Heteroatom Chemistry
Volume 13, Number 4, 2002

Desilylation and Conversion of Trimethylsilylmethyl Epoxides into Ketones under the Influence of a Bulky Base

Yuan Ma

Bioorganic Phosphorus Chemistry Laboratory, Department of Chemistry, School of Life Science, Tsinghua University, Beijing 100084, People's Republic of China

Received 20 July 2001; revised 9 October 2001

ABSTRACT: *Trimethylsilylmethyl epoxides were converted into ketones through a desilylation, epoxide ring-opening, and rearrangement reaction under the influence of a bulky base in the presence of 18-crown-6.*
 Heteroatom Chem 13:310–315, 2002; Published online in Wiley Interscience (www.interscience.wiley.com). DOI 10.1002/hc.10036

INTRODUCTION

Epoxides are very important intermediates in synthetic organic chemistry because of their facile preparation, often with substantial stereochemical control, and their high chemical reactivity, a feature attributable to the ring strain of these small-ring heterocycles [1–3]. Epoxides are typically prepared from olefins by oxidation with peracids or dioxiranes. The preponderance of synthetic applications involves nucleophilic opening of the epoxide ring, and an enormous range of nucleophilic species has been used for this purpose. The conversion of epoxides to their isomeric compounds under the influence of acidic reagents, including protonic acids and Lewis acids, has also been utilized preparatively [1–3]. Recently, much attention has been paid to non-nucleophilic base-promoted ring-opening reactions of epoxides. Organolithiums, lithium dialkylamides, and aluminum dialkylamides have been investigated widely in the reaction. Under these base-promoted ring-opening conditions, epoxides yield generally allylic alcohols; however, sometimes ketones are produced [1]. Trialkylsilylmethyl epoxides are important kinds of functionalized epoxides. They, as synthetic intermediates, have been widely used in the syntheses of bioactive compounds and natural products [2,3]. Trialkylsilylmethyl epoxides can be converted into diol monoesters in the presence of an organic acid [4,5], and converted into trialkylsilyl-substituted allylic alcohols by the action of lithium dialkylamide [6]. They also undergo a desilylation to be converted into allylic alcohols through promotion by tetraalkylammonium fluoride [2,7], a Lewis acid, BF_3 [8], or protonic acids, such as hydrochloric acid [3] and trifluoroacetic acid [9]. Herein, I report a conversion of trimethylsilylmethyl epoxides into ketones under the influence of a bulky base in the presence of 18-crown-6.

RESULTS AND DISCUSSION

Trimethylsilyl olefin **3a** was prepared from cinnamyl alcohol **1a** through esterification with trifluoroacetic anhydride and coupling with hexamethyldisilane $(TMS)_2$ under palladium(0)-catalysis by a procedure described in the literature [10]. Allylic alcohols **1b,c** were prepared from reactions of vinylmagnesium bromide and cyclohexanecarboxaldehyde and heptanal, respectively. After esterification with trifluoroacetic anhydride, their esters underwent a

Correspondence to: Yuan Ma; e-mail; yuan_ma_99@yahoo.com.
Contract grant sponsor: Tsinghua University.

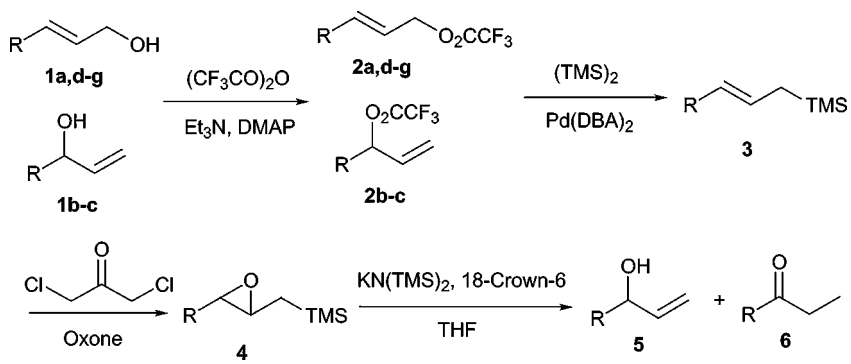
rearrangement and coupling with hexamethyldisilane $(TMS)_2$ under palladium(0)-catalysis to produce trimethylsilyl olefins **3b,c** [10]. The trimethylsilyl olefins **3** were converted into trimethylsilylmethyl epoxides **4** in high yields by oxidation with di(chloromethyl)dioxirane, generated in situ from 1,3-dichloroacetone and Oxone (potassium peroxomonosulfate) [11]. When trimethylsilylmethyl phenyl epoxide **4a** was treated with a bulky base, potassium *tert*-butoxide, not only was a desilylated allylic alcohol (**5a**) obtained, but also desilylated 1-phenyl-1-propanone (**6a**). The yield of **6a** was increased slightly when a more bulky base potassium bis(trimethylsilyl)amide $KN(TMS)_2$ was used instead of potassium *tert*-butoxide. Only **6a** was obtained in almost quantitative yield when an equimolar amount of 18-crown-6 was added with the base. However, two alkyl-substituted trimethylsilylmethyl epoxides (**4b,c**) yielded a mixture of allylic alcohols **5b,c** and ketones **6b,c**, respectively, in the same reaction conditions (Scheme 1).

In earlier papers [12–15] on the reactions of epoxides with strongly basic, nonnucleophilic reagents, two major competing reaction pathways were suggested, the relative efficiencies of which depend on the specific molecule in question. In systems where a favorable cis, coplanar, transition-state geometry can be readily attained, β-elimination to give allylic alcohols is preferred. When such is not the case, the products are thought to evolve from α-elimination at an epoxide ring carbon and carbenoid insertion into a neighboring carbon–hydrogen bond to form multiple ring compounds, or carbenoid rearrangement into ketones. In the latter case, one of the hydrogen atoms in an epoxide ring carbon is more acidic and/or a stronger base is used.

In order to understand this conversion, four deuterio-substituted trimethylsilylmethyl epoxides **4d–g** were also prepared (Table 1). Deuterio-substituted cinnamyl alcohols **1d–f** were prepared from 3-phenyl-2-propyn-1-ol according to a literature procedure [17]. Alcohol **1g** was obtained by reduction of ethyl cinnamate with lithium aluminum deuteride [18]. Transformation of the deuterio alcohols **1d–g** into deuterio trimethylsilylmethyl phenyl epoxides **4d–g** was carried out using the same method as for the alcohol **1a**. The deuterio trimethylsilylmethyl phenyl epoxides **4d–g** were also converted into the corresponding ketones, deuterio 1-phenyl-1-propanones, respectively, in excellent yields in the same reaction conditions. The results are summarized in Table 1.

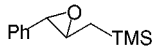
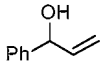
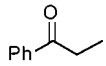
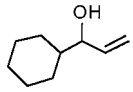
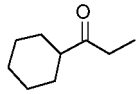
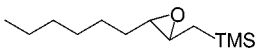
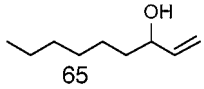
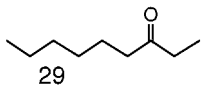
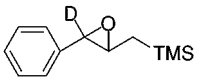
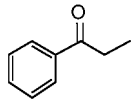
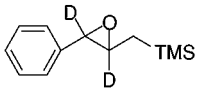
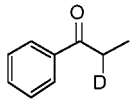
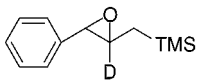
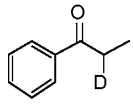
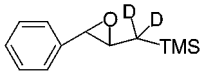
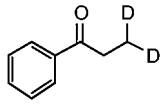
Based on the results and literature, the mechanism for the conversion is suggested as follows (Scheme 2). After the epoxides **4** were attacked on their silicon atoms by a base $^{-}N(TMS)_2$, they undergo a β-elimination to give allyloxide anions **A**, which can form allylic alcohols **5** after treatment with water. The allyloxide anions **A** could lose their α-hydrogens and undergo a double bond rearrangement to give rise to dianions **B** because the α-hydrogens of the allyloxide anions **A** are more acidic because of their location in the allylic position (in both allylic and benzylic positions for **4a,d–g**). After treatment with water, the dianions **B** can form enols **C**, which tautomerize into ketones **6**. The process, in which an allylic alcohol can be converted into a ketone, was confirmed by Crandall and his colleagues [13].

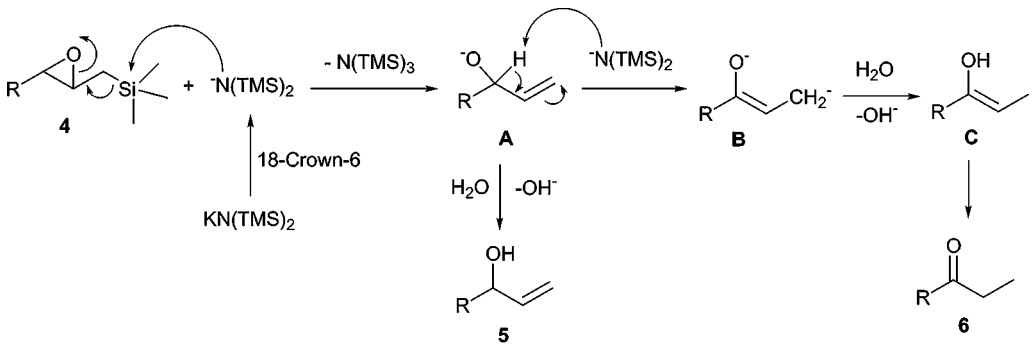
Although a trialkylsilylmethyl epoxide can undergo a β-elimination to produce a trialkylsilyl allylic alcohol through β-abstraction by potassium dialkylamide [6], no trimethylsilyl allylic alcohol was found in my cases. It also supports the suggested mechanism that β,β-dideuterio epoxide **4g** generates 3,3-dideuterio-1-phenyl-1-propanone (**6g**). In the absence of 18-crown-6, both allylic alcohol **5a** and ketone **6a** were obtained from **4a** in the reaction. Epoxide **4a** and its deuterio derivatives **4d–g** yielded ketones **6a,d–g** as the sole products in the presence of 18-crown-6. It is rationalized that 18-crown-6



SCHEME 1 Desilylation and conversion of trimethylsilylmethyl epoxides into ketones under the influence of a bulky base.

TABLE 1 Desilylation and Conversion of Trimethylsilylmethyl Epoxides into Ketones

Entry	*Trimethylsilymethyl Epoxide **4***	*Base*	*Yield of **5** (%)*	*Yield of **6** (%)*
a		*t*BuOK	 41	 52
		$KN(TMS)_2$	23	68
		$KN(TMS)_2$ 18-Crown-6		98
b		$KN(TMS)_2$ 18-Crown-6	 58	 37
c		$KN(TMS)_2$ 18-Crown-6	 65	 29
d		$KN(TMS)_2$ 18-Crown-6		 96
e		$KN(TMS)_2$ 18-Crown-6		 92 [16]
f		$KN(TMS)_2$ 18-Crown-6		 94 [16]
g		$KN(TMS)_2$ 18-Crown-6		 85



SCHEME 2 Suggested mechanism for desilylation and conversion of trimethylsilylmethyl epoxides into ketones under the influence of a bulky base.

prefers to coordinate with a potassium cation so as to increase the basicity of $KN(TMS)_2$. The stronger base $^-N(TMS)_2$ can abstract the α-hydrogen of the allyloxide anion **A** completely when epoxide **4a** is treated by $KN(TMS)_2$ in the presence of 18-crown-6 because the α-hydrogen located in both the allylic and the benzylic position is more acidic. Then, allyloxide **A** could convert into a dianion **B** completely. Thus, only 1-phenyl-1-propanone **6a** is obtained from the epoxide **4a**. For intermediates **A** of the epoxides **4b,c**, their α-hydrogens located in the allylic position are not acidic enough for the base $^-N(TMS)_2$ to abstract their α-hydrogens of the allyloxide anions **A** and convert them into dianions **B** completely. Thus, both allylic alcohols **5b,c** and ketones **6b,c** are obtained.

The proposed structures for all unknown compounds are based on ^1H NMR, ^{13}C NMR, mass spectral, and elemental analyses.

In conclusion, aromatic-substituted trimethylsilylmethyl epoxides were converted into ketones through a desilylation, epoxide ring-opening, and rearrangement reaction under the influence of a bulky base and in the presence of 18-crown-6. However, aliphatic-substituted trimethylsilylmethyl epoxides gave both allylic alcohols and ketones in the same conditions.

EXPERIMENTAL

Melting points were obtained on a Yanaco melting point apparatus and are uncorrected. Elemental analyses were carried out on an Elementar Vario EL elemental analyzer. The ^1H NMR spectra were recorded on a Varian Inova 300 or Brucker AM400 spectrometer with TMS as an internal standard in $CDCl_3$. The IR spectra were taken on a Brucker Vector 22 FT-IR spectrophotometer in KBr. Mass spectra were obtained on a VG ZAB-HS mass spectrometer. TLC separations were performed on silica gel G plates with petroleum ether (30–60°C)/ethyl acetate (10:1), and the plates were visualized with UV light.

Deuterio-substituted cinnamyl alcohols **1d–g** were prepared according to literature procedures [17–19]. 1-En-3-ols **1b,c** were obtained by reaction of cyclohexanecarboxaldehyde and heptanal, respectively, with vinylmagnesium bromide. Their spectral data are in good agreement with literature data [20,21].

Preparation of Trimethylsilyl Olefins **3**

General Procedure. To a solution of allyl alcohol **1** (20.6 mmol) in 19 ml of dichloromethane with stirring at 0°C, 2.87 g of Et_3N, 0.25 g of DMAP, and 5.11 g (24.3 mmol) of trifluoroacetic anhydride were added in the indicated order. The mixture was stirred for 15 h. A brown oil was obtained after removal of solvent. The oil could be used without further purification.

A 150-ml flask was charged with $Pd(DBA)_2$ (255 mg, 0.45 mmol) and 83 ml of THF under N_2. The palladium complex was dissolved with stirring to afford a deep purple solution. Then the ester **2** prepared as described previously (15 mmol) and hexamethyldisilane $(TMS)_2$ (4.38 g, 30 mmol) were added in the indicated order. The reaction mixture turned pale yellow, and the reaction was carried out at RT for 12 h. After the reaction, the reaction mixture was diluted with Et_2O (300 ml), washed with saturated $NaHCO_3$ (300 ml), and dried over Na_2SO_4. After column separation, a colorless oil was obtained.

3-Trimethylsilyl-1-phenyl-1-propene (**3a**): Colorless oil. Yield 73% [22].

1-Cyclohexyl-3-trimethylsilyl-1-propene (**3b**): Colorless oil. Yield 62% [10].

1-Trimethylsilyl-2-nonene (**3c**): Colorless oil. Yield 56% [22].

1-Deuterio-3-trimethylsilyl-1-phenyl-1-propene (**3d**): Colorless oil. Yield 70%. IR (KBr): 3079.4, 3059.0, 2954.4, 2896.1, 1629.4, 1494.5, 1248.2, 1145.6, 1020.4, 846.6, 769.7, 693.2 cm^{-1}. ^1H NMR δ: 7.38–7.21 (5H, m, ArH), 6.30 (1H, tt, $J = 8.4$, 2.4 Hz, CH=), 1.72 (2H, d, $J = 8.4$ Hz, CH_2), 0.11 (9H, s, $SiMe_3$). MS *m/z*: 191 (M^+), 176, 73. HRMS Anal. Calcd. for $C_{12}H_{17}DSi$: 191.1239. Found: 191.1236.

1,2-Dideuterio-3-trimethylsilyl-1-phenyl-1-propene (**3e**): Colorless oil. Yield 73%. IR (KBr): 3078.8, 3058.7, 3022.7, 2954.5, 2896.3, 1610.2, 1494.6, 1248.2, 1149.3, 844.0, 721.2, 692.5 cm^{-1}. ^1H NMR δ: 7.35–7.18 (5H, m, ArH), 1.69 (2H, s, CH_2), 0.08 (9H, s, $SiMe_3$). MS *m/z*: 192 (M^+), 177, 73. HRMS Anal. Calcd. for $C_{12}H_{16}D_2Si$: 192.1301. Found: 192.1307.

2-Deuterio-3-trimethylsilyl-1-phenyl-1-propene (**3f**): Colorless oil. Yield 71%. IR (KBr): 3079.8, 3059.9, 3024.1, 2954.5, 2896.4, 1626.5, 1598.7, 1495.6, 1248.1, 1149.9, 860.8, 718.2, 693.5 cm^{-1}. ^1H NMR δ: 7.34–7.08 (5H, m, ArH), 6.25 (1H, s, CH=), 1.68 (2H, s, CH_2), 0.07 (9H, s, $SiMe_3$). MS *m/z*: 191 (M^+), 176, 73. Anal. Calcd. for $C_{12}H_{17}DSi$: C, 75.32; H + D, 10.01. Found: C, 75.33; H + D, 9.89.

3,3-Dideuterio-3-trimethylsilyl-1-phenyl-1-propene (**3g**): Colorless oil. Yield 68%. IR (KBr): 3023.2, 2954.2, 2897.4, 1639.4, 1495.2, 1247.3, 996.6, 843.3, 691.7 cm^{-1}. ^1H NMR δ: 7.34–7.08 (5H, m, ArH), 6.26 (2H, s, CH=CH), 0.07 (9H, s, $SiMe_3$). MS *m/z*: 192 (M^+), 177, 73. HRMS Anal. Calcd. for $C_{12}H_{16}D_2Si$: 192.1301. Found: 192.1297.

Preparation of Trimethylsilylmethyl Epoxides **4**

General Procedure. To an acetonitrile (14 ml) solution of allylsilane **3** (1 mmol) was added an aqueous Na_2EDTA solution (9 ml, 4×10^{-4} M), followed by addition of 15 mg of Bu_4NHSO_4. The resulting mixture was cooled to 0–1°C and 1,3-dichloroacetone (292 mg, 2.3 mmol) was added. To this solution was added in portions a mixture of sodium bicarbonate (1.43 g, 21 mmol) and Oxone (4.3 g, 7 mmol) over a period of 1.5 h. After the reaction was complete, the product was extracted with hexane (3×30 ml), and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by flash chromatography to give the pure epoxide.

2-Trimethylsilylmethyl-3-phenyl-oxirane (**4a**): Colorless oil. Yield 97%. IR (KBr): 2954.7, 2892.2, 1245.1, 1020.5, 860.9, 747.4, 697.3 cm^{-1}. ^1H NMR δ: 7.37–7.24 (5H, m, ArH), 3.54 (1H, d, $J = 1.8$ Hz, CH), 2.97 (1H, ddd, $J = 1.8$, 5.1, 8.4 Hz, CH), 1.28 (1H, dd, $J = 5.1$, 14.4 Hz, H in CH_2), 0.81 (1H, dd, $J = 8.4$, 14.4 Hz, H in CH_2), 0.09 (9H, s, $SiMe_3$). ^{13}C NMR δ: 137.9 (ArC), 128.3 (ArC), 127.8 (ArC), 125.2 (ArC), 61.5 (CHO), 60.0 (CHO), 21.4 (CH_2), −1.1 ($SiMe_3$). MS *m/z*: 206 (M^+). Anal. Calcd. for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79. Found: C, 70.07; H, 8.72.

2-Cyclohexyl-3-trimethylsilylmethyl-oxirane (**4b**): Colorless oil. Yield 94%. IR (KBr): 2926.2, 2852.8, 1450.1, 1249.1, 859.8 cm^{-1}. ^1H NMR δ: 2.79 (1H, ddd, $J = 2.1$, 5.1, 8.8 Hz, CH), 2.41 (1H, dd, $J = 2.1$, 6.6 Hz, CH), 1.86 (1H, m, CH), 1.76–1.65 (4H, m, $2CH_2$), 1.25–1.05 (6H, m, $3CH_2$), 1.16 (1H, dd, $J = 4.5$, 10.8 Hz, H in CH_2), 0.58 (1H, dd, $J = 8.8$, 10.8 Hz, H in CH_2), 0.09 (9H, s, $SiMe_3$). ^{13}C NMR δ: 64.7 (CHO), 55.82 (CHO), 40.58 (CH), 29.91 (CH_2), 29.29 (CH_2), 26.41 (CH_2), 25.85 (CH_2), 25.67 (CH_2), 21.22 (CH_2), −1.04 ($SiMe_3$). MS *m/z*: 212 (M^+). Anal. Calcd. for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.61; H, 11.27.

2-Hexyl-3-trimethylsilylmethyl-oxirane (**4c**): Colorless oil. Yield 89%. IR (KBr): 2956.6, 2929.1, 2857.9, 1458.3, 1249.7, 1185.4, 860.0, 841.3 cm^{-1}. ^1H NMR δ: 2.72 (1H, ddd, $J = 2.1$, 5.7, 8.1 Hz, CH), 2.60 (1H, ddd, $J = 2.1$, 5.7, 5.4 Hz, CH), 1.52–1.25 (10H, m, $5CH_2$), 1.12 (1H, dd, $J = 5.7$, 14.4 Hz, H in CH_2), 0.88 (3H, t, $J = 7.0$ Hz, Me), 0.61 (1H, dd, $J = 9.1$, 14.4 Hz, H in CH_2), 0.08 (9H, s, $SiMe_3$). ^{13}C NMR δ: 60.3 (CHO), 57.0 (CHO), 32.5 (CH_2), 31.8 (CH_2), 29.3 (CH_2), 26.1 (CH_2), 22.7 (CH_2), 20.9 (CH_2), 14.2 (CH_3), −1.10 ($SiMe_3$). MS *m/z*: 214 (M^+). Anal. Calcd. for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22. Found: C, 67.41; H, 12.27.

3-Deuterio-2-trimethylsilylmethyl-3-phenyl-oxirane (**4d**): Colorless oil. Yield 93 %. IR (KBr): 2954.1, 2892.4, 1249.8, 1020.1, 860.3, 746.9, 697.0 cm^{-1}. ^1H NMR δ: 7.35–7.24 (5H, m, ArH), 2.97 (1H, dd, $J = 5.4$, 8.4 Hz, CH), 1.28 (1H, dd, $J = 5.4$, 13.8 Hz, H in CH_2), 0.81 (1H, dd, $J = 8.4$, 13.8 Hz, H in CH_2), 0.098 (9H, s, $SiMe_3$). ^{13}C NMR δ: 137.9 (ArC), 128.3 (ArC), 127.7 (ArC), 125.2 (ArC), 61.34 (CHO), 59.59 (t, $J = 25.7$ Hz, CDO), 21.32 (CH_2), −1.08 ($SiMe_3$). MS *m/z*: 207 (M^+). Anal. Calcd. for $C_{12}H_{17}DOSi$: C, 69.51; H + D, 9.23. Found: C, 69.39; H + D, 8.96.

2,3-Dideuterio-2-trimethylsilylmethyl-3-phenyl-oxirane (**4e**): Colorless oil. Yield 97%. IR (KBr): 2955.3, 2930.5, 2858.8, 1719.3, 1271.5, 1248.7, 1110.2, 865.0, 838.7, 709.8, 668.1 cm^{-1}. ^1H NMR δ: 7.35–7.24 (5H, m, ArH), 1.28 (1H, d, $J = 13.8$ Hz, H in CH_2), 0.80 (1H, d, $J = 13.8$ Hz, H in CH_2), 0.09 (9H, s, $SiMe_3$). ^{13}C NMR δ: 137.9 (ArC), 128.8 (ArC), 127.8 (ArC), 125.4 (ArC), 60.98 (t, $J = 27.17$ Hz, CDO), 59.54 (t, $J = 25.66$ Hz, CDO), 21.2 (CH_2), −1.04 ($SiMe_3$). MS *m/z*: 208 (M^+). Anal. Calcd. for $C_{12}H_{16}D_2OSi$: C, 69.17; H + D, 9.67. Found: C, 68.99; H + D, 9.49.

2-Deuterio-2-trimethylsilylmethyl-3-phenyl-oxirane (**4f**): Colorless oil. Yield 93%. IR (KBr): 2954.2, 2893.1, 1495.9, 1457.0, 1276.5, 1249.9, 863.8, 841.3, 743.8, 697.1 cm^{-1}. ^1H NMR δ: 7.35–7.25 (5H, m, ArH), 3.55 (1H, s, CH), 1.28 (1H, d, $J = 14.4$ Hz, H in CH_2), 0.81 (1H, d, $J = 14.4$ Hz, H in CH_2), 0.10 (9H, s, $SiMe_3$). ^{13}C NMR δ: 137.9 (ArC), 128.2 (ArC), 127.6 (ArC), 125.1 (ArC), 60.89 (t, $J = 24.91$ Hz, CDO), 59.80 (CHO), 21.09 (CH_2), −1.13 ($SiMe_3$). MS *m/z*: 207 (M^+). Anal. Calcd. for $C_{12}H_{17}DOSi$: C, 69.51; H + D, 9.23. Found: C, 69.77; H + D, 9.36.

2-Trimethylsilyldideuteriomethyl-3-phenyl-oxirane (**4g**): Colorless oil. Yield 96%. IR (KBr): 3033.2, 2954.5, 2897.4, 1496.0, 1457.9, 1249.7, 1009.0, 929.2, 752.6, 731.1, 697.4 cm^{-1}. ^1H NMR δ: 7.35–7.24 (5H, m, ArH), 3.54 (1H, d, $J = 2.1$ Hz, CH), 2.96 (1H, d, $J = 2.1$ Hz, CH), 0.096 (9H, s, $SiMe_3$). ^{13}C NMR δ: 138.00 (ArC), 128.1 (ArC), 127.8 (ArC), 125.2 (ArC), 61.34 (CHO), 59.91 (CHO), 20.56 (quintet, $J = 18.1$ Hz, CD_2), −1.09 ($SiMe_3$). MS *m/z*: 208 (M^+). Anal. Calcd. for $C_{12}H_{16}D_2OSi$: C, 69.17; H + D, 9.67. Found: C, 69.04; H + D, 9.41.

Desilylation and Conversion of Trimethylsilylmethyl Epoxides **4** *into Ketones*

General Procedure. To a solution of a suitable base (0.3 mmol) or a base and 18-crown-6 (79.2 mg, 0.3 mmol) in 2.5 ml of THF at −78°C under a nitrogen atmosphere, 0.25 mmol of epoxide **4** was added. The resulting mixture was stirred for 4–6 h at −78°C and warmed to RT. The mixture was treated with water,

extracted with 3×10 ml of ethyl acetate, washed with water and dried over sodium sulfate. After removal of the solvent, the residue was purified on a silica gel column to give a colorless oil.

3,3-Dideuterio-1-phenyl-1-propanone (**6g**): Colorless oil. Yield 93%. IR (KBr): 3062.6, 2940.1, 1689.8, 1598.3, 1449.7, 1333.2, 1268.3, 1185.4, 950.0, 745.6, 720.7, 691.2 cm^{-1}. ^1H NMR δ: 7.40–7.20 (5H, m, ArH), 2.99 (2H, m CH_2), 1.22 (1H, m, CHD_2). ^{13}C NMR δ: 206.6 (CO), 136.7 (ArC), 132.6 (ArC), 128.3 (ArC), 127.7 (ArC), 31.5 (CH_2), 8.0 (quintet, $J_{CD} = 19.0$ Hz, CHD_2). MS *m/z*: 136 (M^+). Anal. Calcd. for $C_9H_8D_2O$ (136.08): C, 79.37; H + D, 8.88. Found: C, 79.41; H + D, 8.77.

REFERENCES

[1] Crandall, J. K. In Organic Reactions; Duaben, W. G. (Ed.); John Wiley & Sons: New York, 1983; Vol. 29, pp. 345–443.
[2] Tone, H.; Nishi, T.; Oikawa, Y.; Hikota, M.; Yonemitsu, O. Chem Pharm Bull 1989, 1160.
[3] Auyeung, B. W.; Xu, J. W.; Qiu, J. S. Acta Chim Sin 1986, 44, 479.
[4] Badali, F.; Issa, W.; Pool, B.; White, J. M. J Organomet Chem 1999, 575, 251.
[5] Manuel, G.; Boukherroub, R. J Organomet Chem 1993, 447, 167.
[6] Dubac, J.; Laporterie, A.; Manuel, G.; Iloughmane, H.; Beteille, J. P.; Dufour, P. Synth React Inorg Met-Org Chem 1987, 17, 783.
[7] Azzari, E.; Faggi, C.; Gelsomini, N.; Taddei, M. Tetrahedron Lett 1989, 30, 6067.
[8] Lautens, M.; Crudden, C. M. Tetrahedron Lett 1989, 30, 4803.
[9] Russel, A. T.; Procter, G. Tetrahedron Lett 1987, 28, 2045.
[10] Tsuji, Y.; Funato, M.; Ozawa, M.; Ogiyama, H.; Kajita, S.; Kawamura, T. J Org Chem 1996, 61, 5779.
[11] Yang, D.; Wong, M.-K.; Yip, Y.-C. J Org Chem 1995, 60, 3887.
[12] Cope, A. C.; Trumbull, P. A.; Trumbull, E. R. J Am Chem Soc 1958, 80, 2844.
[13] Crandall, J. K.; Lin, L.-H. J Org Chem 1968, 33, 2375.
[14] Rickborn, B.; Thummel, R. P. J Org Chem 1969, 34, 3583.
[15] Thummel, R. P.; Rickborn, B. J Org Chem 1972, 37, 3919.
[16] Gazzard, L. J.; Motherwell, W. B.; Sandham, D. A. J Chem Soc, Perkin Trans 1 1999, 979.
[17] Schwab, J. M.; Ray, T.; Ho, C.-K. J Am Chem Soc 1989, 111, 1057.
[18] Erickson, T. J. J Org Chem 1986, 51, 934.
[19] Cristiano, M. L. S.; Johnstone, R. A. W.; Price, P. J. J Chem Soc, Perkin Trans 1 1996, 1453.
[20] Katritzky, A. R.; Jiang, J. L.; Greenhill, J. V.; Steel, P. J. J Chem Soc, Perkin Trans 1 1992, 3055.
[21] Ueno, Y.; Sano, H.; Okawara, M. Synthesis 1980, 1011.
[22] Fleming, I.; Paterson, I. Synthesis 1979, 446.