylacetic acid (IIa); (2) α-trimethylsiloxyvinyldimethylamine (IIIa); (3) dimethylamide of β-trimethylsiloxyvinylacetic acid (Ia).

this was actually observed with α-trimethylsiloxyvinyldimethylamine (IIIa). CH_2=-protons of the vinylacetic acid derivative (I) proved to be magnetically equivalent and thus gave singlets. The spectra of amides (I) or (II) are peculiar in that they contain the signals of non-equivalent alkyl groups bonded to a nitrogen atom. Diethylamides (Ib, d) have two triplets shifted with respect to another by δ-values 0.9–1.4, and two

* δ(Si–CH_2) 1.82 in esters of trialkylsilylacetic acid[12].

** δ(CH_2–) 3.2 and δ(CH_2=) 4.2 in esters of β-trialkylsiloxyvinylacetic acid[12].

quadruplets by δ-values 3.1–3.4, the multiplets being assigned as those of methyl and methylene groups, respectively, constituting ethyl attached to nitrogen.

A comparison of the spectra taken in aromatic and non-aromatic solvents indicates significant shifts of proton resonance signals caused by anisotropy of magnetic susceptibility of aromatic solvents. As a result, the difference between chemical shifts of resonance signals of protons belonging to non-equivalent alkyls of the dialkylamides increases supposedly because of the formation of an orientated molecular complex between a solvent and a solution[13]. The spectra were taken therefore in benzene if superposition of the signals of interest was observed in CCl_4 or without a solvent. This technique, which produced clear ^1H NMR spectra, enabled the peaks to be unambiguously assigned and the structures of the compounds to be established (see Fig. 2).

The assignment of chemical shifts is confirmed by the intensities ratio of the corresponding signals in all these spectra.

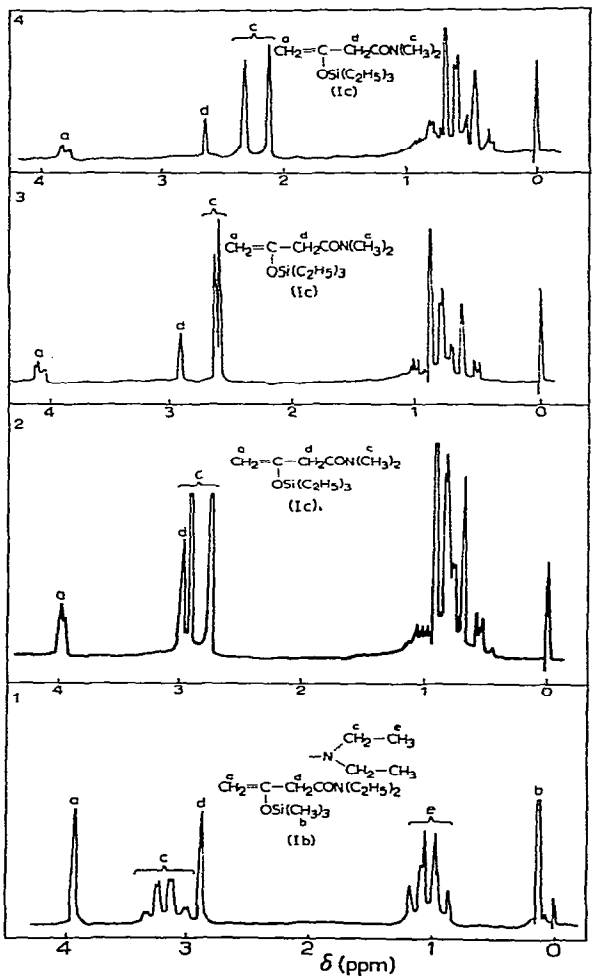


Fig. 2. ^1H NMR spectra: (1) diethylamide of β-trimethylsiloxyvinylacetic acid (Ib) (without a solvent); (2) diethylamide of β-triethylsiloxyvinylacetic acid (Ic) (without a solvent); (3) amide (Ic) (in 50% benzene soln.); (4) amide (Ic) (in 20% benzene soln.).

TABLE 1

PROPERTIES OF THE COMPOUNDS PREPARED IN THIS INVESTIGATION

Methods: 1, reaction with ketene; 2, reaction of acetoacetic diethylamide with bis(trimethylsilyl)acetamide; 3, reaction with diphenylketene; 4, rearrangement; 5, reaction of trialkylsilylketene with amine; 6, Reformatsky reaction; 7, reaction of triethylsilylacetyl chloride with *N*-trimethylsilyl-*N*-methylacetamide

Compound	Method, Yield (%) B.p. (mm)			n_D^{20}	d_4^{20}	Found (%)			Calcd. (%)		
						C	H	Si	C	H	Si
$CH_2=C(OSiMe_3)CH_2CONMe_2$ (Ia)[a]	1	75	78–79° (2)	1.4560	0.9462	53.49	9.31	13.92	53.68	9.51	13.94
$CH_2=C(OSiMe_3)CH_2CONEt_2$ (Ib)	1	81	93–94(2)	1.4558	0.9247	57.49	10.03	12.01	57.60	10.11	12.23
$CH_2=C(OSiEt_3)CH_2CONMe_2$ (Ic)	1	68	122–124(3)	1.4679	0.9487	59.11	10.34	11.95	59.21	10.35	11.53
$CH_2=C(OSiEt_3)CH_2CONEt_2$ (Id)	1	89	134–135(4)	1.4650	0.9311	62.14	10.69	10.86	61.94	10.77	10.35
$CH_2=C[OSi(OMe)_3]CH_2CONEt_2$ (Ie)	1	98	100–102(0.6)	1.4442	1.0907	47.45	8.35	10.41	47.63	8.36	10.12
$CH_2=C(OSiMe_3)CH_2CON\langle^{CH_2CH_2}_{CH_2CH_2}\rangle O$ (If)	1	86	127–128(2)	1.4780	1.0201	54.06	8.98	11.13	54.21	8.69	11.54
$CH_2=C(OSiMe_3)N(CH_3)COCH_3$ (Va)	1	89	80–81(7)	1.4480	0.9503	51.55	8.99	14.70	51.30	9.11	14.90
$CH_2=C(OSiMe_3)N(C_2H_5)COCH_3$ (Vb)	1	81	88–89(8)	1.4458	0.9341	53.85	9.79	13.50	53.69	9.50	13.93
$CH_2=C(OSiMe_3)N(C_4H_9)COCH_3$ (Vc)[b]	1	90	84–85(1)	1.4462	0.9266	57.79	10.28	11.79	57.60	10.11	12.23
$CH_2=C(OSiEt_3)N(CH_3)COCH_3$ (Vd)	1	80	82–83(1)	1.4610	0.9458	57.61	10.01	12.66	57.60	10.11	12.23
$CH_2=C(OSiMe_3)N(CH_3)COC_3H_7$	1	77	70–71(2)	1.4480	0.9312	55.54	9.76	12.38	55.77	9.83	13.00
$CH_2=C[OSi(OMe)_3]N(CH_3)COCH_3$ (Ve)	1	80	70–71(1)	1.4314	1.1060	41.34	7.50	11.98	40.84	7.28	11.94
$CH_2=C(OSiMe_3)CH_2CON(CH_3)COCH_3$ (XIa)	1	90	125–126(8)	1.4650	1.0256	52.75	8.64	11.77	52.37	8.35	12.23
$CH_3C(OSiMe_3)=CHCONEt_2$ (XVIb)	2	80	82–86(1)	1.4670	0.9342	57.70	10.22		57.61	10.11	
$Ph_2C=C(OSiMe_3)CH_2CONMe_2$ (XII)	3	87	150–151(0.01)	1.5565		71.28	7.73	7.97	71.35	7.70	7.94
$Ph_2C=C(OSiMe_3)CH_2CON(CH_3)COCH_3$[c] (XIII)	3	90	c	1.5620		70.07	6.92	6.92	69.26	7.13	7.35
$Me_3SiCH_2CONMe_2$ (IIa)	4	90	54–57(2)	1.4508	0.9016	52.77	10.50	17.43	52.78	10.76	17.60
	5	80	90–91(20)	1.4510	0.9002						
$Me_3SiCH_2CONEt_2$ (IIb)	5	80	92–93(20)	1.4520	0.8804	58.23	11.80	14.26	57.70	11.30	14.76
$Et_3SiCH_2CONEt_2$ (IId)	6	40	90–94(1)	1.4640	0.8958	62.28	11.91	12.76	62.82	11.86	12.23
	5	90	98–99(2)	1.4630	0.8982						
$Et_3SiCH_2CON(CH_3)COCH_3$ (VI)	7	61	106–107(2)	1.4746	0.9708	57.08	10.04	12.78	57.61	10.11	12.23
$Me_3SiCH_2CONHCH_3$ (VIIa)	5	89	63–64(0.01)	1.4450	0.9067	49.25	10.27	18.77	49.61	10.41	19.32
$Me_3SiCH_2CONHC_2H_5$ (VIIb)	5	87	67–68(0.02)	1.4470	0.8988	52.69	10.71		52.78	10.76	
$Me_3SiCH_2CONHC_4H_9$ (VIIc)[b]	5	86	74–76(0.01)	1.4482	0.8929	57.87	11.29		57.70	11.30	
$Et_3SiCH_2CONHCH_3$ (VIId)	5	94	123–124(3)	1.4650	0.9201	57.14	11.24	15.39	57.70	11.30	14.98
$Me_3SiN(C_2H_5)COCH_3$ (IVb)	[d]	80	48–50(7)	1.4396	0.8884	53.12	10.77		52.78	10.76	
$Me_3SiN(C_4H_9)COCH_3$ (IVc)	[d]	93	47–48(1)	1.4410	0.8787	58.22	11.57	15.23	57.70	11.30	14.98
$Et_3SiN(CH_3)COCH_3$ (IVd)	[d]	80	51–53(2)	1.4490	0.8997	57.52	11.50	7.53[e]	57.70	11.30	7.48[e]
$(MeO)_3SiN(CH_3)COCH_3$ (IVe)	[d]	91	86–87(8)	1.4220	1.0930			14.38			14.52

[a] Lit.[11] b.p. 83–85°/3 mm, n_D^{20} 1.4582. [b] In view of the elemental analysis we believe that the substance obtained by Limburg and Post[8] from the reaction of ketene with $Me_3SiNHBu$ (yield 26%, b.p. 67°/0.15 mm; Found: C, 57.9; H, 10.2%) is actually the *O*-derivative (Vc) rather than the *C*-derivative (VIIc). [c] The compound was analyzed without distillation. [d] Reaction of R_3SiCl with $R'N(H)COCH_3$ and Et_3N. [e] %N.

TABLE 2

SOME ^{1}H NMR SPECTRAL DATA FOR THE COMPOUNDS PREPARED IN THIS INVESTIGATION

Compound[a]	*Chemical shifts (ppm) and J-values*									
	CH_2=			$\delta(-CH_2-)$	$\delta(COCH_3)$	$\delta(N-CH_3)$		$\delta(H)$	$J(HN-CH_3)$	$\delta(Si-CH_2)$
	$J(AB)$	$\delta(A)$	$\delta(B)$							
$Me_3SiCH_2CONMe_2$ (IIa)						2.95	3.15			1.95
$Me_3SiCH_2CONEt_2$[b] (IIb)										1.92
$Et_3SiCH_2CONEt_2$[b] (IId)										1.80
$Me_3SiCH_2CONHCH_3$[c] (VIIa)						2.72		8.25	4.1	1.92
$Me_3SiCH_2CONHC_2H_5$[c] (VIIb)								8.25		1.93
$Me_3SiCH_2CONHC_4H_9$[c] (VIIc)								8.25		1.89
$Et_3SiCH_2CONHCH_3$[c] (VIId)						2.65		7.55	4.6	1.87
$Et_3SiCH_2CON(CH_3)COCH_3$ (VI)					2.23	3.08				2.44
CH_2=$C(OSiMe_3)NMe_2$ (III)	2	2.86	2.96			2.49				
CH_2=$C(OSiMe_3)N(CH_3)COCH_3$ (Va)		4.11			2.01	2.89				
CH_2=$C(OSiMe_3)N(C_2H_5)COCH_3$ (Vb)	1.7	3.84	3.91		1.99					
CH_2=$C(OSiMe_3)N(C_4H_9)COCH_3$ (Vc)	1.64	4.06	4.13		1.99					
CH_2=$C(OSiEt_3)N(CH_3)COCH_3$ (Vd)		4.15			2.05	2.98				
CH_2=$C[OSi(OMe)_3]N(CH_3)COCH_3$[d] (Ve)	1.6	4.32	4.43		2.04	2.94				
CH_2=$C(OSiMe_3)CH_2CON(CH_3)COCH_3$ (XIa)		4.05		3.28	2.25	3.09				
CH_2=$C(OSiMe_3)CH_2CONMe_2$[e] (Ia)		4.15		3.07		2.85	3.03			
CH_2=$C(OSiMe_3)CH_2CONEt_2$[f] (Ib)		4.06		2.96						
CH_2=$C(OSiEt_3)CH_2CONMe_2$ (Ic)		3.97		3.00		2.77	2.95			
CH_2=$C(OSiEt_3)CH_2COEt_2$ (Id)		4.15		2.95						
CH_2=$C[OSi(OMe)_3]CH_2CONEt_2$[g] (Ie)	1	4.11	4.30	3.05						
CH_2=$C(OSiMe_3)CH_2CON\langle CH_2CH_2\rangle O$ (If)		4.05		3.01						
$Me_3SiO(CH_3)C{=}C(H)CONEt_2$ *cis*-(XVIb)[h]		5.35[i]		2.13[j]						
$Me_3SiO(CH_3)C{=}C(CONEt_2)H$ *trans*-(XVIb)[k]		5.15[i]		1.81[j]						

[a] The spectra were obtained without a solvent. [b] $\delta(N-CH_2)$ = 3.15–3.45. [c] The spectra were obtained in CCl_4 (1 : 1) soln. [d] $\delta[OSi(OMe)_3]$ = 3.51. [e] Lit.[31] $\delta(CH_2=)$ = 4.09, $\delta(-CH_2-)$ = 2.98. [f] Lit.[31] $\delta(CH_2=)$ = 4.17, $\delta(-CH_2-)$ = 3.05. [g] $\delta[Si(OMe)_3]$ = 3.56. [h] Lit.[31] $\delta(CH=)$ = 5.40, $\delta(CH_3-)$ = 2.18. [i] $\delta(CH_3)$. [k] Lit.[31] $\delta(CH=)$ = 5.23, $\delta(CH_3-)$ = 1.87.

IR spectra of amides (I) or (II) contain intensive absorption bands at 1640–1670 cm^{-1}, *i.e.*, the stretching vibration bands of a tertiary amido group[14]. These broad absorption bands may mask the C=C stretching vibration bond in the case of vinylacetic acid derivatives (I). Examples of IR spectra are given in Fig. 3.

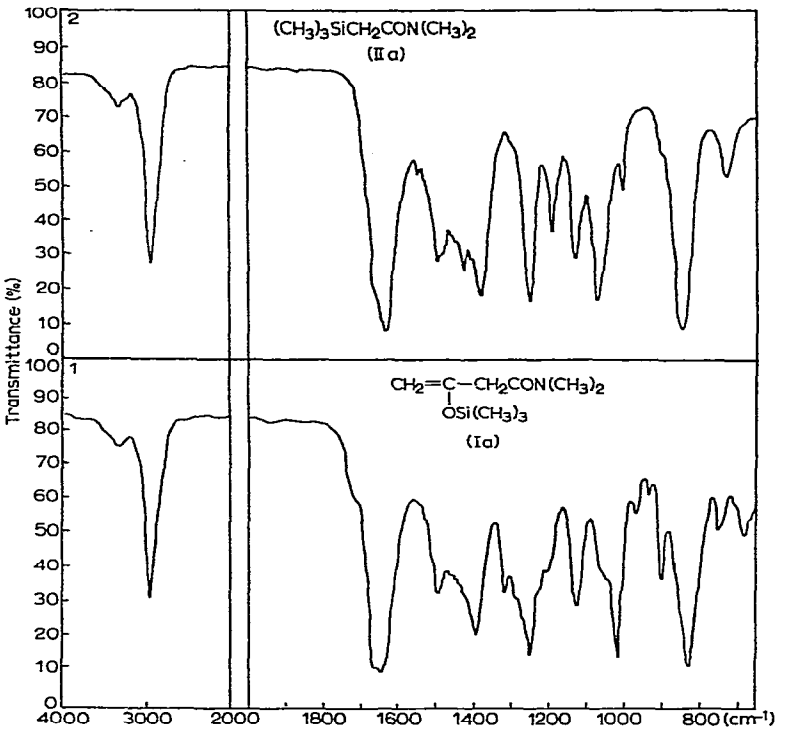
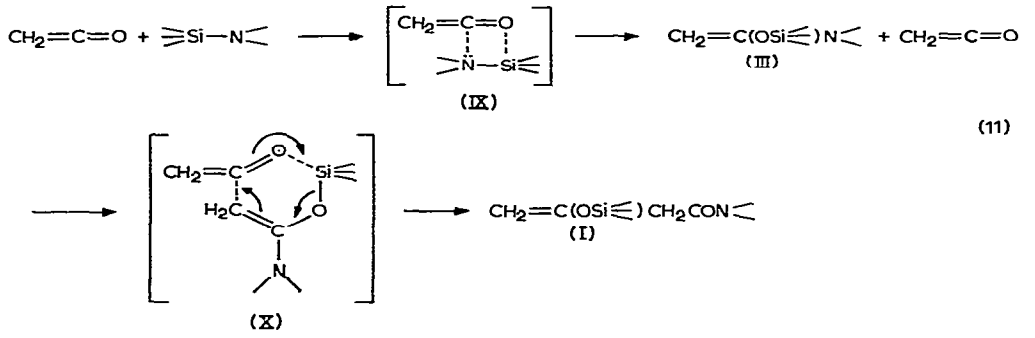


Fig. 3. (1) IR spectrum of dimethylamide of β-trimethylsiloxyvinylacetic acid (Ia); (2) IR spectrum of dimethylamide of trimethylsilylacetic acid (IIa).

The mechanism of ketene reactions with dialkylaminosilanes

A consideration of the mechanism of the reactions under study suggests that the addition of dialkylaminosilanes to ketene involves the concerted interaction of dipole–dipole type leading to a four-centre transition state (IX), although the nucleo-



philic attack of the nitrogen at the carbonyl carbon of ketene may proceed somewhat faster than the attack of the silicon at oxygen.

Further, the interaction of ketene with α-siloxyvinyldialkylamines is accompanied by the rupture of the Si–O bond (the reaction may proceed *via* a six-membered cyclic transition state (X)) rather than insertion of ketene into the C–N bond as proposed by Mironov and co-workers[11]. Evidence for the rupture of the Si–O bond* is given by the interaction of diphenylketene with α-trimethylsiloxyvinyldimethylamine (IIIa) as well as ketene reactions with *O*-silyl-*O*-methylketeneacetals which involve the rupture of the Si–O bond[4].

$$\underset{\text{(IIIa)}}{CH_2{=}C(OSiMe_3)NMe_2} + Ph_2C{=}C{=}O$$

$$\begin{cases} \xrightarrow{\text{rupture of Si–O}} Ph_2C{=}C(OSiMe_3)CH_2CONMe_2 \\ \xrightarrow[C-N]{\text{insertion into}} CH_2{=}C(OSiMe_3)C(Ph_2)CONMe_2 \end{cases} \quad (12)$$

Reactions of ketene with silylated amides (routes "g", "h", "k")

The easy reaction of ketene with α-siloxyvinyldialkylamines (III) and the fact that the compounds can rearrange into *C*-derivatives (II) result from the high nucleophilicity of their vinyl carbon. The reactivity of compounds (III) was shown to vary significantly when electron-withdrawing substituents were attached to the silicon or nitrogen atoms, *e.g.*, ketene interaction with *N*-trimethoxysilyl-*N*-methylacetamide (IVe) involves no more than one equivalent of ketene, and *O*-trimethoxysilyl-*N*-acetyl-*N*-methylketeneacetal (Ve), which does not react with ketene, is isolated from the reaction mixture in 80% yield.

$$\underset{\text{(IVe)}}{(MeO)_3SiN(CH_3)COCH_3} + CH_2{=}C{=}O \longrightarrow \underset{\text{(Ve)}}{CH_2{=}C\begin{matrix}OSi(OMe)_3\\ N(CH_3)COCH_3\end{matrix}} \quad (13)$$

If the trimethoxysilyl group is exchanged for a trialkylsilyl group, the reactivity of the compound increases thus enabling the reaction with ketene to be used for obtaining either the keteneacetal derivative (V) or a product of its further reaction with ketene—a derivative of β-siloxyvinylacetic acid (XI)—or a mixture of both compounds.

$$\underset{\text{(IV)}}{R_3SiN\begin{matrix}R'\\ COCH_3\end{matrix}} \xrightarrow{CH_2=C=O} \underset{\text{(V)}}{CH_2{=}C\begin{matrix}OSiR_3\\ N(R')COCH_3\end{matrix}} \xrightarrow{CH_2=C=O} \underset{\text{(XI)}}{CH_2{=}C(OSiR_3)CH_2CON(R')COCH_3} \quad (14)$$

(Va, R = R′ = CH_3; Vb, R = CH_3, R′ = C_2H_5; Vc, R = CH_3, R′ = C_4H_9; Vd, R = C_2H_5, R′ = CH_3; Ve, R = OCH_3, R′ = CH_3)

* Furthermore, *O,N*- or *O,O*-keteneacetals when acted upon by ketene, are known to give either cyclobutanones or the products of acylation of the keteneacetal methylene group rather than to undergo insertion of ketene into =C–O or =C–N bonds[15].

Structures and spectra of compounds of type (V) or (XI), the products of ketene reactions with silylated amides

The ^{1}H NMR spectrum of the ketenacetal derivative (Ve), Fig. 1, contains three singlets, $\delta_1 = 2.04$ (three protons), $\delta_2 = 2.94$ (three protons), $\delta_3 = 3.56$ (nine protons), assigned as the signals of CH_3CO-, CH_3N-, $(CH_3O)_3Si-$, respectively. $CH_2=$ protons are magnetically non-equivalent and give a characteristic *AB* spin system spectrum with $\delta_A = 4.32$, $\delta_B = 4.43$ and $J(AB) = 1.6$ cps. Similarly, the structures of other compounds of type (V) can be established by their spectra (Table 2). It should be noted that the ^{1}H NMR spectrum of compound (Va) contains only a singlet within the olefin region, *i.e.*, terminal methylene protons are here magnetically equivalent as with compounds of type (I).

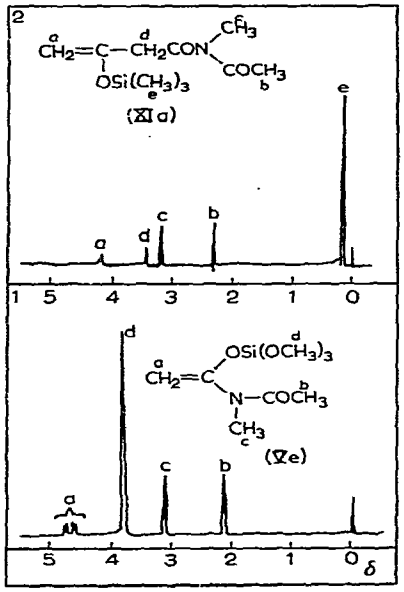


Fig. 4. ^{1}H NMR spectra (without a solvent): (1) *N*-methyl-α-trimethoxysiloxyvinylacetamide (Ve); (2) *N*-acetyl-*N*-methylamide of β-trimethylsiloxyvinylacetic acid (XIa).

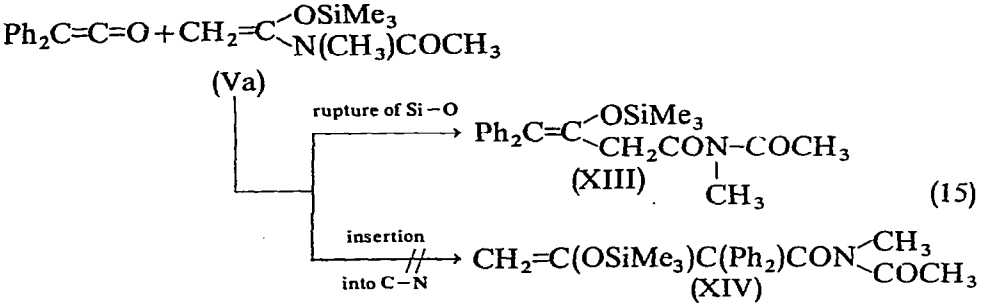
The ^{1}H NMR spectrum of the *N*-methyl-*N*-acetylamide of β-trimethylsiloxyvinylacetic acid (XIa) is similar to the spectra of amides (I). The spectrum contains (Fig. 4) five singlets with chemical shifts, $\delta_1 = 0.19$ (nine protons), $\delta_2 = 2.25$ (three protons), $\delta_3 = 3.09$ (three protons), $\delta_4 = 3.28$ (two protons), $\delta_5 = 4.05$ (two protons) assigned as the signals from protons of the $(CH_3)_3Si-$, CH_3CO-, CH_3N-, $-CH_2-$, $=CH_2$ groups, respectively. The assignment requires the structure, $CH_2=C(OSiMe_3)CH_2CON(CH_3)COCH_3$.

The mechanism of ketene reactions with silylated amides

Klebe[16] considered that silicon was five-coordinated in silylated amides and the reaction under discussion could therefore be assumed to involve a six-membered transition state where the silicon is six-coordinated.

The interaction of ketene with compounds (V) involves the rupture of the

Si–O bond; the process may pass through a six-membered cyclic transition state similar to (X). This is confirmed by the result of the diphenylketene reaction with compound (Va) leading to the formation of amide (XIII) rather than (XIV).



Isomerization of N-alkyl-N-acetylamides of silylated acetic acid (VI) to N-alkyl-α-siloxyvinylacetamides (V), route "k"

In the study of amides (V) the silicon atom has never been observed to migrate from oxygen to carbon. Unlike α-siloxyvinyldialkylamines (III) which on heating easily isomerizes to the corresponding *C*-derivatives (II), compounds (V) when heated at 180–200° loose ketene giving silylated acetamides (IV).

$$\underset{\text{(V)}}{CH_2{=}C\!\begin{smallmatrix}\diagup OSiR_3\\ \diagdown N(CH_3)COCH_3\end{smallmatrix}} \xrightarrow{180-200^\circ} CH_2{=}C{=}O + \underset{\text{(IV)}}{R_3SiN(CH_3)COCH_3} \quad (16)$$

Consequently, it could be supposed that the *C*-derivatives corresponding to compounds (V), *i.e.*, acylated *N*-alkylamides of trialkylsilylacetic acid (VI), should be less thermodynamically stable isomers that under certain conditions would isomerize to the stable *O*-derivatives (V). In fact, compounds (VI) were shown to undergo the rearrangement when heated for 15 min at 160–180°. The starting compounds, *C*-derivatives (VI),were synthesized by the interaction of silylated acetyl chloride (VIII) with amides (IV)

$$\underset{\text{(VIII)}}{Et_3SiCH_2COCl} + \underset{\text{(IVa)}}{Me_3SiN(CH_3)COCH_3} \rightarrow \underset{\text{(VId)}}{Et_3SiCH_2CON(CH_3)COCH_3} \quad (17)$$

$$\underset{\text{(VId)}}{Et_3SiCH_2CON(CH_3)COCH_3} \xrightarrow{t^\circ} \underset{\text{(Vd)}}{CH_2{=}C(OSiEt_3)N(CH_3)COCH_3} \quad (18)$$

^{1}H NMR control of the isomerization was possible, because the signal of the $-CH_2-$ group (at about $\delta = 2.4$) bonded directly with the silicon atom disappeared in the course of the reaction whereas that of olefin protons appears at about $\delta = 4.5$ (see Fig. 8).

Irreversible isomerizations reported in this paper (eqns. (9) and (18)) should be considered together with earlier results concerning the relative stability of *O*- or *C*-isomeric silicon or germanium ketoenol derivatives (see Table 3). Although there is insufficient evidence to come to decisive conclusions on the difference in relative stability of the isomers, it is clear that even small variations in the donor–acceptor properties of a group bonded to the central carbon of the triad system (C=C(R)–O) may alter the direction of isomerization.

TABLE 3

RELATIVE STABILITY OF ISOMERIC *O*- OR *C*-SILICON OR -GERMANIUM ORGANIC DERIVATIVES OF KETOENOL SYSTEMS

O-derivative	Direction of rearrangement	*C*-derivative	Ref.	*O*-derivative	Direction of rearrangement	*C*-derivative	Ref.
$CH_2=C(OCH_3)OSiR_3$	→	$R_3SiCH_2COOCH_3$	12	$CH_2=C(OSiR_3)CH_3$	←	$R_3SiCH_2COCH_3$	28
$CH_2=C(OCH_3)OSiCl_3$	→	$Cl_3SiCH_2COOCH_3$	12	$CH_2=C(OSiR_3)N(CH_3)COCH_3$	↓	$R_3SiCH_2CON(CH_3)$ $\vert$ $COCH_3$	[a]
$CH_2=C(OSiR_3)OSiR_3$	→	$R_3SiCH_2COOSiR_3$	29	$CH_2=C(OGeMe_3)CH_3$	⇄	$Me_3GeCH_2COCH_3$	30[b]
$CH_2=C(OSiR_3)NMe_2$	→	$R_3SiCH_2CONMe_2$	[a]				

[a] This paper. [b] Equilibrium mixture contains 4% of *O*-isomer at 20° and 12.5% at 170°.

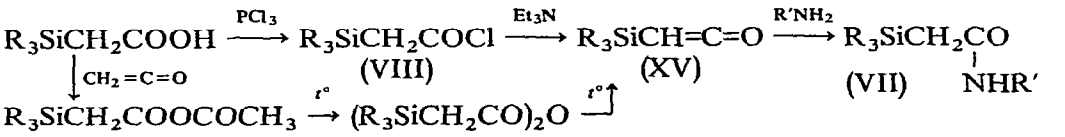
Reactions of ketene with monoalkylsilylamines and isomerization of monoalkylamides of silylacetic acid (VII) to silylated alkylacetamides (IV), route "d" and "e"

Further investigation of ketene interaction with aminosilanes showed that *N*-alkyl-α-siloxyvinylacetamides (V) could also be obtained by the reaction of ketene with *N*-alkylaminosilanes. For example, compound (Va) is formed as the main product when ketene reacts with trimethylsilylmethylamine*.

$$Me_3SiNHCH_3 \xrightarrow{CH_2=C=O} Me_3SiN(CH_3)COCH_3 \xrightarrow{CH_2=C=O} CH_2=C(OSiMe_3)N(CH_3)COCH_3 \quad (19)$$

(Va)

These results suggest that Limburg and Post[8] who considered the product of ketene reaction with trimethylsilylbutylamine to have the structure of substituted amide of trimethylsilylacetic acid, made this conclusion rather arbitrarily. We obtained monoalkylamides (VII) *via* the various routes shown in Scheme C**.



Scheme C

Physical constants as well as spectral properties of silylated acetamides (IV) are distinctly different to those of *N*-alkyl-α-siloxyvinylacetamides (V) or the amides of silylated acetic acid (VII).

The assignment of the structures of the compounds formed in the reactions discussed above must be approached with caution as demonstrated by the reactions of silylated ketenes (XV) with primary amines. The reaction products—secondary amides (VII)—may be isolated in almost quantitative yield if the reaction mixture is rapidly distilled without a Vigreux column in a moderately high vacuum; but if a slow distillation is used, compounds (VII) are isomerized to silylated acetamides (IV).

$$\underset{\text{(VIIa–d)}}{R_3SiCH_2CONHR'} \xrightarrow{180-200^\circ} \underset{\text{(IVa–d)}}{R_3SiN(R')COCH_3} \quad (20)$$

The rearrangement is complete after 15 min at 180–200°. Structures of the initial secondary amides (VII) are confirmed by the IR spectra (see Fig. 5) which contain absorption bands corresponding to stretching vibrations of free or bonded NH-groups of secondary amides within 3050–3400 cm^{-1}, and by ^1H NMR spectra (see Fig. 6) where there is a characteristic doublet of methyl protons at the nitrogen atom at about $\delta=2.65$, $J(H-CH_3)=4.1$ cps in the case of compounds (VIIa, d). The rear-

* Lower temperatures do not affect the reaction course.

** A silylated ketene was reacted with a primary amine for the first time by Shchukovskaya and coworkers[17].

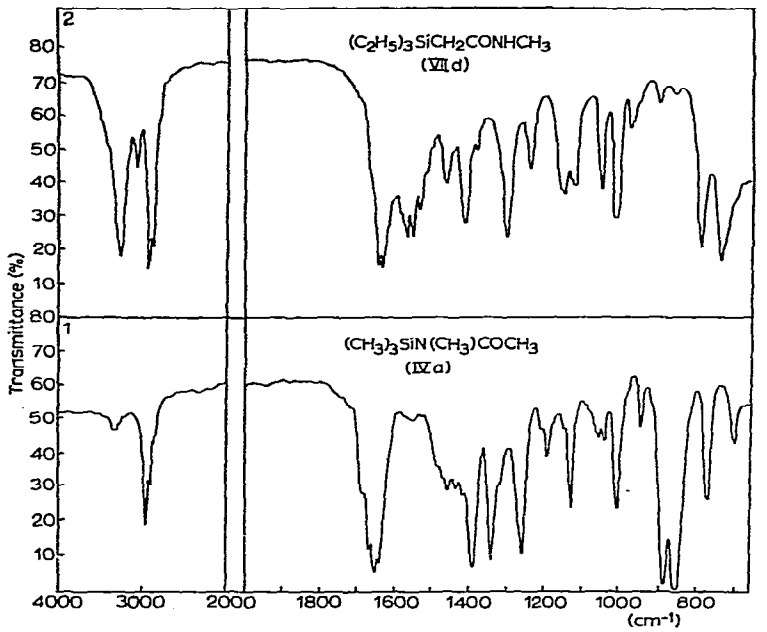


Fig. 5. (1) IR spectrum of *N*-trimethylsilyl-*N*-methylacetamide (IVa); (2) IR spectrum of *N*-methylamide of triethylsilylacetic acid (VIIa).

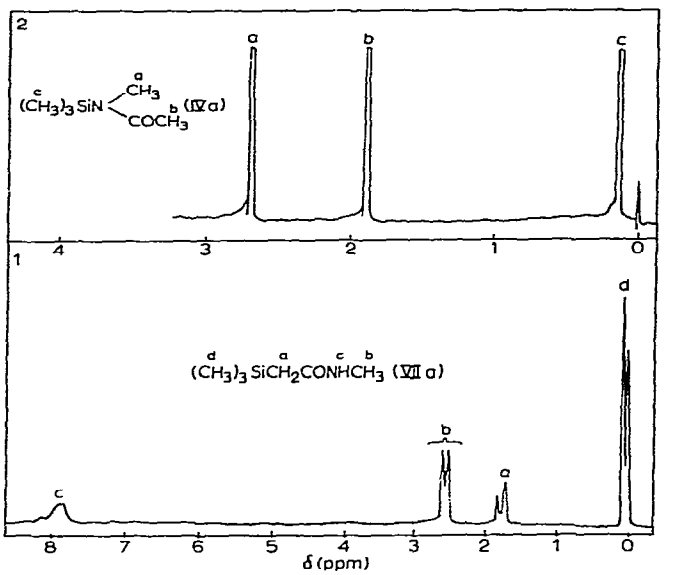


Fig. 6. ^{1}H NMR spectra: (1) *N*-methylamide of trimethylsilylacetic acid (VIIa) (in CCl_4 50% soln.); (2) *N*-trimethylsilyl-*N*-methylacetamide (IVa) (without a solvent).

rangement may be controlled by means of IR as well as ^{1}H NMR spectra in which the disappearance of the absorption bands or proton signals may be seen.

Silylated ketenes (XV) readily react with secondary amines as well, and give

stable dialkylamides of silylated acetic acid (II). These compounds may also be obtained through the Reformatsky reaction of trialkylhalosilanes with the dialkylamides of bromoacetic acid.

$$\underset{\text{(XV)}}{R_3SiCH{=}C{=}O} + R'_2NH \longrightarrow \underset{\text{(II)}}{R_3SiCH_2CONR'_2} \quad (21)$$

$$R_3SiCl + Zn + BrCH_2CONR'_2 \longrightarrow \underset{\text{(II)}}{R_3SiCH_2CONR'_2} \quad (22)$$

Physical constants and spectra of compounds (II) obtained through reaction (9) are identical with those of compounds (II) obtained through reactions (21) or (22).

Properties of compounds obtained above

The *C*-structure of the dimethylamide of trimethylsilylacetic acid (IIa) is confirmed by the reduction of the compound with lithium aluminium hydride to give the corresponding amine, eqn. (23). When reduced under the same conditions, the *O*-derivative (Ic), gave triethylsilane and 4-*N*,*N*-dimethylamino-2-butanol in yields as high as 71 and 61%, respectively (eqn. (24)).

$$\underset{\text{(IIa)}}{Me_3SiCH_2CONMe_2} \xrightarrow{LiAlH_4} Me_3SiCH_2CH_2NMe_2 \quad (23)$$

$$\underset{\text{(Ic)}}{CH_2{=}C(OSiEt_3)CH_2CONMe_2} \xrightarrow{LiAlH} CH_3CH(OH)CH_2CH_2NMe_2 + Et_3SiH \quad (24)$$

The action of water or methanol on *N*-alkyl-α-siloxyvinylacetamides (V) or on β-siloxyvinylacetic acid derivatives (I) leads to the cleavage of the compounds (eqns. (25)–(27)).

$$\underset{\text{(Va)}}{CH_2{=}C(OSiMe_3)N(CH_3)COCH_3} \xrightarrow{MeOH} Me_3SiOMe + CH_3N(COCH_3)_2 \quad (25)$$

$$\underset{\text{(Ia)}}{CH_2{=}C(OSiMe_3)CH_2CONMe_2} \xrightarrow{MeOH} Me_3SiOMe + CH_3COCH_2CONMe_2 \quad (26)$$

$$CH_2{=}C(OSiEt_3)CH_2CONEt_2 \xrightarrow{H_2O} Et_3SiOH + CH_3COCH_2CONEt_2 \quad (27)$$

Catalytic amounts of water lead to the isomerization of vinylacetic acid derivatives (I) to those of crotonic acid (XVI), the isomerization is, however, much slower than that of the corresponding esters[2] and becomes much faster in the presence of catalytic amounts of sulphuric acid.

$$\underset{\text{(Ib)}}{CH_2{=}C(OSiMe_3)CH_2CONEt_2} \longrightarrow \underset{\text{(XVIb)}}{CH_3C(OSiMe_3){=}CHCONEt_2} \quad (28)$$

We have also studied the interaction of diketene with trialkylsilyldialkylamines. Here, the products are a mixture of the isomeric amides (I) with *cis*–*trans*-(XVI).

Only one example of the reaction is given in this paper because similar results have already been reported by Mironov and co-workers[11] who consider that the formation of mixtures of various compounds is accounted for by a series of parallel reactions. However, taking into account rearrangement (28) we believe that the reaction under study passes through the initial formation of the vinylacetic acid derivative (I) which is further partially rearranged *in situ** to give a derivative of crotonic acid (XVI)

$$CH_2{=}C(O{-}C{=}O){-}CH_2 + Me_3SiNEt_2 \rightarrow CH_2{=}C(OSiMe_3){-}CH_2CONEt_2 \rightarrow$$

(Ib)

$$\rightarrow CH_3C(OSiMe_3){=}CHCONEt_2 \qquad (29)$$

(XVIb)

The formation of a mixture of amides (I) and (XVI) in a reaction of ketene with dialkylaminosilanes carried out by Mironov and co-workers[11] may be rationalized in the same manner.

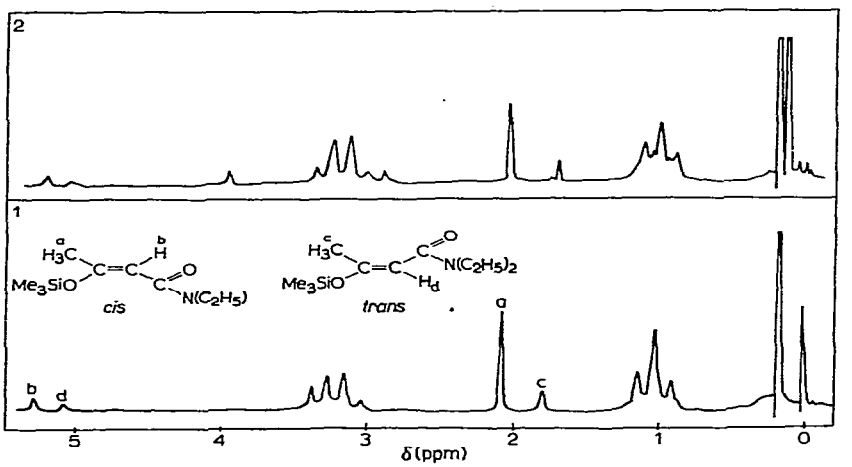


Fig. 7. ^{1}H NMR spectra (without a solvent): (1) diethylamide of β-trimethylsiloxyvinylcrotonic acid (XVIb); (2) mixture of amide (XVIb) and diethylamide of β-trimethylsiloxyvinylacetic acid (Ib), the products of the reaction between diketene and trimethylsilyldiethylamine.

EXPERIMENTAL

The IR spectra were taken in thin films using a spectrometer IKS-22 (NaCl), calibrated with a polystyrene film. The ^{1}H NMR spectra were obtained in CCl_4 (1 : 1) or benzene solutions, or without a solvent, with hexamethyldisiloxane or benzene as internal reference, with a RS-60 spectrometer.

Silylated amides were synthesized by the procedure for trimethylsilyl-*N*-

* This may be accounted for by the fact that diketene is itself a weak acid[18].

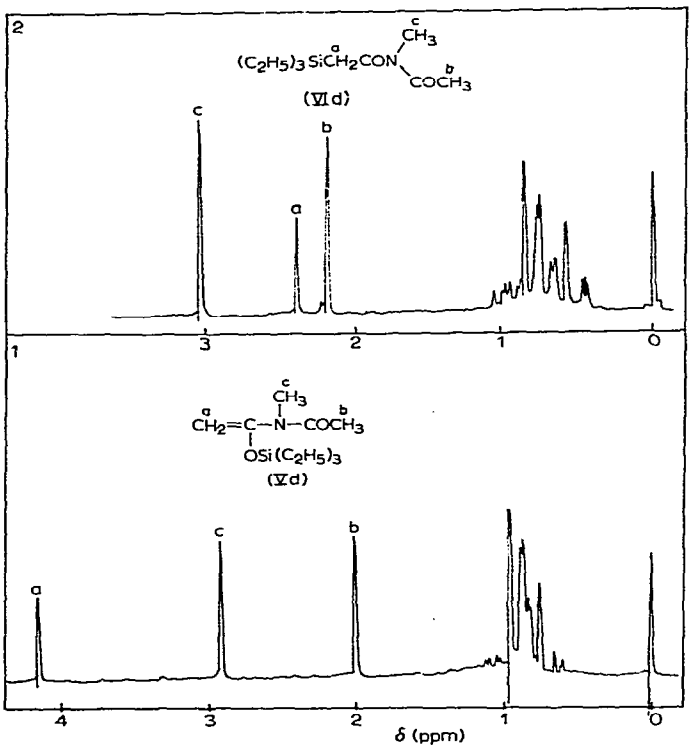


Fig. 8. ^{1}H NMR spectra (without a solvent): (1) *N*-methyl-α-triethylsiloxyvinylacetamide (Vd); (2) *N*-acetyl-*N*-methylamide of triethylsilylacetic acid (VId).

methylacetamide[19]. Trimethylsilylacetic acid was obtained by the carboxylation of siliconeopentylmagnesium chloride according to a procedure reported by Sommer[20]. Triethylsilylacetic acid was obtained similarly, yield 70%, b.p. 100–102°/2 mm, n_D^{20} 1.4548, d_4^{20} 0.9333, MR_D 50.63. (Found: C, 55.19; H, 10.31; Si, 16.35. $C_8H_{18}SiO_2$ calcd.: C, 55.13; H, 10.41; Si, 16.10%; MR_D 50.30.)

Triethylsilylacetyl chloride (VIII)

Phosphorus trichloride (13.7 g, 0.1 mole) was added slowly dropwise with stirring to triethylsilylacetic acid (17.4 g, 0.1 mole). The reaction mixture heated up spontaneously to 35°; it was then cooled by water and stirred for 15 min. The upper layer was separated and fractionated to give 12 g (62%) of (VIII), b.p. 51–53°/1 mm, n_D^{20} 1.4612.

Thionyl chloride (8.9 g, 0.075 mole) was added slowly dropwise to triethylsilylacetic acid anhydride (25 g, 0.075 mole), see below. Spontaneous heating to 30° was observed. The mixture was stirred for 45 min at 50°, and fractionated to give 23.5 g (80%) of the chloride (VIII), b.p. 52–53°/1 mm, n_D^{20} 1.4622, d_4^{20} 0.9751. (Found: C, 50.15; H, 9.01; Si, 14.77. $C_8H_{17}SiOCl$ calcd.: C, 49.85; H, 8.89; Si, 14.56%.)

Triethylsilylketene (XVb)

Dry triethylamine (4.04 g, 0.04 mole) in absolute ether (20 ml) was placed into a three-necked bulb fitted with a stirrer, a drop funnel and a condenser, and the

chloride (VIII) (8 g, 0.04 mole) was added dropwise. The reaction mixture was refluxed for 30 min. The precipitate formed, $Et_3N \cdot HCl$, was filtered and washed with ether. The solvent was removed from the filtrate and the latter fractionated to give 5 g (80%) of triethylsilylketene, b.p. 57–59°/17 mm, n_D^{20} 1.4420 (lit.[21] b.p. 61.5–62.5°/20 mm, n_D^{20} 1.4410).

Excess ketene was bubbled through 15 g (0.08 mole) of triethylsilylacetic acid. The progress of the reaction was controlled by the disappearance of the COOH band in the IR spectrum. The mixture was heated in a water bath at 2 mm reduced pressure whereupon acetic anhydride was quantitatively distilled. The residue was triethylsilylacetic anhydride, n_D^{20} 1.4630 (Found: C, 57.61; H, 10.02; Si, 17.54. $C_{16}H_{34}Si_2O_3$ calcd.: C, 58.14; H, 10.36; Si, 16.98%) which was further pyrolysed at 140–150° and reduced pressure, 30–40 mm. Ketene (XVb) (5 g) was isolated, b.p. 75–80°/35 mm. Triethylsilylacetic acid remaining in the bottle was again saturated with ketene to give another 3 g of compound (XVb). The ketene fractions were collected and refractionated to give (XVb), 7.5 g (83%), b.p. 65–68°/30 mm, n_D^{20} 1.4440.

Trimethylsilylketene (XVa) was obtained similarly, yield 30% of theory, b.p. 82°/760 mm, n_D^{20} 1.4120 (lit.[17] b.p. 82°/755 mm, n_D^{20} 1.4111).

Reaction of ketene with trimethylsilyldimethylamine

Ketene was obtained through pyrolysis of acetone[22] and purified in a trap cooled to about −30°. The procedure gives 0.1–0.2 mole of ketene/h.

Excess ketene was bubbled through 24.9 g (0.21 mole) of trimethylsilyldimethylamine at 50–60° (thermometer in the mixture). Fractionation gave 3.7 g of the initial amine and 26 g (75%) of the dimethylamide of β-trimethylsiloxyvinylacetic acid (Ia), b.p. 78–79°/2 mm, n_D^{20} 1.4560. Compounds, I, b–f were obtained in a similar manner.

Prolonged interaction (45 min) of ketene with 25 g (0.21 mole) of trimethylsilyldimethylamine at −20° followed by fractionation gave 15 g (45%) of α-trimethylsiloxyvinyldimethylamine (IIIa), b.p. 50–52°/8 mm, n_D^{20} 1.4330 and 5 g (15%) of the dimethyl amide of trimethylsilylacetic acid (IIa), b.p. 80–81°/7 mm, n_D^{20} 1.4520, together with 12 g (27%) of the vinylacetic acid derivative (Ia), b.p. 98–102°/7 mm, n_D^{20} 1.4560.

Small amounts of ketene were passed through 21 g (0.18 mole) of trimethylsilyldimethylamine at −10 to −15° for 20 min, with ^1H NMR control of the reaction mixture. The ketene input was stopped when traces of amide (Ia) appeared in the reaction mixture. Fractionation gave 16 g of the initial compound and 6 g (89%) of compound (IIIa), b.p. 48–50°/8 mm, n_D^{20} 1.4330. The compound, identified according to ^1H NMR spectra (Fig. 1) was analysed after its isomerization to the *C*-derivative (IIa).

Excess ketene was passed through 15 g (0.13 mole) of trimethylsilyldimethylamine at −10 to −15°, five drops of trimethylbromosilane being preliminarily added to the reaction mixture. Strong resinification of ketene was observed. Fractionation gave 9 g (45%) of the *C*-derivative (IIa), b.p. 79–80°/7 mm, n_D^{20} 1.4510 and 7 g (27%) of the vinylacetic acid derivative (Ia), b.p. 98–100°/7 mm, n_D^{20} 1.4560.

Reaction of ketene with α-trimethylsiloxyvinyldimethylamine (IIIa)

Excess ketene was passed through 7 g (0.04 mole) of compound (IIIa). Intense

heating of the reaction mixture was observed. The mixture was cooled with water. Fractionation gave 8 g (87%) of the vinylacetic acid derivative (Ia), b.p. 100–102°/7 mm, n_D^{20} 1.4560.

α-Trimethylsiloxyvinyldimethylamine (IIIa) isomerization to the dimethylamide of trimethylsilylacetic acid (IIa)

Compound (IIIa) (0.5 g) was placed into an ampoule of the NMR spectrometer and heated for 20 min at 140°. The complete transformation to the *C*-derivative (IIa) was verified from the ^{1}H NMR spectrum. Two other ampoules containing compound (IIIa) contained also two drops of trimethylbromosilane or trimethylchlorosilane, respectively. Trimethylbromosilane completed the isomerization in 15 min; trimethylchlorosilane brought about 60% isomerization in 1 h. The *O*-derivative (IIIa) alone was rearranged into the *C*-derivative (IIa) after 2–3 days at room temperature.

Reaction of ketene with N-trimethoxysilyl-N-methylacetamide (IVe)

Excess ketene was bubbled through 15 g (0.12 mole) of amide (IVe). Spontaneous heating of the reaction mixture (50–60°) was observed. Fractionation gave 14.6 g (80%) of *N*-methyl-α-trimethoxysiloxyvinylacetamide (Ve), b.p. 70–71°/1 mm, n_D^{20} 1.4314.

Reaction of ketene with N-trimethylsilyl-N-methylacetamide (IVa)

Small amounts of ketene were passed through 20 g (0.14 mole) of amide (IVa) with ^{1}H NMR control of the reaction mixture. The addition of ketene was stopped when traces of amide (XIa) appeared in the reaction mixture. Fractionation gave 23 g (89%) of *N*-methyl-α-trimethylsiloxyvinylacetamide (Va), b.p. 80–81°/7 mm, n_D^{20} 1.4480. Compound (V b–d) were obtained similarly.

In another experiment, excess ketene was passed through 11.8 g (0.08 mole) of amide (IVa). Fractionation gave 15 g (82%) of the *N*-acetyl-*N*-methylamide of β-trimethylsiloxyvinylacetamide (XIa), b.p. 125–126°/8 mm, n_D^{20} 1.4650.

Excess ketene was passed through 10 g (0.05 mole) of compound (Va). Fractionation gave 11 g (90%) of amide (XIa), b.p. 125–126°/8 mm, n_D^{20} 1.4650.

Thermolysis of N-methyl-α-trimethylsiloxyvinylacetamide (Va)

Compound (Va) (12 g, 0.06 mole) was heated at 180–200°, at a reduced pressure of 180 mm, for 2 h. The distilled mixture was fractionated to give 6.5 g of amide (IVa), b.p. 47–48°/10 mm, n_D^{20} 1.4380, and 2 g of the initial compound, (Va).

N-acetyl-N-methylamide of triethylsilylacetic acid (VI)

N-trimethylsilyl-*N*-methylacetamide (IVa) (5.2 g, 0.036 mole) was added dropwise with stirring to triethylsilylacetyl chloride (VIII) (7.2 g, 0.036 mole). The reaction mixture was heated for 1.5 h at 100°. Fractionation gave 5 g (61%) of amide (VI), b.p. 106–107°/2 mm, n_D^{20} 1.4746.

Isomerization of the N-acetyl-N-methylamide of triethylsilylacetic acid (VI) to N-methyl-α-trimethylsiloxyvinylacetamide (Va)

Amide (VI) (0.5 g) was placed into an ampoule of the ^{1}H NMR spectrometer and heated for 12 min at 170–180°. The ^{1}H NMR spectrum demonstrated the complete transformation to compound (Va).

Reaction of α-trimethylsiloxyvinyldimethylamine (IIIa) with diphenylketene

Diphenylketene (4.2 g, 0.022 mole) was added to compound (IIIa) (3.5 g, 0.022 mole). The mixture was heated (water bath) for 3.5 h. The completion of the reaction was determined by the disappearance of the C=C=O absorption band of diphenylketene in the reaction mixture. Fractionation gave 6.8 g (87%) of the dimethyl amide of β-trimethylsiloxy-γ-diphenylvinylacetic acid (XVII), (b.p. 150–151°/0.01 mm, n_D^{20} 1.5565).

The *N*-methyl-*N*-acetylamide of β-trimethylsiloxy-γ-diphenylvinylacetic acid (XIII) was obtained similarly.

The ^{1}H NMR spectra of amides (XVII) and (XIII) show signals of $-CH_2-$ protons, $\delta = 3.29$ and 3.61; the olefin region of the spectra contains no terminal $CH_2=$ group signals, confirming the rupture of Si–O rather than the C–N bond during the reaction of diphenylketene with compounds (IIIa) and (Va).

Reaction of triethylsilylketene (XVb) with methylamine

Ketene (XVb) (4.5 g, 0.026 mole) was added dropwise to methylamine (1 g, 0.03 mole) at −40°. Fractionation gave 5 g (94%) of triethylsilylacetic acid *N*-methylamide (VIId), b.p. 122–123°/3 mm n_D^{20} 1.4650.

Amides (VII a–c) and (IIa, b) were obtained similarly. The addition of diethylamine was carried out at room temperature.

Rearrangement of the N-methylamide of triethylsilylacetic acid (VIId) to triethylsilyl-N-methylacetamide (IVd)

Amide (VIId) (3.5 g) was heated for 15 min at 180–200°. Fractionation gave 3.1 g (88%) of amide (IVd), b.p. 50–53°/2 mm, n_D^{20} 1.4529.

Amides (VIIa–c) underwent a similar rearrangement when distilled at a reduced pressure of 8 mm.

Reaction of triethylchlorosilane with bromoacetic acid diethylamide in the presence of zinc

Triethylchlorosilane (18 g, 0.12 mole) and bromoacetic acid diethylamide (34 g, 0.17 mole) dissolved in absolute benzene (70 ml) were added slowly dropwise to 17 g of zinc with heating. The heating was stopped once the reaction had started. When all the solution had been added, the mixture was further heated for 1 h and then decomposed by the addition of a saturated solution of ammonium chloride, and dried over anhydrous $MgSO_4$. Fractionation gave 12 g (40%) of triethylsilylacetic acid diethylamide (IId), b.p. 90–94°/1 mm, n_D^{20} 1.4640.

Reaction of ketene with trimethylsilylbutylamine

Small amounts of ketene were passed through 18 g (0.13 mole) of trimethylsilylbutylamine at −5 to −10° for 20 min, with ^{1}H NMR control of the reaction mixture. The addition of ketene was stopped when traces of *N*-butyl-α-trimethylsiloxyvinylacetamide (Vc) appeared in the reaction mixture. Fractionation gave 5.5 g of the initial compound and 13 g (80%) of *N*-trimethylsilyl-*N*-butylacetamide (IVc), b.p. 74–78°/11 mm, n_D^{20} 1.4398.

Prolonged interaction (40 min) of ketene with 12 g (0.08 mole) of trimethylsilylbutylamine at room temperature followed by fractionation gave 9.6 g (64%) of amide

(Vc), b.p. 78–80°/1 mm, n_D^{20} 1.4470, and 2.2 g (12%) of the *N*-acetyl-*N*-butylamide of β-trimethylsiloxyvinylacetic acid (XIc), b.p. 107–109°/1 mm, n_D^{20} 1.4580.

The reaction of ketene with trimethylsilylmethylamine was carried out in a similar manner and analogous results were obtained. ^{1}H NMR spectra of the reaction mixtures contain no signals of trimethylsilylacetic acid methylamide (VIIa).

Reduction of the dimethylamide of trimethylsilylacetic acid (IIa) with lithium aluminium hydride

Amide (IIa) (6.1 g, 0.03 mole) was added slowly dropwise to a suspension of lithium aluminium hydride (2 g, 0.05 mole) in absolute ether (50 ml). The mixture was refluxed for 4 h, decomposed first by moist ether with cooling, and then by water. The usual procedure gave β-(*N*,*N*-dimethylamino)trimethylsilylethane, 4 g (84%), b.p. 130–132°/760 mm, n_D^{20} 1.4192, d_4^{20} 0.7666, MR_D 47.90. (Found: C, 57.98; H, 12.78. $C_7H_{19}SiN$ calcd.: C, 57.87; H, 13.08%; MR_D 47.98.)

Reduction of the dimethylamide of β-triethylsiloxyvinylacetic acid (Ic) with lithium aluminium hydride

Amide (Ic) (10 g, 0.04 mole) was added slowly dropwise to a suspension of lithium aluminium hydride (6 g, 0.15 mole) in absolute ether (200 ml). The mixture was refluxed for 32 h. The usual procedure gave triethylsilane, 3.4 g (71%), b.p. 106–108°/760 mm, n_D^{20} 1.4118 (lit.[23] b.p. 108.2°, n_D^{20} 1.4117). In addition, there was isolated 2.9 g (61%) of 4-(*N*,*N*-dimethylamino)-2-butanol, b.p. 74–76° at 47 mm, n_D^{20} 1.4310 (lit.[24] b.p. 75–79°/50 mm, n_D^{20} 1.4290).

Reaction of N-methyl-α-trimethylsiloxyvinylacetamide (Va) with methanol

Amide (Va) (8 g, 0.04 mole) was added dropwise to methanol (12 g, 0.37 mole) and the mixture was stirred for three days. Fractionation gave 3.5 g (70%) of *N*-methyldiacetamide, b.p. 69–70°/7 mm, n_D^{20} 1.4540 (lit.[25] b.p. 194.5°/741 mm, n_D^{25} 1.4502).

Methanolysis of the *N*,*N*-dimethylamide of trimethylsiloxyvinylacetic acid (Ia) was carried out at 60° for 30 min and gave the dimethylamide of acetoacetic acid, yield 70%, b.p. 104–106°/8 mm, n_D^{20} 1.4700 (lit.26 b.p. 109°/10 mm, n_D^{20} 1.4710).

The diethylamide of β-triethylsiloxyvinylacetic acid (Id) (6.4 g, 0.028 mole) was hydrolyzed by water (0.5 g, 0.028 mole) under ambient conditions for 12 h to give triethylsilanol, 1 g (89%), b.p. 98–99°/760 mm, n_D^{20} 1.3880 (lit.[27] b.p. 98.6/760 mm, n_D^{20} 1.3880), and acetoacetic acid diethylamide, 3.8 g (87%), b.p. 100–104°/4 mm, n_D^{20} 1.4725 (lit.[26] b.p. 127–129°/9 mm, n_D^{20} 1.4728).

Isomerization of the diethylamide of β-trimethylsiloxyvinylacetic acid (Ib) to the diethylamide of trimethylsiloxycrotonic acid (XVIb)

Four drops of concentrated sulphuric acid were added to amide (Ib) (9 g, 0.04 mole), and the mixture was heated at 80° for 1.5 h. Fractionation gave 8 g (89%) of amide (XVIb), the mixture containing 71.5% of the *cis*-isomer and 28.5% of the *trans*-isomer, b.p. 116–121°/7 mm, n_D^{20} 1.4660. Amide (XVIb) was synthesized independently from the diethylamide of acetoacetic acid and bis(trimethylsilyl)acetamide, yield 80%. The two amides are identical. The ^{1}H NMR spectrum of the amide (XVIb) is shown in Fig. 7.

Reaction of trimethylsilyldiethylamine with diketene

Diketene (5.2 g, 0.062 mole) was added dropwise to trimethylsilyldiethylamine

(9 g, 0.062 mole). The reaction mixture was heated to 80–100° with stirring for 1.5 h. Fractionation gave 10 g (71%) of a mixture containing amide (Ib) and amide (XVIb), b.p. 118–124°/8 mm, n_D^{20} 1.4650. The mixture consists of amide (Ib) (21%), *cis*-(XVIb) (58%), and *trans*-(XVIb) (21%). The ^{1}H NMR spectrum of the mixture is shown in Fig. 7.

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