Synthesis and Reactions of Bis(p-methoxyphenyl)tellurone

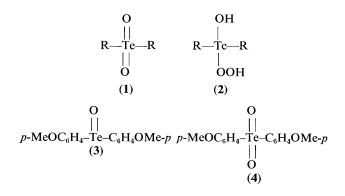
Lars Engman and Michael P. Cava*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, U.S.A.

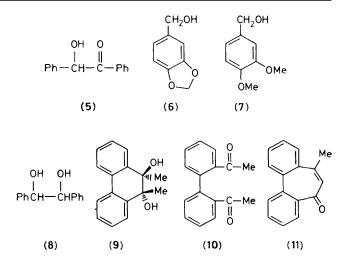
Bis(*p*-methoxyphenyl)tellurone, the first definitely characterized tellurone, has been prepared by periodate oxidation of the corresponding telluroxide and its oxidizing properties have been studied.

Diaryl and dialkyl tellurones, R_2TeO_2 (1), the tellurium analogues of the well known sulphones, are ill defined substances. It is doubtful whether a substance corresponding to the formula R_2TeO_2 has ever been obtained in pure form.¹ Early attempts to oxidize diaryl and dialkyl tellurides and telluroxides with hydrogen peroxide,^{2,3} probably resulted in formation of 'hydroxy-perhydrates' (2), instead of the purported tellurones. These compounds possessed all the characteristics of a peroxide; thus they had explosive properties and oxidized halogen acids to the corresponding halogen.⁴

Recent interest in the mild oxidizing properties of bis(*p*-methoxyphenyl)telluroxide (3),^{5,6} prompted us to investigate its further oxidation to the tellurone. We have found that this transformation can be effected readily using NaIO₄, to give bis(*p*-methoxyphenyl)tellurone (4) in 82% yield as a high-melting white material giving satisfactory analytical data.[†]



† NaIO₄ (8.4 mmol) in H₂O (50 ml) was added dropwise at room temperature to a solution of bis(*p*-methoxyphenyl)telluroxide (8.4 mmol) in MeOH (50 ml). After 3 h the white product was filtered and dried at 70 °C. The crude tellurone was then dissolved in boiling CHCl₈ (150 ml) and filtered from some insoluble material. Evaporation, recrystallization from MeOH-H₂O, and drying at 70 °C afforded 2.59 g (82%) of bis(*p*-methoxyphenyl)-tellurone, m.p. > 300 °C. The material gave satisfactory analytical data (C, H, Te \pm 0.4%).



Further evidence for the structure was obtained by reduction of the tellurone with methanolic hydrazine hydrate to give bis(p-methoxyphenyl)telluride (87%).

We have found that bis(p-methoxyphenyl)tellurone is a relatively mild oxidant, capable of effecting a variety of organic transformations. These reactions were typically carried out in refluxing toluene and the products isolated by column chromatography. Thus, benzenethiol was oxidized to diphenyl disulphide (97%) and hydroquinone converted into *p*-benzoquinone (39%). Bis(*p*-methoxyphenyl)telluroxide (3) does not react with simple alcohols.⁵ However, the corresponding tellurone (4) oxidizes benzylic alcohols to the corresponding carbonyl compounds. Benzoin (5), piperonyl alcohol (6), and veratryl alcohol (7) could be oxidized to benzil (89%), piperonal (72%), and veratraldehyde (79%), respectively.

Attempted oxidation of hydrobenzoin (8) with the tellurone (4) gave, surprisingly, a 79% yield of benzaldehyde. The formation of a substantial amount of bis(p-methoxyphenyl)-telluride in this experiment, indicated that the telluroxide (3) also might be capable of effecting this cleavage reaction. That

this is indeed the case was shown in a separate experiment (75%) yield of benzaldehyde).

The diol (9) was cleaved by the tellurone (4) to give a mixture of 2,2'-diacetylbiphenyl(10)(38%) and the unsaturated ketone (11) (51%), a secondary cyclization product.

The recently postulated thermal rearrangement of an alkyl aryl tellurone (or its hydrate), to a tellurinic ester $(12) \rightarrow (13)$,⁷ was not observed for bis(*p*-methoxyphenyl)tellurone (boiling 24 h in *N*,*N*-dimethylformamide followed by NaBH₄-reduction gave no phenolic products).

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$$\begin{array}{ccc} O & O \\ || & || \\ R-Te-Ar & R-O-Te-Ar \\ || \\ O \\ (12) & (13) \end{array}$$

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