Catalytic Debromination of Vicinal Dibromides *via* Phase Transfer of Diaryltellurium Compounds

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Synopsis. Several vicinal dibromides were debrominated to olefins by potassium disulfite in the presence of catalytic amounts of bis(4-methoxyphenyl) telluride in a two-phase system.

In recent years, there has been remarkable interest in the development of new synthetic methods using organotellurium compounds.[1] However, there have been only a limited number of successes involving the catalytic use of organotellurium compounds and/or tellurium salts.[2,3] Now we wish to report that several vicinal dibromides have been debrominated to their corresponding olefins by potassium disulfite in the presence of catalytic amounts of diaryltellurium compounds.

First, the debromination of *erythro*-1,2-dibromo-1,2-diphenylethane (**1**) in the presence of bis(4-methoxyphenyl) telluride (**3**) was investigated. The reaction system was composed of an aqueous potassium disulfite solution (0.5 mol dm^{-3}, 20 cm^3) and benzene (30 cm^3) as an organic phase that included the dibromide (**1**) and catalytic amounts of **3**. Upon stirring the two-phase system at a benzene-refluxing temperature, dibromide **1** was reduced to *trans*-stilbene (**2**) at varying rates, depending upon the amounts of **3** (Fig. 1). In this experiment, *cis*-stilbene was not found in detectable amounts by GLPC (<1%). In a blank experiment without **3**, the formation of **2** was not observed even after 24 h. Thus, apparently the presence of the diaryl telluride **3** is necessary for the conversion of **1** into **2**. It is interesting that **1** was quantitatively reduced to **2** in the presence of only 5% mol amounts of **3** after a 24 h run (Run 3, Fig. 1). Debromination was speeded up as the concentration of **3** was increased. Thus, in the presence of 10 and 20% mol amounts of **3**, debromination was complete in 12 h and 2 h, respectively (Runs 1 and 2, Fig. 1). On the other hand, in experiments with much smaller amounts of **3**, debromination was incomplete even after prolonged heating; 63% in the presence of 2% mol amounts of **3** and 33% in the presence of 1% mol amounts of **3** (Runs 4 and 5, Fig. 1). From the latter two experiments, the maximum turnover number of the diaryl telluride **3** can be roughly estimated to be 30.

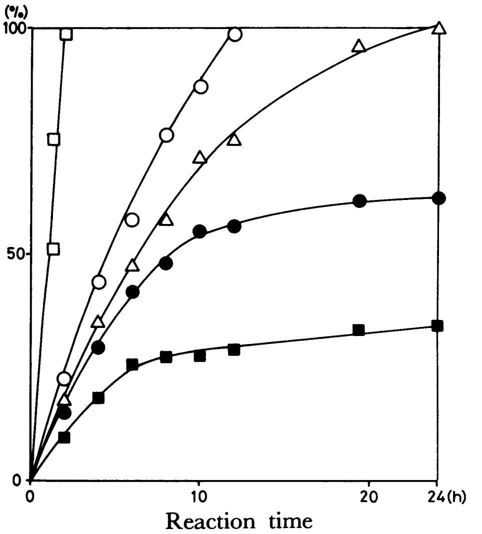
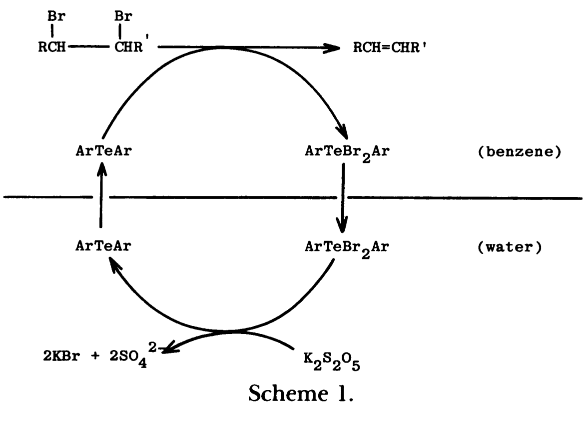


Fig. 1. Catalytic debromination of *meso*-1,2-dibromo-1,2-diphenylethane by $K_2S_2O_5$ using bis(4-methoxyphenyl) telluride (**3**).
Run 1, □: 20% mole amounts, Run 2, ○: 10% mole amounts, Run 3, △: 5% mole amounts, Run 4, ●: 2% mole amounts, Run 5, ■: 1% mole amounts.

It is widely known that a class of diaryltellurium(II) species are easily brominated to diaryltellurium(IV) dibromides with a variety of brominating reagents, including vicinal dibromide, and that the debromination of diaryltellurium(IV) dibromides can be achieved upon treatment with potassium disulfite in hot water.[4] Therefore, the catalytic cycle of the debromination of **1** can be plausibly depicted as shown in Scheme 1, where the diaryltellurium compound, itself, acts as an electron carrier. Indeed, bis(4-methoxyphenyl) tellurium dibromide (**4**) is soluble enough in water to be consistent with the mechanism in Scheme 1. Further, the addition of **4**, instead of **3**, to the reaction mixture also effected the debromination of **1** with a similar efficiency.

The debromination of other vicinal dibromides was tried under the same conditions as Run 3 in Fig. 1. The results are summarized in Table 1. Only *trans*-stilbene and *trans*-4-styrylpyridine were obtained from *erythro*-dibromides, whereas debromination from *threo*-1,2-dibromo-1,2-diphenylethane was modestly stereoselective. Chalcone and ethyl cinnamate were similarly obtained from corresponding dibromides in 61 and 57% yields, respectively. However, 1,2-dibromocyclohexadecane was not debrominated under these conditions.[6]



Scheme 1.

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Table 1. Two-phase debromination of vicinal dibromides by potassium disulfite using bis(4-methoxyphenyl) telluride

	Dibromide [$R^1CH(Br)CH(Br)R^2$]	Olefin (*trans/cis*)	Yield/%[b]
1	R^1=R^2=Ph *erythro*	PhCH=CHPh (100/0)	100 (92)[c]
2	R^1=R^2=Ph *threo*	PhCH=CHPh (6/94)	100 (88)[c]
3	R^1=Ph, R^2=4-pyridyl *erythro*	PhCH=CH-4-pyridyl (100/0)	100
4	R^1=Ph, R^2=COPh	PhCH=CHCOPh (100/0)	61
5	R^1=Ph, R^2=CO_2Et	$PhCH=CHCO_2Et$ (100/0)	57
6	R^1=H, R^2=$C_{14}H_{29}$	$CH_2=CHC_{14}H_{29}$	0

a) All reactions were performed as described in detail in the text. b) GLPC yield. c) Isolated yield.

Experimental

Bis(4-methoxyphenyl) telluride was prepared according to the method of Bergman.[5]

General Procedure for the Catalytic Debromination of Vicinal Dibromides by Potassium Disulfite Using Bis(4-methoxyphenyl) Telluride. To a solution of vicinal dibromide (1 mmol) and bis(4-methoxyphenyl) telluride (17 mg, 0.05 mmol) in 30 cm^3 of benzene was added a solution of potassium disulfite (2.22 g, 10 mmol) in 20 cm^3 of water. The resulting mixture was refluxed with vigorous stirring for a suitable time. The progress of the reaction was followed by GLPC (a Hitachi Model 163, using a 3 mm×2 m stainless steel column packed with 10% SE 30 on Celite 545 AW). After completion of the reaction , the reaction mixture was cooled to room temperature. The organic layer was separated, washed with water, dried over Na_2SO_4, and evaporated to give the crude product, which was purified by chromatography over silica gel. The products were identified by comparison with the authentic samples.

References

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6) Irradiation with high-pressure Hg lamp of benzene solution of 1,2-dibromohexadecane and equimolar amounts of bis(4-methoxyphenyl) telluride gave rise to the formation of 1-hexadecene in 70% yield. However, irradiation of two-phase system described in this paper in the presence of catalytic amounts of **3** did not give the olefin.