Tetrahedron Letters Vol. 21, pp 2329 - 2332
©Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/0608-2329$02.00/0

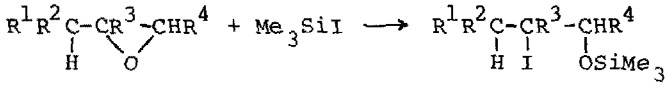
STEPWISE CONVERSION OF OXIRANES TO ALLYLIC ALCOHOLS BY IODOTRIMETHYLSILANE AND DBU[1]

Hideki Sakurai,*Koshi Sasaki and Akira Hosomi
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

Summary: Iodotrimethylsilane, prepared from hexamethyldisilane and iodine, reacts smoothly with oxiranes to give (2-iodoalkoxy)trimethylsilanes which can be converted to allylic alcohols with DBU in good yields. The whole conversion can be carried out in one-pot operation.

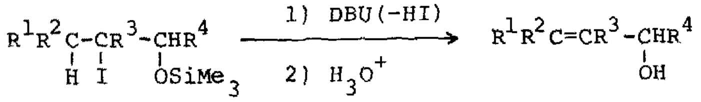
In a previous paper,[2] we have described a facile method of preparing iodotrimethylsilane from hexamethyldisilane and iodine together with some new reactions of the reagent.[3] During the course of the study on the application of the reagent, we have found an unprecedented reaction of iodotrimethylsilane with oxiranes, which results in the quantitative formation of (2-iodoalkoxy)trimethylsilane. The latter can be further converted to allylic alcohols (or allyloxysilanes before hydrolysis) by treatment with base such as 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU).

$$Me_3Si\text{-}SiMe_3 + I_2 \longrightarrow 2Me_3SiI \qquad (1)$$



$$R^1R^2\underset{H}{C}\text{-}\underbrace{CR^3\text{-}CHR^4}_{O} + Me_3SiI \longrightarrow R^1R^2\underset{H}{C}\text{-}\underset{I}{C}R^3\text{-}\underset{OSiMe_3}{C}HR^4$$

(2)



$$R^1R^2\underset{H}{C}\text{-}\underset{I}{C}R^3\text{-}\underset{OSiMe_3}{C}HR^4 \xrightarrow[2)\ H_3O^+]{1)\ DBU(-HI)} R^1R^2C{=}CR^3\text{-}\underset{OH}{C}HR^4$$

(3)

Isomerization of an oxirane to an allylic alcohol is one of the important processes in organic synthesis and therefore many reagents have been proposed for the purpose.[4] An advantage of the present method lies in that the whole reaction can be carried out in one-pot operation. Therefore, the essential reagent is hexamethyldisilane which is thermally and hygroscopically stable, non-toxic and readily available.[5] The results are listed in Tables 1 and 2.

A typical procedure follows. Iodine (254mg, 1.0mmol) was added to a small excess amount of hexamethyldisilane (150mg, 1.02mmol) and the mixture was heated to 60-70° to yield iodotrimethylsilane (100% conversion), to which benzene (2ml) was added. 1,2-Epoxycyclohexane (206mg, 2.1mmol) was added at room temperature and the mixture was stirred for 1h. GLC and TLC examinations showed quantitative conversion of the oxirane to (2-iodocyclohexyloxy)trimethylsilane. Then DBU (350mg, 2.3mmol) was added and the mixture was heated at 75° for 25h. The mixture was passed through a short column packed with silica gel and eluted with hexane/ether (2/1). The solvent was evaporated and the residue was subjected to preparative TLC by using benzene/hexane (1/3) as an eluent. Pure 2-cyclohexenyloxytrimethylsilane (275mg, 1.62mmol) was obtained in 81% yield.

The general feature of the reaction is rather similar to the recently reported reaction of oxiranes with trimethylsilyl trifluoromethanesulfonate.[4] The reactivity of iodotrimethylsilane with oxirane (reaction 2) seems to be higher than that of trimethylsilyl trifluoromethanesulfonate. Base-induced elimination of HI from (2-iodoalkoxy)trimethylsilane (reaction 3) is slow but very selective. For efficient and selective conversion of oxiranes to allylic alcohols both reactivity of the reaction 2 and selectivity of the reaction 3 are important. As a consequence even 1,2-epoxybutane can be converted to (2-butenyloxy)trimethylsilane. This may be the second advantage of the present method.

In this connection, we have examined the reaction of bromotrimethylsilane generated similarly to the reaction 1.

$$Me_3Si{-}SiMe_3 + Br_2 \longrightarrow 2Me_3SiBr \qquad (4)$$

The reaction of bromotrimethylsilane with 1,2-epoxycyclohexane (0°, 5min → rt, 20min) resulted in the quantitative formation of (2-bromocyclohexyloxy)trimethylsilane. DBU-induced conversion of the latter was slow, the yield of (2-cyclohexenyloxy)trimethylsilane being 56% after 45h at 80°.

In conclusion, *in situ* generated iodotrimethylsilane is a useful new entrant for conversion of oxirane to allylic alcohol. Related works are in progress.

Acknowledgment: We thank Toshiba Silicone Co., Ltd., Takasago Perfumary Co., Ltd. and Sanyo Kasei Co., Ltd. for gifts of chlorosilanes, terpene alcohols and DBU, respectively. The work was supported in part by the Mitsubishi Foundation.

References and Notes

(1) Chemistry of Organosilicon Chemistry, 138.

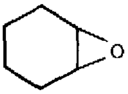
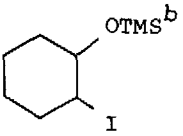
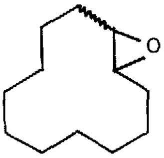
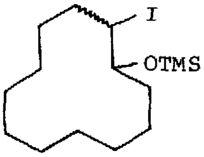
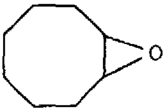
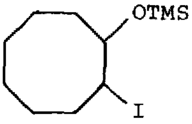
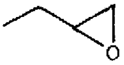
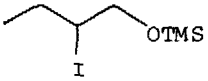
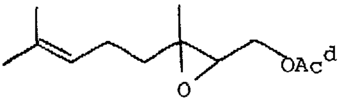
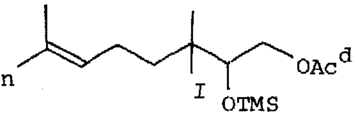
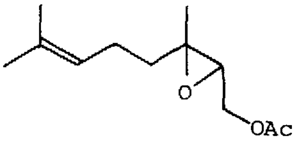
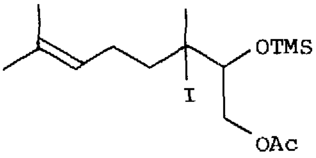
(2) H. Sakurai, A. Shirahata, K. Sasaki and A. Hosomi, Synthesis, 740 (1979), see also G. A. Olah, S. C. Narang, B. G. B. Gupta, and R. Malhorta, Angew. Chem. Int. Ed. Engl., 18, 612 (1979).

(3) For the reaction of iodotrimethylsilane, see M. E. Jung, T. A. Bumenkopf, Tetrahedron Lett., 3675 (1978), and references cited therein.

(4) S. Murata, M. Suzuki and R. Noyori, J. Am. Chem. Soc., 101, 2738 (1979), and references cited therein.

(5) Hexamethyldisilane may be obtained commercially. For the preparation, see a) H. Sakurai and A. Okada, J. Organometal. Chem., 36, C13 (1972); b) H. Sakurai and F. Kondo, ibid., 117, 149 (1976); and references cited therein.

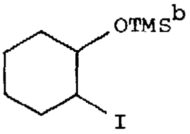
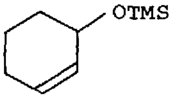
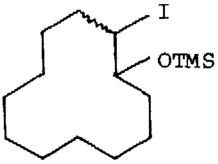
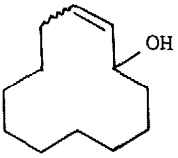
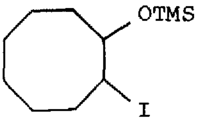
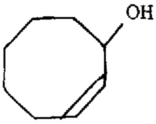
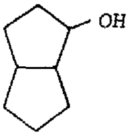
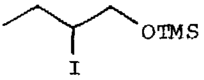
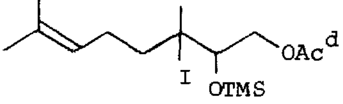
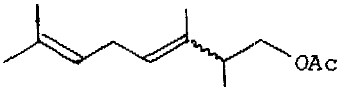
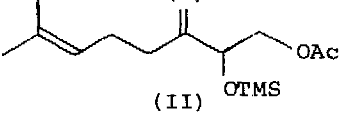
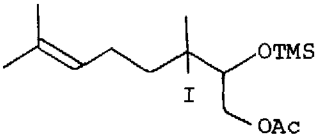
Table 1 Reaction of Oxiranes with Iodotrimethylsilane

Entry	Oxirane	Conditions	Product	(%conversion)[a]
1		PhH, rt, 1h		(100)
2		PhH, rt, 1h		(100)
3		$PhCH_3$, -78°, 10min then rt, 1h		(100)
4		$PhCH_3$, -78°, 30min then rt, 1h		(100)
5		$PhCH_3$, -78°, 4h then -30°, 20min		(100)[c]
6		$PhCH_3$, -78°, 2h then rt, 20min		(100)[c]

---

[a] Determined by GLC unless otherwise stated. [b] TMS = Me_3Si. [c] Determined by TLC. [d] Ac = CH_3CO.

Table 2 Reaction of (2-Iodoalkoxy)trimethylsilane with DBU

Entry	2-Iodoalkoxy-trimethylsilane	Conditions	Products	(% yield)[a]
1		75°, 25h		(81)
2		i) 70°, 30h ii) H^+, MeOH		(80)
3		i) 80°, 28h ii) H^+, MeOH		(49)
				(32)
4		80°, 38h		(70)[c]
5		rt, 38h	 (I)  (II) (I)/(II) = 85/15[e]	(53)
6		rt, 46h	(I) + (II) (I)/(II) = 35/65[e]	(63)

---

[a] Yields after isolation by TLC. [b] TMS = Me_3Si. [c] Determined by GLC.

[d] Ac = CH_3CO. [e] Determined by NMR.

(Received in Japan 22 March 1980)