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OXIDATION OF ALKENYLDISILANES BY *m*-CHLOROPERBENZOIC ACID

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Summary

Oxidation of vinylpentamethyldisilane by *m*-chloroperbenzoic acid (MCPBA) yields 1-(α,β-epoxyethyl)-1,1,2,2,2-pentamethyldisilane as major product. Conversely, the oxidation of allylpentamethyldisilane yields approximately equal amounts of allylpentamethyldisiloxane and 3-pentamethyldisilanylpropanal. These results have been accounted for in terms of the relative rates of oxidation of the various carbon—carbon double bonds and silicon—silicon single bonds which have been determined.

Silicon often modifies the properties and reactivity of adjacent unsaturated functional groups [1—4]. Recently, there has been interest in the oxidation of vinylsilanes by peracids to yield α,β-epoxysilanes because these can easily be converted to carbonyl compounds on treatment with acid [5,6]. There have been several reports that alkenylsilanes are relatively unreactive toward epoxidation by peracids [7—9]. This low reactivity may require that the carbonyl group of a ketoalkenyltrimethylsilane be protected as a ketal to prevent Baeyer—Villiger oxidation of the ketone in competition with oxidation of the vinylsilane functionality [7]. This problem might be expected since it has been reported that vinyltrimethylsilane is epoxidized about three times slower than 1-heptene by perbenzoic acid [10].

We have been interested in the effect of a pentamethyldisilanyl group on the oxidation of an adjacent C—C double bond. Both C—C double bonds [11] and Si—Si single bonds [12—14] are known to be oxidized by *m*-chloroperbenzoic acid (MCPBA) to yield respectively epoxides and disiloxanes. In fact, oxidation of vinylpentamethyldisilane with MCPBA has been reported to yield 1-(α,β-epoxyethyl)-1,1,3,3,3-pentamethyldisiloxane as the only reaction product [15].

In our hands, oxidation of vinylpentamethyldisilane with one equivalent of MCPBA yields 1-(α,β-epoxyethyl)-1,1,2,2,2-pentamethyldisilane as the major product (79%) with lesser amounts of 1-(α,β-epoxyethyl)-1,1,3,3,3-pentamethyl-

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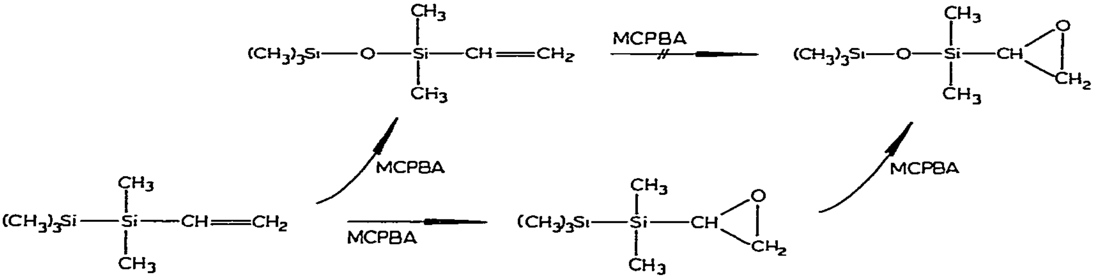
[12]

disiloxane and vinylpentamethyldisiloxane. While the relative amounts of these products varies with reaction conditions, in particular the amount of MCPBA (see experimental), under no conditions was vinylpentamethyldisiloxane the major product.

These results indicate that the C—C double bond of vinylpentamethyldisilane is more easily oxidized than the Si—Si single bond. If this is correct, the formation of 1-(α,β-epoxyethyl)-1,1,3,3,3-pentamethyldisiloxane must occur by a two-step oxidation process. Most of the time, the C—C double bond is oxidized first; the Si—Si single bond is oxidized in a second step.

To test this hypothesis, a 1/1 mixture of vinylpentamethyldisilane and vinylpentamethyldisiloxane was oxidized by one equivalent of MCPBA. Based on the amount of starting materials consumed 1-(α,β-epoxyethyl)-1,1,2,2,2-pentamethyldisilane (19%) and 1-(α,β-epoxyethyl)-1,1,3,3,3-pentamethyldisiloxane (27%) were formed. Vinylpentamethyldisilane (46%) and vinylpentamethyldisiloxane (108%) were recovered. Apparently both the C—C double bond and the Si—Si bond of vinylpentamethyldisilane are oxidized faster than the C—C double bond of vinylpentamethyldisiloxane. Oxidation of the Si—Si bond of vinylpentamethyldisilane results in formation of vinylpentamethyldisiloxane. Overall vinylpentamethyldisiloxane is produced in this reaction, not consumed.

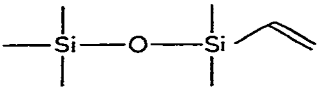
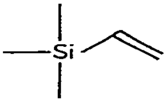
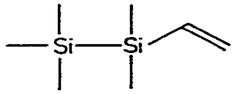
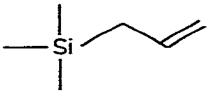


The C—C double bond of vinylpentamethyldisilane is oxidized much more rapidly than the C—C double bond of vinylpentamethyldisiloxane. This is in accord with previous observations that epoxidation of vinyldisiloxanes with peracetic acid was very sluggish [16]. Conversely, the Si—Si single bond of 1-(α,β-epoxyethyl)-1,1,2,2,2-pentamethyldisilane must be more readily oxidized than the Si—Si single bond of vinylpentamethyldisilane. While MCPBA oxidizes both C—C double bonds and Si—Si single bonds, tertiary amine oxides have been found to oxidize Si—Si single bonds selectively in the presence of C—C double bonds [17].

In competition experiments, we have determined the relative rates of oxidation of C—C double bonds by MCPBA for a series of alkenyl silanes (See Table 1). The results indicate that the C—C double bond of vinylpentamethyldisilane

TABLE 1

RELATIVE RATES OF CARBON—CARBON BOND OXIDATIONS BY MCPBA

	1.0
	2.1
	5.6
	13.0
	29.0

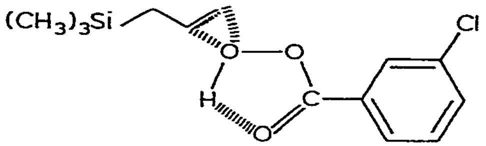
is approximately three times more reactive toward oxidation with MCPBA than the C—C double bond of vinyltrimethylsilane. Our results also indicate that 1-hexene is oxidized fifteen times faster than vinyltrimethylsilane. This is in contrast to the reported rates of oxidation of 1-heptene and vinyltrimethylsilane with perbenzoic acid [10]. This difference may be attributed to the change of solvent and peracid used.

Both trimethylsilyl and pentamethyldisilanyl groups are known to affect adjacent unsaturated functionalities by a combination of σ-donor and π-acceptor interactions [18]. Apparently, in oxidation reactions, the pentamethyldisilanyl group serves predominantly as a σ-donor which increases the electron density of the adjacent C—C double bond. This would simultaneously decrease the electron density of the Si—Si σ-bond. The combination of these effects would make the C—C bond more reactive toward oxidation by MCPBA than the Si—Si bond.

Oxidation of allylpentamethyldisilane with MCPBA yields almost equal amounts of allylpentamethyldisiloxane and 3-pentamethyldisilanylpropanal. Allyltrimethylsilane has an oxidation rate comparable to 1-hexene, the C—C double bond and Si—Si single bond of vinylpentamethyldisilane are not oxidized at comparable rates, and both bonds are of lowered reactivity (See Table 1).

3-Pentamethyldisilanylpropanal probably arises from acid-catalyzed rearrangement of 3-pentamethyldisilanyl-1,2-epoxypropane. This epoxide has been previously proposed as an intermediate in the base-initiated cyclization of 1-chloro-3-trimethylsilyl-2-propanol [19]. The rearrangement of the epoxide to the aldehyde is expected to be facile due to the ability of trimethylsilyl groups to stabilize β-carbocations. No evidence for the formation of 3-pentamethyldisiloxanylpropanal was found.

The rate of oxidation of the allyl silanes reflects the symmetric nature of the transition state in the oxidation with MCPBA.



If there was charge localization at the position β to the trimethylsilyl group, a rate acceleration for the oxidation of allyltrimethylsilane compared to 1-alkenes would be expected. In fact, 1-hexene is oxidized about twice as fast as allyltrimethylsilane.

Finally, oxidation of 2-pentamethyldisilanylethyl ethyl sulfide with MCPBA yields 2-pentamethyldisilanylethyl ethyl sulphone. This indicates that the dialkyl sulfide and dialkyl sulfoxide intermediates are both oxidized by MCPBA more readily than the Si—Si σ-bond.

In conclusion, vinylpentamethyldisilane is oxidized in a two-step process. The C—C double bond is oxidized in the first step, and the Si—Si single bond is oxidized in the second step. On the other hand, the C—C double bond and Si—Si single bond of allylpentamethyldisilane are oxidized at comparable rates. The adjacent vinyl and disilanyl groups of vinylpentamethyldisilane are mutually deactivating. Relative rate studies show that isolated Si—Si bonds and C—C double bonds in a molecule are oxidized at rates similar to 1-alkenes. Not surprisingly, dialkyl sulphides and sulphoxides are oxidized more rapidly than Si—Si single bonds.

Experimental

NMR spectra were recorded on Varian XL-100 spectrometer operated in the FT mode with 1% solutions in $CDCl_3$ as solvent and $CHCl_3$ as internal standard. IR spectra were run as CCl_4 solutions on a Perkin—Elmer 281 spectrometer. Spectra were calibrated against known bands of a polystyrene film. Ultraviolet spectra were run on a Beckman Acta M spectrometer. All samples were purified by preparative GLC on a Gow Mac 550 using a 14 ft by 1/4 in 20% SE-30 on Chromosorb W column. Competition experiments were analyzed on a Hewlett—Packard 5710 A gas chromatograph equipped with a flame ionization detector on a 15 ft by 1/8 in 10% SE-30 on Cromosorb P column. Yields were determined by GLC using decane as an internal standard. Low resolution mass spectra were obtained on a Hewlett—Packard 5985 GC-MS. Elemental analysis were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Most starting materials and some products are known compounds. Their spectral properties are in full agreement with literature values. In those cases where complete spectral information has not been previously reported, we have included these data.

Ethyl ether and tetrahydrofuran were distilled from the sodium ketyl of benzophenone. Chloroform and dichloromethane were reagent grade and used without further purification.

Chlorosilanes were purchased from Petrarch Systems, Inc. and were distilled immediately before use. *m*-Chloroperbenzoic acid was purchased from Aldrich.

Vinylpentamethyldisilane [20] was prepared by reaction of dimethylvinylchlorosilane, trimethylchlorosilane and magnesium turnings in THF. Mass spectrum: *m/e* (parent) 158 (28%); ($M-15$) 143 (31%); ($M-27$) 131 (2%); ($M-73$) 85 (64%); ($M-85$) 73 (100%).

Allylpentamethyldisilane [21] was prepared by reaction of allylmagnesium bromide with pentamethylchlorodisilane [22]. NMR: δ 5.8 (m, 1H); 4.87 (d of m, 1H); 4.73 (br. s, 1H); 1.57 (d, 2H, J 8.3Hz); 0.05 (s, 9H), 0.02 ppm (s, 6H). Mass spectrum: *m/e* (parent) 172 (10%); ($M-15$) 157 (5%); ($M-41$) 131 (100%). Pentamethylchlorodisilane was prepared by the method of Carberry, Keene, and Johnson [22].

2-Pentamethyldisilanylethyl ethyl sulphide. Vinylpentamethyldisilane (0.288 g, 1.8 mmol), ethyl mercaptan (0.2 g, 3.2 mmol) and a catalytic amount of 2,2-azobis[2-methylpropionitrile] in 1 ml dichloromethane were photolyzed with a sunlamp for 3 h [23]. Solvent and excess ethyl mercaptan were removed by evaporation under reduced pressure. GLC analysis showed quantitative conversion of the vinyldisilane to the sulphide. NMR: δ 2.54 (q, 2H, J 7.3 Hz); 2.55 (m, 2H, $(J_{AX}+J_{AX'})/2$ 8.8 Hz); 1.24 (t, 3H, J 7.3 Hz); 0.92 (m, 2H, $(J_{AX}+J_{AX'})/2$ 8.8 Hz) 0.05 ppm (s, 15H); IR: ν(Si—CH_3) 1255 cm^{-1}; Mass spectrum: *m/e* ($M-15$) 205 (0.3%), ($M-73$) 147 (31%), ($M-101$) 119 (100%). Anal. Found: C, 49.59; H, 11.00. $C_9H_{24}Si_2S$ calcd.: C, 49.42; H, 10.97%.

Vinylpentamethyldisiloxane [24,25] was prepared by cohydrolysis of trimethylchlorosilane and vinyldimethylchlorosilane in moist ethyl ether in 60% yield. Mass spectrum: *m/e* (M+) 174 (0.1%), ($M-15$) 159 (100%), ($M-27$) 147 (11.8%).

Vinyltrimethylsilane [26] was prepared by the addition of vinylmagnesium bromide in THF to trimethylchlorosilane.

Allyltrimethylsilane [26] was prepared by the addition of allylmagnesium bromide in ether to trimethylchlorosilane.

The oxidation of vinylpentamethyldisilane. MCPBA (80—90%, 870 mg, 5.04 mmol) was added to a stirred solution of vinylpentamethyldisilane (800 mg, 5.06 mmol) in 2 ml dichloromethane. This mixture was stirred for 16 h at room temperature. The mixture was then washed with water, saturated sodium carbonate, and water. The organics were dried over magnesium sulfate and filtered. GLC analysis indicated formation of 1-(α,β-epoxyethyl)-1,1,2,2,2-pentamethyldisilane (56%), 1-(α,β-epoxyethyl)-1,1,3,3,3-pentamethyldisiloxane [15,16] (10%), and vinylpentamethyldisiloxane (5%). Vinylpentamethyldisilane (29%) was recovered.

1-(α,β-Epoxyethyl)1,1,2,2,2-pentamethyldisilane. NMR: δ 2.89 (m, 1H), 2.53 (m, 1H), 2.26 (m, 1H), 0.09 (s, 9H), 0.02 ppm (s, 6H); IR: ν(Si—CH_3) 1260, (C—O) 1250 cm^{-1}. Mass spectrum: *m/e* ($M-15$) 159 (3.3%); ($M-43$) 131 (29.4%), ($M-101$) 73 (100%); Anal. Found: C, 48.17; H, 10.41. $C_7H_{18}OSi$ calcd.: C, 48.22; H, 10.33%.

1-(α,β-Epoxyethyl)-1,1,3,3,3-pentamethyldisiloxane [15,16]. IR: ν(Si—CH_3) 1260, (Si—O) 1050 cm^{-1}; Mass spectrum: *m/e* ($M-43$) 147 (62.1%), ($M-57$) 133 (45.3%), ($M-59$) 131 (29.6%), ($M-117$) 73 (100%).

The oxidation of allylpentamethyldisilane. Allylpentamethyldisilane (261 mg, 1.52 mmol), MCPBA (261 mg, 1.52 mmol) and 2 ml dichloromethane were stirred for 15 h at room temperature. Work-up and analysis were carried out as above. 3-Pentamethyldisilanylpropanal (48%), allylpentamethyldisiloxane

(39%) [27] and recovered allylpentamethyldisilane (13%) were found.

3-Pentamethyldisilanylpropanal. NMR: δ 9.21 (br, s, 1H), 2.36 (*m*, 2H), 0.82 (m, 2H), 0.05 (s, 9H), 0.03 (s, 6H); IR: ν(C=O) 1733, ν(Si—CH$_3$) 1255 cm^{-1}. Mass spectrum: *m*/*e* (*M* — 15) 173 (1%); (*M* — 57) 131 (24%); (*M* — 73) 115 (100%). Anal. Found: C, 51.04; H, 10.80. $C_8H_{20}OSi_2$ calcd.: C, 51.00; H, 10.70%. UV (methylcyclohexane) λ_{max} 291 nm, ϵ 17.4.

Allylpentamethyldisiloxane [27]. NMR: δ 5.8 (m, 1H); 4.87 (d of m, 1H); 4.75 (br. s, 1H); 1.65 (d, 2H, *J* 8.0 Hz); 0.15 (s, 9H); 0.12 ppm (s, 6H). Mass spectrum: *m*/*e* (*M* — 41) 147 (100%), (*M* — 55) 133 (18%), (*M* — 57) 131 (18%), (*M* — 103) 85 (20.4%), (*M* — 115) 73 (71.7%).

The oxidation of 2-pentamethyldisilanylethyl ethyl sulfide. 2-Pentamethyldisilanylethyl ethyl sulfide (166 mg, 0.75 mmol) in 2 ml chloroform was added to MCPBA (130 mg, 0.75 mmol). The reaction mixture was stirred for 16 h at room temperature. Reaction was worked-up and analyzed as above. The sole product was 2-pentamethyldisilanylethyl ethyl sulphone (32%).

2-Pentamethyldisilanylethyl ethyl sulphone. NMR: δ 2.98 (q, 2H, *J* 7.4 Hz), 2.86 (m, 2H, $(J_{AX} + J_{AX'})/2$ 8.9 Hz), 1.38 (t, 3H, *J* 7.4 Hz), 1.07 (m, 2H, $(J_{AX} + J_{AX'})/2$ 8.9 Hz); 0.07 (s, 15H); IR: ν(O=S=O) 1332, 1141, (Si—CH$_3$) 1255 cm^{-1}. Mass spectrum: *m*/*e* (*M* — 73) 179 (22%), (*M* — 101) 151 (100%). Anal. Found: C, 42.70; H, 9.63. $C_9H_{24}O_2SSi_2$ calcd.: C, 42.81; H, 9.58%.

Competitive oxidation of vinylpentamethyldisilane and vinylpentamethyldisiloxane. A mixture of vinylpentamethyldisilane (76 mg, 0.48 mmol) and vinylpentamethyldisiloxane (80 mg, 0.46 mmol) in 2 ml chloroform was added to MCPBA (83 mg, 0.48 mmol) and stirred for 16 h at room temperature. Work-up was as previously described. Vinylpentamethyldisiloxane (0.50 mmol, 108%), vinylpentamethyldisilane (0.22 mmol, 46%) 1-(α,β-epoxyethyl)-1,1,2,2,2-pentamethyldisilane (0.09 mmol, 19%), and 1-(α,β-epoxyethyl)-1,1,3,3,3-pentamethyldisiloxane (0.13 mmol, 27%) were found.

Competitive oxidation of 1-hexene and vinylpentamethyldisilane. A solution composed of 2 ml dichloromethane, 1-hexene (20 mg, 0.24 mmol), vinylpentamethyldisilane (26 mg, 0.16 mmol) and MCPBA (7 mg, 0.04 mmol) was stirred for 16 h at room temperature. It was worked up as above. GLC analysis indicated formation of 1,2-epoxyhexane [28] and 1-(α,β-epoxyethyl)-1,1,2,2,2-pentamethyldisilane in a ratio of 5.2/1.

Competitive oxidation of vinyltrimethylsilane and vinylpentamethyldisiloxane. MCPBA (13 mg, 0.08 mmol) was added to a mixture of vinyltrimethylsilane (51 mg, 0.51 mmol) and vinylpentamethylsiloxane (54 mg, 0.31 mmol) in 2 ml dichloromethane. The mixture was reacted and worked-up as previously described. GLC analysis showed formation of α,β-epoxyethyltrimethylsilane [29—31] and 1-(α,β-epoxyethyl)-1,1,3,3,3-pentamethyldisiloxane in a ratio of 2.1/1.

Competitive oxidation of 1-hexene and allyltrimethylsilane. A solution of allyltrimethylsilane (34 mg, 0.30 mmol), 1-hexene (29 mg, 0.34 mmol), MCPBA (17 mg, 0.1 mmol), and 2 ml dichloromethane was stirred for 16 h at room temperature. Work-up was as previously described. GLC analysis indicated 1-hexene had been oxidized 2.2 times faster than allyltrimethylsilane.

Competitive oxidation of 1-hexene and vinylpentamethyldisiloxane. A mixture of 1-hexene (46 mg, 0.55 mmol) and vinylpentamethylsiloxane (66 mg, 0.38 mmol) in 2 ml dichloromethane was oxidized with MCPBA (17 mg, 0.1 mmol) as described above. GLC analysis indicated formation of 1,2-epoxyhexane and 1-(α,β-epoxyethyl)-1,1,3,3,3-pentamethyldisiloxane in a ratio of 29.0/1.

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