Monodebromination of *gem*-Dibromocyclopropanes by Sodium Hydrogentelluride

Atsuhiro Osuka,* Keita Takechi, and Hitomi Suzuki*
Department of Chemistry, Faculty of Science, Ehime University, Bunkyo-cho 2-5, Matsuyama 790

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Synopsis. *gem*-Dibromocyclopropanes were effectively reduced to monobromocyclopropanes by sodium hydrogentelluride.

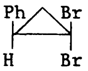
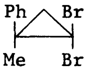
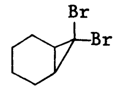
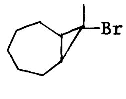
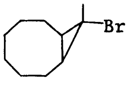
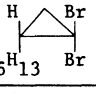
Much attention has been focused in recent years on the application of tellurium in organic syntheses.[1] Among these, sodium hydrogentelluride (NaHTe),[2] which was prepared *in situ* from tellurium and sodium borohydride ($NaBH_4$), has been reported to possess considerable versatility as selective reagent for the reduction of a wide variety of organic molecules.[2–5] While NaHTe effects the hydrogenation of α,β-unsaturated carbonyl compounds, it does not reduce simple ketones or aldehydes.[3b,4] Several observations that anionic tellurium species have strong affinity toward activated halogen have led to the development of their uses for dehalogenation reactions.[3a,5,6,7] In this note, we wish to report an effective monodebromination of *gem*-dibromocyclopropanes by NaHTe.

Monobromocyclopropanes were obtained by treatment of *gem*-dibromocyclopropanes with 2.5 equiv. of NaHTe in refluxing ethanol. A further reduction of the resultant monobromides was not observed under the reaction conditions employed. For comparison, the reduction of *gem*-dibromocyclopropanes with $NaBH_4$ was also investigated. The yields and trans/cis ratios of the present reactions are given in the Table 1. Apparently, the reduction with NaHTe is faster and more selective than that with $NaBH_4$ in ethanol. A similar debromination may be expected in the reaction with NaHSe,[8] but neither 1,1-dibromo-2-phenylcyclopropane, nor 1,1-dibromo-2-methyl-2-phenylcyclopropane, nor 7,7-dibromobicyclo[4.1.0]heptane underwent reduction upon treatment with 2.5 equiv. of NaHSe in refluxing ethanol. It should be noted here that NaHTe has strong affinity for activated halogens, which property is not shared by NaHSe. 1,1-Dichloro-2-phenylcyclopropane and 7,7-dichlorobicyclo[4.1.0]heptane were quantitatively recovered after prolonged treatment with NaHTe, while dichlorodiphenylmethane was readily reduced by NaHTe to give tetraphenylethylene and diphenylmethane in 37 and 33% yields, respectively.

$$Ph_2CCl_2 \xrightarrow[EtOH]{NaHTe} Ph_2C{=}CPh_2 + Ph_2CH_2.$$

It was indeed true that numerous methods are availabe to bring about the monodebromination of *gem*-

Table 1. Reduction of *gem*-dibromocyclopropanes to monobromocyclopropanes by sodium hydrogentelluride[a)]

Reactant	Reducing reagent	Reaction time/h	Conversion/%	Yield/%[b)]	Trans/Cis[c)]
	NaHTe	3.5	100	64	72:28
	$NaBH_4$	3.5	17	(14)[d)]	65:35
	NaHTe	3	100	61	63:37
	$NaBH_4$	3	20	(16)[d)]	54:46
	NaHTe	9	98	55	24:76
	NaHTe	8	100	56	33:67
	NaHTe	9	98	59	33:67
	NaHTe	9	98	63	30:70

a) All reactions were performed as described in detail in the text. b) Values reported are isolated yields for mixtures of *trans*- and *cis*-bromocyclopropanes. c) The trans/cis ratios were determined by GLPC. d) GLPC yields.

dibromocyclopropanes⁹⁾ but the present method would be a simple and convenient addition to them.

Experimental

gem-Dibromocyclopropanes and *gem*-dichlorocyclopropanes were prepared according to the reported procedures.¹⁰⁾

General Procedure for the Reduction of gem-*Dibromocyclopropanes with Sodium Hydrogentelluride.* To a hot solution of sodium hydrogentelluride, prepared in situ by reacting tellurium (1.30 g, 10 mmol) and sodium borohydride (0.90 g, 24 mmol) for 1 h in refluxing ethanol (40 ml) under argon atmosphere, *gem*-dibromocyclopropane (4 mmol) in 4 ml of ethanol was added. The resulting mixture was refluxed for a suitable time as indicated in the Table 1. The progress of the reaction was followed by GLPC (a Hitachi Model 163, using a 3 mm×2 m strainless steel column packed with 10% SE-30 on Celite 545 AW.) After completion of the reaction, the reaction mixture was cooled to room temperature, 50 ml of water was added, and the resulting mixture was left open to air with stirring. The solution became clear after about 3 h with the deposition of tellurium species as tellurium powder. It was then filtered through Celite 545 and *the filtrate was extracted with three portions of hexane* (30 ml). The extracts were washed with water, dried over Na_2SO_4, and evaporated to give the crude product, which was purified by Kugel-rohr distillation. The products were identified by comparison with authentic samples.

NaHSe was preprared by the method of Klayman⁸⁾ and used directly.

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