

0040-4039(95)00960-4

Epoxidation versus Allylic Oxidation (CH Insertion) in the Oxyfunctionalization of Vinylsilanes and β-Hydroxy Derivatives by Dimethyldioxirane

Waldemar Adam*, Frank Prechtl, Markus J. Richter, Alexander K. Smerz

Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany

Abstract: Epoxidation of acyclic vinylsilanes by dimethyldioxirane affords α,β -epoxysilanes in high yields, whereas for cyclic vinylsilanes appreciable amounts of allylic oxidation is observed. These competitive pathways become more pronounced, when the reactivity of the double bond is decreased by electronic and/or steric factors.

Dimethyldioxirane has been well established as an extraordinary oxidizing agent during the last decade¹. Thus, olefin epoxidations, heteroatom oxidations and CH insertions can be performed very selectively under mild conditions with isolated dimethyldioxirane². It is widely accepted that dimethyldioxirane is an electrophilic oxidant³, but so far no consistent mechanistic picture for the different oxidation reactions exists.

To broaden the scope of the synthetic applicability of dioxiranes, we have investigated the oxidation of vinylsilanes 1, which should give rise to α,β -epoxy silanes 2, a class of compounds that has attracted considerable synthetic interest. For instance, α,β -epoxy silanes can be used as vinyl cation equivalents, they can be transformed to β -hydroxysilanes by regioselective epoxide ring opening, and their hydrolysis yields the corresponding α -hydroxy carbonyl compounds⁴.

For acyclic vinylsilanes, the reaction with dimethyldioxirane proceeded straightforwardly and the expected epoxy silanes were obtained in high yields (Table 1). It is noteworthy that the epoxides can be obtained cleanly

Table 1: Dimethyldioxirane Oxidation of Acyclic Vinylsilanes 5

R ¹		$ \begin{array}{c c} SIMe_2R^4 & & & \\ & $			R^1 SiMe ₂ R^4 R^2 R^3		
	1 R ¹	R ²	R ³	R ⁴	2 conv. [%] ^a	yield [%]ª	
1a	н	ⁿ Bu	Н	Me	> 95	> 95	
1 b	Me	н	Me	Me	> 95	> 95 ^b	
1 c	Et	н	Me	Ph	> 95	> 95°	
1 d	Me	ⁿ Bu	Н	Me	86	> 95	
1 e	Et	ⁿ Bu	н	Mic	> 95	> 95	
1f	Mc	Cyclohexyl	н	Mic	> 95	> 95	
1 g	Me	Mc	Me	Ph	> 95	> 95	

^a Determined by ¹H NMR analysis directly on the crude product mixture (error ± 5%). ^b A 64:36 E/Z mixture of vinylsilane 1b yielded a 63:37 *trans/cis* mixture of the corresponding epoxides. ^cA 78:22 E/Z mixture of vinylsilane 1c yielded a 75:25 *trans/cis* mixture of the corresponding epoxides. in acetone as solvent, despite the fact that examples have been reported, in which carbonyl functionalities promote ring-opening of epoxy silanes⁶.

For cyclic substrates, in addition to the expected epoxides 2, the dimethyldioxirane oxidation gave also the two regioisomeric silylated enones 3 and 4 (Table 2). The allylic alcohols, the primary oxidation products, could not

Table 2: Dimethyldioxirane Oxidation of Cyclic Vinylsilanes⁵



^a Determined by ¹H NMR analysis directly on the crude product mixture (error \pm 5%). ^b The diastereometric epoxides 2 were obtained in a 62:38 *anti/syn* ratio.

be detected in these reactions. The epoxide/enone ratio and the regioselectivity in the formation of enones 3 and 4 depend on the ring size and the substitution pattern of the cyclic vinylsilane. Thus, the eight-membered ring vinylsilane 1h does not afford any enone, whereas the six- and five-membered ring trisubstituted vinylsilanes 1i, 1k and 1l do to an appreciable extent. However, the tetra-substituted, electron-rich double bond of (2-methyl-1-cyclohexenyl)trimethylsilane (1j) is sufficiently reactive to lead exclusively to the epoxide.

Interestingly, these dioxirane oxidations closely resemble those of the corresponding allylic alcohols, in that the eight-membered ring derivative gives exclusively the epoxy alcohol, while cyclopent-2-en-1-ol and cyclohex-2-en-1-ol afford appreciable amounts of the enones as byproducts⁷. In contrast to cyclohex-2-en-1-ol, which gave 30% CH insertion and 70% epoxidation⁷, dimethyldioxirane oxidation of its silyl derivative **5a** formed exclusively (> 95%) the enone. A similar trend is also observed in the oxidation of the acyclic substrates in Eq. 1. Again, the enone is the major product in the dioxirane oxidation of the silylated substrate **5b**⁸, whereas the corresponding desilylated allylic alcohol **5d** yielded exclusively the diastereomeric epoxides Moreover, even more enone was formed for the sterically more demanding dimethylphenylsilyl derivative **5c**.

To assess the kinetic effect of a trimethylsilyl substituent at the double bond in the dimethyldioxirane oxidation, a competition experiment between trimethylsilylcyclohexene and cyclohexene (Eq. 2) was performed. Cyclohexene was oxidized faster by dimethyldioxirane than trimethylsilylcyclohexene, since on treatment of a 1:1 mixture of the two olefins with one equivalent of dioxirane, the cyclohexene was consumed to the extent of 87% versus 13% for the silyl derivative. This is in contrast to peracid epoxidations, in which vinylsilanes are



generally more reactive than the corresponding alkenes⁴. Thus, the oxidation of the 1:1 mixture with mCPBA yielded a 34:66 mixture of epoxide and α , β -epoxy silane when the total conversion was 36%. The



reduced reactivity of the vinylsilanes versus the corresponding alkenes in the dioxirane reactions is attributed to the steric hindrance exerted by the trialkylsilyl group⁹, which is more pronounced for the bulkier DMD compared to mCPBA. Mechanistically more revealing is the fact that for mCPBA only epoxidation took place, while for DMD also appreciable amounts of allylic oxidation were observed (Eq. 2).

Were it only for the acyclic vinylsilanes **1a-g**, for which analogous to mCPBA⁴ exclusively epoxidation and no allylic oxidation is observed (Table 1), unquestionably the well-established "butterfly" mechanism for the peracid oxidation¹⁰ would also apply for the present dioxirane oxygen transfer^{11,12}. However, this straightforward mechanistic rationale is complicated by the fact that for the cyclic vinylsilanes **1h-I** (Table 2) and the cyclic and acyclic β -hydroxy vinylsilanes (Eq.1) appreciable allylic oxidation to the silyl enones is also found. In fact, for the trialkylsilyl-bearing allylic alcohols such allylic oxidation dominates over epoxidation since the silyl enone product is the major if not exclusive oxidation product. Therefore, the hydroxy functionality activates the allylic CH bond towards oxygen atom insertion. This is particularly evident for 2-trimethylsilylcyclohex-1-en-2-ol (**5a**) versus 1-trimethylsilylcyclohexene (**1i**). For the former, exclusive (100%) CH insertion takes place at the hydroxy-bearing allylic position, none at the other allylic methylenic groups and no epoxidation, while for the latter about equal amounts (ca. 10%) of allylic oxidation is observed at the two possible allylic methylene groups and predominantly epoxidation (82%). A similar trend applies for the DMD oxidation of acyclic allylic substrates in Eq. 1.

In view of the recent additional evidence that CH insertions by DMD involve free radical-chain reactions¹³, it would be tempting to propose such a mechanism for the allylic oxidation observed here for the vinylsilanes and

 β -hydroxy derivatives. However, the unsymmetrically substituted cases 5b,c should have afforded, besides the silyl enones 7b,c, also regioisomerically oxyfunctionalized products at the methylene terminal through the intermediary mesomeric allyl radical generated by H abstraction at the hydroxy site; but these were not observed. Furthermore, for vinylsilane 1i (Table 2), the allyl radical generated after H abstraction at the 3-position should afford cyclohex-2-en-1-one by hydroxylation at the silyl-substituted terminal and subsequent loss of silanol, but again this allylic oxidation product is not detected even in traces. Indeed, the fact that radicalchain products are observed does not necessitate a free radical mechanism in the CH insertion by the dioxirane. Instead, the dioxirane may initiate the radical-chain, and if the latter is efficient, the true CH insertion process will not come to fruition. Besides, the proposed¹³ radical-chain mechanism for CH insertion by DMD completely ignores the fact that 100% retention of configuration is documented¹⁴ for the α -hydroxylation of optically active 2-phenylbutane. Surely, the intermediary radical generated after benzylic H abstraction by DMD would be expected to racemize appreciably.¹⁵

We contend that the activation barriers for DMD epoxidations and allylic oxidation lie close together (a few kcal/mol), so that subtle structural changes push the chemoselectivity in one or the other oxidation mode through electronic and/or steric effects. The electronic effects are convincingly expressed by the vinylsilane pair li and 1j, for which the additional methyl group enhances the π reactivity of the double bond towards epoxidation such that allylic oxidation is completely supressed (Table 2). The importance of structural effects is evident in the silyl alcohol pair 5b,c, for which the bulkier PhMe₂Si group discourages epoxidation and, thus, allylic oxidation dominates. More such chemoselective studies will be essential to understand the mechanistic complexities of dioxirane oxyfunctionalizations, but in the meantime Ockhams razor should be our guide.¹⁶

Acknowledgement: Financial support by the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm "Peroxidchemie: Mechanistische und präparative Aspekte des Sauerstofftransfers") and the Fonds der Chemischen Industrie is gratefully acknowledged.

References and Notes:

- a.) W. Adam, R. Curci, J. O. Edwards, Acc. Chem. Res. 1989, 22, 205-211. b.) R. W. Murray, 1 Chem. Rev. 1989, 89, 1187-1201. c.) R. Curci, in Advances in Oxygenated Processes; A. L. Baumstark, Ed.; JAI: Greenwich, CT, 1990; Vol 2, Chapter I. d.) W. Adam, L. P. Hadjiarapoglou, R. Curci, R. Mello in Organic Peroxides; W. Ando, Ed.; Wiley, New York, 1992; Chapter 4, pp 195-219. e.) W. Adam, L. Hadjiarapoglou, Top. Curr. Chem. 1993, 164, 45-62.
- 2 3 W. Adam, L. Hadjiarapoglou, J. Bialas, Chem. Ber. 1991, 124, 2377.
- W. Adam, D. Golsch, Chem. Ber. 1994, 127, 1111-1113.
- 4 P. F. Hudrlik, A. M. Hudrlik, Advances in Silicon Chemistry 1993, 2, 1-93.
- 5 6 Dimethyldioxirane was used as a 0.070 - 0.100 M solution in acetone.
- G. Stork, M. E. Jung, J. Am. Chem. Soc. 1974, 96, 3682-3684.
- 7 W. Adam, F. Prechtl, M. J. Richter, A. K. Smerz, Tetrahedron Lett. 1993, 34, 8427-8430.
- In this context it is worth noting that the corresponding stannylated allylic alcohols also yield a mixture of epoxides (23%, d.r. 80:20) and enone (77%) when treated with dioxirane, e.g.

$$Me_{3}Sn \qquad CH_{3} \xrightarrow{O} \\ CH_{2}Cl_{2}/acetone, r.t., 3.5 h \qquad O \\ CH_{3} \xrightarrow{O} \\ CH_{2}Cl_{2}/acetone, r.t., 3.5 h \qquad O \\ CH_{3} + Me_{3}Sn \qquad CH_{3} + Me_{3}Sn \\ CH_{3$$

- 9 For a sterically hindered vinylsilane which could not be epoxidized by dimethyldioxirane cf. G. D. Maynard, L. A. Paquette, J. Org. Chem. 1991, 56, 5480-5482.
- 10 B. Plesnicar in The Cemistry of Peroxides; S. Patai, Ed.; John Wiley, NewYork, 1983, p. 521.
- a.) A. L. Baumstark, C. J. McCloskey, Tetrahedron Lett. 1987, 28, 3311-3114. b.) A. L. Baumstark, P. C. Vasquez, J. Org. Chem. 1988, 53, 3437-3439. 11
- R. D. Bach, A. L. Owensby, J. L. Andres, H. B. Schlegel, J. Am. Chem. Soc. 1991, 113, 2338-2341. 12
- a) F. Minisci, L. Zhao, F. Fontana, A. Bravo, Tetrahedron Lett. 1995, 36, 1697-1700. b) F. Minisci, L. 13 Zhao, F. Fontana, A. Bravo, Tetrahedron Lett. 1995, 36, 1895-1898.
- 14 W. Adam, G. Asensio, R. Curci, M. E. Gonzales-Nunes, R. Mello, J. Org. Chem. 1992, 57, 953-955.
- K. P Kopecky, T. Gillan, Can. J. Chem. 1969, 47, 2371-2386. 15
- 16 W. H. Jefferys, J. O. Berger, Am. Sci. 1992, 80, 64-72.

(Received in Germany 28 April 1995; accepted 22 May 1995)