Journal of Organometallic Chemistry, 280 (1985) 31–37
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

EFFECT OF RING SIZE ON THE ACID-CATALYSED HYDROLYSIS OF CYCLIC α,β-EPOXYSILANES

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(Received December 22nd, 1983; in revised form July 3rd, 1984)

Summary

Acid-catalysed hydrolysis of epoxysilanes derived from common-, medium- and large-ring vinylsilanes is described. Whereas the large-ring epoxysilanes give ketones, the medium-ring epoxysilanes give transannular products and the common-ring epoxysilanes provide α,β-dihydroxysilanes. The results are explained as due to the conformational rigidity in the common-ring silyldiols and the conformational freedom in the large-ring silyldiols to achieve antiperiplanar geometry for 1,2-elimination of trimethylsilanol.

Introduction

Acyclic α,β-epoxysilanes are known to give aldehydes or ketones on acid-catalysed hydrolysis, α,β-dihydroxysilanes being formed as isolable intermediates [1–5]. However, when the cyclic α,β-epoxysilane, 1-trimethylsilylcyclohexene oxide (VII), gave only the silyldiol XII and no cyclohexanone, Hudrlik et al. concluded that only epoxysilanes derived from acyclic vinylsilanes can give carbonyl compounds [3]. The results could be different with cyclic α,β-epoxysilanes of different ring sizes, because, unlike common-ring compounds ($C_{n'}$, $n' = 5$, 6), large-ring compounds ($n' \geqslant 12$) behave like acyclic compounds due to greater conformational flexibility and the medium-ring compounds ($n' = 7$–11) give transannular products [6,7].

Results and discussion

The starting epoxides VI–X were obtained in excellent yields by the reaction of 1-trimethylsilylcycloalkenes I–V [9] with *m*-chloroperbenzoic acid (Scheme 1).

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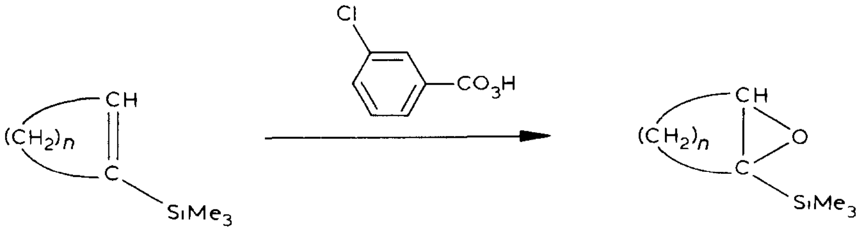
SCHEME 1



(I	$n = 3$	(VI
II	$n = 4$	VII
III	$n = 5$	VIII
IV	$n = 6$	IX
Va (*cis*) Vb (*trans*)	$n = 10$	Xa Xb)

The acid-catalysed reactions of the epoxysilanes VII [3,10] and IX [8] are described elsewhere. The hydrolysis of the remaining epoxides for the present study was carried out in dioxane using 0.8–1.0 *M* sulphuric acid. Hydrolysis of the silylepoxide VIII, both at room temperature and around 100°C for varying periods of time, produced no cycloheptanone nor 1-trimethylsilylcycloheptane-1,2-diol but a complex mixture of products, and no further discussion on this is included here.

Hydrolysis of 1-trimethylsilylcyclopentene oxide

The epoxysilane VI underwent complete hydrolysis at room temperature in about 2 h to silyldiol XI, which exhibited spectral characteristics similar to those of the diol XII. Extending the reaction for 72 h or heating the reaction mixture on water bath for 5 h did not provide any cyclopentanone and the silyldiol XI was recovered unchanged.

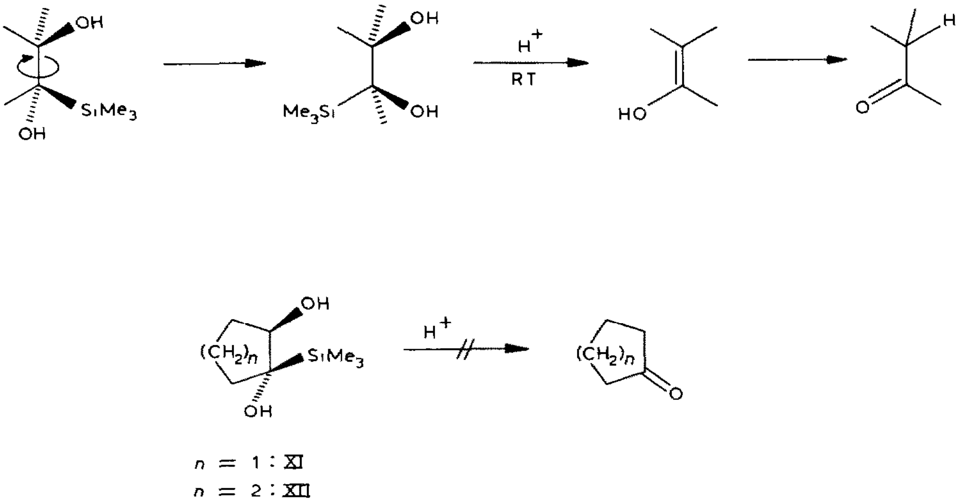
Hydrolysis of 1-trimethylsilylcyclododecene oxide

The diastereomeric mixture of the epoxides Xa and Xb obtained from 1-trimethylsilylcyclododecene (42% *cis* + 58% *trans* [9]) was hydrolysed as such to silyldiols XIIIa and XIIIb at room temperature, the conversion being 95% in 48 h. The diols XIIIa and XIIIb could not be separated and were identified as a mixture by means of spectral data.

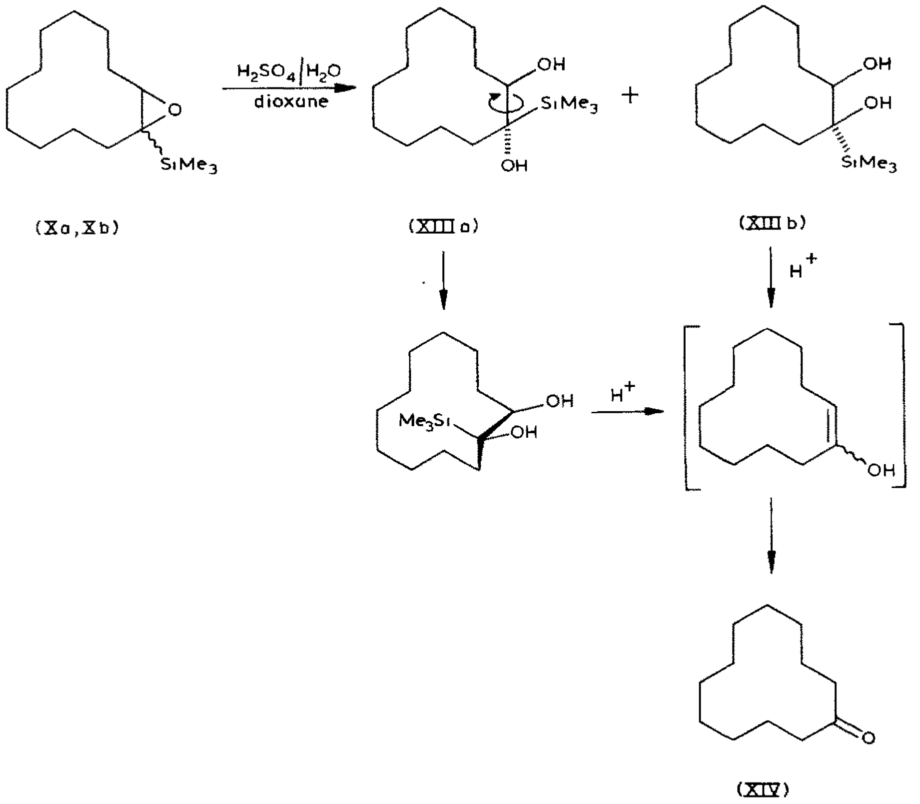
When the hydrolysis of X was continued beyond 48 h at room temperature, cyclododecanone (XIV) began to form and the conversion was about 80% in 7 days. Heating either the epoxides Xa, Xb or the diols XIIIa, XIIIb in the same medium on a boiling water bath also gave XIV in more than 95% yield in just 5 h.

It has been shown that, under mild hydrolytic conditions, α,β-epoxysilanes, through *trans*-opening of the epoxide ring, give α,β-dihydroxysilanes, which lead to aldehydes or ketones by elimination of trimethylsilanol if trimethylsilyl and β-hydroxy groups can assume antiperiplanar positions [2,3], (Scheme 2). This conformational requirement is not satisfied in the case of the diol XII and as such it does not provide cyclohexanone. The five-membered ring system exhibits similar or even more severe conformational restrictions [6a] and in the diol XI the β-hydroxy and the trimethylsilyl groups cannot attain the necessary *anti* position and therefore no

SCHEME 2



SCHEME 3



cyclopentanone could form, (Scheme 2). We have observed earlier in the case of hydrolysis of 1-trimethylsilylcyclooctene oxide (IX) that, subsequent to transannular hydride migration, trimethylsilanol is eliminated from the likely intermediates 2- and 5-trimethylsilylcyclooctane-1,4-diol [8].

The twelve-membered ring, considered as the first among the large-ring compounds, possesses much greater conformational flexibility than the common rings and is also largely free from the transannular interactions encountered in the medium rings [6g]. Therefore, 1-trimethylsilyl-1,2-cyclododecanediol (XIIIa and XIIIb), once formed from the hydrolysis of X, can assume a conformation, wherein the β-hydroxy and the silyl groups are antiperiplanar like in acyclic α,β-dihydroxysilanes (Scheme 3). The accomplishment of the *anti*-conformation of these groups may also be helped by the coming together of the two vicinal hydroxy groups in XIIIa, XIIIb as the stable conformation of *trans*-1,2-cyclododecanediol is one in which the two hydroxy groups are close to each other [13]. Thus β-hydroxy and silyl groups in XIIIa, XIIIb can achieve the required *anti*-conformation for the smooth *trans*-elimination of trimethylsilanol to result in the formation of cyclodocecanone (XIV).

In conclusion, the cyclic α,β-epoxysilanes of different ring sizes behave differently towards acid-catalysed hydrolysis, and as such large-ring vinylsilanes can be used as ketone precursors in contrast to other cyclic vinylsilanes.

Experimental

The melting and boiling points are uncorrected. The IR spectra of the liquids were run as thin films and those of solids in KBr pellets or $CDCl_3$, on Beckman Acculab-1 instrument. The NMR spectra were taken on Bruker Data System Model MTC-120 (60 MHz) instrument using $CDCl_3$ as solvent. The chemical shifts are measured from chloroform or TMS as internal standard respectively for silylated or unsilylated compounds and reported in ppm (δ). The GC/MS analyses were conducted on Varian Mat-111 and Hewlett-Packard HP 5985 instruments. The GC analyses were performed on Varian Aerograph 1400 with temperature programme. Thin layer chromatography (TLC) was carried out on silica gel-coated glass plates and column chromatography was done using 60–120 mesh silica gel (BDH chemicals). The vinylsilanes and the epoxides were prepared by methods described previously [8,9] using chemicals from Aldrich Chemical Co., England and Fluka AG, Switzerland.

1-Trimethylsilylcyclopentene oxide (VI)

From 1.49 g (10.64 mmol) of the vinylsilane I, 1.51 g (90.9% yield) of the epoxide VI was obtained, b.p. 65°C/50 torr. IR (cm^{-1}), 3000, 2960, 2910 (sh), 2850, 1430, 1375, 1250, 975, 940, 915, 880, 840, 815, 785, 745. NMR, δ 0.06 (s, 9H), 1.23–1.85 (m, 4H) overlapping with 1.85–2.23 (m, 2H), 3.30 (s, 1H). MS, m/e (intensity, %), 156 (6.3, M^+), 155 (11.9), 141 (5.3), 125 (5.9), 97 (8.9), 75 (100), 73 (67.3), 67 (8.9), 59 (18.8).

1-Trimethylsilylcycloheptene oxide (VIII)

From 10.34 g (61.54 mmol) of the vinylsilane III was obtained 9.80 g (86.5% yield) of the epoxide VIII, b.p. 77°C/5 torr. IR (cm^{-1}), 2960, 2940, 2860, 1470, 1455, 1420, 1250, 1050, 960, 940, 910, 840, 750. NMR, δ 0.03 (s, 9H), 1.33–1.67 (broad s, 6H) overlapping with 1.67–2.16 (illresolved m, 4H), 2.86–3.13 (dd, J 6.5 and 4.5 Hz, 1H). MS, m/e (intensity, %), 184 (4.2, M^+), 183 (4.0), 169 (15.2), 155 (9.8), 141 (8.3), 130 (8.3), 115 (12.6), 94 (7.6), 79 (7.6), 75 (78.3), 73 (100), 59 (12.6), 45 (14.1).

1-Trimethylsilylcyclododecene oxide (X)

The epoxide X was obtained in 89.6% yield from 6.03 g (21.13 mmol) of V (42/58 Va and Vb), b.p. 127–134°C/1 torr. It was freed from small amounts of starting vinylsilane and *m*-chlorobenzoic acid (total ~ 2–3%) by eluting through a short column of silica gel with petroleum ether (b.p. 40–60°C). (Found: C, 70.61; H, 11.95; $C_{15}H_{30}OSi$ calcd.: C, 70.86; H, 11.81%). IR (cm^{-1}), 2920, 2850, 1250, 840, 780. NMR, δ 0.06 (s), 0.16 (s) (together 9H), 1.18–1.76 (m, 20H), 2.65 (broad s, 1H). MS, m/e (intensity, %), 239 (0.2, $M^+ - CH_3$), 197 (1.4), 183 (4.1), 169 (4.9), 155 (5.9), 143 (22.2), 130 (14.7), 129 (9.6), 115 (8.9), 75 (60.6), 73 (100), 67 (7.3), 59 (14.5), 55 (18.4), 45 (17.3), 41 (19.0).

Hydrolysis of VI

A mixture of 0.93 g (5.96 mmol) of VI in 3.5 ml of 0.8 *M* H_2SO_4 and 10 ml of dioxane was stirred magnetically at room temperature. The reaction was complete in 2 h as indicated by the disappearance of the epoxide peak in GC. The acid was neutralised with saturated aqueous $NaHCO_3$. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 ml). The combined organic layers were washed with water (3 × 20 ml) saturated aqueous NaCl (20 ml) and dried ($MgSO_4$). The solvent was removed on a rotary evaporator and the remaining white solid was recrystallized from pentane. Yield of XI, 0.86 g (83.2%), m.p. 98–99°C. (Found: C, 56.2; H, 10.51; $C_8H_{18}O_2Si$ calcd.: C, 56.38; H, 10.3%). IR ($CDCl_3$, cm^{-1}), 3620, 3480, 2960, 2900 (sh), 2860 (sh), 1435, 1250, 1070, 950, 835. NMR, δ 0.10 (s, 9H), 1.33 (s, 2H, *−OH*) superimposed on 1.16–2.40 (m, 6H), 4.2 (m, 1H). MS, m/e (intensity, %), 174 (1.2, M^+), 159 (5.1), 141 (8.6), 125 (4.3), 97 (8.5), 75 (100), 73 (69.2), 67 (7.8), 59 (16.4).

Hydrolysis of X at room temperature

(a) to diol XIII. A solution of 0.49 g (1.93 mmol) of the epoxide X in 2 ml 1 *M* H_2SO_4 and 6 ml dioxane was stirred at room temperature. The reaction was followed by TLC, and most of the epoxide was found to have reacted in 48 h. The mixture was neutralised with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 10 ml). The combined CH_2Cl_2 extracts were washed with 5% aqueous $NaHCO_3$ (15 ml), water (3 × 15 ml), saturated aqueous NaCl (20 ml) and dried ($MgSO_4$). The solvent was removed under vacuum and the solid obtained was chromatographed on a short silica gel column using petroleum ether (50–55°C) as solvent to remove traces of unreacted epoxide and cyclododecanone, a small amount of which had formed by now. Yield of XIIIa + XIIIb, 0.39 g (74.5%). (Found: C, 66.31; H, 11.64; $C_{15}H_{32}O_2Si$ calcd.: C, 66.17; H, 11.76%). IR ($CDCl_3$, cm^{-1}), 3560, 3430, 2930, 2850, 1245, 835. NMR, δ 0.07 (s) and 0.13 (s)(together 9H), 1.01–1.92 (m, 22H), 3.87 (broad d, J 4.0 Hz, 1H). MS, m/e (intensity, %), 257 (3.3, $M^+ - CH_3$), 256 (9.4), 223 (6.2), 213 (9.8), 199 (6.9), 197 (6.9), 185 (12.0), 168 (14.9), 155 (12.7), 149 (11.2), 143 (26.4), 129 (15.9), 127 (14.1), 115 (28.6), 109 (16.3), 97 (53.3), 85 (27.5), 83 (54.0), 81

(39.1), 77 (29.7), 75 (23.9), 73 (93.1), 71 (51.1), 69 (83.0), 67 (31.2), 60 (76.1), 57 (69.9), 55 (85.5), 45 (100).

(b) to cyclododecanone. In another run the reaction was allowed to proceed for 7 days, and the product worked up as described above. The unreacted silyldiol XIIIa, XIIIb and cyclododecanone were separated on silica gel column with petroleum ether/benzene (1/1) as eluent. The conversion to cyclododecanone was about 80%. It was identified as described in the next experiment.

Hydrolysis of X at 100°C

A solution of 0.42 g (1.65 mmol) of epoxide X in 2 ml 1 *M* H_2SO_4 and 6 ml dioxane was heated on a boiling water bath. At the end of 5 h most of the epoxide had disappeared and the reaction mixture, after cooling, was worked up as usual. Cyclododecanone (XIV) was separated from traces of X and XIIIa, XIIIb by chromatographing on a silica gel column using petroleum ether (50–55°C) and petroleum ether/benzene (1/1) as eluents, and further purified by vacuum sublimation. Yield, 0.26 g (79.4%), m.p. 59°C, mixed m.p. with authentic (Aldrich) sample, 59–60°C (lit. [14] m.p. 59°C). IR spectrum superimposable on that of authentic XIV. Oxime, m.p. 127°C, mixed m.p. 127–129°C (lit. [15] m.p. 132°C); semicarbazone, m.p. 219–220°C, mixed m.p. 220°C (lit. [14] m.p. 226°C).

Hydrolysis of XIII(a,b) at 100°C

A solution of 0.27 g (1.0 mmol) of the diol XIIIa, XIIIb in 1.5 ml 1 *M* H_2SO_4 and 5 ml dioxane was heated on a water bath for 3 h. After the usual work up 0.14 g (71.2%) of cyclododecanone was obtained and was identified as above.

Acknowledgements

G.N. thanks the Alexander von Humboldt-Stiftung, Bonn, for a fellowship during part of the work. Sincere gratitude is due to Prof. Dr. K. Griesbaum for encouragement and providing facilities. The authors thank the UAS authorities for their support.

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