Syntheses of Alkyl Bromides from Ethers and Bromotrimethylsilane*

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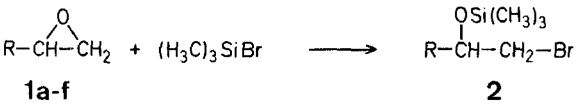
Previously, we have demonstrated[1] that lactones undergo ring-opening when heated with bromotrimethylsilane, while non-cyclic esters are not attacked. It is also known that oxiranes[2] and tetrahydrofuran[3,4,5] react with bromotrimethylsilane, while linear ethers are not cleaved. We have reinvestigated the cleavage of ethers focussing our interest on the following points:

(a) regioselectivity of the cleavage of epoxides,

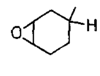
(b) influence of ring size on the reactivity, and

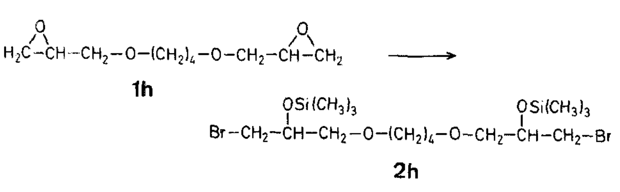
(c) reactivity of ethers with primary, secondary, and tertiary carbon atoms.

The oxiranes **1 a-f, h** and **3** were found to undergo a highly exothermic reaction with bromotrimethylsilane. When the conversion was conducted in solution and under cooling an almost quantitative and highly selective reaction was observed. Non-cyclic ester or ether groups, such as those of **1 f** and **1 h**, were not attacked. The ring-standing epoxide group of **1g** also remained unaffected when the reaction was run at about $-60\,^{\circ}C$. In all cases, the CH_2—O bond was cleaved exclusively, so that the primary alkyl bromides **2a-h** were isolated.

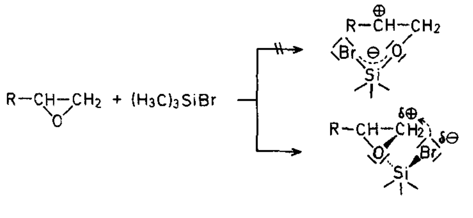


1a-f **2**

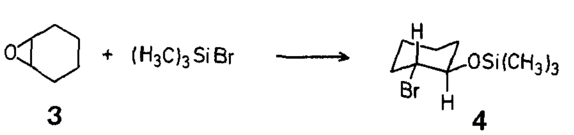
1,2	R	1,2	R
a	H	e	Cl-CH_2-
b	CH_3	f	$H_2C{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}$
c	C_2H_5		
d	C_6H_5	g	 (at -60°C)



These observations lead us to the conclusion that the ring fission involves a four-membered cyclic transition state.



Carbenium ions as intermediates are unlikely for the following reasons: (a) the "Anti-Markownikow" course of the reaction, (b) the sterically clean reaction of **3** to a product with two equatorial substituents (**4**).



3 **4**

In this connection it is noteworthy that 90 or 250 MHz ^{1}H-N.M.R. spectra were used to characterize the structure of the reaction products. Thus, the formation of the alkyl bromides **2a-h**, **6**, and **7** was easily detectable by a ~ 0.4 ppm upfield shift of the CH_2 protons (relative to the starting material). In the case of **4**, the axial positions of the two methine protons were identified by the coupling constant of 9.5 Hz, observed after selective decoupling of the neighbored CH_2 protons.

Four-membered cyclic ethers such as **5a, b** also react exothermically with bromotrimethylsilane while the conversion of tetrahydrofuran to the ω-bromoalkoxysilane **7** requires 40 h of reflux with pure bromotrimethylsilane. No conversion was observed when tetrahydropyran or 1,4-dioxane were refluxed with bromotrimethylsilane for 7 days. Under the same conditions, 15% conversion was found with oxepane. Hence, the reactivity of cyclic ethers decreases in the following order (n = ring size): $n=3>n\approx4>n=5>n=7>n=6$, in contrast to the order found for lactones[1], namely $n=4>n=6\approx n=7>n=5$.

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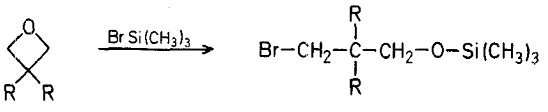
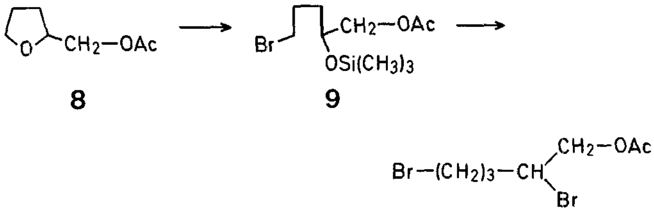


5a R = H
5b R = $-CH_2Cl$

6a,b

7

When tetrafurfuryl acetate (**8**) was heated with bromotrimethylsilane, 2,5-dibromo-1-pentanol acetate (**10**) was obtained via the intermediate **9** which was characterized by ^{1}H-N.M.R. spectra. That primary carbon atoms of cyclic ethers are more reactive than secondary ones is confirmed by our observation that 2,5-dimethyltetrahydrofuran is inert towards boiling bromotrimethylsilane. Interestingly, non-cyclic ethers show a different behavior which also supports the above reaction scheme. In the case of **11a,b** and **12a,b** seven days of reflux with excess bromotrimethylsilane is required to bring about 40–50% conversion. However, the secondary and tertiary ethers **13a,b**, **14a,b**, **15**, and **16** are cleaved almost quantitatively within 12 h. The corresponding alkyl bromides were isolated in yields of 89–93%. However, if an electronegative substituent is attached to the secondary or tertiary carbon atom, as is true for silylated lactic acid ethyl ester or citric acid, the O—C bond is inert towards boiling bromotrimethylsilane. Thus, we may conclude that the reaction mechanism of the cleavage of cyclic and non-cyclic ethers is somewhat different. In the latter case the transition state seems to involve a nonsolvated carbenium ion.



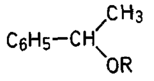
8 **9** **10**

$C_6H_5-CH_2-O-R$

11a,b

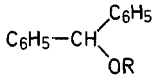
$H_3C-(CH_2)_5-O-R$

12a,b



$C_6H_5-CH\begin{smallmatrix}CH_3\\ OR\end{smallmatrix}$

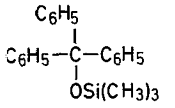
13a,b



$C_6H_5-CH\begin{smallmatrix}C_6H_5\\ OR\end{smallmatrix}$

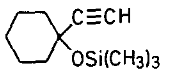
14a,b

a R = C_2H_5
b R = $Si(CH_3)_3$



$$\begin{array}{c} C_6H_5 \\ | \\ C_6H_5-C-C_6H_5 \\ | \\ OSi(CH_3)_3 \end{array}$$

15



16

3-(2-Bromo-1-trimethylsiloxyethyl)-7-oxabicyclo[4.1.0]heptane (2 g):
Bromotrimethylsilane (46 g, 0.3 mol) is added dropwise to a stirred solution of 3-oxiranyl-7-oxabicyclo[4.1.0]heptane (**1g**; 42 g, 0.3 mol) in dry chloroform (50 ml) at about −60 °C, in such a manner that the temperature does not exceed −40 °C. The mixture is then allowed to warm to room temperature and the product is isolated by distillation in vacuo; yield: 54.5 g (62%); b.p. 93–95 °C/0.5 torr. A residue of polymerized product remains in the distillation flask.

In the case of epoxides **1a–e**, cooling with ice is sufficient.

2,2-Bis[chloromethyl]-3-bromo-1-trimethylsiloxypropane (6b):
Bromotrimethylsilane (47 g, 0.3 mol) is added dropwise, with stirring, to 3,3-bis[chloromethyl]-oxetane (**5b**; 45 g, 0.3 mol) cooled in ice. After the addition is complete the mixture is heated at 100 °C for 2 h. The product is isolated by distillation in vacuo; yield: 85 g (93%); b.p. 82–84 °C/12 torr.

4-Bromo-1-trimethylsiloxybutane (7):
A mixture of dry tetrahydrofuran (28.8 g, 0.4 mol) and bromotrimethylsilane (70 g, 0.4 mol) is refluxed for ~40 h and the product then isolated by distillation in vacuo; yield: 73 g (82%); b.p. 82–84 °C/12 torr. [The conversion may be monitored by ^{1}H-N.M.R. spectroscopy ($CDCl_3$/TMS) since the CH_2Br group absorbs ~0.4 ppm upfield of the CH_2—O protons while bromotrimethylsilane absorbs ~0.4 ppm downfield of TMS].

2,5-Dibromo-1-pentanol Acetate (10):
Furfuryl acetate (57.5 g, 0.4 mol) and bromotrimethylsilane (153 g, 1.0 mol) are refluxed for 48 h. Then hexamethyldisiloxane and excess bromotrimethylsilane are removed in vacuo, and the product is isolated by vacuum distillation over a short column; yield: 100 g (87%); b.p. 89–91 °C/0.1 torr; n_D^{20}: 1.4987.

1-Bromo-1-phenylethane:
O-Trimethylsilyl-1-phenylethanol (77.6 g, 0.4 mol) and bromotrimethylsilane (77 g, 0.5 mol) are refluxed for 12 h; afterwards the product is isolated by distillation; yield: 69 g (93%).

Table. Bromotrimethylsiloxyalkanes prepared

Product	Yield [%]	b.p./torr [°C]	n_D^{20}	Molecular formula[a]	
2a	69	34–36°/12	1.4362	$C_5H_{13}BrOSi$	(197.2)
2b	61	40–42°/12	1.4400	$C_6H_{15}BrOSi$	(211.2)
2c	88	60–62°/12	1.4418	$C_7H_{17}BrOSi$	(225.2)
2d	71	69–71°/0.06	1.5162	$C_{11}H_{17}BrOSi$	(273.3)
2e	89	79–81°/12	1.4633	$C_6H_{14}BrClOSi$	(245.6)
2f	85	86–88°/0.7	1.4630	$C_{10}H_{19}BrOSi$	(295.2)
2g	62	93–95°/0.5	1.4843	$C_{11}H_{21}BrO_2Si$	(293.3)
2h	59	160°/0.001	1.4723	$C_{14}H_{32}Br_2O_2Si_2$	(508.4)
4	57	46–48°/0.5	1.4728	$C_9H_{19}BrOSi$	(251.2)
6a	73	55–57°/12	1.4410	$C_6H_{15}BrOSi$	(211.2)
6b	93	82–84°/12	1.4805	$C_8H_{17}BrCl_2OSi$	(309.1)
7	82	82–84°/12	1.4483	$C_7H_{17}BrOSi$	(225.2)

[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.32; H, ±0.34; Br, ±0.35.

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