Journal of Organometallic Chemistry, 77 (1974) C19—C21

Preliminary communication

1,4-SILYL REARRANGEMENTS OF SILOXYALKENES TO SILOXYKETONES DURING PEROXIDATION

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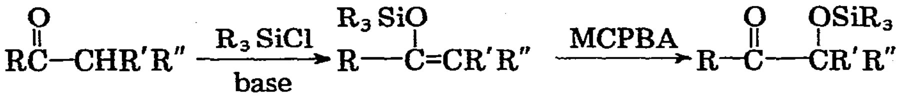
(Received June 10th, 1974)

Summary

Peroxidation of siloxyalkenes yields α-siloxyketones, which appear to arise as the result of a 1,4 shift of silicon from oxygen to oxygen.

Rearrangements involving 1,2, 1,3, 1,4 and 1,5 shifts of organosilyl groups are well-documented in the literature [1] and a rapid, reversible 1,9 silyl shift (involving a 1,4 shift between atoms) has been proposed to account for the NMR spectra of a tropolone silyl ether [2].

We have now found that a rearrangement occurs during the peroxidation of siloxyalkenes II, which yields siloxyketones III. This is best explained as resulting from a 1,4 oxygen-to-oxygen silyl shift.



$$R\overset{\overset{O}{\|}}{C}\text{—}CHR'R'' \xrightarrow[\text{base}]{R_3SiCl} R\text{—}\overset{\overset{R_3SiO}{|}}{C}=CR'R'' \xrightarrow{\text{MCPBA}} R\text{—}\overset{\overset{O}{\|}}{C}\text{—}\overset{\overset{OSiR_3}{|}}{C}R'R''$$

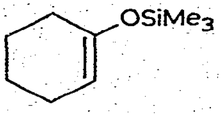
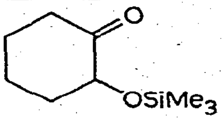
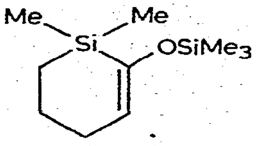
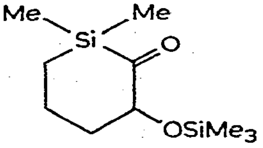
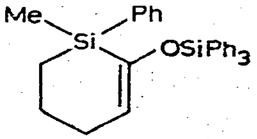
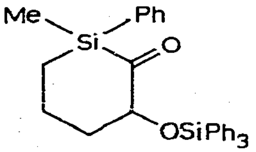
(I) (II) (III)

Siloxyalkenes II are readily prepared from enolizable ketones I using base and chlorosilane [3—5]. The siloxyalkene was treated with a slight excess of *m*-chloroperbenzoic acid (MCPBA) in methylene chloride at 0°. Workup by addition of pentane, filtration to remove precipitated *m*-chlorobenzoic acid and then rapid chromatography through neutral alumina (eluting with ether) gave the siloxyketones III, generally as oils which were then distilled. Typical results are given in Table 1.

It is evident from the results that the carbon atom to which the siloxy group was initially attached becomes the carbonyl group, and that the siloxy group becomes attached to the other end of the original carbon—carbon double bond. Formally analogous rearrangements have been observed in the peroxidation of enol acetates [6], and in the conversion of enamines to acetoxyketones [7].

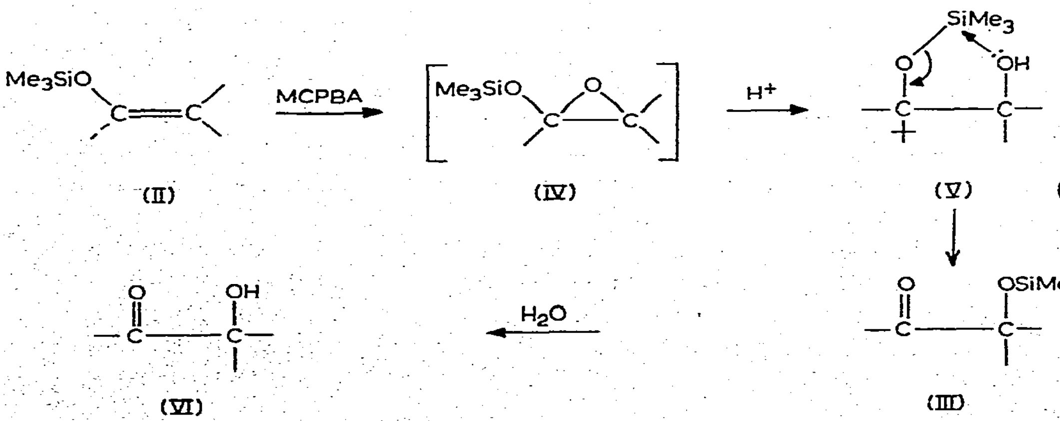
TABLE 1

PERACID OXIDATION OF SOME SILOXYALKENES

Siloxyalkene	Preparation [a]	Siloxyketone	Yield (%)
	I		68 [b,c]
$PhC(OSiMe_3)=CH_2$	I, II	$PhCOCH_2OSiMe_3$	70 [d,g]
$PhC(OSiPh_3)=CH_2$	II	$PhCOCH_2OSiPh_3$	61 [b]
$MeC(OSiMe_3)=CHPh$	III	$MeCOCHPhOSiMe_3$	3
$MeC(OSiMe_3)=CH_2$	I	$MeCOCH_2OSiMe_3$	60 [e,g]
	I, II		75 [b]
	II		74 [b,f]

[a] Methods of Siloxyalkene preparation:
I, ketone, trimethylchlorosilane and triethylamine refluxed in DMF [2]; II, enolate ion from ketone and sodium bis(trimethylsilylamine) treated with chlorosilane [1]; III, ketone treated with NaH, followed by chlorosilane [2]. No attempt to optimize yields has been made. [b] New compound, which had analyses and spectra consistent with the proposed structures. [c] Gave 90% 2-hydroxycyclohexane on hydrolysis. [d] Gave 70% α-hydroxyacetophenone on hydrolysis. [e] Gave 70% hydroxyacetone on hydrolysis. [f] Peroxidation in ether and workup yielded the epoxide, which on reflux with a trace of p-toluenesulphuric acid in ether over one hour, yielded the siloxyketone as a mixture of diastereomers which were not separated. [g] See ref. 3.

The present reaction is of interest because of the 1,4 silyl rearrangement, and a likely mechanism is illustrated in equation 2. While the rearrangement logically involves the more stable oxacarbonium ion V as an intermediate, it is not clear whether this forms directly from the siloxyalkene on reaction



(2)

with MCPBA, or whether an intermediate siloxyepoxide, IV is formed which on subsequent protonation opens to V. Attempts to isolate or detect the epoxide in methylene chloride have been unsuccessful and the siloxyketones are normally isolated directly from the reaction. The siloxyketones are readily hydrolyzable to the expected hydroxyketones VI using mild base. Further studies are in progress.

This research was supported by the National Research Council of Canada.

References

1 For summaries see A.G. Brook, Accounts Chem. Res., 7 (1974) 77 and R. West, Pure Appl. Chem., 19 (1969) 291.
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