Organotellurium Chemistry. The Telluroxide Elimination Reaction[1]

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Summary In an effort to clarify the nature of the organotelluroxide elimination reaction, dodecyl-(4-methoxyphenyl)tellurium oxide and dioxide were thermolysed; mechanisms involving tellurenic acid for the oxide and a 1,2-oxygen shift for the dioxide are proposed.

THE synthesis of olefins by the *syn*-elimination of a selenoxide, although first discovered only a decade ago, has been the subject of intense investigation and has become one of the most widely employed modern synthetic reactions.[2] In contrast, the corresponding behaviour of telluroxides has remained obscure, to our knowledge the only specific report being that by Sharpless *et al.*,[3] who reported that t-butyl hydroperoxide oxidation of several tellurides in benzene gave mixtures of olefins, presumably *via syn*-elimination of the corresponding telluroxides. 3α-Phenyltellurocholestane was oxidized in the same manner to give an approximately equal mixture of olefins and alcohols.

The alcohol products were ascribed to the result of a 1,2-shift in *either* the corresponding oxide or the dioxide. Intermediate oxidation products were not isolated. We now report preliminary studies which clarify the nature of the telluroxide elimination reaction.

4-Methoxyphenyl n-dodecyl telluride (**1**)† was converted into the corresponding oxide (**2**) (or oxide hydrate) by a method which is known not to cause overoxidation of the tellurium atom.[4] Thus, reaction of (**1**) with *N*-bromosuccinimide (NBS) in methanol–dichloromethane, followed by aqueous sodium hydroxide, gave (**2**) which was also formed in high yield by addition of bromine in CCl_4 to (**1**) to give the corresponding alkyl-aryl-tellurium dibromide (m.p. 34 °C), followed by alkaline hydrolysis.‡ The purity of (**2**) was confirmed by its quantitative reduction to (**1**) by sodium borohydride.

A solution of (**2**) in CCl_4 was unchanged after several hours at room temperature, but after refluxing (80 °C) for 24 h, the

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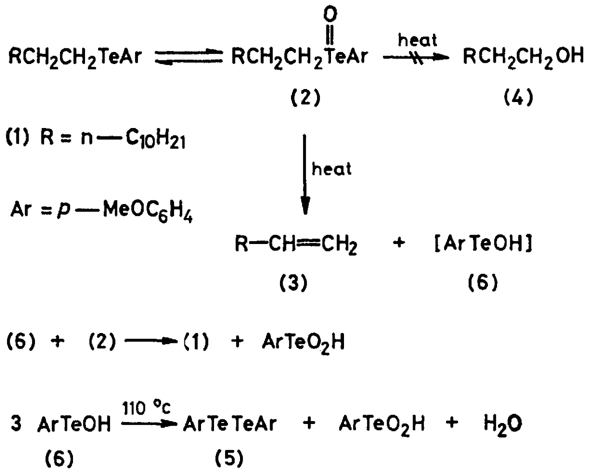
† The telluride (**1**) (m.p. 26—28 °C) was prepared by the reduction of the ditelluride (**5**) with $NaBH_4$ in propan-2-ol, followed by reaction with 1-bromododecane.

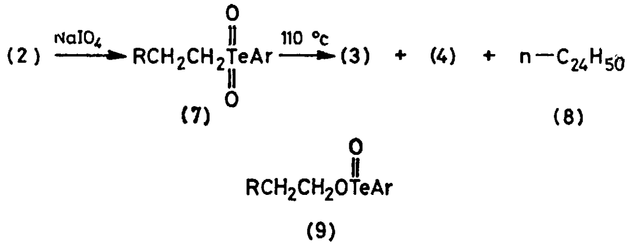
‡ Diaryl telluroxides have been prepared in this manner: K. Lederer, *Liebig's Ann. Chem.*, 1912, **391**, 326.

oxide decomposed with the formation of an equimolar mixture of dodec-1-ene (**3**) and the telluride (**1**); dodecan-1-ol (**4**) was not produced. When (**2**) was thermolysed in toluene (110 °C) for 12 h, a *ca.* 7:5 ratio of olefin (**3**) to telluride (**1**) was observed, in addition to a small amount of the brown diaryl ditelluride (**5**), but again no alcohol (**4**) was detected. The thermal decomposition of the oxide (**2**) thus parallels the known decomposition of n-decyl phenyl selenoxide in CCl_4 to an equimolar mixture of dec-1-ene and the parent selenide;[5] a similar mechanism may be proposed, in which an arenetellurenic acid intermediate (**6**) reduces half of the original oxide back to the corresponding telluride. The formation of some ditelluride (**5**) and an observed ratio of olefin to telluride of $>1:1$ at 110 °C, are consistent with the competitive thermal disproportionation of the tellurenic acid (**6**) at this higher temperature (Scheme 1).



SCHEME 1

Sodium periodate oxidation of the oxide (**2**) affords a new species, formulated as the dioxide (**7**) (or its hydrate). Thermolysis of (**7**) in toluene (110 °C) for 40 h gave none of the telluride (**1**); the major products were the olefin (**3**) (55%) and the alcohol (**4**) (15%), along with a small amount of n-tetracosane (**8**). The alcohol (**4**) is probably derived from (**7**) *via* its rearrangement product, the tellurinic ester (**9**), which may also be the precursor of (**3**) and (**8**) in this reaction (Scheme 2).



SCHEME 2

Finally, oxidation of the telluride (**1**) in benzene with 1 equiv. of t-butyl hydroperoxide affords a 1:2:1 mixture of the telluride (**1**), the oxide (**2**), and the dioxide (**7**). This oxidant is not, therefore, suitable for the selective oxidation of a telluride to the corresponding telluroxide.

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[1] For Part 4 of the series Organotellurium Chemistry, see S. J. Falcone and M. P. Cava, *J. Org. Chem.*, 1980, **45**, 1044.

[2] For a recent review, see H. J. Reich, *Acc. Chem. Res.*, 1979, **12**, 22.

[3] K. B. Sharpless, K. M. Gordon, R. F. Lauer, D. W. Patrick, S. P. Singer, and M. W. Young, *Chem. Scr.*, 1975, **8*A***, 9.

[4] M. J. Detty, *J. Org. Chem.*, 1980, **45**, 274.

[5] R. D. Clark and C. J. Heathcock, *J. Org. Chem.*, 1976, **41**, 1396.