

NOVEL OXIDATION OF ALKYL PHENYL TELLURIDES AND TELLUROXIDES WITH
meta-CHLOROPERBENZOIC ACID: REPLACEMENT OF TELLURIUM MOIETY BY
METHOXY GROUP ACCOMPANIED BY RING-CONTRACTION AND PHENYL MIGRATION

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Summary: Oxidation of alkyl phenyl tellurides and telluroxides with meta-chloroperbenzoic acid in methanol at room temperature afforded the corresponding alkyl methyl ethers in high yields. The reaction was accompanied by phenyl migration and ring-contraction respectively when applied to the compounds having phenyl group next to the tellurium moiety and to the methoxytelluration products of cyclic olefins.

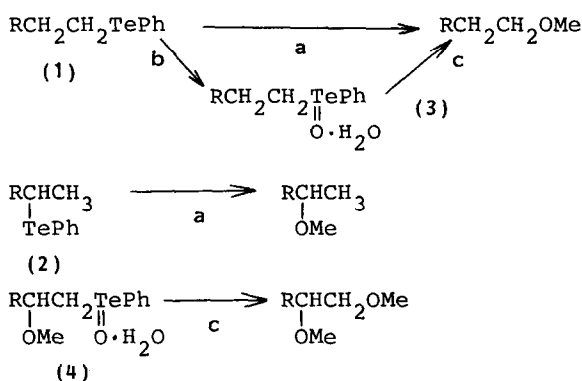
Development of synthetic methods based on tellurium chemistry is growing and of current interest,¹⁻³ though it is still far behind from that of fruitful organosulfur and organoselenium chemistry. Recently a facile elimination of some telluroxides leading to olefins, allylic alcohols, and allylic ethers was reported.⁴ We now find that a novel and facile carbon-tellurium bond fission occurs in tellurides and telluroxides to give alkyl methyl ethers when they are treated with m-chloroperbenzoic acid (MCPBA) in methanol. The reaction may provide a new method for the transformation of C-Te bond to C-O bond.

Oxidation of alkyl phenyl tellurides (1,2) and telluroxides (3,4)^{4,5} with MCPBA in methanol at room temperature afforded the corresponding alkyl methyl ethers in good yields (Scheme I), none of methyl phenyl ether (anisole) being formed. Generally, 3-5 and 1-2 equivalents of MCPBA to organotellurium compounds were necessary in the cases of tellurides and telluroxides, respectively. The expected tellurones, $[\text{PhTe}(\text{O})_2\text{R}]$, one of which having been prepared by the NaIO_4 oxidation of 4-methoxyphenyl dodecyl telluroxide,⁶ were not isolated at all under the present reaction conditions. The treatment of (3; $\text{R}=\text{n-C}_{10}\text{H}_{21}$) with other oxidants than MCPBA such as H_2O_2 , $\text{H}_2\text{O}_2/\text{HClO}_4$, $\text{H}_2\text{O}_2/\text{BF}_3 \cdot \text{Et}_2\text{O}$, t-BuOOH, and NaIO_4 did not afford any dodecyl methyl ether under the conditions where 95% of the ether was produced by using MCPBA.

When the phenyl group was situated at a vicinal position to tellurium moiety as in the cases of (5)-(7), the replacement of tellurium moiety by the methoxy group was accompanied by phenyl migration as shown in Scheme II.

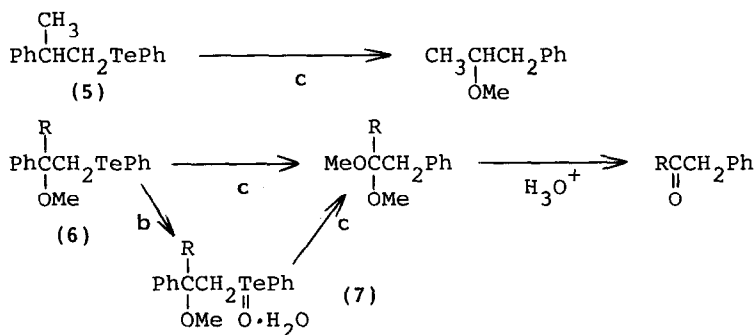
By similar treatment the methoxytelluration products of cyclic olefins such as (8) and (11) where the methoxy group was situated at a vicinal position^{3a,b} afforded readily the dimethylacetals of the ring-contracted cyclic aldehydes (10)

Scheme I



Conditions: a; 3-5 equiv. MCPBA/MeOH (20-25°C for 0.5-1 h).
 b; Br₂/CCl₄ (0°C) and aq. 0.5N NaOH (20°C for 5 min).
 c; 1-2 equiv. MCPBA/MeOH (20-25°C for 0.5-1 h).

Scheme II



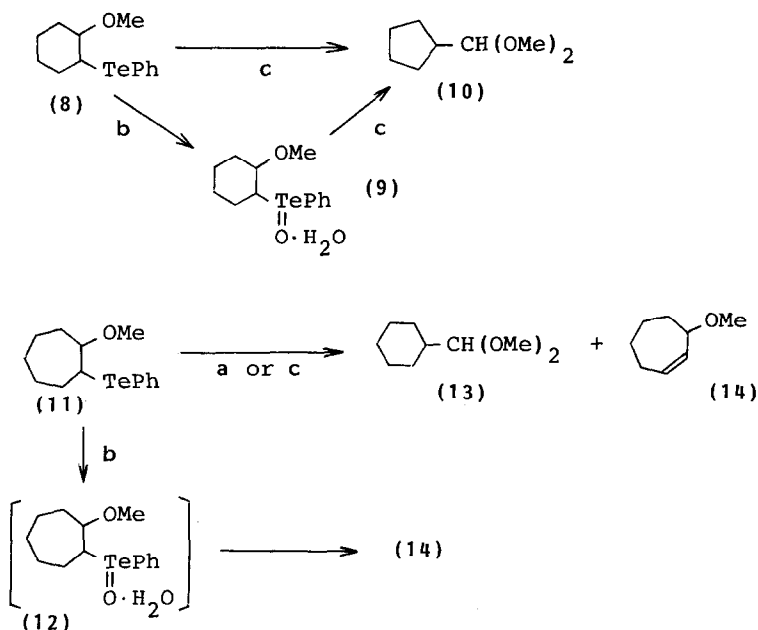
and (13) respectively in high yields (Scheme III). In the oxidation of (11) using one equivalent of MCPBA, allylic ether (14) is the major product as expected from the formation of the unstable telluroxide (12) and its rapid telluroxide elimination,⁴ while the use of excess MCPBA resulted in a selective formation of (13). In contrast to the case of (3), such oxidants as NaIO₄, H₂O₂, and t-BuOOH also promoted the respective transformation of (8) and (11) to (10) and (13), though the yields were lower in all cases compared with the MCPBA oxidation.

Typical results are summarized in Table I. Further work to elucidate the reaction mechanism and the scope and limitations of this novel oxidation is currently in progress.⁷

Acknowledgement

We thank Professor Masaya Okano of Kyoto University for his helpful discussion and encouragement throughout the work.

Scheme III



References and Notes

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- (a) S. Uemura, S. Fukuzawa, A. Toshimitsu, and M. Okano, Tetrahedron Lett., **23**, 1177(1982). (b) S. Uemura, S. Fukuzawa, and A. Toshimitsu, J. Organometal. Chem., **250**, 203(1983). (c) S. Uemura and S. Fukuzawa, Tetrahedron Lett., **23**, 1181(1982). (d) S. Uemura, S. Fukuzawa, and S. R. Patil, J. Organometal. Chem., **243**, 9(1983).
- S. Uemura and S. Fukuzawa, J. Am. Chem. Soc., **105**, 2748(1983).
- In the case of R=Ph, (3) could not be isolated by the treatment of the dibromide of (1; R=Ph) with aq. NaOH and instead only styrene was isolated almost quantitatively.

Table I. MCPBA Oxidation of Alkyl Phenyl Tellurides and Telluroxides^a

Te compound (2 mmol)	MCPBA ^b (equiv.)	Product and isolated yield(%)
(1; R=n-C ₁₀ H ₂₁)	3	n-C ₁₀ H ₂₁ CH ₂ CH ₂ OMe 50
(1; R=Ph)	5	PhCH ₂ CH ₂ OMe 67 PhCH=CH ₂ 14
(2; R=n-C ₁₂ H ₂₅)	5	n-C ₁₂ H ₂₅ CH(OMe)CH ₃ 86
(3; R=n-C ₁₀ H ₂₁)	2	n-C ₁₀ H ₂₁ CH ₂ CH ₂ OMe 95
(3; R=n-C ₁₀ H ₂₁)	2	n-C ₁₀ H ₂₁ CH ₂ CH ₂ OEt ^c 70
(4; R=n-C ₈ H ₁₇)	2	n-C ₈ H ₁₇ CH(OMe)CH ₂ OMe 84
(5)	3	PhCH ₂ CH(OMe)CH ₃ 90
(6; R=H)	2	PhCH ₂ CH(OMe) ₂ 90
(7; R=H)	1	PhCH ₂ CH(OMe) ₂ 73
(7; R=CH ₃)	1	PhCH ₂ COCH ₃ 84 ^d
(8) ^e	2	(10) 77 ^f
(9) ^e	1	(10) 84 ^f
(11) ^e	5	(13) 90 ^f
(11) ^e	1	(13) 6 ^f (14) 54 ^f

^a Carried out in MeOH (10-20 ml) at 20-25°C for 0.5-1 h.

^b Equivalent to Te compound. ^c Carried out in EtOH as solvent.

^d After hydrolysis with dil. HCl. ^e 1 mmol. ^f GLC yield with internal standard.

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7. Although the details on the mechanism of this reaction are not yet clear, the tellurinic acid ester PhTe(O)OR, which might be formed by the Baeyer-Villiger type oxidation, and/or the tellurone PhTe(O)₂R seem to be involved as the intermediate which may afford the product ether in the presence of acid (meta-chlorobenzoic acid in this case).

(Received in Japan 25 June 1983)