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TELLUROXIDE ELIMINATION BY DIRECT OXIDATION OF ALKYL PHENYL TELLURIDE

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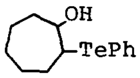
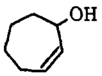
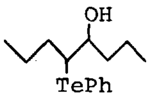
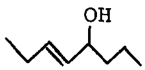
Summary: Treatment of sec-alkyl phenyl tellurides, except for the cyclohexyl system, with m-chloroperbenzoic acid(MCPBA) in diethyl ether readily afforded the corresponding olefins in good yields presumably via telluroxide elimination together with small amounts of alcohols and ketones. In the pri-alkyl and cyclohexyl cases the adducts between MCPBA and the tellurides were isolated as stable organotellurium(IV) compounds which gave similar elimination products by neat pyrolysis at 220-250°C.

It has been reported that a facile elimination of sec-alkyl phenyl telluroxides leading to olefins, allylic alcohols, and allylic ethers occurred by treating the corresponding stable organotellurium(IV) dibromides with aqueous NaOH.[1] We now succeed in a similar elimination by the direct oxidation of sec-alkyl phenyl tellurides with m-chloroperbenzoic acid(MCPBA)[2] and also in an isolation of the adducts between MCPBA and pri-alkyl and cyclohexyl phenyl tellurides.

When 2-tetradecyl phenyl telluride was reacted with 1~1.5 equivalents of MCPBA in diethyl ether at 25°C for 2 h, 1- and 2-tetradecenes were obtained in over 50% yield together with small amounts of 2-tetradecanol and 2-tetradecanone(Scheme 1: R = n-$C_{12}H_{25}$). Similar reaction also proceeded by using other oxidants such as hydrogen peroxide and t-butyl hydroperoxide, but the yield of the alcohol and the ketone was increased in these cases. Treatment of several other sec-alkyl phenyl tellurides with MCPBA also resulted in a facile formation of the expected olefins in good yields together with variable amounts of the corresponding alcohols and ketones. Typical results are shown in Table 1. The ratio of terminal to internal olefins observed here in the formation of linear olefins when R = n-C_6H_{13} and n-C_8H_{17} (1.5~1.7/1) is lower than that observed in the alkaline treatment of the corresponding organotellurium(IV) dibromide (ca. 2.5/1; elimination from dihydroxytelluranes)[1] and seems to be governed statistically by the number of hydrogen (CH_3 vs. CH_2) as in the cases

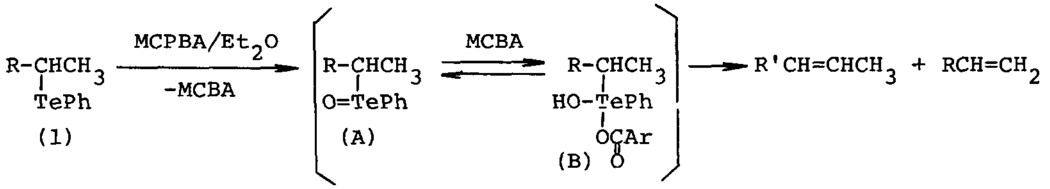
Table 1. Oxidation of tellurides with 1~1.5 equiv. oxidizing agents at 25°C for 2 h.

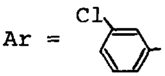
telluride	oxidant (equiv.)	solvent (5 ml)	product (yield, %)[a]
(1; R=n-C_6H_{13})	MCPBA(1)	Et_2O	1-octene(33), trans-2-octene(15), cis-2-octene(4), 2-octanol(10), 2-octanone(14)
(1; R=n-C_8H_{17})	MCPBA(1)	Et_2O	1-decene(29), 2-decenes(19),[b] 2-decanol(8), 2-decanone(10)
(1; R=n-$C_{12}H_{25}$)	MCPBA(1.5)	Et_2O	1- and 2-tetradecenes(54), 2-tetradecanol(1), 2-tetradecanone(2)
"	MCPBA(1)	EtOAc	1- and 2-tetradecenes(64), 2-tetradecanol(6), 2-tetradecanone(7)
"	H_2O_2(1.5)	THF/H_2O	1- and 2-tetradecenes(53), 2-tetradecanol(3), 2-tetradecanone(12)
"	t-BuOOH(1.5)	benzene	1- and 2-tetradecenes(48), 2-tetradecanol(15), 2-tetradecanone(26)
cycloheptyl phenyl telluride	MCPBA(1)	Et_2O	cycloheptene(70), cycloheptanol(1), cycloheptanone(8)
"	MCPBA(1)	EtOAc	cycloheptene(55), cycloheptanol(trace), cycloheptanone(trace)
cyclooctyl phenyl telluride	MCPBA(1)	Et_2O	cyclooctene(69), cyclooctanol(7), cyclooctanone(19)
cyclododecyl phenyl telluride	MCPBA(1)	Et_2O	trans-cyclododecene(67), cyclododecanol(7), cyclododecanone(7)
	MCPBA(1)	Et_2O	 (46)[c]
	MCPBA(1)	Et_2O	 (42)[c]

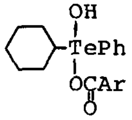
[a] Glpc yield with internal standard unless otherwise stated. [b] A cis/trans mixture. [c] Isolated yield. Several unidentified compounds were also detected.

of the selenoxide[3] and sulfoxide[4] eliminations. This may suggest that the elimiantion proceeded mainly through the telluroxide (A).

Scheme 1







(C)

It is known that pri-alkyl[1,5] and cyclohexyl phenyl telluroxides[1] are thermally stable enough to be isolated. In agreement with this fact the oxidation of 1-tetradecyl and cyclohexyl phenyl tellurides with MCPBA under similar conditions as above did not afford any corresponding olefins, alcohols, and ketones, and instead, organotellurium compounds were obtained as a yellow oil and a white solid, respectively. The pyrolysis of the yellow oil by Kugelrohr distillation apparatus(250°C/7 torr) afforded 1-tetradecene(42%), 1-tetradecanol(7%), and 1-tetradecanal(2%), while that of the white solid at 220-250°C/760 torr gave cyclohexene(19%) and cyclohexanol(1%). From spectral data the structure of the white solid(mp 166-169°C, ca. 30% isolated yield) can be assigned as (C), namely, the compound derived from oxidative addition of MCPBA to cyclohexyl phenyl telluride.[6] The yellow oil seems to have a similar structure as (C) since its IR spectrum is nearly the same as that of (C). These facts suggest that (A) in Scheme 1 may exist in equilibrium with its MCBA(m-chlorobenzoic acid) addition compound (B) in solution. Further studies to elucidate the relation between these adducts and telluroxide elimination are currently in progress.

References and Notes

1. S. Uemura and S. Fukuzawa, J. Am. Chem. Soc., **105**, 2748(1983).
2. It has been reported that the oxidation of three alkyl phenyl tellurides with t-butyl hydroperoxide gave olefins in relatively low yields, though the detailed reaction conditions are not known: K. B. Sharpless, K. M. Gordon, R. F. Lauer, D. W. Patrick, S. P. Singer, and M. W. Young, Chem. Scr., **8A**, 9(1975).

3. K. B. Sharpless, M. W. Young, and R. F. Lauer, Tetrahedron Lett., 1979 (1973).
4. J. R. Shelton and K. E. Davis, Int. J. Sulfur Chem., **8**, 197(1973).
5. H. Lee and M. P. Cava, J. Chem. Soc., Chem. Commun., 277(1981).
6. ^{1}H-NMR(CDCl$_3$) δ 0.8-2.6(m, 11H, including OH proton), 3.1-3.8(m, 1H), 6.9-7.7 (m, 5H), 7.7-8.1(m, 4H): ^{13}C-NMR(CDCl$_3$) δ 25.7(t), 28.2(t), 29.5(t), 60.6 (d, $\underline{C}$-Te), 127.7(d), 129.2(d), 129.5(d), 129.7(d), 130.0(s), 131.0(d), 131.2 (d), 133.0(d), 134.0(s), 136.4(s), 171.2(s): IR(KBr disk), 3600-3300(br), 3050(m), 2940(s), 2850(m), 1605(s), 1560(s), 1475(m), 1450(m), 1420(m), 1335(vs), 1260(m), 1180(m), 1065(m), 990(m), 865(m), 760(vs), 735(vs), 680(m), 610(s) cm^{-1}. Anal. for $C_{18}H_{21}O_3ClTe$, Found(Calcd); C 50.41(49.57), H 4.30(4.60).

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