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ISOMERIZATION OF OXIRANES TO ALLYLIC ALCOHOLS WITH DIALKYLBORYL TRIFLUOROMETHANESULFONATES

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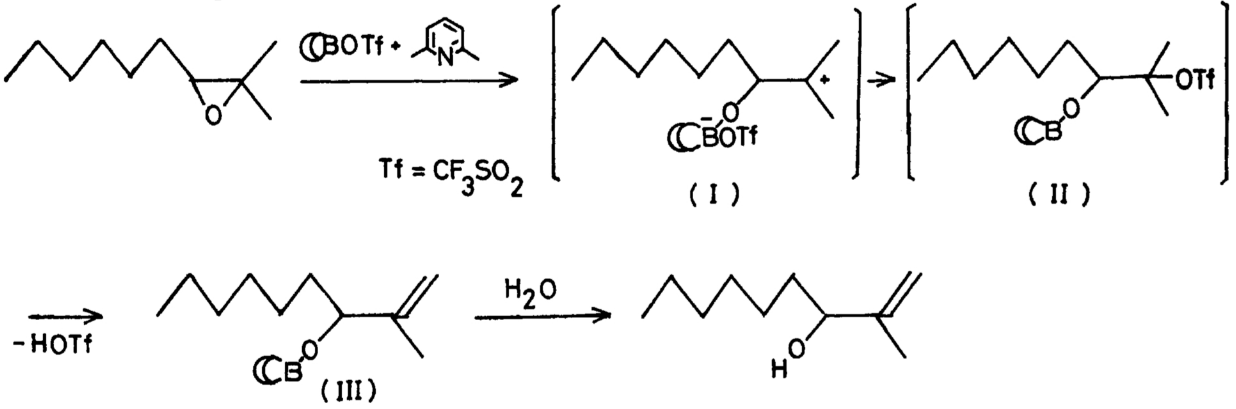
Isomerization of oxiranes to allylic alcohols by treatment with dialkylboryl trifluoromethanesulfonates and tertiary amines is described. Several reactions proceed in regioselective manner.

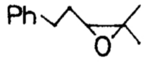
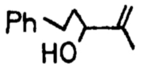
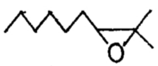
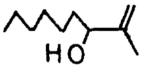
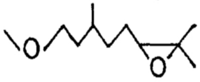
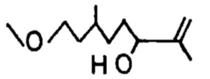
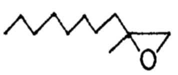
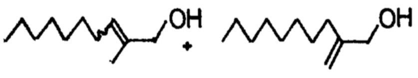
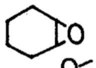
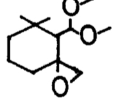
We recently reported a useful regiospecific cross-aldol reaction between ketones and aldehydes or two different ketones by use of dialkylboryl trifluoromethanesulfonates (triflates) and tertiary amines.$^{1)}$ As a part of our continuing study, we have now found that combined use of the trifluoromethanesulfonates and tertiary amines exhibits remarkable reactivity in the isomerization of oxiranes to allylic alcohols. The reaction sequence is exemplified for 2-methyl-2,3-epoxynonane in the scheme depicted below.



To a solution of 9-borabicyclo[3.3.1]non-9-yl trifluoromethanesulfonate (9-BBNOTf) (0.180 g, 0.67 mmol) and 2,6-dimethylpyridine (0.071 g, 0.67 mmol) in 1 ml of ether was added 2-methyl-2,3-epoxynonane (0.100 g, 0.59 mmol) in 1.5 ml of ether at room temperature under argon. After the mixture was stirred for 10 minutes, the resulting solution was poured into 5 ml of water and extracted with hexane. The extract was washed with brine, dried over Na$_2$SO$_4$ and concentrated in vacuo. The crude oil was purified by preparative tlc to afford 3-hydroxy-2-methyl-1-nonene (0.096∼0.100 g, 96%∼quant.) The absorption in the nmr at ca. δ 5.3, which is characteristic of the chemical shift of the disubstituted olefinic protons corresponding to the regioisomer of the product, was not observed, suggesting this reaction proceeds regioselectively.

As indicated in the scheme, dialkylboryl triflate, possessing strong affinity toward oxygen atom, and oxirane initially forms the complex molecule (I), which is in turn converted to the second unstable intermediate (II) by the intramolecular migration of triflate anion, an excellent leaving group, to the carbonium ion. The intermediate (II) decomposes to give the borate (III) in the presence of tertiary amine and finally allylic alcohol is produced by hydrolysis of the resulting borate. It can be also seen from the scheme that the regioselectivity of the present reaction is necessarily determined by the step of the carbon-oxygen bond cleavage of oxirane to form the stable carbonium ion at tertiary carbon. The results of the reaction with various kind of oxiranes carried out according to the above mentioned procedure are summarized in Table 1.

Table 1. Reaction of 9-BBNOTf and 2,6-dimethylpyridine with oxiranes[a]

Oxirane	Product	Reaction Time	Yield (%)
(E)-1,2-epoxycyclododecane	(E)-2-cyclododecen-1-ol	1.5 hr[b]	85
(Z)-1,2-epoxycyclododecane	(E)-2-cyclododecen-1-ol	1.5 hr[b]	15
		overnight	51[c]
		10 min	96 ∼ quant.
		10 min	99[d]
		10 min	94 ∼ quant.
	(ca. 2.6 : 1)		
	-	overnight	no reaction[e]
	-	overnight	— [f]

a) All of the products gave satisfactory ir and nmr data for assigned structures.

b) Reactions were terminated at this point for comparison.

c) Reaction temperature was gradually raised up from -78°C to room temperature. As a side reaction, intramolecular substitution at phenyl ring was observed.

d) One and a half equiv. of dibutylboryl triflate and ethyldiisopropylamine were used.

e) Most of oxirane was recovered.

f) About 70% of oxirane was recovered. Small amounts of unidentified products were observed.

Similarly, the isomerization of 2-methyl-2,3-epoxynonane also took place with catalytic amount of dialkylboryl triflate to afford 3-hydroxy-2-methyl-1-nonene in reasonable yield. Contrary to this result, the reagents, such as lithium amide,$^{2)}$ dialkylaluminium amide,$^{3)}$ or sodium selenide,$^{4)}$ employed in the previous reports, always requires one to four molar equivalents to oxirane. The detailed mechanism of the above mentioned reaction is under investigation.

Table 2. Isomerization of 2-methyl-2,3-epoxynonane to 3-hydroxy-2-methyl-1-nonene by the use of dialkylboryl triflate or dialkylboryl triflate and 2,6-dimethylpyridine$^{a)}$

	Molar equivalents to oxirane	Reaction time	Yield (%)
Bu_2BOTf	0.07	30 min	38
9-BBNOTf	0.05	30 min	41
9-BBNOTf+2,6-dimethylpyridine	0.06	30 min	45
	0.14	1.5 hr	70
	0.25	overnight	69
	1.1	10 min	96∼quant.

a) All of the reactions were conducted under the same conditions employed for Table 1. All of the products gave satisfactory ir and nmr data.

These results indicate that the reaction pathway of the isomerization of oxirane to allylic alcohol with dialkylboryl triflate is obviously distinct from the other reagents reported and it provides a convenient and useful method for the isomerization of some kind of oxiranes. The extension of the reactions using dialkylboryl triflate is now in progress.

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