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Preliminary communication

THERMAL REARRANGEMENTS OF EPOXYSILANES

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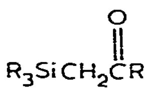
Summary

Siloxyalkenes are formed, often with considerable stereospecificity, from the thermolysis of epoxysilanes which appear to rearrange by two different pathways depending on structure and geometry.

We have recently described thermal rearrangements of acylsilanes (I) [1] and of β-ketosilanes (II) [2], each of which undergo clean and facile intramolecular reactions leading to siloxyalkenes (III). Because of the obvious similarities in bonding and spatial relationships which exist, particularly between oxygen and silicon, it appeared important to investigate the thermal behaviour of epoxysilanes (silyl epoxides) (IV).

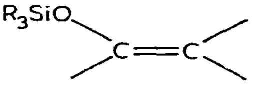

$R_3Si\overset{\overset{O}{\|}}{C}CHR_2$

(I)


$R_3SiCH_2\overset{\overset{O}{\|}}{C}R$

(II)

(III)



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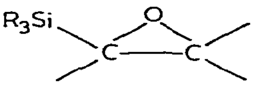

(IV)

In contrast to the behaviour of epoxides, which often decompose at high temperatures to a complex mixture of products [3-5], it was found that the epoxysilanes rearranged cleanly to siloxyalkenes at relatively low temperatures (170-310 °C). The structures of the products isolated indicated that two different rearrangement pathways existed: which pathway was followed depended on the substituents attached to the epoxide ring and their relative geometry. With some epoxysilanes a "double migration" process occurred in which the silyl group migrated from C(1) to oxygen becoming a siloxy group attached to C(2), while R^3 (or R^2) migrated from C(2) to C(1) [path a]. In other cases, the rearrangement in-

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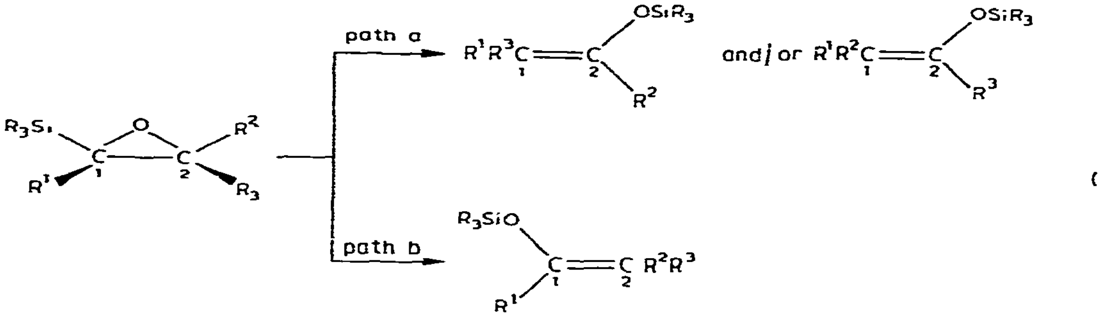
volved only the migration of the silyl group from C(1) to oxygen, to form the siloxy group attached to C(1) [path b], hereafter referred to as "silyl migration".



(1)

The experimental data are presented in Tables 1 and 2, including stereochemical assignments for the reactants and products based on chemical grounds (*cis* epoxidation of alkenes using *m*-chloroperbenzoic acid) and NMR data (where it was assumed that $J(trans) > J(cis)$ in the siloxyalkenes).

Table 1 lists the results of thermolyses which appear to proceed by the "double migration" mechanism. It is evident that many of the reactions proceed with considerable stereospecificity. Thus rearrangement of II indicated that R^1 and silyl, both originally attached to C(1), ended up on different carbon atoms, and that 95% of the rearrangement led to products in which R^1 had a *cis* relationship with the siloxy group in the product. This is interpreted most simply as the migration of H (R^3 or R^2) from C(2) to C(1) as the silyl group bonds to oxygen becoming the siloxy group attached to C(2). In the light of this interpretation, the rearrangement of III indicated that at least 80% of the migration from C(2) to C(1) was by R^3, the group (deuterium) originally *trans* to the silyl group.

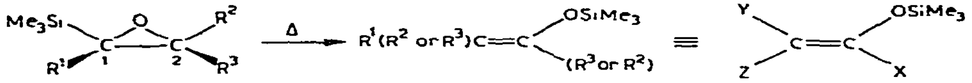
The results for the other compounds examined, IV-VII, all follow the above pattern, namely the migration of H from C(2) to C(1) while Si migrates to oxygen which remains bonded to C(2). However, these rearrangements were less stereospecific than was observed with II and III, since mixtures of geoisomeric siloxyalkenes were produced.

Before discussing the details of path a further, it is necessary to consider the rearrangements which follow the "silyl migration" pathway. Examples are listed in Table 2. The first two examples, VIII and IX, show unambiguously that in the course of forming the new Si—O and C=C bonds, no migration of R groups between C(1) and C(2) occurred and that the newly formed Me_3SiO group was attached to C(1). Thermal rearrangement of IX at 170 °C gave only the more stable *trans* isomer, but at higher temperatures a *cis*/*trans* mixture was formed, with the *trans* isomer predominating.

While the products isolated from the thermolyses of X and XI do not themselves unambiguously reveal whether a "silyl migration" or a "double migration" involving phenyl migration occurred, it follows from the results of IX that X rearranged by the "silyl migration" pathway. Since the behaviour of IX indicated no tendency for phenyl migration to occur in these sorts of compounds, it follows that phenyl migration is equally unlikely with compound XI, which must likewise rearrange by the "silyl migration" pathway.

TABLE 1

REARRANGEMENTS OF EPOXYSILANES INVOLVING DOUBLE MIGRATION

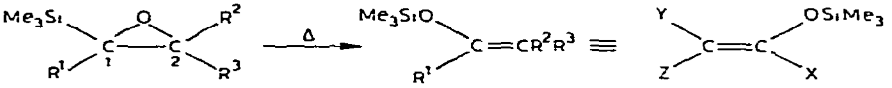


Compound	R^1	R^2	R^3	Temperature (° C)	Time (min)	X	Y	Z	Yield (%)
I	H	H	H	310	100	H	H	H	100
II	D	H	H	310	100	H	D	H	95
						H	H	D	4
						D	H	H	<1
III	H	H	D	310	100	H	H	D	70
						H	D	H	10
						D	H	H	20
IV	Me_3Si	H	H	256	120	H	H	Me_3Si	50
						H	Me_3Si	H	50
V	Ph	H	H	250	15	H	H	Ph	55
						H	Ph	H	45
VI	Me	H	H	256	60	H	H	Me	50
						H	Me	H	50
VII	H	Me	H	256	315	Me	H	H	50[a]

[a] 50% starting material recovered.

TABLE 2

THERMAL REARRANGEMENTS OF EPOXYSILANES INVOLVING SILYL MIGRATION



Compound	R^1	R^2	R^3	Temperature (° C)	Time (min)	X	Y	Z	Yield (%)
VIII	H	Me	Me	233	120	H	Me	Me	70[a]
IX	D	H	Ph	170	1320	D	H	Ph	100
				310	30	D	H	Ph	85
						D	Ph	H	15
X	H	H	Ph	200	150	H	H	Ph	60[b]
				250	134	H	H	Ph	55
						H	Ph	H	45
XI	H	Ph	H	160	1200	H	H	Ph	50[c]
				320	60	H	H	Ph	85
						H	Ph	H	15
XII	H	H	Me	256	315	Me	H	H	50
						H	H	Me	50
XIII	H	H	Me_3Si	258	240	H	H	Me_3Si	80
						H	Me_3Si	H	20

[a] 30% starting material recovered. [b] 40% starting material recovered. [c] 40% starting material recovered. In addition, 10% of the isomeric epoxide was obtained, the only case where isomerism of starting material was observed.

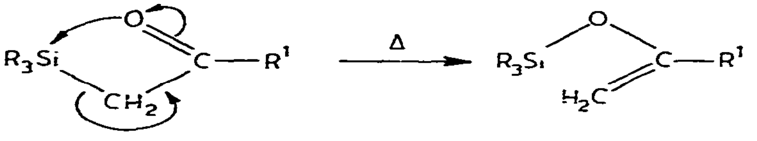
In all of the examples considered so far, where migration has been clearly demonstrated, only H (or D) migration has been observed, with no evidence for the migration of Ph, Me_3Si or Me[*]. These observations are relevant to the thermolysis of XII, where the results can be explained either on the basis of the occurrence of two competing "double migrations", with H (R^2) migration giving the siloxyalkene XIV (X = Me; Y = Z = H) and Me (R^3) migration giving the siloxyalkene XV (X = Y = H; Z = Me) or alternatively, on the basis that part of the reaction involves the "double migration" process with H (R^2) migration yielding XIII, and part of the rearrangement follows the "silyl migration" pathway, yielding XV. Since alkyl migrations are usually less facile than H or aryl migrations, regardless of the type of reaction, we prefer the second explanation for the results from XII.

A similar ambiguity applies to XIII, where the results can be explained either on the basis of "silyl migration" or "double migration" with Me_3Si the migrating group, or a mixture of both pathways.

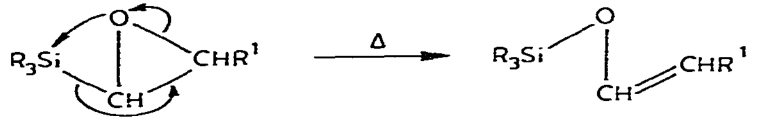
A preliminary investigation of the kinetics of the rearrangement of VI (double migration) and VIII, (silyl migration), indicated that each was a clean first-order process.

It is evident that no single mechanism can account for all of the observations given above, and that different mechanisms must apply to the "double migration" and "silyl migration" pathways. Each pathway displays high stereospecificity in some cases, consistent with a concerted intramolecular process, but in other cases particularly at higher temperatures, there is a loss of stereospecificity; It is not yet clear whether the loss of stereospecificity is due to competing mechanisms, one of which might involve the homolytic or heterolytic opening of the epoxide ring prior to rearrangement, or to other processes, but it appears significant that both, V and X, when rearranged at 250 °C gave the same 55/45 proportions of the same *trans* and *cis* isomers, even though different pathways were followed.

Since the rearrangements that occur by the "silyl migration" pathway parallel very closely the previously described concerted intramolecular rearrangements of β-ketosilanes, which also yield siloxyalkenes (eqn. 2), a formally related mechanism, also involving nucleophilic attack of oxygen on silicon as shown in eqn. 3, seems a reasonable explanation for this pathway.



(2)



(3)

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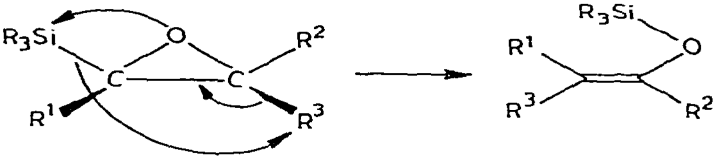
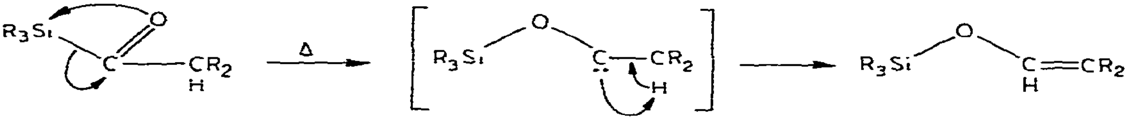
[*] In one set of runs only (of several) using VIII, evidence for a small amount (15%) of methyl migration was found, but this was not duplicated in subsequent runs.

The mechanism for the "double migration" pathway necessarily differs from that for "silyl migration". A concerted process, involving in effect inversion of configuration at C(1) as hydrogen (R^3) migration occurs to the backside of the C—Si bond during its cleavage and formation of the siloxy group, appears to account for the observed stereospecificity. Clearly in this case also, other pathways, which may involve preliminary ring opening, must be available in cases where little or no stereospecificity is observed.



The concerted pathway for "double migration" appears to be closely related to the recently described thermal isomerisation of acylsilanes in which siloxyalkenes are also formed, possibly via an intermediate or transition state having carbene character, which subsequently acquires hydrogen from an adjacent C—H bond.



Our studies of these interesting rearrangements are continuing.

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