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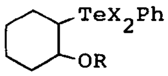
A FACILE METHOD FOR OXYTELLURATION OF OLEFINS

Sakae Uemura,* Shin-ichi Fukuzawa, Akio Toshimitsu, and Masaya Okano
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

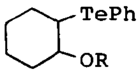
Summary: Treatment of olefins with phenyltellurium(II) or (IV) species [$(PhTe)_2$, PhTeCN, $PhTeBr_3$] in alcohol at room to reflux temperature for 1-24 h produces the corresponding (2-alkoxyalkyl)phenyltellurium dihalides in good yields, the reaction being trans-stereoselective and highly regioselective.

Organic synthesis using tellurium salt and/or organotellurium compounds is of current interest and is growing.[1] One of the key reactions in this field is the introduction of tellurium into organic compounds. Oxytelluration of olefins seems to be an effective method for this purpose, but so far a facile method has been scarcely explored. Recent publication on intramolecular oxytelluration of some hydroxy olefins[2] prompted us to communicate our new facile method for oxytelluration of olefins to produce (2-alkoxyalkyl)phenyltellurium dihalides which can be easily converted to the corresponding tellurides and telluroxides.[3,4]

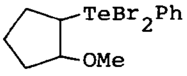
In a typical experiment, cyclohexene(10 mmol) was added to a yellow homogeneous solution of diphenyl ditelluride(2.5 mmol),[5] bromine(7.5 mmol), and methanol (5 ml) and the mixture was stirred at reflux for 1 h, during which period a pale yellow solid was precipitated. After being cooled down to 0°C, the solid was filtered, dried under vacuum, and recrystallized from methanol-chloroform(10:1). Combustion analysis and several spectroscopic analysis showed this to be (2-methoxycyclohexyl)phenyltellurium dibromide (1; R=Me, X=Br); 1.44 g(3.0 mmol, 60%,



(1)



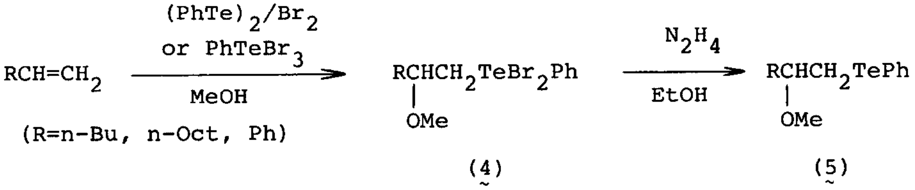
(2)



(3)

m.p. 180-181°C). The reaction proceeded even at room temperature for a longer time and also by using phenyltellurium tribromide[6] in the place of diphenyl ditelluride and bromine. Other alcohols such as ethanol, n-butanol, and i-propanol can be used, but the yield of (1) was lower. Similar reaction also occurred by using phenyltellurocyanate[7] or diphenyl ditelluride in the presence of copper(II) chloride to give the corresponding dichloro-analogue (1; R=Me, X=Cl; m.p. 183-184°C). Reduction of (1) by N_2H_4, $Na_2S_2O_3$, or Na_2S readily gave the telluride (2), this result being in a sharp contrast with that of (2-chloroalkyl)tellurium-(IV) compound from which the parent olefin, diaryl ditelluride, and/or elemental tellurium are produced.[4,8]

The reaction can be applied well to cyclopentene, styrene, 1-hexene, 1-decene, cis- and trans-2-butenes. Here, oxytelluration of terminal olefins occurred completely regioselectively to give (4) as an oil,[†] tellurium moiety attacking on terminal carbon as shown in Scheme 1.[‡] The addition to cis-2-butene occurred completely in a trans fashion to give threo-(6) (m.p. 139 °C) and then (7) (oil), an authentic sample of (7) being prepared by several steps shown in Scheme 2 (the retention time of GLC and ^{1}H-NMR spectrum being completely the same). The same conclusion was obtained by using trans-2-butene [erythro-(6); m.p. 105-106°C]. Typical results are shown in Table.



$$RCH{=}CH_2 \xrightarrow[\text{MeOH}]{(PhTe)_2/Br_2 \text{ or } PhTeBr_3} \underset{\text{OMe}}{\underset{|}{RCHCH_2TeBr_2Ph}} \xrightarrow[\text{EtOH}]{N_2H_4} \underset{\text{OMe}}{\underset{|}{RCHCH_2TePh}}$$

Scheme 1

Treatment of (1; R=Me, X=Br) with aqueous NaOH afforded the corresponding telluroxide (8) as a colorless oil. When this compound (5.70 mmol) was thermally

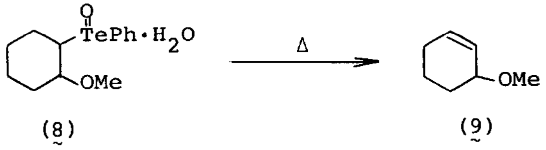
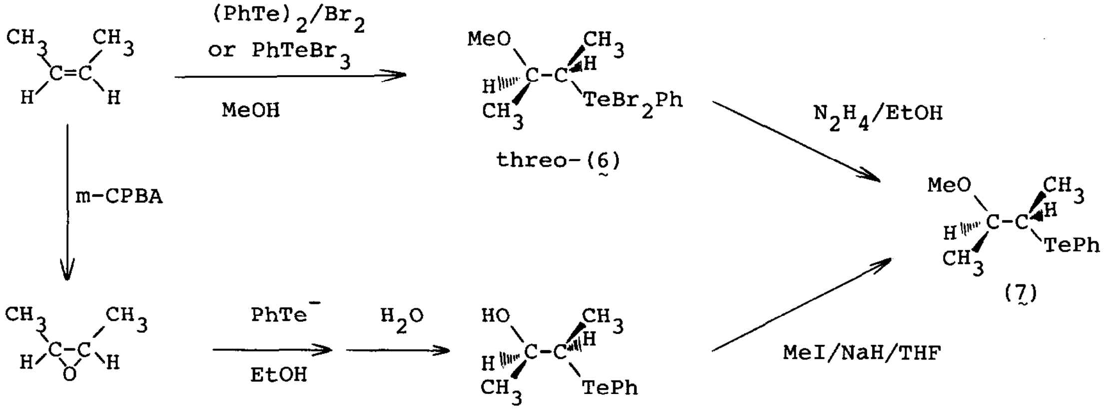


Table. Oxytelluration of olefins.[a)]

Olefin	Temp(°C)	Time(h)	Product[b)] & yield(%)[c)]	
Cyclohexene	65	1	(1; R=Me, X=Br)	60
Cyclohexene	20	24	(1; R=Me, X=Br)	60
Cyclohexene	78[d)]	2	(1; R=Et, X=Br)	48
Cyclohexene	82[e)]	2	(1; R=i-Pr, X=Br)	31
Cyclohexene[f)]	65	1	(1; R=Me, X=Br)	65
Cyclohexene[g)]	65	1	(1; R=Me, X=Cl)	77
Cyclopentene	20	24	(3)[h)]	55
Styrene	20	24	(4; R=Ph)	47
1-Hexene[f)]	65	3	(4; R=n-Bu)	63
1-Decene	65	2	(4; R=n-Oct)	66
cis-2-Butene[i)]	20	24	threo-(6)	54
cis-2-Butene[f,i)]	65	3	threo-(6)	46
trans-2-Butene[i)]	20	24	erythro-(6)	61

a) Carried out using diphenyl ditelluride(2.5 mmol), bromine(7.5 mmol), and olefin (10 mmol) in methanol(5 ml). b) Satisfactory ^{1}H- and ^{13}C-NMR data, as well as combustion analytical data, were obtained for all compounds. c) Isolated yield; based on charged Te reagent. d) EtOH as solvent. e) i-PrOH as solvent. f) $PhTeBr_3$(5 mmol) and methanol(10 ml) were used. g) PhTeCN(2 mmol), $CuCl_2$(2 mmol), and methanol(10 ml) were used. h) M.p. 105°C. i) Carried out in a glass pressure bottle; olefin(25 mmol).



Scheme 2

decomposed at 200°C in Kugelrohr, 3-methoxycyclohexene (9) (3.88 mmol, 70%) and diphenyl ditelluride were obtained as products. This result shows that the direction of telluroxide elimination giving allylic ether is the same as that of the corresponding selenoxide, although the telluroxide is very stable compared to the selenoxide [which is unstable and decomposes rapidly at 0-20°C to give (9)].

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† The reaction mixture was added with water and (4) was extracted with chloroform.

‡ This was confirmed by ^{13}C-NMR of the crude product of (4) and (5), and also by GLC analysis of the crude (5).

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