Synthesis and Reactions of Bis(*p*-methoxyphenyl)tellurone

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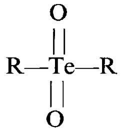
Bis(*p*-methoxyphenyl)tellurone, the first definitely characterized tellurone, has been prepared by periodate oxidation of the corresponding telluroxide and its oxidizing properties have been studied.

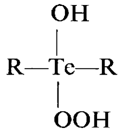
Diaryl and dialkyl tellurones, R_2TeO_2 (**1**), the tellurium analogues of the well known sulphones, are ill defined substances. It is doubtful whether a substance corresponding to the formula R_2TeO_2 has ever been obtained in pure form.[1] Early attempts to oxidize diaryl and dialkyl tellurides and 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 $NaIO_4$, to give bis(*p*-methoxyphenyl)tellurone (**4**) in 82% yield as a high-melting white material giving satisfactory analytical data.†



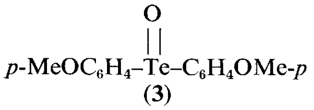
$$R-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Te}}-R$$

(**1**)



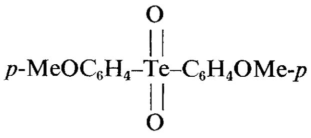
$$R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OOH}{|}}{Te}}-R$$

(**2**)



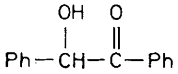
$$p\text{-}MeOC_6H_4-\overset{\overset{\displaystyle O}{\|}}{Te}-C_6H_4OMe\text{-}p$$

(**3**)



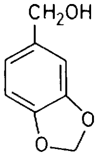
$$p\text{-}MeOC_6H_4-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Te}}-C_6H_4OMe\text{-}p$$

(**4**)

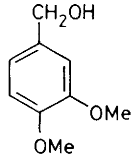


$$Ph-\overset{\overset{\displaystyle OH}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}-Ph$$

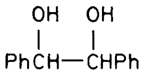
(**5**)



(**6**)

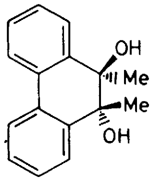


(**7**)

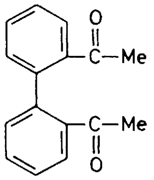


$$Ph\overset{\overset{\displaystyle OH}{|}}{CH}-\overset{\overset{\displaystyle OH}{|}}{CH}Ph$$

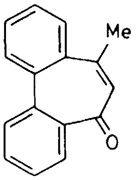
(**8**)



(**9**)



(**10**)



(**11**)

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

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† $NaIO_4$ (8.4 mmol) in H_2O (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 $CHCl_3$ (150 ml) and filtered from some insoluble material. Evaporation, recrystallization from MeOH–H_2O, 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 ± 0.4%).

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)** → **(13)**,[7] was not observed for bis(*p*-methoxyphenyl)tellurone (boiling 24 h in *N*,*N*-dimethylformamide followed by $NaBH_4$-reduction gave no phenolic products).

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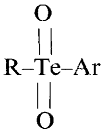
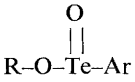


$$\mathrm{R{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Te}}{-}Ar}$$

(12)



$$\mathrm{R{-}O{-}\overset{\overset{O}{\|}}{Te}{-}Ar}$$

(13)

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