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ALLYLIC ALCOHOLS FORMATION BY OXIDATION OF ALLYLIC PHENYL TELLURIDES. A POSSIBLE [2,3]SIGMATROPIC REARRANGEMENT OF ALLYLIC TELLUROXIDES

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Summary: Treatment of cinnamyl, 3-methyl-2-butenyl, and 2-cyclohexenyl phenyl tellurides with an oxidizing agent such as H_2O_2, $NaIO_4$, or t-BuOOH at room temperature under nitrogen affords 1-phenyl-2-propenol, 2-methyl-3-butene-2-ol, and 2-cyclohexenol as a sole or main product respectively in a high yield. The formation of these allylic alcohols can be best explained by assuming a [2,3]-sigmatropic rearrangement of the intermediate allylic telluroxides. These tellurides also react with oxygen, the formation of α,β-unsaturated carbonyl compounds being much increased in this oxidation.

In contrast to the well-known [2,3]sigmatropic rearrangement of allylic selenoxides,[1] the chemical behavior of telluroxide analogues is completely unknown to our knowledge. We report here the first example of the oxidation of allylic phenyl tellurides, the formation of main products being best explained by assuming a [2,3]sigmatropic rearrangement of the intermediate allylic telluroxides.

Treatment of a pale yellow heterogeneous ethanol solution of cinnamyl phenyl telluride(1), prepared from cinnamyl bromide and phenyl telluride anion($PhTe^-$) in freshly distilled ethanol under nitrogen, with an oxidizing agent such as hydrogen peroxide, sodium periodate, or tert-butyl hydroperoxide under nitrogen followed by normal workup procedure afforded four oxidation products, 2-5, the rearranged allylic alcohol 2 being the major product(Scheme 1). Allylic tellurides 6 and 10, prepared similarly in situ from the corresponding bromides, were also oxidized readily to give a good yield of allylic alcohols 7 and 11, respectively. Some of the results are aummarized in Table 1.

Contrary to air stable cinnamyl phenyl selenide, 1 was revealed to be very

Scheme 1

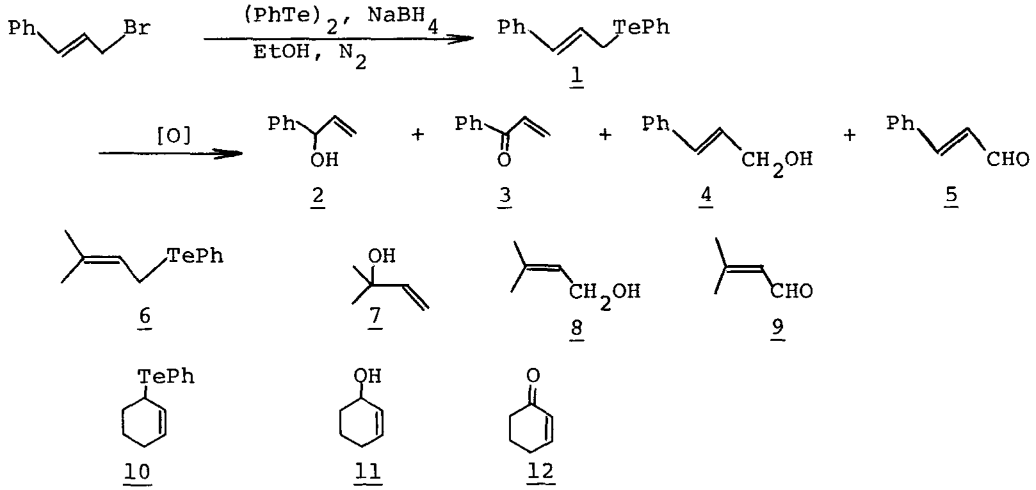


Table 1. Oxidation of allylic phenyl tellurides

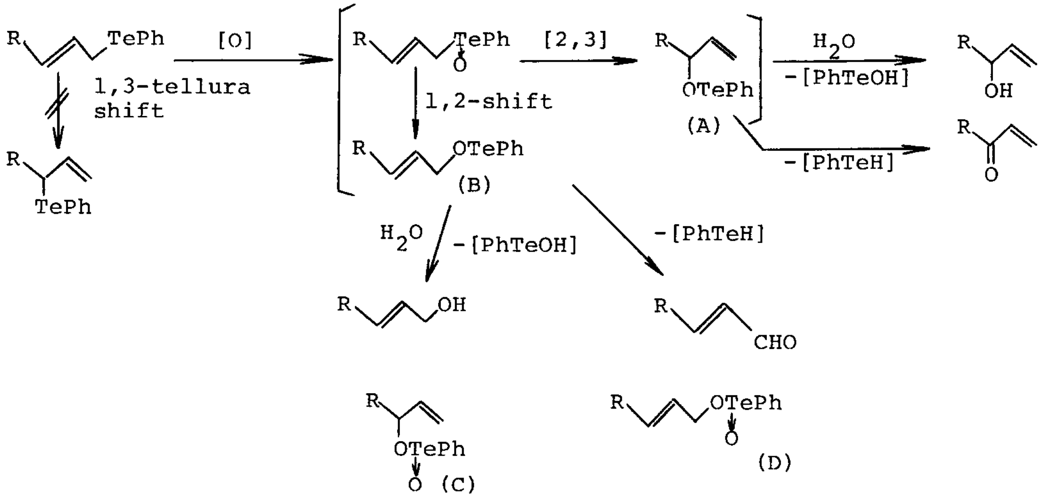
entry	telluride[a]	oxidant[b]	time, h[c]	product yield, %(ratio)[d]
				2:3:4:5
1	1	H_2O_2	2	57 (68:7:13:12)
2	1	t-BuOOH	1	90 (70:22:3:5)
3	1	$NaIO_4$	1.5	63 (68:5:14:13)
4	1	air	1	75 (19:46:4:31)
5	1	air	24	82 (24:43:4:29)
				7:8:9
6	6	H_2O_2	2	55 (94:4:2)
7	6	t-BuOOH	1	72 (93:1:6)
8	6	O_2	1	87 (82:10:8)
				11:12
9	10	H_2O_2	1	70 (86:14)
10	10	$NaIO_4$	1	96 (100:0)
11	10	O_2	1	100 (50:50)

[a] Prepared from allylic bromide(5 mmol), $(PhTe)_2$(2.5 mmol), $NaBH_4$(7 mmol) in freshly distilled EtOH(20 ml) at 15-20°C for 1-2 h. [b] Excess of air or O_2 and 15 mmol of other oxidant(30% H_2O_2, 70% t-BuOOH). [c] Time for oxidation at 15-20°C. [d] Determined by GLC. Compounds except 3 are commercial products. Compound 3 was prepared by Jones oxidation of 2.

air sensitive and could not be isolated under ambient atmosphere.[2] Eventually, it was disclosed that the introduction of air or oxygen to the pale yellow ethanol solution of 1 with stirring at room temperature also results in a formation of 2-5, α,β-unsaturated carbonyl compounds 3 and 5 being the major products in this case(entries 4 and 5 of Table 1). The tellurides 6 and 10 were also air sensitive and gave readily good yields of oxidation products by similar treatments(entries 8 and 11). On the other hand, allyl phenyl telluride[3] was revealed to be more stable to air and it can be handled in an open air for a while with a slight decomposition to allyl alcohol and acrolein.[4]

Considering a known [2,3]sigmatropic rearrangement of allylic selenoxides[1] together with known facts of direct oxidation of tellurides to telluroxides[5,6] and also with our finding that 1,3-tellura shift of 1 to 1-phenyl-2-propenyl phenyl telluride does not occur under the present conditions,[7] the formation of the rearranged allylic alcohols such as 2, 7, and probably 11 can be best explained by assuming Scheme 2: i.e., oxidation of allylic telluride to the telluroxide followed by its [2,3]sigmatropic rearrangement to tellurenic ester(A) and then its hydrolysis. On the other hand, non-rearranged allylic alcohols such as 4 and 8 are presumably formed by the hydrolysis of the tellurenic ester(B) which is produced by a 1,2-tellurium oxygen shift[5] of the allylic telluroxides.

Scheme 2



α,β-Unsaturated carbonyl compounds(enones) may arise from (A) and (B) by the intramolecular elimination of phenyltellurol(PhTeH). Tellurinic esters (C) and (D) derived from (A) and (B) by further oxidation may also be the precursors. Such precursor has already been postulated in selenium chemistry at the formation of an enone.[8] Phenyltellurol is rapidly oxidized to diphenyl ditelluride, while phenyltellurenic acid(PhTeOH) disproportionates to diphenyl ditelluride and $PhTeO_2H$. In the case of oxidation by oxygen there might be a possibility of the intervention of some alkoxy radical species as speculated in the reaction of benzyl tellurocyanate with oxygen under hν.[9] Further studies on the reaction mechanism are now in progress.

References and Notes

1. See for example, (a) D. L. J. Clive, Tetrahedron, 34, 1049(1978). (b) H. J. Reich, "Oxidation in Organic Chemistry", Academic Press: New York, NY, 1978, p. 1.
2. Under N_2 atmosphere 1 was isolated as a yellow solid: ^1H NMR(100 MHz, degassed $CDCl_3$) δ 3.76(2H, d, J=8 Hz), 6.02(1H, d, J=15.5 Hz), 6.40(1H, dt, J=15.5 and 8 Hz), 7.1-7.3(8H, m), 7.7-8.0(2H, m).
3. D. Seebach and A. K. Beck, Chem. Ber., 108, 314(1975).
4. By similar treatment of allyl phenyl telluride with air (at 30°C for 1 h) as entry 4 of Table 1, allyl alcohol(16%) and acrolein(14%) were obtained.
5. K. B. Sharpless, K. M. Gordon, R. F. Lauer, D. W. Patrick, S. P. Singer, and M. W. Young, Chem. Scr., 8A, 9(1975).
6. S. Uemura, K. Ohe, and S. Fukuzawa, submitted.
7. The ^1H NMR spectrum(100 MHz) of 1 in degassed $CDCl_3$ did not change at all even after 20 h at 25°C, the fact showing that isomerization of the double bond by a 1,3-tellura shift does not occur under this condition: cf. D. L. J. Clive, P. C. Anderson, N. Moss, and A. J. Singh, J. Org. Chem., 47, 1641 (1982). A facile thermal 1,3-selena shift has been known: K. B. Sharpless and R. F. Lauer, J. Org. Chem., 37, 3973(1972).
8. R. S. Brown, S. C. Eyley, and P. J. Parsons, J. Chem. Soc., Chem. Commun., 438(1984) and references therein.
9. H. K. Spencer, M. V. Lakshmikantham, M. P. Cava, J. Am. Chem. Soc., 99, 1470 (1977).

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