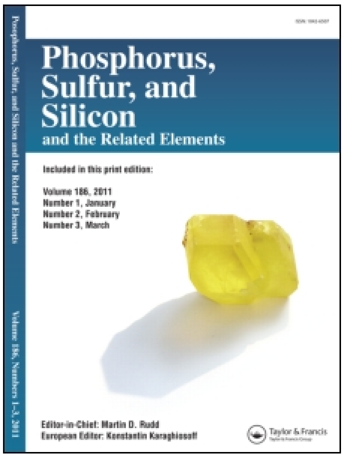

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Hirai, Yasuyuki , Ohe, Kouichi , Toshimitsu, Akio and Uemura, Sakae(1992) 'Oxidative substitution of PhTe and PhSe Moieties in Alkyl Phenyl Tellurides and Selenides Leading to Esters and Alcohols', Phosphorus, Sulfur, and Silicon and the Related Elements, 67: 1, 173 — 176

To link to this Article: DOI: 10.1080/10426509208045835

URL: http://dx.doi.org/10.1080/10426509208045835

Phosphorus, Sulfur, and Silicon, 1992, Vol. 67, pp. 173–176

OXIDATIVE SUBSTITUTION OF PhTe AND PhSe MOIETIES IN ALKYL PHENYL TELLURIDES AND SELENIDES LEADING TO ESTERS AND ALCOHOLS

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Abstract Oxidation of alkyl phenyl tellurides and/or selenides with sodium periodate($NaIO_4$) in aqueous acetic acid or with meta-chloroperbenzoic acid(MCPBA) in N,N-dimethylformamide or N,N-dimethylacetamide affords a mixture of the corresponding alkyl esters(acetates or formates) and/or alcohols in 20-94% yield under mild conditions(at 20-80°C for 0.5-24 h).

INTRODUCTION

Many functional group transformations involving alkyl phenyl selenides and tellurides have been developed recently,[1] and yet a facile and general method for the preparation of alcohols and their synthon esters by replacing PhM(M=Se, Te) moiety with oxygen-functional group (C-MPh $\longrightarrow$ C-OH, C-OCOR) has not been well established.[2] We describe here preliminary results of several attempts for such conversion.

$NaIO_4$ OXIDATION OF ALKYL PHENYL TELLURIDES IN AQUEOUS AcOH

First we tried oxidation of cyclohexyl phenyl telluride with an excess of various oxidants(5 eq. to the telluride) in some solvents at 25°C for 24 h. As a result it was disclosed that the use of sodium periodate($NaIO_4$) in aqueous 50% acetic acid is most fruitful for obtaining a higher yield of a mixture of cyclohexanol and cyclohexyl acetate, none of cyclohexene, phenol, and phenyl acetate being formed. In aqueous tetrahydrofuran the main product was cyclohexene, while in aqueous methanol both cyclohexanol and cyclohexene were produced in low yields. Other oxidants such as meta-chloroperbenzoic acid(MCPBA) and hydrogen peroxide(H_2O_2) were also used in place of $NaIO_4$ in aqueous

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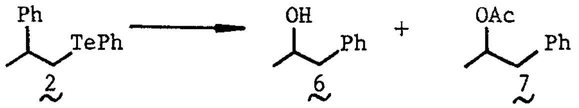
AcOH, but the yield of the desirable products was slightly lower than that obtained by $NaIO_4$ oxidation.

Then we applied this oxidation system($NaIO_4$/aq. AcOH) to some alkyl phenyl tellurides(eq. 1). Typical results are shown in Table 1. When a phenyl group is present at a vicinal position to PhTe moiety, the oxidation was accompanied by phenyl migration(eq. 2). In the oxidation of 2-methoxycyclohexyl phenyl telluride ring-contraction occurred to produce cyclopentanecarbaldehyde(eq. 3).

$$\underset{\mathbf{1}}{\text{RTePh}} \xrightarrow[\text{aq. AcOH, 25°C, 24h}]{NaIO_4} \underset{\mathbf{4}}{\text{ROH}} + \underset{\mathbf{5}}{\text{ROAc}} \qquad (1)$$



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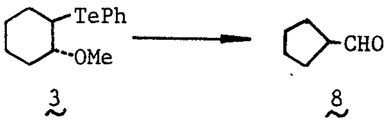


(3)

Table 1. $NaIO_4$ Oxidation of Organic Tellurides in aq. AcOH[a]

Telluride	Product & yield(%)[b]				Others
1($R=C_{12}H_{25}-$)	**4**	16	**5**	4	
1($R=C_6H_{13}(CH_3)CH-$)	**4**	26	**5**	15	2-octanone 9%
1(R=cyclohexyl)	**4**	25	**5**	39	
1(R=cycloheptyl)	**4**	33	**5**	19	
1(R=cyclododecyl)	**4**	10	**5**	11	cyclododecanone 20% cyclododecenes 37%
2	**6**	49	**7**	20	2-phenylpropene 15%
3	**8**	60			

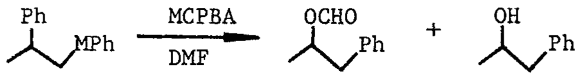
[a] Telluride 2 mmol, $NaIO_4$ 10 mmol, aq. 50% AcOH 20 ml; 25°C, 24 h.
[b] Glc yield.

Oxidation of alkyl phenyl telluroxides such as dodecyl and cyclohexyl ones, prepared separately by hydrolysis of the corresponding organotellurium dibromide, under various conditions did not improve the yield of the corresponding alcohols and acetates.

MCPBA OXIDATION OF ALKYL PHENYL SELENIDES AND TELLURIDES IN DMF OR DMA

We found that treatment of alkyl phenyl tellurides and selenides with an excess of MCPBA in N,N-dimethylformamide(DMF) or N,N-dimethylacetamide(DMA) generally produces the corresponding alkyl esters(formates or acetates) and alcohols by the substitution of PhTe or PhSe moiety with ester and hydroxy groups. Thus, oxidation of dodecyl phenyl telluride with MCPBA(5 equiv.) in DMF at 25°C for 3 h afforded a mixture of dodecyl formate(43%) and dodecanol(15%). When DMA was used as solvent, dodecyl acetate was obtained in place of the formate(eq. 4). A similar reaction occurred also with the corresponding selenide as well as other primary alkyl tellurides and the secondary alkyl tellurides and selenides. Typical results are shown in Table 2. As in the case of $NaIO_4$ oxidation, when a phenyl group is present at a vicinal position to PhTe or PhSe moiety, the replacement of such moieties by OCHO and OH was accompanied by phenyl migration(eq. 5). All reactions proceeded more smoothly at 80°C and alkenes which might be formed by telluroxide or selenoxide elimination were not detected in the products.

$$\underset{\mathbf{9}}{\mathrm{RMPh}} \xrightarrow[\substack{\mathrm{Me_2NCHO(DMF)} \\ \text{or} \\ \mathrm{Me_2NCOMe(DMA)} \\ 25\text{-}80^\circ\mathrm{C},\ 0.5\text{-}24\mathrm{h}}]{\mathrm{MCPBA}} \underset{\substack{\mathbf{12}\ (\mathrm{R'=H}) \\ \mathbf{13}\ (\mathrm{R'=Me})}}{\mathrm{ROCOR'}} + \underset{\mathbf{14}}{\mathrm{ROH}} \qquad (4)$$



10 (M=Te)
11 (M=Se)
15
16
(5)

By considering the proposed mechanism for alkoxy group substitution,[3] we assume that the reaction giving the ester takes place by a nucleophilic attack of the carbonyl oxygen of DMF or DMA upon the MCPBA adduct(A) of a tellurone or selenone. The produced carbonium and/or iminium ions are hydrolyzed by water which might be obtained in the solvent to produce the ester. Direct nucleophilic attack of water upon (A) produces the alcohol. We confirmed separately that the formate is not converted into the alcohol, and vice versa, under the employed reaction conditions.

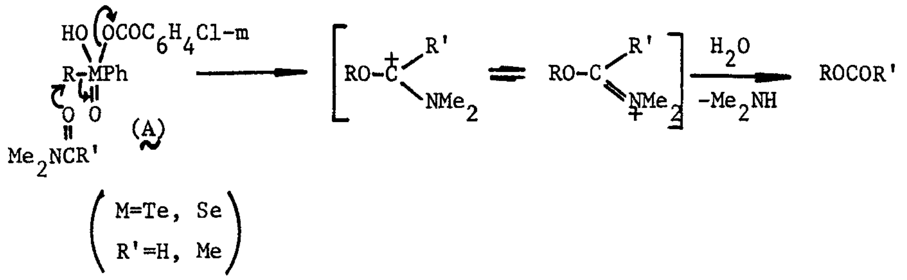


Table 2. Oxidative Conversion of Tellurides and Selenides to Esters and Alcohols by Use of MCPBA in DMF or DMA[a]

R in 9	M	Solvent	Temp/°C	Time/h	Product and Isolated yield(%)			
$C_{12}H_{25}$	Te	DMF	25	3	12	43	14	15
$C_{12}H_{25}$	Te	DMF	80	2	12	74	14	20
$C_{12}H_{25}$	Te	DMA	80	2	13	69	14	22
$C_{12}H_{25}$	Se	DMF	25	24	12	57	14	22
$C_{12}H_{25}$	Se	DMF	80	0.5	12	67	14	13
$C_{12}H_{25}$	Se	DMA	80	1	13	44	14	50
$C_{16}H_{33}$	Te	DMF	80	2	12	69	14	14
$C_{12}H_{25}CHMe$	Te	DMF	80	2	12	65	14	0
$C_{12}H_{25}CHMe$	Se	DMF	80	2	12	46	14	0
10		DMF	80	2	15	33[b]	16	25[b]
11		DMF	80	2	15	27[b]	16	23[b]

[a] Telluride or selenide 1 mmol, MCPBA 5 mmol, solvent 5 ml.

[b] G.l.c. yield.

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