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Preliminary communication

SILOXYCARBENES FROM THE THERMOLYSIS OF ACYLSILANES

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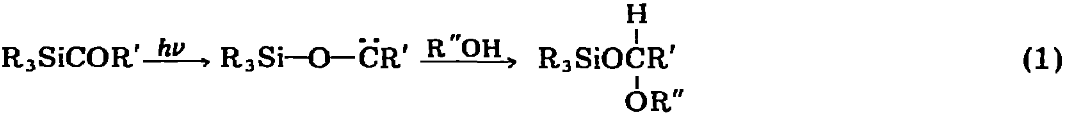
Summary

Acylsilanes undergo a first-order thermal rearrangement to yield products derived from the insertion of an intermediate siloxycarbene into adjacent C—H bonds.

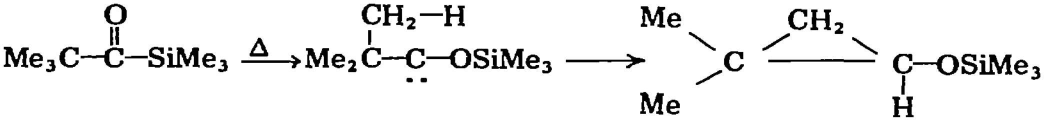
It is now well established that acylsilanes (R_3SiCOR') are photochemically isomerised under appropriate conditions to siloxycarbenes: these intermediates have been trapped by a variety of reagents including alcohols (eqn. 1) [1].



$$R_3SiCOR' \xrightarrow{h\nu} R_3Si{-}O{-}\ddot{C}R' \xrightarrow{R''OH} R_3SiO\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OR''}{|}}{C}}R' \qquad (1)$$

Similar behaviour has also been observed with cyclobutanones and other strained cyclic ketones [2, 3], but to date there appears to be no evidence of the thermal isomerisation of carbonyl compounds to oxacarbenes.

We have recently observed that a variety of acylsilanes are rearranged when heated to 200°C or higher to products* which appear to be derived from intermediate siloxycarbenes, as shown in Table 1. Thus pivaloyltrimethylsilane (I), when heated in a sealed tube, rearranged smoothly to give 2,2-dimethylcyclopropyloxytrimethylsilane (II) as the only product (eqn. 2). The isolation of the



(2)

(I) (II)

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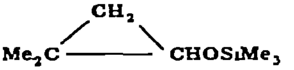
[*] The identity of products was established by analyses, spectroscopic properties, and the identity of their hydrolysis products with authentic samples.

TABLE 1

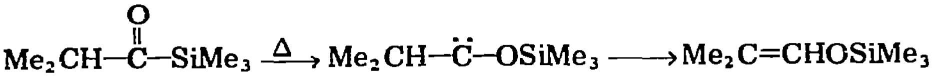
THE THERMAL ISOMERISATION OF SOME ACYLSILANES

Acylsilane	Temperature (°C)	Time (h)	Products	Yield [a] (%)
$Me_3CCOSiMe_3$	350	24		98
$Me_2CHCOSiMe_3$	320	2	$Me_2C{=}CHOSiMe_3$	95
$MeCOSiMe_3$	230	1.25	CH_3CHO [b]	30
			$CH_2{=}C(SiMe_3)OSiMe_3$	30
			$CH_2{=}CHOSiMe_3$	20
$PhCH_2COSiMe_3$	250	0.33	*cis*-$PhCH{=}CHOSiMe_3$	20
			trans-$PhCH{=}CHOSiMe_3$	20
			$PhCH_2CHO$	15
			$PhCH{=}C(SiMe_3)OSiMe_3$	15
			$PhCH_2SiMe_3$	trace
$CH_3COSiMe_2Ph$	300	1	$CH_2{=}CHOSiMe_2Ph$	25
			CH_3CHO	25
			$CH_2{=}C(SiMe_2Ph)OSiMe_2Ph$	25
$CH_3COSiMe_2Ph$	ca. 650	1	$CH_2{=}CHOSiMe_2Ph$	98
(−)-$CH_3COSiMePhNp$	ca. 650	1	(−)-$CH_2{=}CHOSiMePhNp$ [c]	96

[a] By NMR. [b] Inclusive of paraldehyde. [c] Reduction gave R_3Si^*H, 91% optical purity, corresponding to retention of configuration during the rearrangement.

cyclopropane is consistent with the formation of the siloxycarbene, which then inserts into the γ C—H bond [4].

Similarly, isobutyroyltrimethylsilane (III) thermally rearranged cleanly to 2-methylpropenoxytrimethylsilane (IV) involving insertion of an intermediate siloxycarbene into the β C—H bond (eqn. 3). Preliminary studies in the temperature range 205-225°C have shown that the rearrangement followed clean first-order kinetics.



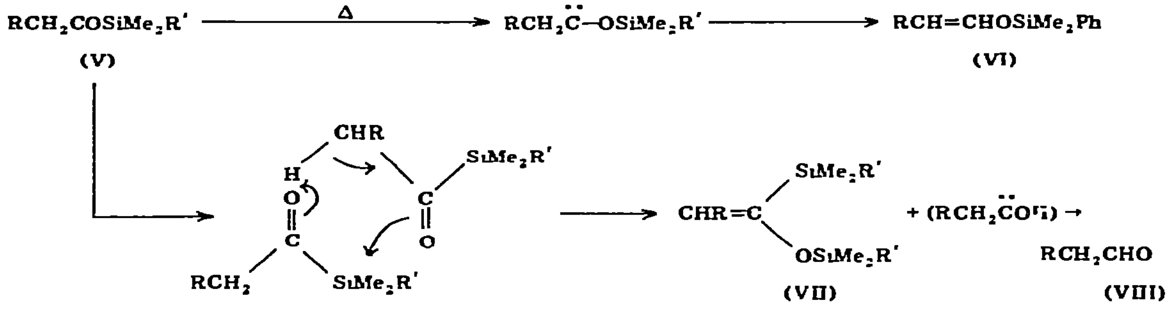
$$Me_2CH{-}\overset{O}{\overset{\|}{C}}{-}SiMe_3 \xrightarrow{\Delta} Me_2CH{-}\ddot{C}{-}OSiMe_3 \longrightarrow Me_2C{=}CHOSiMe_3 \qquad (3)$$

(III) (IV)

The thermal behaviour of the acetylsilanes investigated was more complex. Thermolysis of acetyltrimethylsilane (V) (Scheme 1, R = H, R′ = Me) in a sealed tube at 230°C gave vinyloxytrimethylsilane (VI) presumably from insertion of an intermediate siloxycarbene into the adjacent C—H bonds, and two other major products, 1-trimethylsilyl-1-trimethylsiloxyethylene (VII) and acetaldehyde (VIII). Similar results were obtained from the other acetyl- and phenylacetyl-silanes investigated.

The aldehyde isolated in each case almost certainly does not arise as a result of a free radical type process: a wealth of evidence indicates that under such thermal conditions any precursor acetyl (or phenylacetyl) radicals formed would decarbonylate prior to hydrogen abstraction or other reaction, giving rise not to aldehydes, but to methylated derivatives [5-7]. Thus the formation of the silylsiloxyalkene (VII) and aldehyde (VIII) seems best explained as arising from a competing bimolecular process such as shown in Scheme 1, a pathway which should be more accessible to the less sterically hindered acetylsilanes than to the acylsilanes discussed earlier. As would be anticipated, under conditions of higher temperature and lower concentration (drops of liquid were allowed to fall on the

SCHEME 1



walls of an evacuated flask heated to ≈ 650°C) the bimolecular process became less favourable and vinyloxyphenyldimethylsilane (VI) produced by the intramolecular process, was the only product obtained from acetylphenyldimethylsilane (R = H, R' = Ph) under these conditions.

The stereochemistry of the thermal rearrangement has also been established. Optically pure (—)-1-naphthylphenylmethylacetylsilane, under similar conditions at 650°C for 1 h, yielded 96% of (—)-vinyloxy-1-naphthylphenylmethylsilane, which on reduction with $LiAlH_4$ under conditions known to involve retention of configuration at silicon [8], gave an 82% yield of (—)-R_3Si^*H, $[\alpha]_D$ —31°, corresponding to an optical purity of 91% and the retention of configuration during the course of the rearrangement. Thus the stereochemistry of the thermal rearrangement is the same as that observed for the photochemical isomerisation of an acylsilane to a siloxycarbene [1].

The above data clearly indicate that a variety of acylsilanes undergo stereospecific intramolecular thermal rearrangements. Whether siloxycarbenes are actual intermediates in the rearrangement, or whether the C—H insertion is concerted with the Si—C bond cleavage is not clearly established at present, since preliminary attempts to trap the carbenes with other reagents have so far been unsuccessful.

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