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Preparation of Some Silyl Esters and Study of Their Vibration Spectra in Gas and Condensed Phases

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A new preparative route for silyl esters is described, involving reaction of silyl bromide and trisalkyltin esters. The far infrared spectrum of some simple esters are reported; an investigation of the shifts in the carbonyl stretching band on condensation shows no significant differences in behaviour between methyl and silyl esters.

(Keywords: Silyl esters, preparation; Vibration spectra)

Darstellung einiger Silylester und Untersuchung der Vibrationsspektren in der Gasphase und in kondensierter Phase

Es wird ein neuer präparativer Weg (über Silylbromid und Trisalkylzinnester) für die Synthese von Silylestern beschrieben. Das ferne IR einiger Ester wird angeführt; eine Untersuchung der Verschiebung der Carbonyl-Streck-Frequenz bei Kondensation zeigt keine signifikanten Unterschiede zwischen Methyl- und Silyl-Estern.

Introduction

Silyl esters $SiH_3O(C{=}O)R$ have been prepared previously using the reactions of trisilylamine $[(SiH_3)_3N]$ with organic acids RCOOH in the vapour phase (R = H, Me, CF_3, HC = C-)[1]. We have investigated an alternative route involving the reaction of silylbromide with a trisalkyltin ester:

$$SiH_3Br + R_3SnO(C{=}O)R^1 \rightarrow SiH_3O(C{=}O)R^1 + R_3SnBR$$

Here we report the successful use of this reaction to prepare silyl formate, acetate, thioacetate, propionate, isobutyrate and trifluoracetate and the results of some spectroscopic and structural studies on these compounds.

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Experimental

Silyl bromide was prepared from phenyl silane by cleavage with HBr at low temperature; tributyltin esters were prepared from bis(tributyltin)oxide and the free acid in toluene[2].

In a typical preparation, silyl bromide (3.50 mmol) was condensed into a greaseless tap ampoule containing tributyltin formate (1.339 g; 4.0 mmol) using a vacuum line and the ampoule and contents allowed to warm to room temperature with shaking. After 1 min the volatile contents were removed and fractionated by trap-to-trap distillation in the vacuum line. The product, silyl formate (0.189 g, 2.62 mmole, 75%) was trapped at 195 K.

Silyl formate, acetate, monothioacetate and trifluoracetate were characterised by comparison of their mid-infrared spectra[3,4] and ^1H(and ^{19}F)nmr spectra with published results. The isobutyrate was identified using infrared, *Raman* and ^1H nmr spectra, by mass spectroscopy, by SiH analysis (calculated 570 ml H_2/g, found 564), and by vapour density.

Infrared spectra were recorded using a Perkin Elmer 577 grating spectrophotometer (4,000–200 cm^{-1}) or a Beckman RIIC IR720 interferometer (400–40 cm^{-1}), *Raman* spectra using a Cary 83 laser *Raman* spectrometer with Ar^+ excitation. ^1H nmr spectra were recorded on a Varian HA100 instrument.

Results and Discussion

a) Preparations

The yields in the preparative reaction were high (Table 1), and the new route to silyl esters is clearly superior to the earlier method on this count, as well as eliminating the need to prepare trisilylamine. We observed the production of silane in most cases, indicating the occurrence of some disproportionation reactions involving SiH bonds, but only to a small degree. No less volatile products containing SiH bonds were identified, but it was shown that the involatile liquid residue, largely Bu_3SnBr, also contained SiH-containing species.

Table 1. *Yields of preparative reaction*

Silyl Ester	Yield/%
Formate	75
Acetate	64
iso-Butyrate	53
Thioacetate	70
Trifluoracetate	75

b) Characterisation of Silyl Isobutyrate

This, a wholly new ester, was essentially characterised by spectroscopic means, with the volume of H_2 released by alkaline hydrolysis (see above) as a check. The ^{1}H nmr spectrum (Table 2) showed all the expected resonances and couplings, with no other significant peaks, while the mass spectrum confirmed the molecular formula as $C_4H_{10}O_2Si$ (parent ion $m/e = 118$) and showed prominent fragment peaks at $m/e = 75$ ($SiH_3CO_2^+$) and 43 [$(CH_3)_2CH^+$]. The vapour pressure of the compound over the compound over the range 278–289 K could be expressed in the usual form as $\log_{10} (P/\text{mm Hg}) = 8.814\text{–}2{,}105/(T/\text{K})$.

The vibrational spectrum showed the expected strong infrared peaks at 1,750, 1,270 and 1,070 cm^{-1} due to the stretching of the CO—O—Si skeleton, with characteristic SiH_3 group bands at 2,200, 950 and 700 cm^{-1}. A fuller discussion of some aspects of these spectra appears below.

Table 2. ^{1}H-NMR *Parameters of silyl esters*

	$HCOOSiH_3$	$CH_3COOSiH_3$	$(CH_3)_2CHCOOSiH_3$
δ **CH**/ppm	8.05	—	2.55 (septet) $^3J(HH) = 7.4$ Hz
δ **CH$_3$**/ppm	—	1.94	1.13 (doublet)
δ SiH$_3$/ppm	4.55	4.47	4.49
$^1J(^{29}SiH)$Hz	234.9	231.03	232.0

c) *Far Infrared Spectra of Gaseous Silyl Esters*

Previous infrared spectra studies[2] of the silyl esters have omitted the low-frequency region below about 400 cm^{-1}; we have obtained spectra for silyl formate, acetate, thioacetate and trifluoracetate in the 400–40 cm^{-1} region. According to the analysis of the spectra proposed earlier[2] the low-frequency modes expected are torsions about Si—O and C—O bonds and bending at oxygen, together with C—C bond torsions for the acetate and trifluoracetate. We do not believe that the Si—O bond torsions give rise to any detectable absorptions, and assign the two bands observed for the formate to the bend at oxygen and the C—O bond torsion. The *Raman* spectra of the liquid shows that the higher frequency band is depolarised, and the lower frequency band polarised, strongly suggesting that the former (at 223 cm^{-1} in the IR spectrum of the gas) is due to the torsion about the C—O bond and the latter (at 160 cm^{-1}) is due to the C—OSi bend. In the acetate there are again only two discernible bands in the gas-phase infrared, neither of which gives rise to a distinct band in the *Raman* spectrum of the liquid. It is reasonable to suppose that substitution of a methyl group for the formyl hydrogen atom would decrease both the vibration frequencies

Table 3. *Vibrational bands of silyl isobutyrate*

Infrared		*Raman*	Proposed
Vapour	Solid	Liquid	Assignment
2980 ms		2980 w	νCH
2942 m		2950 w	
2882 mw		2930 w	
		2880 w	
2198 vs		2195 vs	νSiH
1740 s		1717 w	$\nu C=O$
1474 m		1453 mw	δCH_3
1389 m		1350 vw	
1350 m		1300 vw	
1267 ms			
1200 s		1200 vw	δCH,
1160 s		1160 vw	νC—O,
1120 m		1120 w	νSiO,
1070 m		1100 mw	νC—C
		982 w	
945 vvs		945 s	δSiH_3
843 m		850 vs	ρCH_3? CH?
792 ms		792 s	ρSiH_3,
698 m		706 s	δCCC,
595 w		600 w	etc.
515 vw		570 mw	
300 w		520 vw	
		450 s	
		315 m	
		250 m	

concerned here, so we suggest the same assignment as for the formate, the stronger, higher frequency band being the C—O torsion and the lower frequency, weaker band the SiOC band. However, the spectrum of the thioacetate, where the organic group has suffered a similar mass increase with substitution of the $C=O$ oxygen by sulphur, shows two bands almost identical in position and intensity to the acetate, so it is clear that mass changes are not the only factor involved; the correct assignments for the acetate and thioacetate must remain in some doubt.

In the trifluoracetate there are the expected peaks between 300 and 200 cm^{-1} due to deformations of the CF_3 group, together with a moderate band at 163 cm^{-1} and a stronger band at 116 cm^{-1}. Again no distinct bands are observed in the *Raman* spectrum of the liquid below

200 cm^{-1}, and with the possibility of CF_3 rocking motions, which may well couple with both the C—O torsion and the SiOC bend, we are unable to propose an assignment at this stage.

d) Vibrational Spectrum of Silyl Isobutyrate

Vibrational bands observed for silyl isobutyrate in the range 4,000–200 cm^{-1} in the infrared and *Raman* effects are listed in Table 3 with suggested assignments. In the absence of any sign of two $C=O$ stretching frequencies we are reluctant to invoke more than one conformation of the $(CH_3)_2CH$ moiety relative to the carbonyl; a complete assignment is clearly impossible at this stage, but it is tempting to see in the gas-phase IR bands at 1,070 cm^{-1} and 1,267 cm^{-1}, which shift to higher frequency on condensation, the two normal modes resulting from the coupled Si—O and C—O stretches. These shifts to higher frequency may be related to the corresponding phase shift to lower frequency of the $C=O$ stretch, implying a reduced coupling between the single and double bond stretches in condensed phases.

e) Shifts in $C=O$ *Stretching Band on Condensation*

It has been reported[5] that substantial shifts of the CO stretch to low frequency occur on condensation of some silicon esters, and it was suggested that these are related to incipient coordination of the carbonyl group to silicon atoms in neighbouring molecules. However, we have noted that significant shifts (~ 25 cm^{-1}) also occur for methyl esters, and have recorded gas-phase and solid-phase infrared spectra and liquid-phase *Raman* spectra of all our samples to establish the extent of the effect over a range of esters. The results are listed in Table 4; it is clear that there is a shift of between 19 and 32 cm^{-1} between gas and liquid phases, with a further shift of ~ 10 cm^{-1} on solidification. Very similar behaviour occurs for methyl esters. results for some which are also included in the Table. There is therefore evidence for some intermolecular interaction in both silyl and methyl esters. It may be noted that the gas → solid shift for formic acid is about -150 cm^{-1}, while acetic acid *dimer*, known to be present in both liquid and solid, undergoes a shift of -61 cm^{-1} from liquid to solid. The esters by comparison show smaller shifts and we do not feel that there is any evidence for special effects in the silyl esters.

The similar behaviours of methyl and silyl esters in this respect may be reasonably correlated with their similar structures; as for methyl formate in the gas phase we find essentially *cis*-planar arrangements of carbonyl oxygen and silyl groups for silyl formate[6] and silyl acetate[7] in the gas phase and for the acetate in the crystalline solid[7]. The solid

Table 4. *Carbonyl stretching frequencies in various phases*

	$HCOOSiH_3$			$CH_3COOSiH_3$			$CH_3CH_2COOSiH_3$			$(CH_3)_2CHCOOSiH_3$			$CF_3COOSiH_3$		
Gas (IR)	1734			1750			1743			1740			1790		
		31			32						23			19	
Liq (*R*)	1703		39	1718		43	—		34	1717		40	1771		28
		8			11						17			9	
Solid (IR)	1695			1707			1709			1700			1762		

	$HCOOCH_3$			CH_3COOCH_3			$CH_3CH_2COOCH_3$		
Gas	1754			1774			1767		
		27			27			24	
Liq	1727		61	1747		43	1743		39
		34			16			15	
Solid	1693			1731			1728		

structure contains a short $C=O \cdots Si$ interaction between neighbouring molecules, the $O \cdots Si$ distance being 2.72 Å; the crystal structure of methyl acetate is under investigation.

f) Other Uses of the Preparative Reaction

We have used the preparative reaction described here to prepare silyl propionate (some data for which are included above) and germyl thioacetate (using germyl bromide as starting material). It appears that many other silyl and germyl esters may readily be prepared in this way.

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