Debromination of *vic*-dibromides with 1,5-dichalcogenacyclooctane induced by transannular chalcogen–chalcogen interaction: the first example of the *vic*-dibromide–alkene functional group interconversion by organic selenide

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Vicinal dibromoalkanes are debrominated to alkenes by treatment with 1,5-dichalcogenacyclooctane under neutral conditions induced by transannular interaction. The first example of dehalogenation by using an organoselenium compound is described.

Recent reports on the halogenation of alkenes to *vic*-dihalogenides by treatment with diaryltellurium(IV) derivatives as well as the reported debromination of *vic*-dibromides to afford olefins with diaryl telluride(II) derivatives suggest that these reactions are reversible and the equilibria is shown in eqn. (1).[1–4] On the other hand, organoselenium(IV) derivatives are useful as halogenating agents for olefinic substrates since similar reactions with organoselenium(II) compounds involve equilibria which lie far to the left [eqn. (1)].[2] However, debromination of *vic*-dibromides with diorgano selenides has never been reported. In order to obtain evidence for this equilibrium of diorganoselenium derivatives, it was necessary to test diorgano selenides in the debromination of *vic*-dibromides occurring according to eqn. (1).

1a Y = Te
1b Y = Se

X = Br, Cl

2a Y = Te, X = Br
2b Y = Se, X = Br

Scheme 1
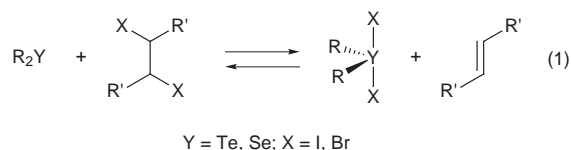
Meanwhile, there has been considerable interest in transannular interaction or bond formation (*e.g.*, dication formation) between chalcogen atoms in medium-sized heterocyclic compounds.[5–8] This paper describes the debromination of *vic*-dibromides to alkenes with 1,5-dichalcogenacyclooctane **1** induced by transannular interaction between the two chalcogen atoms, especially, the first example to gain carbon–carbon unsaturation starting from *vic*-dibromides, employing a diorgano selenide.

During our studies on the cyclic bis-chalcogenide mediated organic reactions, we found that transannular interaction between the two tellurium atoms of 1,5-ditelluracyclooctane (**1a**) accelerated the debromination reaction of various *vic*-dibromides (Scheme 1).

In a typical run, a mixture of *erythro*-1,2-dibromo-1,2-diphenylethane (100 mg, 0.294 mmol) and 1,5-ditelluracyclooctane **1a** (200 mg, 0.589 mmol) in chloroform (1 ml) was stirred vigorously at 90 °C in a sealed tube under a N₂ atmosphere for 0.5 h. The dibromoditellurane (**2a**) was formed as a yellow precipitate and was separated by filtration. The crude product was purified by silica gel column chromatography (eluent 1:1 hexane–benzene) to afford *trans*-stilbene (53 mg, 0.294 mmol) in 100% yield, which was characterized by ¹H NMR spectroscopy and GLC with an authentic sample. On the other
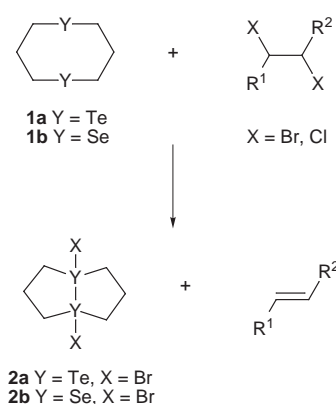
hand, debromination of *erythro*-1,2-dibromo-1,2-diphenyl-ethane upon treatment with di-*n*-hexyl telluride, in which there is no transannular interaction, took 30 h to give *trans*-stilbene in 98% yield.[1] This result suggests that debromination with 1,5-ditelluracyclooctane was induced and accelerated by transannular tellurium–tellurium interaction.

When a variety of *vic*-dibromides were treated with 2.0 equiv. of 1,5-ditelluracyclooctane **1a**, excellent or moderate yields of debrominated olefins were produced, and no side-reactions were observed. The results are given in Table 1.

Although so far *vic*-dibromides used for debromination with diorgano tellurides have been required to have carbocation-stabilizing substituents (*e.g.*, alkyl or phenyl groups) on the carbons bearing the bromo substituents, it must be noted that the debromination reaction could proceed smoothly even when 2,3-dibromopropionamide, having only an amide group which cannot stabilize the cationic intermediate, was used as substrate, and hence 1,5-ditelluracyclooctane **1a** appears to drive the equilibrium to the right as well as to accelerate the rate of debromination (Entry 5a). Furthermore, it is noteworthy that *trans*-10,11-dichlorodibenzosuberone was dechlorinated to give dibenzosuberenone in 17% yield, since dechlorination of *vic*-dichlorides to alkenes with organotellurium compound was hitherto unknown (Entry 12a).

Various *vic*-dihalogenides were thus treated with 1,5-diselenacyclooctane (**1b**), the selenium analogue of **1a**. Surprisingly, this afforded the dehalogenated products in marked contrast to acyclic selenides[2] as shown in Table 1. Apparently, the dehalogenation reactions were induced by transannular selenium–selenium interaction. However, the reactivity of bis-selenide **1b** was relatively low in comparison with that of bis-telluride **1a**; these transformations required long reaction times.

The results described herein show the first example of a

Table 1 Reductive debromination of *vic*-dihalogenides with 1,5-dichalcogenacyclooctane (**1**) in CHCl₃ at 90 °C

Entry	Substrate	Y	Reaction Time (h)	Product	Yield (%)[a]
(1a)		Te	1		79
(1b)		Se	21		39
(2a)		Te	1		100
(2b)		Se	23		65
(3a)		Te	1		99
(3b)		Se	23		45
(4a)		Te	1		100
(4b)		Se	19		94
(5a)[b]		Te	15		62
(5b)[b]		Se	74		15
(6a)		Te	71		23
(6b)		Se	100		—
(7a)[b]		Te	1		14[c]
(7b)[b]		Se	170		42[c]
(8a)		Te	0.5		100
(8b)		Se	26		37
(9a)		Te	0.5		28
(9b)		Se	70		16
(10a)		Te	66		6
(10b)		Se	100		5
(11a)		Te	20		trace
(11b)		Se	100		—
(12a)		Te	74		17
(12b)		Se	95		28

[a] GLC yields based on the dibromides. Each product from a larger scale experiment was isolated by silica gel column chromatography and identified by ¹H NMR spectroscopy with an authentic sample. [b] THF was used as solvent. [c] The product was isolated as the methyl ester. [d] Only *trans*-stilbene was detected. An analogous result was reported in ref. 1.

dehalogenation reaction of a *vic*-dihalogenide upon treatment with an organoselenium(II) derivative induced by transannular interaction. The equilibrium was reconfirmed by debromination of various *vic*-dibromides with bis-selenide **1b**. Furthermore, these results indicate that the debromination with 1,5-ditelluracyclooctane **1a** is of considerable synthetic utility, particularly when a dihalogenide possesses other reducible groups such as carbonyl, carboxy, ester, nitro and sulfonyl groups, because all of these remain unaffected during the debromination. Further work is in progress to explore applications and advantages of the transannular interaction of cyclic bis-chalcogenide.

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