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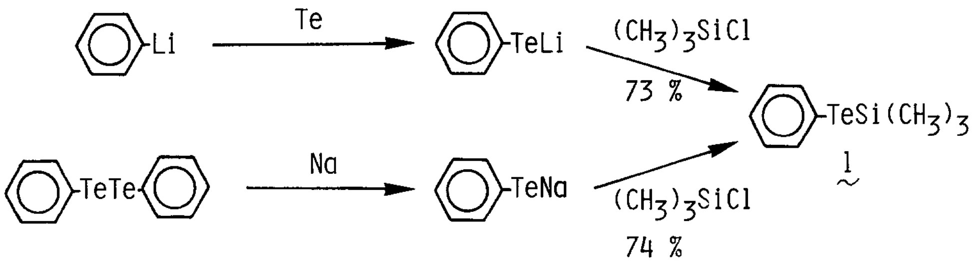
NUCLEOPHILIC CLEAVAGES OF ESTERS AND ETHERS WITH PHENYLTELLUROTRIMETHYLSILANE[1)]

Kazuaki Sasaki, Yoshio Aso, Tetsuo Otsubo, and Fumio Ogura*
Department of Applied Chemistry, Faculty of Engineering,
Hiroshima University, Saijo, Higashi-Hiroshima 724, Japan

Abstract: The title tellurosilane **1** reacted with esters and ethers in the presence of catalytic zinc iodide under very mild conditions, giving the corresponding products with C-telluration and O-silylation via nucleophilic cleavages of the C-O bonds.

In past years, thiosilanes and selenosilanes have been developed as effective oxygenophiles due to the weak chalcogen-silicon bonds.[2,3,4)] On the other hand, little has been known about tellurosilanes as the counterpart. A few of typical tellurosilanes such as phenyltellurotrimethylsilane **1** were recently synthesized, but their reactivities except for ready protolytic cleavages have not been revealed yet.[5,6)] As part of our interest in utilizing organotelluriums for organic synthesis, we have investigated some reactions of phenyltellurotrimethylsilane **1**. Based on the weak Te-Si bond and the high nucleophilicity of PhTe group, it is anticipated to be a promising reagent for organotelluration.

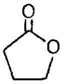
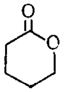
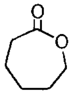
Scheme



The tellurosilane **1** was accessible not only from phenyllithium according to the method reported by Drake and Hemmings[5)] but also from diphenyl ditelluride as shown in Scheme.[7)] Because of its sensitivity toward moisture and oxygen, it could be conveniently stored as a 2.5 M hexane solution in a Schlenk flask and handled by a syringe technique under an inert gas.

The tellurosilane **1** like the other chalcogenosilanes[4,8)] reacted with esters in the presence of a catalytic Lewis acid (ZnI_2), resulting in the ready cleavages of the C-O bonds. As a result, lactones led to ω-phenyltelluro trimethylsilyl esters which were isolated as the corresponding

Table 1. Reactions of esters with phenyltellurotrimethylsilane 1[a]

No.	Ester	Temp(°C)	Time(h)	Product	Yield(%)[b]
1		RT	3	$PhTe(CH_2)_3COOH$	98
2		RT	3	$PhTe(CH_2)_4COOH$	86
3		RT	21	$PhTe(CH_2)_5COOH$	79
4	n-BuOAc	RT	24	n-BuTePh	30

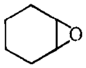
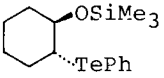
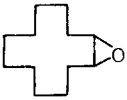
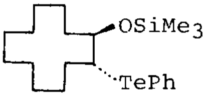
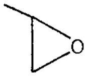
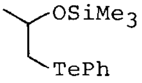
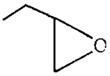
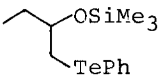
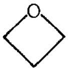
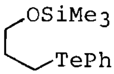
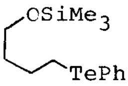
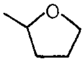
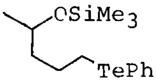
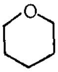
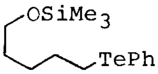
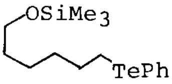
a) Ester (1.0 mmol) was allowed to react with 1 (1.45 mmol) and ZnI_2 (0.01 mmol) in dry dichloromethane (3 ml).
b) Isolated yield.

carboxylic acids.9) Some results are shown in Table 1. The ring opening proceeded at room temperature, in contrast to similar reactions with thiosilanes (70°C)8) and selenosilanes (80-110°C).4)

The high reactivity of 1 was further demonstrated by effecting the ready cleavages of various ethers involving a series of cyclic ethers (see Table 2). The reactions of oxiranes occurred at 0°C or less, giving β-siloxyalkyl phenyl tellurides in high yields. The ring opening is stereospecific on the basis of predominance of trans siloxy telluride from cycloalkene oxide and regiospecific on the basis of predominance of primary alkyl telluride from acyclic alkene oxide. These results indicate S_N2-like cleavages. The four and five-membered ether rings like the above three-membered ring smoothly reacted with tellurosilane 1, whereas the cleavages of six and seven-membered ring required a somewhat higher temperature (40°C). The cleavages of unsymmetrical acyclic ethers proceeded with a certain regioselectivity, as indicated by the predominant formations of methyl phenyl telluride from n-butyl methyl ether, n-dodecyl methyl ether or anisole and of benzyl phenyl telluride from benzyl methyl ether. The directions of such cleavages are determined by the relative ease of ether bond breakings by S_N2 process.

It is thus understandable that tellurosilane 1 posseses much higher reactivity than the other chalcogenosilanes and accordingly reacts with esters and ethers under very mild conditions, giving the corresponding products with C-telluration and O-silylation via nucleophilic cleavages of the C-O bonds. On considering that phenyltelluro group is convertible into a variety of functional groups such as olefinic10), halogen11), and methoxy12), it is possible to effect some useful synthetic transformations starting with the nucleophilic cleavages of esters and ethers by tellurosilane 1.

Table 2. Reactions of ethers with phenyltellurotrimethylsilane **1**[a]

No.	Ether	Temp(°C)	Time(h)	Product	Yield(%)[b]
1		0	4		91
2		0	1		67
3		-20	5		71
4		0	3		83
5		0	5		83
6		0	4		96
7		RT	6		71
8		40[c]	30		21
9		40[c]	4		50
10	$CH_3(CH_2)_3OCH_3$	RT	19	CH_3TePh[d]	60
11	$CH_3(CH_2)_{11}OCH_3$	RT	24	CH_3TePh $CH_3(CH_2)_{11}OSiMe_3$	30 46
12	$PhOCH_3$	40[c]	40	CH_3TePh $PhOSiMe_3$	29 10
13	$PhCH_2OCH_3$	RT	16	$PhCH_2TePh$ CH_3TePh $PhCH_2OSiMe_3$ CH_3OSiMe_3	42 15 14[e] 79[e]

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a) Ether (1.0 mmol) was allowed to react with **1** (1.35 mmol) and ZnI_2 (0.01 mmol) in dry dichloromethane (3 ml).
b) Isolated yield.
c) Refluxed temperature of dichloromethane.
d) The siloxy counterpart was not isolated because of its volatility.
e) The yield was determined by NMR analysis.

References and Notes

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4) N. Miyoshi, H. Ishii, S. Murai, and N. Sonoda, Chem. Lett., 873 (1979).

5) J. E. Drake and R. T. Hemmings, Inorg. Chem., 19, 1879 (1980).

6) K. Praefcke and C. Weichsel, Synthesis, 216 (1980).

7) The preparation of tellurosilane 1 from diphenyl ditelluride was carried out as follows; A mixture of diphenyl ditelluride (20.5 g, 50 mmol) and small pieces of sodium (3.5 g, 152 mmol) in dry tetrahydrofuran (50 ml) was refluxed under argon. Sodium gradually dissolved within 18 h. Freshly distilled trimethylsilyl chloride (14 ml, 110 mmol) was slowly added into the mixture at room temperature. It was then stirred for one h, and directly distilled in vacuo to give an yellow oil of 1 (20.5 g, 74 %, bp 77-79°C/2 mmHg).

8) E. W. Abel and D. J. Walker, J. Chem. Soc. (A), 2338 (1968).

9) After the reactions of esters or ethers with tellurosilane 1 were carried out under conditions indicated in Table 1 or 2 and then the reaction mixture was worked up as usual, all the telluro products were isolated by preparative gel-permeation liquid chromatography using chloroform as eluent and characterized by elemental and spectroscopic analyses.

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11) K. Chikamatsu, T. Otsubo, F. Ogura, and H. Yamaguchi, Chem. Lett., 1081 (1982).

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