

## Double Bond Geometry of the Alkenes produced by Oxidative Elimination of Alkyl Phenyl Selenides and Tellurides

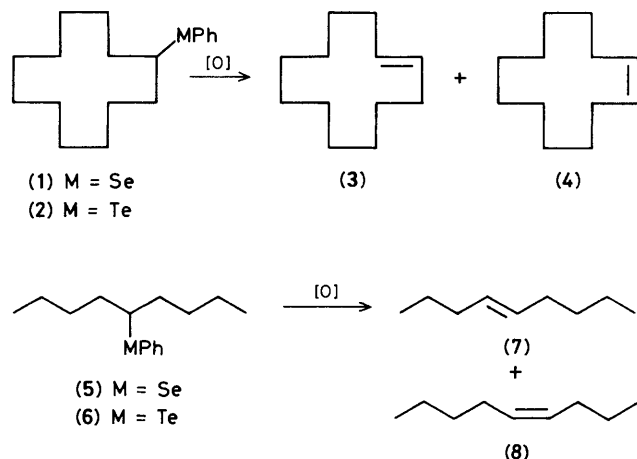
Sakae Uemura,\* Yasuyuki Hirai, Kouichi Ohe, and Nobuyuki Sugita

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

Treatment of secondary-alkyl phenyl selenides with various oxidants affords the corresponding *trans*-alkene highly selectively irrespective of the amount of oxidant, while in the case of the tellurium analogues the double bond geometry of the product alkene depends markedly on the amount of oxidant, the *trans*-isomer being formed highly selectively with 1 equiv. oxidant and the proportion of the *cis*-isomer being increased with excess (2–10 equiv.) of oxidant.

Oxidation of cyclododecyl phenyl selenide (1) is known to give a 1:1 mixture of *trans*- and *cis*-cyclododecene [(3) and (4) respectively] by selenoxide elimination,<sup>1</sup> while treatment of the dibromide of cyclododecyl phenyl telluride (2) with aqueous NaOH affords only (3) *via* the telluroxide or its hydrate.<sup>2</sup> We were concerned by this discrepancy as fragmentation of both selenoxides and telluroxides is assumed to be a *syn* elimination process.<sup>1,3</sup> Herein, we report new evidence which clarifies the relationship between the double bond geometry of the alkene obtained from secondary-alkyl phenyl selenides and tellurides and the amount of oxidant used.

First, we re-examined the experiment by Sharpless *et al.*<sup>1</sup> on the oxidation of (1) with H<sub>2</sub>O<sub>2</sub> (70%) under conditions as similar as possible to those employed by them and found that the main products are (3) and cyclododecene oxide together with a small amount of (4), in a sharp contrast to their result of a quantitative yield of a 1:1 mixture of (3) and (4).<sup>†</sup> Oxidation of (1) with various oxidizing agents such as H<sub>2</sub>O<sub>2</sub> (30%), *m*-chloroperbenzoic acid, and NaIO<sub>4</sub> at 25 °C for 2–24 h afforded (3) in excellent yield irrespective of the amount of oxidant used (1–10 equiv. to the selenide). In almost all cases (3) is the sole product. Oxidation of cyclododecyl phenyl telluride (2) was similarly carried out as in the case of (1) to give also (3) and (4) as main products (54–77% yield),

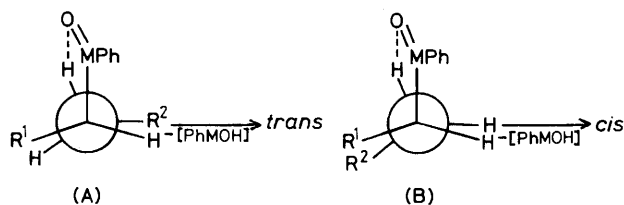


<sup>†</sup> The selenide (1) was dissolved in tetrahydrofuran (THF), and excess (10 equiv.) of 70% H<sub>2</sub>O<sub>2</sub> was added, with cooling in an ice bath. Upon completion of oxidation (0 °C for 3 h), as determined by t.l.c. (Merck, Silica Gel 60 F<sub>254</sub>), the reaction mixture was kept at 25 °C for 3 h. G.l.c. analysis was carried out using an EGSS-X(15%)-Chromosorb W (3 m) column at 110 °C for (3) and (4), and using a Silicone DC QF-1(30%)-Chromosorb W (1 m) column at 160 °C for cyclododecene oxide (N<sub>2</sub> as carrier gas). The alkene (3) [contaminated by a small amount of (4)] and cyclododecene oxide were isolated by column chromatography using hexane and hexane–ethyl acetate as eluants, respectively, their <sup>1</sup>H-n.m.r. and i.r. spectra being identical with those of authentic samples. Results (Table 1) were reproducible.

although their yields were slightly lower than those from the selenide because of the formation of side products such as cyclododecanol (3–15%) and cyclododecanone (1–7%). In contrast to the selenide, with telluride the double bond geometry of the product alkene was markedly dependent upon the amount of oxidant employed. When 1 equiv. of oxidant with respect to the telluride was used, (3) was nearly the sole product. On the other hand, the use of excess of oxidant (even 2 equiv.) resulted in formation of a mixture of (3) and (4), in some case (4) being the major product. Typical results are shown in Table 1. We confirmed separately that interconversion between (3) and (4) did not occur at all under these reaction conditions in both selenide and telluride cases.

A similar phenomenon was also observed in the oxidation of 5-nonyl phenyl selenide (5) and telluride (6) to afford the corresponding alkenes, *trans*- and *cis*-non-4-ene (7) and (8) respectively. Thus, in the case of (5) the formation of (7) was overwhelming and the ratio of (7) to (8) was not affected by the amount of oxidant, whereas in the case of (6) the proportion of the *cis*-alkene was increased by use of excess of oxidant (Table 1).

To consider the mechanism for the formation of the *trans*- and *cis*-alkene, the following facts should be noted. First, selenoxide elimination proceeds much faster than telluroxide elimination.<sup>2,4</sup> Secondly, in contrast to the slow oxidation of selenoxide to selenone,<sup>5</sup> the oxidation of telluroxide to tellurone seems to be rather fast since the clean oxidation of tellurides to telluroxides is difficult and often results in over-oxidation to afford a mixture of telluroxides and tellurones.<sup>4,6</sup> In oxidation with 1 equiv. of oxidant alkenes will be produced *via* selenoxides and telluroxides (*E*<sub>1</sub> mechanism), and two conformers (A) and (B) (or their hydrates) are conceivable; (A) is much more stable than (B) owing to the steric repulsion of the two bulky alkyl groups and should give mainly the *trans*-isomer in agreement with experimental results. The sole or highly selective formation of the *trans*-isomer from the selenide even in the presence of excess of oxidant can be explained by the above reasons. On the other hand, the *cis*-isomer from the telluride in the presence of excess of oxidant might be derived from a further oxidized species, the tellurone PhTe(O)<sub>2</sub>R, or its 1,2 tellurium–oxygen shift product, the tellurinic ester PhTe(O)OR (R = cyclo-



M = Se, Te  
R<sup>1</sup> R<sup>2</sup> = –[CH<sub>2</sub>]<sub>10</sub>–  
R<sup>1</sup> = Bu<sup>n</sup>, R<sup>2</sup> = Pr<sup>n</sup>

**Table 1.** Oxidation of alkyl phenyl selenides and tellurides.<sup>a</sup>

Substrate	Oxidant <sup>b</sup>	Mol equiv. <sup>c</sup>	Reaction time/h	Yield of alkenes/% <sup>d</sup>	Molar ratio <sup>d</sup> <i>trans</i> : <i>cis</i>
(1)	H <sub>2</sub> O <sub>2</sub>	1	2	94	100 : 0
(1)	H <sub>2</sub> O <sub>2</sub>	10	3	83	100 : 0
(1) <sup>e</sup>	70% H <sub>2</sub> O <sub>2</sub>	10	6	54 <sup>f</sup>	95 : 5
(2)	H <sub>2</sub> O <sub>2</sub>	1	2	56	91 : 9
(2)	H <sub>2</sub> O <sub>2</sub>	10	2	65	51 : 49
(2)	NaIO <sub>4</sub>	1	24	54	100 : 0
(2)	NaIO <sub>4</sub>	5	24	77	30 : 70
(5)	H <sub>2</sub> O <sub>2</sub>	1	2	96	84 : 16
(5)	H <sub>2</sub> O <sub>2</sub>	10	2	96	83 : 17
(5)	NaIO <sub>4</sub>	5	24	100	84 : 16
(6)	H <sub>2</sub> O <sub>2</sub>	1	2	57	82 : 18
(6)	H <sub>2</sub> O <sub>2</sub>	10	2	53	65 : 35
(6)	NaIO <sub>4</sub>	1	24	64	83 : 17
(6)	NaIO <sub>4</sub>	5	24	72	59 : 41

<sup>a</sup> Carried out at 25 °C using 0.5–2 mmol of substrate and THF and 50% aq. THF (10–20 ml) as solvent for H<sub>2</sub>O<sub>2</sub> and NaIO<sub>4</sub> respectively.

<sup>b</sup> H<sub>2</sub>O<sub>2</sub> = 30% aqueous H<sub>2</sub>O<sub>2</sub>. <sup>c</sup> Oxidant to substrate. <sup>d</sup> Determined by g.l.c. <sup>e</sup> Re-examination of ref. 1. <sup>f</sup> Isolated yield. Cyclododecene oxide was also isolated in 39% yield.

C<sub>12</sub>H<sub>23</sub>, CHBu<sup>n</sup><sub>2</sub>), although direct evidence for this has not yet been obtained.

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#### References

- 1 K. B. Sharpless, M. W. Young, and R. F. Lauer, *Tetrahedron Lett.*, 1973, 1979.
- 2 S. Uemura and S. Fukuzawa, *J. Am. Chem. Soc.*, 1983, **105**, 2748.
- 3 K. B. Sharpless, K. M. Gordon, R. F. Lauer, D. W. Patrick, S. P. Singer, and M. W. Young, *Chem. Scr.*, 1975, **8A**, 9.
- 4 H. Lee and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 1981, 277.
- 5 For example, H. J. Reich, 'Oxidation in Organic Chemistry,' part C, ed. W. S. Trahanovsky, Academic Press, New York, 1978, pp. 7–12.
- 6 M. R. Detty, *J. Org. Chem.*, 1980, **45**, 274.