CHEMISTRY LETTERS, pp. 415-418, 1991.

Nucleophilic Reactions of Acetals, Alkyl Sulfonates, and Oxiranes with Diisobutylaluminum Benzenetellurolate1)

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Diisobutylaluminum benzenetellurolate was proved to be an effective nucleophilic reagent toward acetals, alkyl sulfonates, and oxiranes to give the corresponding tellurides. These reactions showed the characteristics of an S_N2 type. When the substitution reactions were sterically hindered, olefins and allylic alcohols were obtained from alkyl sulfonates and oxiranes, respectively.

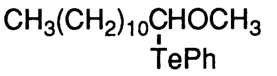
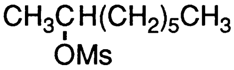
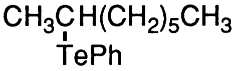
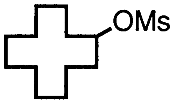
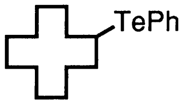
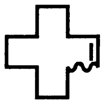
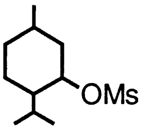
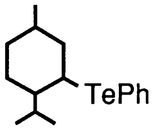
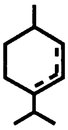
Recently, much attention is focused on utilization of organotellurium compounds for organic synthesis.2) Nucleophilic substitution of alkyl halides with lithium, sodium, or halomagnesium tellurolates under basic conditions offers a convenient method for the introduction of a tellurium functional group into organic structure. These tellurolates are, however, unreactive to esters and the ethers other than oxiranes. We previously reported phenyltellurotrimethylsilane (**1**) as an effective nucleophile for cleavage of the C–O bond of esters and ethers in the presence of a Lewis acid catalyst (ZnI_2).3) Aluminum tellurolate is expected to have a potential reactivity like **1** toward oxygen functional groups due to its weak Te–metal bond and high Lewis acidity of the counter metal.4) We have recently found that diisobutylaluminum benzenetellurolate (**2**) undergoes a facile conjugate addition to α,β-unsaturated carbonyl compounds.5) Here we wish to report reactions of **2** with acetals, alkyl sulfonates, and oxiranes under noncatalyzed conditions.

$Me_3SiTePh$ **1**

$i\text{-}Bu_2AlTePh$ **2**

When diisobutylaluminum benzenetellurolate (**2**), generated in situ from diphenyl ditelluride and diisobutylaluminum hydride,5) was treated with 1-methoxybutane in dichloromethane at room temperature under argon, a substitution reaction proceeded slowly and formed methyl phenyl telluride as a sole product in 14% yield after 24 h, whereas no substitution product was obtained by the treatment of 1-bromooctane with **2** under the same conditions. This obviously indicates the specific reactivity of **2** to oxygen functional groups. The high reactivity was demonstrated by nucleophilic reactions to acetals and alkyl sulfonates. Results are summarized in Table 1.6) Aldehyde dimethyl acetals were smoothly

Table 1. Reactions of acetals and alkyl sulfonates with **2** in dichloromethane

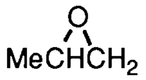
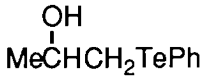
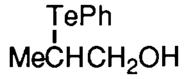
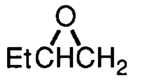
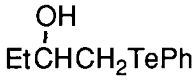
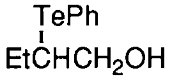
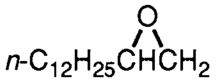
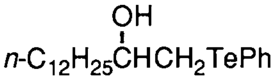
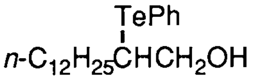
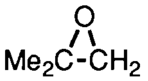
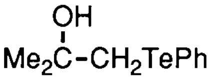
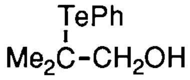
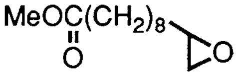
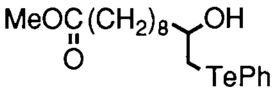
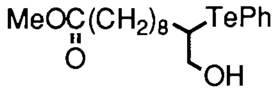
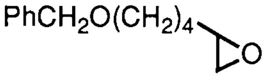
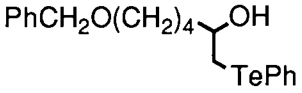
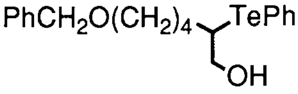
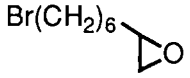
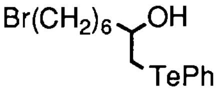
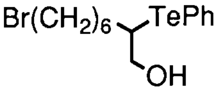
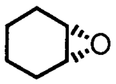
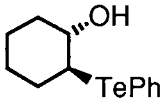
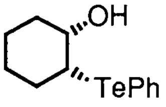
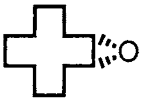
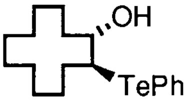
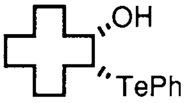
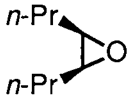
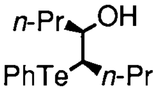
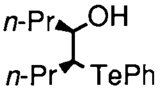
Run	Substrate	Temp/°C	Time/h	Product (Isolated yield/%)	
1	$CH_2(OCH_3)_2$	r t	7	CH_3OCH_2TePh	(42)
2	$CH_3(CH_2)_{10}CH(OCH_3)_2$	r t	3	 $CH_3(CH_2)_{10}\underset{\mathrm{TePh}}{C}HOCH_3$	(80)
3[a]	$CH_3(CH_2)_{10}CH(OCH_3)_2$	reflux	24	$CH_3(CH_2)_{10}CH(TePh)_2$	(50)
4	$CH_3(CH_2)_5OMs$	0	2	$CH_3(CH_2)_5TePh$	(72)
5	$CH_3(CH_2)_5OTs$	0	3	$CH_3(CH_2)_5TePh$	(72)
6	$Ph(CH_2)_3OMs$	0	1	$Ph(CH_2)_3TePh$	(84)
7	 $CH_3\underset{\mathrm{OMs}}{C}H(CH_2)_5CH_3$	-15	4	 $CH_3\underset{\mathrm{TePh}}{C}H(CH_2)_5CH_3$	(54)
8		- 40	5.5	 (46) 	(43)[b]
9		0	2.5	 (42) 	(24)[b]

a) Excess **2** (2.5-fold the molar quantity) was used. b) Determined by GLC analysis.

converted to monotelluroacetals, and, under forced conditions with excess **2**, to the corresponding ditelluroacetal. The nucleophilic substitutions of alkyl methanesulfonates and *p*-toluenesulfonate proceeded at 0 °C or below, in contrast to a similar reaction with sodium benzenetellurolate (at reflux temperature of EtOH–THF (1:1)).[7] Primary alkyl sulfonate esters were converted to alkyl tellurides in high yields, whereas *sec*-alkyl methanesulfonates produced both *sec*-alkyl tellurides and olefins, β elimination products, even at sufficiently low temperature. This indicates the S_N2-type nucleophilicity and basicity of **2**. These reactions were markedly retarded in THF, which solvates aluminum species, suggesting that the C–O bond activation by the coordination of the oxygen atom to **2** is important to smooth reactions.

The high reactivity of **2** toward oxygen functional groups was also substantiated by the ready reactions with oxiranes under neutral conditions. As shown in Table 2, the nucleophilic ring opening of mono-, 2,2-di-, and *cis*-2,3-disubstituted oxiranes proceeded at room temperature to afford β-hydroxy tellurides in high yields and tolerated the coexistence of ester, ether, and halide groups. The ring opening is highly regiospecific as demonstrated in the predominant formation of primary alkyl tellurides from monosubstituted oxiranes and especially from 2,2-dimethyloxirane (Runs 1–4), which produce the other regioisomers in the nucleophilic reaction under acidic conditions or catalytic influence of a Lewis acid.[8] Moreover, the reactions of *cis*-2,3-disubstituted oxiranes gave stereospecifically *threo*-β-hydroxy tellurides. Evidently the ring opening follows an S_N2 mechanism.

Table 2. Reactions of mono-, 2,2-di-, and *cis*-2,3-disubstituted oxiranes with **2**[a)]

Run	Substrate	Time/h	Product		Yield/% (Ratio)[b)]
1	 $MeCHCH_2$ (epoxide)	3	 $MeCH(OH)CH_2TePh$	 $MeCH(TePh)CH_2OH$	88 (94:6)
2	 $EtCHCH_2$ (epoxide)	3	 $EtCH(OH)CH_2TePh$	 $EtCH(TePh)CH_2OH$	79 (95:5)
3	 $n\text{-}C_{12}H_{25}CHCH_2$ (epoxide)	1.5	 $n\text{-}C_{12}H_{25}CH(OH)CH_2TePh$	 $n\text{-}C_{12}H_{25}CH(TePh)CH_2OH$	70 (91:9)
4	 $Me_2C\text{-}CH_2$ (epoxide)	3	 $Me_2C(OH)\text{-}CH_2TePh$	 $Me_2C(TePh)\text{-}CH_2OH$	64 (99>1)
5		2			72 (97:3)
6		2			70 (97:3)
7		2			59 (87:13)
8		4.5			80 (93:7)
9		1.5			79 (99>1)
10		1.5			71 (99>1)

a) The reactions were carried out in dichloromethane at room temperature. b) Determined by ^{13}C NMR analysis.

On the other hand, the ring opening of *trans*-disubstituted and trisubstituted oxiranes competed with isomerization to allylic alcohols as summarized in Table 3. The formation of allylic alcohols preceded the ring opening when the S_N2 attack was sterically hindered, though it was suppressed in a concentrated solution (Run 3) or in THF (Run 4). Moreover, aluminum tellurolate **2** preferentially abstracts α-proton of alkyl group located on the less hindered side of the oxirane group (Run 6). These results support that the isomerization to allylic alcohols proceeds via a cyclic *syn*-elimination mechanism involving the coordination of oxirane to **2** as illustrated in Fig. 1.[9)]

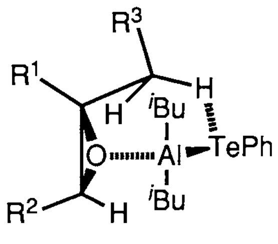
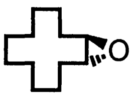
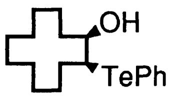
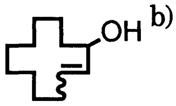
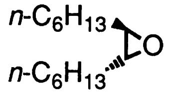
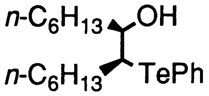
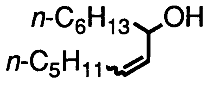
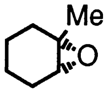
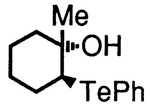
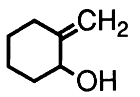
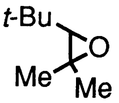
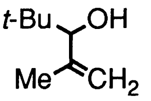


Fig. 1.

In conclusion, these unique oxygenophilic reactivities of **2** are attributable to high polarizability of the Te–metal bond

Table 3. Reactions of *trans*-2,3-disubstituted and trisubstituted oxiranes with **2**a)

Run	Substrate	Solvent	Time/h	Product (Isolated yield/%)			
1		hexane	2		(47)	 b)	(42)
2		CH$_2$Cl$_2$	2		(40)		(48)
3c)		CH$_2$Cl$_2$	2		(60)		(32)
4		THF	24		(35)		(8)
5		CH$_2$Cl$_2$	2		(80)		(3)
6		CH$_2$Cl$_2$	2		(62)		(18)
7		CH$_2$Cl$_2$	2	——			(76)

a) The reactions were carried out at room temperature. b) *E*/*Z* = 2:1 by ^{13}C NMR analysis. c) In a fivefold-concentrated solution compared to that of Run 2.

induced by coordination of the oxygen atom of a substrate to the aluminium site.

The present work was supported by a Grant-in-Aid of Scientific Research from the Ministry of Education, Science and Culture, Japan.

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5) K. Sasaki, Y. Aso, T. Otsubo, and F. Ogura, *Chem. Lett.*, **1989**, 607.
6) All new compounds in the present paper were characterized by elemental and spectroscopic analyses.
7) D. L. J. Clive, G. J. Chittattu, V. Farina, W. A. Kiel, S. M. Menchen, C. G. Russell, A. Singh, C. K. Wong, and N. J. Curtis, *J. Am. Chem. Soc.*, **102**, 4438 (1980).
8) The reaction of 2,2-dimethyloxirane with **1** in the presence of ZnI$_2$ gave a 1:1 mixture of regioisomeric β-silyloxy tellurides; K. Sasaki, Y. Aso, T. Otsubo, and F. Ogura, unpublished result. See also J. G. Smith, *Synthesis*, **1984**, 629.
9) Similar isomerizations with aluminum amides or strong bases have been reported; A. Yasuda, H. Yamamoto, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **52**, 1705 (1979) and references cited therein.

(Received December 1, 1990)