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A MILD AND EFFICIENT DEBROMINATION OF VICINAL DIBROMOALKANES WITH SODIUM TELLURIDE PREPARED FROM TELLURIUM AND RONGALITE

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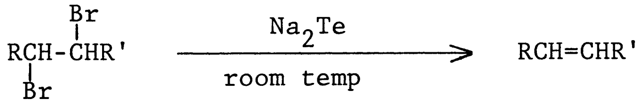
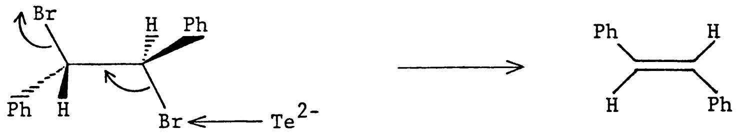
Vicinal dibromoalkanes are debrominated to alkenes with remarkable ease by treatment with sodium telluride prepared from tellurium and Rongalite in aqueous alkaline medium.

When gently heated with Rongalite (sodium formaldehydesulfoxylate dihydrate; $HOCH_2SO_2Na \cdot 2\ H_2O$) in dilute aqueous sodium hydroxide, tellurium is reduced to afford sodium telluride as a wine-colored solution.[1)] We wish to report herein that vicinal dibromoalkanes are rapidly debrominated with this solution to give alkenes in good yields. The debromination proceeds smoothly and cleanly to completion at room temperature, and no side-reactions are observed.



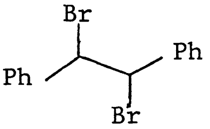
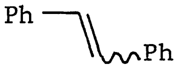
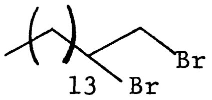
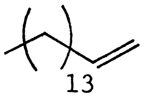
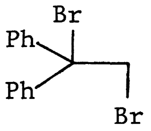
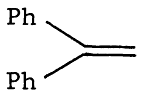
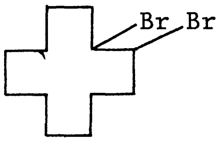
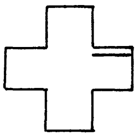
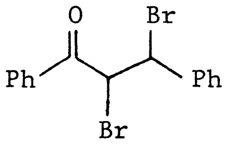
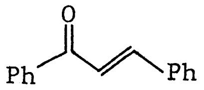
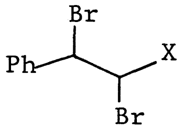
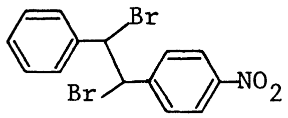
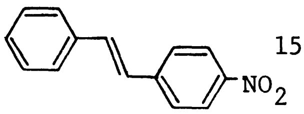
$$\underset{\mathrm{Br}}{\mathrm{RCH}}-\overset{\mathrm{Br}}{\mathrm{CHR'}} \xrightarrow[\text{room temp}]{\mathrm{Na_2Te}} \mathrm{RCH{=}CHR'}$$

The reaction is of considerable synthetic interest, particularly when a molecule contains other reducible groups such as carbonyl, carboxyl, ester and nitro groups, because all of these remain unaffected during the debromination. The elimination of bromine atoms is apparently stereoselective and the stereochemical results support the concerted *anti*-elimination process in which one might postulate a nucleophilic attack of telluride ion on bromine atom as shown below:



The debromination of vicinal dibromoalkanes with sodium telluride leads to the liberation of elementary tellurium, which suggests that the reaction may be

Table 1. Debromination of vicinal dibromides with sodium telluride

Substrate	Method	Product	Mp θm/°C or Bp θm/°C(Torr)	Yield/%a)
				
meso-	B	only Eb)	126-128	98
d,l-	A	E/Z=16/74	—	90
	B		168-173(15)	82
	A		168-173(32)	92
	B		140-144(32)	77
	A		53-55	91
				
X=CO_2H	A		134-135	90
X=CO_2Et	A		165-173(33)	80
	Ac)		153-155	89

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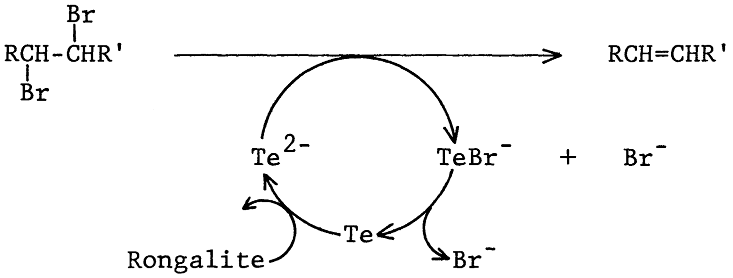
a) Yield is based on the isolated compounds. Products are all known, and identified by IR, NMR, and MS spectra as well as by direct comparison with authentic specimens.

b) Isomeric ratio was determined by GLC.

c) Partial reduction of nitro group occurred with Method B.

carried out using a catalytic amount of tellurium, since sodium telluride is readily regenerated in the presence of excess Rongalite. This is indeed the case when dibromoalkanes which are stable toward moderate heating are used (heating is essential to convert tellurium into telluride). Thus, *meso*-1,2-dibromo-1,2-diphenylethane, 1,2-dibromohexadecane and 1,2-dibromocyclododecane are successfully debrominated by this procedure to give parent olefines in 98, 82 and 77% isolated yields respectively. Without tellurium, debromination does not take place. A probable reaction sequence followed by the tellurium-catalyzed debromination may be depicted as below:[2)]



Addition of bromine to double bond and subsequent debromination of dibromides to regenerate original double bond have been accepted as a useful method for protecting the olefinic functions toward oxidizing and reducing agents. Although there are a wide variety of methods available to effect such transformations,[3)] our procedure is an attractive addition to the existing methodology in that a combination of tellurium and Rongalite is cheap and readily available, the manipulation is simple to perform, the chemoselective reaction completes instantaneously under mild conditions, and good yields of olefinic products are obtained in a state of high purity.

The typical procedures are illustrated below by two examples, one of which uses a stoichiometric amount (Method A), and the other a catalytic amount of tellurium (Method B).

Method A: To a wine-colored solution of sodium telluride, prepared by heating a mixture of powdered tellurium (3.0 mmol), Rongalite (6.0 mmol), and 1 M sodium hydroxide solution (15 ml) at 70 °C, ethyl 2,3-dibromo-3-phenylpropionate (3.0 mmol) in dioxane (5 ml) was added dropwise under nitrogen at room temperature. The reaction immediately proceeded to completion with the separation of elementary tellurium. The mixture was then filtered through a thin bed of Celite 535, and the filtrate was extracted with ether. The extract was washed with water, dried over sodium sulfate, and evaporated to leave a colorless oil, which was distilled by Kugelrohr apparatus under reduced pressure to give pure ethyl cinnamate. Yield, 80%.

Method B: A solution of 1,2-dibromohexadecane (3.0 mmol) in ethanol (5 ml) was added to a mixture of powdered tellurium (0.3 mmol), Rongalite (6.0 mmol), and 1 M sodium hydroxide solution (15 ml) under nitrogen at room temperature. After being stirred at 70 °C until the color of the solution turned deep red, excess reagent was destroyed by the addition of 2 M hydrochloric acid (10 ml). The resulting black suspension was worked up as described for Method A to afford 1-hexadecene. Yield, 82%.

References

1) L. Tschugaeff and W. Chlopin, Chem. Ber., 47, 1269 (1914). Other methods for preparation of this reagent are:
Tellurium/sodium in liquid ammonia: F. H. Burstall and S. Sugden, J. Chem. Soc., 1930, 229.
Tellurium/sodium borohydride: J. Bergman and L. Engman, Z. Naturforsch., B, 35B, 217 (1980).
Tellurium/sodium in DMF: D. J. Sandman, J. C. Stark, L. A. Acampora, and P. Gange, Organometallics, 2, 549 (1983).

2) Catalytic debromination of vicinal dibromides has been recently reported, where sodium borohydride/bis(2-thienyl)ditelluride was used as the debrominating reagent: L. Engman, Tetrahedron Lett., 23, 3601 (1982). Literature so far contains several examples of dehalogenation based on sodium telluride:
W. Mack, Angew. Chem., Int. Ed. Engl., 6, 1083 (1967);
E. Cuthbertson and D. D. MacNicol, J. Chem. Soc., Chem. Commun., 1974, 498;
E. Luppold and W. Winter, Chem.-Ztg., 101, 303 (1977).

3) For a general survey, see: M. Schlosser, "Houben-Weyl, Methoden der Organischen Chemie," 4th ed, ed by E. Müller, Georg Thieme Verlag, Stuttgart (1972), Vol. 5/1b, p. 180; D. W. Young, "Protective Group in Organic Chemistry," ed by J. F. W. McOmie, Plenum Press, London (1973), p. 309. Also see, I. M. Mathai, K. Schug, and S. I. Miller, J. Org. Chem., 35, 1733 (1970); J. E. Gordon and V. S. K. Chang, ibid., 38, 3062 (1973) and references cited therein.

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