

CATALYTIC DEBROMINATION OF VICINAL DIBROMIDES

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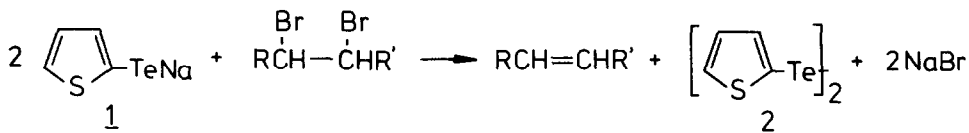
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Abstract: A number of vicinal dibromides were debrominated using sodium borohydride and a catalytic amount of bis(2-thienyl)ditelluride.

Olefins are commonly protected as dibromides through reaction sequences involving strongly oxidizing or reducing agents.<sup>1</sup> Debromination has been accomplished with a large variety of reagents<sup>2-4</sup> including metals (zinc, magnesium, sodium) metal ions (Cr(II), Fe(II), Ti(II), Sn(II)) and different nucleophilic reagents (halide ions, thiolates, phosphites, phosphines, metal hydrides). More recently reagents like Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>,<sup>5</sup> NaHSe,<sup>6</sup> NaHTe,<sup>7</sup> iron-graphite<sup>8</sup> and electrochemical methods<sup>9</sup> have been employed for regeneration of the double bond.

We would like to report the first catalytic laboratory procedure for debromination of vicinal dibromides using sodium borohydride together with a catalytic amount of bis(2-thienyl)ditelluride(2).<sup>10</sup> The ditelluride 2 is readily reduced by sodium borohydride in EtOH to give sodium 2-thiophenotelluroolate(1), a highly potent nucleophile which readily debrominates vicinal dibromides to olefins according to Scheme 1.

Scheme 1



The reaction is conveniently performed as a "titration" of the dibromide with sodium borohydride, the ditelluride serving as an "indicator" changing colour from deep red to colourless when all the dibromide is consumed. A number of representative examples are presented in the Table. All debrominations gave good to excellent yields and were performed at or below room temperature using 3-9 mole-% of the catalyst. In a typical procedure NaBH<sub>4</sub> (5% in 5% aq. NaOH) was added dropwise under N<sub>2</sub> to a solution of 5α, 6β-dibromocholestan-3β-ol (1.50 g, 2.73 mmol) and bis(2-thienyl)ditelluride (0.10 g, 0.24 mmol) in ethanol (20 ml) at room temperature until the red colour of the ditelluride just disappeared. At this point air was introduced into the system to oxidize the catalyst back to the ditelluride state. The reaction mixture was then dissolved in ether/water and the organic phase washed several times with water. Drying, evaporation and chromatography (CH<sub>2</sub>Cl<sub>2</sub>/5% MeOH) afforded cholesterol 0.95 g (90%), m.p. 149-50° (lit. 148.5°).<sup>11</sup>

TABLE Debromination of vic-dibromides to olefins.

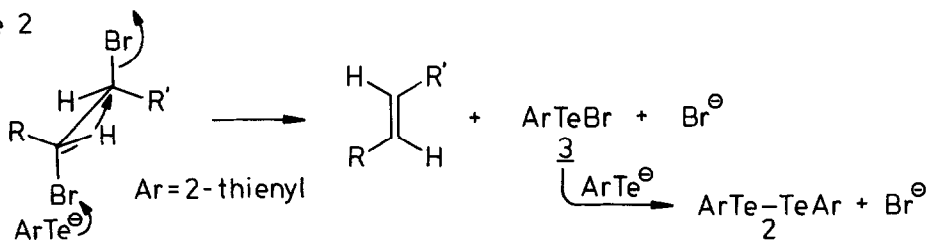
Substrate	Product	Yield(%)
meso-stilbene dibromide	stilbene (100% <u>trans</u> )	92
d,1-stilbene dibromide	stilbene ( <u>cis/trans</u> =93/7)	99
meso-2,3-dibromobutane	2-butene ( 98% <u>trans</u> )	— <sup>a</sup>
d,1-2,3-dibromobutane	2-butene ( 98% <u>cis</u> )	— <sup>a</sup>
1,2-dibromodecane	1-decene	92
1,2-dibromocyclooctane	cyclooctene	85
dibromodihydrocinnamic acid	cinnamic acid	93
dibromodihydrocrotonic acid	crotonic acid	75
diethyl meso-2,3-dibromosuccinate	diethyl fumarate	90 <sup>b</sup>
5 $\alpha$ , 6 $\beta$ -dibromocholestan-3 $\beta$ -ol	cholesterol	90

<sup>a</sup>No yield was determined. The dibromide was added to a preformed stoichiometric amount of sodium 2-thiophenellurolate in EtOH and the gaseous products analyzed.

<sup>b</sup>Run at 5° to minimize formation of diethyl succinate, a by-product.

Concerning the stereochemistry of the tellurolate-induced debromination reaction, all examples where this can be seen show a high degree of anti-stereospecificity in the products (Table), comparable to the best results obtained by other methods.<sup>4</sup> From the mechanistic point of view, the results given are consistent with a nucleophilic attack on bromine as shown in Scheme 2. The 2-thienyltellurenyl bromide(3) is readily attacked by another molecule of tellurolate ion to regenerate ditelluride 2.

Scheme 2



Although numerous methods are available for the debromination of vic-dihalides, we consider the present mild catalytic procedure a valuable addition to them in view of the high anti-stereospecificity, the consistently good yields and the absence of side-reactions.

#### References

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