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Selenium-Catalyzed Debromination of *vic*-Dibromoalkanes and α-Bromo Ketones with Carbon Monoxide and Water

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ABSTRACT

Selenium has been found to be an excellent catalyst for the reductive debromination of some organic bromides with carbon monoxide and water: vic*-dibromoalkanes and α-halo ketones can be reduced to the corresponding alkenes and ketones respectively in moderate to high yields.*

INTRODUCTION

Carbon monoxide is widely accepted as a useful reducing agent [1] as well as an extremely important agent for introducing carbonyl functions into organic molecules [2]. As to the synthetic reactions utilizing the reducing ability of carbon monoxide, the reaction system in combination with water has been utilized for the reduction or reductive carbonylation of various organic compounds, in which transition metal complexes are usually employed as the catalyst [3]. For example, nitrobenzenes and olefins underwent reduction or reductive carbonylation in the presence of a catalytic amount of transition metal complexes. Contrary to this, little is known about a catalytic reduction of organic halides with carbon monoxide and water, probably because these organic halides form unreactive complexes with metal catalysts.

We have found that elemental selenium, a nontransition metal, acts as a unique catalyst for the reduction of some functional groups with carbon monoxide and water in the presence of a tertiary amine [4]. Successful isolation of hydrogen selenide from the stoichiometric reaction of selenium with carbon monoxide and water suggests that the active reducing species in this catalytic reduction system is the amine salt of hydrogen selenide, which may be formed in situ by release of carbon dioxide from selenolcarboxylic acid as shown in Equation 1 [5].

The use of selenium as the catalyst to effect the reduction of organic halides such as *vic*-dihalides [6] and α-halo ketones [7] with carbon monoxide and water is believed to be related to the fact that some selenolate anions such as NaSeH [8], Na_2Se [9], and PhSeNa [10], are known to reduce these halides in a stoichiometric manner. This paper provides evidence that selenium does indeed act as an efficient catalyst for the reductive dehalogenation

$$\mathrm{Se} \xrightarrow[R_3N]{CO} \mathrm{SeCO} \xrightarrow[R_3N]{H_2O} [\mathrm{HOC(=O)Se}]^-[R_3NH]^+ \xrightarrow{-CO_2} [\mathrm{HSe}]^-[R_3NH]^+ \quad (1)$$

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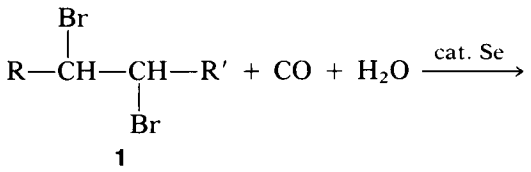
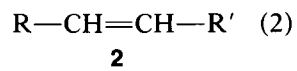


1



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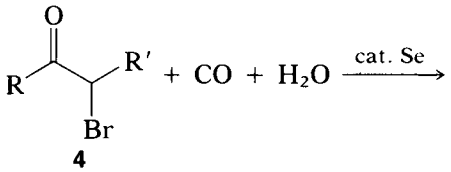

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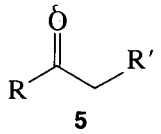


5 (3)

of *vic*-dibromoalkanes and α-halo ketones with carbon monoxide and water under mild conditions (Equations 2 and 3).

RESULTS AND DISCUSSION

Treatment of *vic*-dibromoalkanes with carbon monoxide (5 atm) and water in the presence of 0.2 equivalent of selenium at 50°C for 24 h gave rise to the corresponding alkenes in good yields, as summarized in Table 1 [11]. This method is quite general and applicable to various *vic*-dibromoalkanes with a high chemoselectivity. For example, several carbonyl functions (ketones **1e** and **1f**, an ester **1g**, and a carboxylic acid **1h**) have remained unchanged under the reaction conditions employed. Isomerization of the carbon-carbon double bond of alkenes produced (**1c, 1d,** and **1i**) was not observed during the reaction. It is possible to reduce the amount of selenium still further under a somewhat higher pressure and a higher temperature (run 2). This method is usable for the debromination of a *vic*-dibromoalkene to an alkyne (runs 14 and 15). To gain an insight into the stereoselectivity of this debromination, the reduction of *meso*- and *d,l*-1,2-dibromo-1,2-diphenylethane (**1a** and **1b**) was examined: debromination of the *meso*-isomer (**1a**) led to *trans*-stilbene (**2a**) exclusively, whereas the *d,l*-isomer (**1b**) provided an isomeric mixture (*cis*/*trans* = 69/31) (runs 1 and 3). The stereoselectivity of product formation was found to be independent of the amount of selenium used (run 4). The lower selectivity in the debromination of **1b** may be due to the isomerization of *cis*-stilbene to the *trans*-isomer in the presence of HBr formed during the reaction [12]. When the reduction was carried out in the presence of sodium hydroxide as a capturing agent of HBr, selective formation of *cis*-stilbene from **1b** was attained (run 5). In view of this stereospecificity (retention), some possible reaction paths are imaginable: (1) an E2 type mechanism by the direct attack of the selenolate anion (HSe^-) on the bromine atom [13]; (2) the displacement of bromine atom by HSe^- leading to a β-bromoselenol, followed by *syn* elimination of two heteroatom moieties [14, 15]; (3) the displacement of both bromine atoms by HSe^- leading to a β-diselenol, followed by an E2 type elimination by the attack of HSe^- on the selenium. In addition, a proposal in the literature on a pathway for the reductive debromination of *vic*-dibromoalkanes by sodium sulfide suggests that the one electron transfer mechanism may be involved in this reaction [17]. However, if this reaction follows the SET mechanism, the reduction of a *d,l*-isomer should proceed with poor stereoselectivity [18]. Nevertheless, at this point, evidence for and/or against these reaction mechanisms cannot be provided. Further studies to investigate the mechanism are necessary.

In an attempt to extend the scope of the reaction, we undertook the reductive elimination of bromohydrin derivatives (Table 2) [19]. Bromohydrin derivatives **3** have been found to react with carbon monoxide and water in the presence of a catalytic amount of selenium to give the expected alkenes in good yields. The stereoselectivity is sensitive to the nature of substituent groups (Y) on the bromohydrin **3** [20].

As with *vic*-dibromoalkanes, reductive debromination of α-bromo ketones proceeded smoothly in this reaction system [21]. Representative results are listed in Table 3. α-Bromoacetophenones (**4b-4e**) bearing bromo-, hydroxy-, and methoxy-groups on the benzene ring underwent debromination without affecting these functional groups. Similarly, 5-bromo-6-undecanone (**4g**) and *exo*-α-bromocamphor (**4h**) are efficiently converted into the corresponding ketones. α-Chloroacetophenone (**4f**) could be reduced to acetophenone by the same procedure.

In summary, a catalytic method for reductive dehalogenation has been developed. A characteristic feature of the present debromination is that selenium, a nontransition metal, shows excellent catalytic activity for the reduction of organic bromides with carbon monoxide and water.

EXPERIMENTAL SECTION

Instruments and Materials

The instruments used were as follows: ^{1}H-NMR, JEOL PS-100; IR, JASCO R-400; Mass, JEOL JMS-QH100. Metallic selenium (99%) from Wako Chemical Co. and carbon monoxide (99.9%) from Seitetsu Chemical Co. were used. 4-tert-Butylcyclohexene (**2d**) [22], α-bromo ketones (**4b** [23], **4c** [24], and **4h** [24]), and bromohydrin derivatives (**3a** [19a], **3b** [19a], **3c** [19a], **3d** [19a], and **3e** [19a]) were prepared according to the literature. Other olefins, α-halo ketones, phenylacetylene, *N*-methylpyrrolidine, and tetrahydrofuran (THF) were all purchased from

TABLE 1 Reductive Debromination of *vic*-Dibromoalkanes[a]

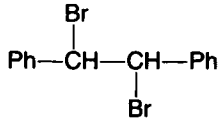
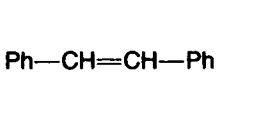
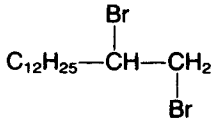
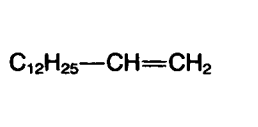
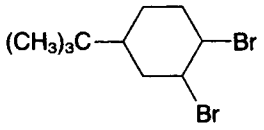
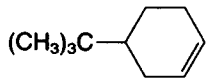
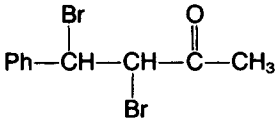
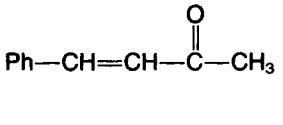
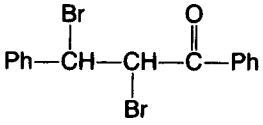
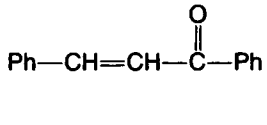
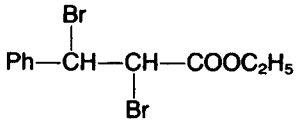
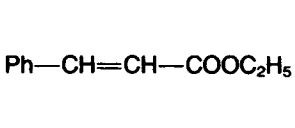
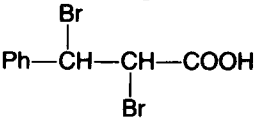
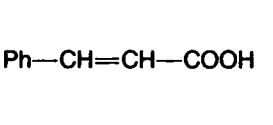
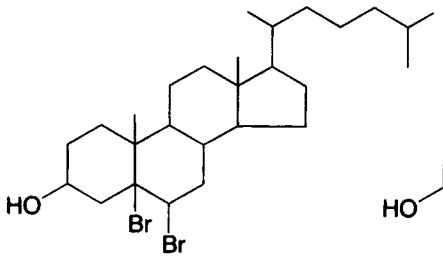
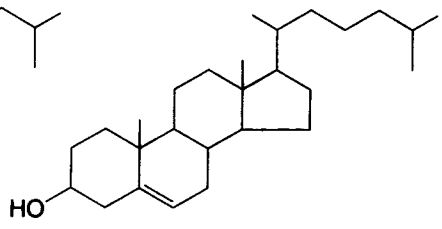
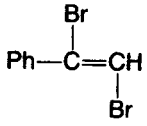
Run	Dibromide	Product	Yield, %[b] (trans/cis)[c]
1			92 (100/0)
	[meso]		
	1a	**2a**	
2[d]	**1a**	**2a**	91 (100/0)
3	[*d,l*]		85 (31/69)
	1b	**2a**	
4[e]	**1b**	**2a**	96 (26/74)
5[f]	**1b**	**2a**	76 (0/100)
6			82
	1c	**2c**	
7			79
	1d	**2d**	
8			86 (100/0)
	1e	**2e**	
9			96 (100/0)
	1f	**2f**	
10			88 (100/0)
	1g	**2g**	
11			51 (100/0)
	1h	**2h**	
12[e]	**1h**	**2h**	78 (100/0)
13			87
	1i	**2i**	

TABLE 1 Reductive Debromination of *vic*-Dibromoalkanes[a] (*continued*)

Run	*Dibromide*	*Product*	*Yield, %[b] (trans/cis)[c]*
14		PhC≡CH	49
	1j	**2j**	
15[e]	**1j**	**2j**	89

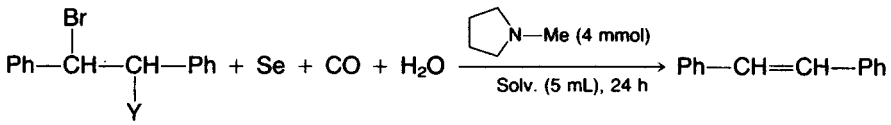
[a] Reaction conditions: substrate (2 mmol), selenium (0.4 mmol), water (10 mmol), *N*-methylpyrrolidine (4 mmol), THF (5 mL), and CO (5 atm) at 50°C for 24 h.
[b] Isolated yield.
[c] Ratio of stereoisomers was determined by ^{1}H-NMR and GLC.
[d] Reaction using selenium (0.1 mmol) at 80°C for 48 h.
[e] One equivalent of selenium was used.
[f] NaOH (3 equiv) was added.

commercial sources and purified by distillation or recrystallization. *vic*-Dibromoalkanes and a *vic*-dibromoalkene were prepared by the reaction of corresponding alkenes and an alkyne with bromine.

General Procedure for the Debromination of vic*-Dibromoalkanes and a* vic*-Dibromoalkene with Carbon Monoxide and Water Using a Catalytic Amount of Selenium*

In a 50 mL stainless steel autoclave were placed a given *vic*-dibromoalkane (2 mmol), selenium (0.03 g, 0.4 mmol), water (0.18 mL, 10 mmol), *N*-methylpyrrolidine (0.34 g, 4 mmol), and THF (5 mL), and the mixture was heated at 50°C for 24 h under CO (5 atm: initial pressure at 25°C). After the reaction, carbon monoxide was purged in a well-ventilated hood, and the air was blown into the solution for 10 min in order to oxidize remaining hydrogen selenide to elemental selenium. Selenium that deposited was filtered off, the filtrate was slightly acidified by the addition of hydrochloric acid (2*N*), and then the product was extracted with diethyl ether (20 mL × 3). The combined extracts were dried over $MgSO_4$. Evaporation of the solvent and purification by column chromatography on silica gel gave the corresponding alkenes. The similar treatment of a *vic*-dibromoalkene gave the corresponding alkyne. Results are given in Table 1. The structure of the products was assigned by a comparison of their ^{1}H-NMR, IR, and mass spectra with those of authentic materials.

TABLE 2 Reductive Elimination of Bromohydrin Derivatives



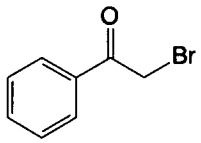
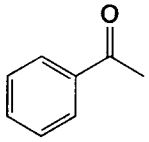
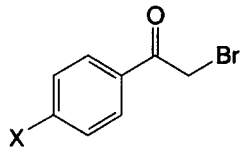
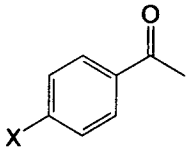
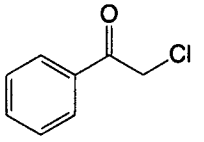
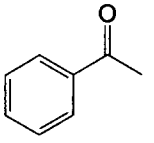
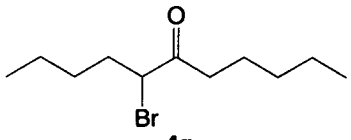
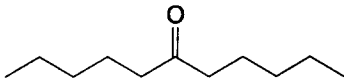
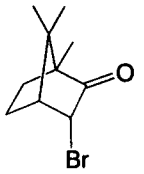
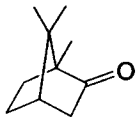
3 **2**

2 mmol | 0.4 mmol | 30 atm | 10 mmol

Run	*Substrate[a] (Y=)*	*Solv.*	*Temp. (°C)*	*Yield, %[b,c] (trans/cis)*
1	—OH **3a**	CH_3CN	80	96 (93/7)
2	—OCH_3 **3b**	DMF	120	77 (28/72)
3[d]	—OCH_3 **3c**	DMF	120	82 (91/9)
4	—$OCOCH_3$ **3d**	THF	50	99 (61/39)
5	—OSO_2CH_3 **3e**	DMF	80	77 (96/4)

[a] Erythro isomer.
[b] Isolated yield.
[c] Ratio of isomers was determined by ^{1}H-NMR and GLC.
[d] Threo isomer.

TABLE 3 Reductive Dehalogenation of α-Halo Ketones[a]

Run	Substrate	Product	Yield, %[b]
1	 **4a**	 **5a**	88
2	 X = Br **4b**	 **5b**	87
3	X = OH **4c**	**5c**	95
4	X = CH_3O **4d**	**5d**	95
5	X = CH_3 **4e**	**5e**	86
6	 **4f**	 **5f**	81
7	 **4g**	 **5g**	74
8	 **4h**	 **5h**	96

[a] Reaction conditions: substrate (2 mmol), selenium (0.4 mmol), water (10 mmol), *N*-methylpyrrolidine (4 mmol), THF (5 mL), CO (5 atm) at 80°C for 24 h.
[b] Isolated yield.

trans-*Stilbene* (**2a**). 0.33 g (92%), mp 122–123.5°C (lit. [25] 123°C): ^{1}H-NMR (CCl_4) δ 7.04 (s, 2H), 7.26–7.58 (m, 10H); IR (KBr) 1590, 1490, 960 cm^{-1}; mass spectrum, m/e 180 (M^+).

1-Tetradecene (**2c**). 0.32 g (82%): ^{1}H-NMR (CCl_4) δ 0.87 (t, J = 8 Hz, 3H), 1.16–2.08 (c, 22H), 4.94 (dd, J = 16, 8 Hz, 1H), 5.24–5.36 (m, 1H), 5.56–5.84 (m, 1H); IR (neat) 2950, 2830, 1640, 990, 905 cm^{-1}; mass spectrum, m/e 196 (M^+).

4-tert-Butylcyclohexene (**2d**). 0.22 g (80%): ^{1}H-NMR (CCl_4) δ 0.98 (s, 9H), 1.28–2.20 (c, 7H), 5.68–5.70 (c, 2H); IR (neat) 2940, 2845, 1360 cm^{-1}; mass spectrum, m/e 138 (M^+).

Benzalacetone (**2e**). 0.25 g (86%): ^{1}H-NMR (CCl_4) δ 2.16 (s, 3H), 6.58 (d, J = 16 Hz, 1H), 7.26 (s, 5H), 7.42 (d, J = 16 Hz, 1H); IR (neat) 1675, 1600, 1490, 970 cm^{-1}; mass spectrum, m/e 146 (M^+).

Chalcone (**2f**). 0.40 g (96%), mp 55–56°C (lit. [25] 55–57°C): ^{1}H-NMR (CCl_4) δ 7.26–7.57 (m, 10H), 7.68–7.82 (m, 2H); IR (KBr) 1660, 1600, 1450, 1220 cm^{-1}; mass spectrum, m/e 208 (M^+).

Ethyl cinnamate (**2g**). 0.31 g (88%): ^{1}H-NMR (CCl_4) δ 1.27 (t, J = 8 Hz, 3H), 4.20 (q, J = 8 Hz, 2H), 6.38 (d, J = 16 Hz, 1H), 7.24–7.45 (m, 5H), 7.61 (d, J = 16 Hz, 1H); IR (neat) 1730, 1460, 1270, 950 cm^{-1}; mass spectrum, m/e 176 (M^+).

Cinnamic acid (**2h**). 0.15 g (51%), mp 133.5–134°C (lit. [25] 133–134°C): ^{1}H-NMR (CCl_4) δ 6.35 (d, J = 16 Hz, 1H), 7.24–7.49 (m, 5H), 7.67 (d, J = 16 Hz, 1H), 14.20 (br s, 1H); IR (neat) 1610, 1490, 1445, 1320 cm^{-1}; mass spectrum, m/e 148 (M^+).

Cholesterol (**2i**). 0.67 g (87%), mp 148–149°C (lit. [25] 147–149°C): ^{1}H-NMR (CCl_4) δ 0.68–1.10 (c, 15H), 1.16–2.20 (c, 28H), 3.24–3.56 (m, 1H), 5.20–5.26 (m, 1H); IR (KBr) 3300, 2100 cm^{-1}; mass spectrum, m/e 386 (M^+).

Phenylacetylene (**2j**). 0.10 g (49%): ^{1}H-NMR (CCl_4) δ 2.93 (s, 1H), 7.08–7.22 (m, 3H), 7.30–7.42 (m, 2H); IR (neat) 2100 cm^{-1}; mass spectrum, m/e 102 (M^+).

Debromination of vic*-Dibromoalkanes with CO and H_2O in the Presence of a Stoichiometric Amount of Selenium*

A stirred mixture of a given *vic*-dibromoalkane (2 mmol), Se (2 mmol), water (10 mmol), *N*-methylpyrrolidine (4 mmol), and THF (5 mL) was heated under CO (5 atm) at 50°C for 24 h. The subsequent workups were carried out as described in the general procedure for a catalytic debromination.

Stereoselective Reductive Debromination of d,l*-1,2-Dibromo-1,2-diphenylethane* (**1b**) *with Se, CO, and H_2O*

A stirred mixture of *d,l*-1,2-dibromo-1,2-diphenylethane (2 mmol), Se (2 mmol), water (10 mmol), *N*-methylpyrrolidine (4 mmol), NaOH (6 mmol), and THF (5 mL) was heated under CO (5 atm) at 50°C for 24 h. The same workup was carried out to give 0.26 g (72%) of *cis*-stilbene (**2b**). ^{1}H-NMR (CCl_4) δ 6.43 (s, 2H), 7.01 (s, 10H); IR (neat) 1575, 1495, 755 cm^{-1}; mass spectrum, m/e 180 (M^+).

Typical Procedure for Reductive Elimination of Bromohydrin Derivatives

A mixture of *erythro*-1-bromo-2-hydroxy-1,2-diphenylethane (2 mmol), Se (0.4 mmol), H_2O (10 mmol), *N*-methylpyrrolidine (4 mmol), and CH_3CN (5 mL) was heated at 80°C for 24 h under the pressure of carbon monoxide (30 atm). The subsequent workup was carried out as described in the general procedure for a catalytic debromination of *vic*-dibromoalkanes. The results are given in Table 2.

A Catalytic Reduction of α-Halo Ketones

A mixture of α-halo ketone (2 mmol), selenium (0.4 mmol), water (10 mmol), *N*-methylpyrrolidine (4 mmol), and THF (5 mL) was stirred at 80°C for 24 h under 5 atm of CO (initial pressure at 25°C). The subsequent workups were carried out as described above in the general procedure for a catalytic debromination of *vic*-dibromoalkanes. The results are given in Table 3.

Acetophenone (**5a**). 0.21 g (88%): ^{1}H-NMR (CCl_4) δ 2.43 (s, 3H), 7.08–7.33 (m, 3H), 7.62–7.78 (m, 2H); IR (neat) 1670 cm^{-1}; mass spectrum, m/e 120 (M^+).

4'-Bromoacetophenone (**5b**). 0.35 g (88%), mp 51–52°C (lit. [25] 50–52°C): ^{1}H-NMR (CCl_4) δ 2.46 (s, 3H), 7.37 (d, J = 8 Hz, 2H), 7.59 (d, J = 8 Hz, 2H); IR (KBr) 1670 cm^{-1}; mass spectrum, m/e 199 (M^+).

4'-Hydroxyacetophenone (**5c**). 0.26 g (96%), mp 108.5–110°C (lit. [25] 109–111°C): ^{1}H-NMR (CCl_4) δ 2.56 (s, 3H), 6.67 (d, J = 8 Hz, 2H), 7.81 (d, J = 8 Hz, 2H), 8.15 (s, 1H); IR (KBr) 3325, 1650 cm^{-1}; mass spectrum, m/e 136 (M^+).

4'-Methoxyacetophenone (**5d**). 0.29 g (97%), mp 36–37°C (lit. [25] 36–38°C: ^{1}H-NMR (CCl_4) δ 2.38 (s, 3H), 3.73 (s, 3H), 6.71 (d, J = 8 Hz, 2H), 7.67 (d, J = 8 Hz, 2H); IR (KBr) 1670, 1260 cm^{-1}; mass spectrum, m/e 150 (M^+).

4'-Methylacetophenone (**5e**). 0.23 g (86%): ^{1}H-NMR (CCl_4) δ 2.28 (s, 3H), 2.37 (s, 3H), 7.01 (d, J = 8 Hz, 2H), 7.62 (d, J = 8 Hz, 2H); IR (neat) 1680 cm^{-1}; mass spectrum, m/e 134 (M^+).

6-Undecanone (**5g**). 0.25 g (74%): ^{1}H-NMR (CCl_4) δ 0.90 (t, J = 7 Hz, 4H), 1.00–1.90 (m, 12H), 2.40 (t, J = 6 Hz, 6H); IR (neat) 1725 cm^{-1}; mass spectrum, m/e 170 (M^+).

Camphor (**5h**). 0.29 g (95%), mp 175–176 (lit. [25] 175–177°C): ^{1}H-NMR (CCl_4) δ 0.80–1.00 (c, 9H), 1.20–2.40 (c, 8H); IR (KBr) 1745 cm^{-1}; mass spectrum, m/e 152 (M^+).

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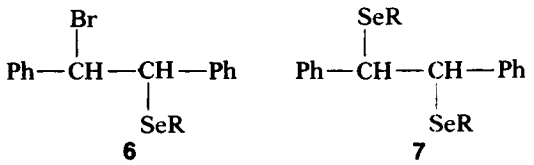
[11] The reaction was affected by tertiary amine, reaction time, and reaction temperature: *N*-methylpyrrolidine is effective for the present reduction. A weaker base such as triethylamine, a shorter reaction time, and a lower reaction temperature are not preferable to the reaction.

[12] Isomerization of *cis*-stilbene to *trans*-isomer did not occur under the standard conditions where the debromination takes place: *cis*-stilbene (2 mmol), Se (2 mmol), water (10 mmol), *N*-methylpyrrolidine (4 mmol), carbon monoxide (5 atm), and THF (5 mL) at 50°C for 24 h. However, the addition of HBr to the system caused the isomerization to *trans*-stilbene (36%).

[13] In the cases of reductive debromination of *vic*-dibromoalkanes by sodium selenide [9b] and sodium methylselenolate or phenylselenolate [10a], E2 type mechanism path has been suggested.

[14] In order to gain further insight into the details of this mechanism, the model reaction of 1,2-dibromo-1,2-diphenylethane with PhSeNa or NaSeH was monitored by measurement of the ^{1}H and ^{13}C-NMR spectra. A decrease in the amount of starting dibromide and an increase in the amount of stilbene was observed. However, ^{1}H and ^{13}C-NMR spectra of the substitution products (**6** or **7**) were not detected [16].



6 **7**

R = H and Ph

[15] The model reaction of erythro- and threo-β-bromoalkyl phenylselenide, generated from *trans*- and *cis*-stilbene and benzeneselenenyl bromide [16], with Se, CO, and H_2O was examined. However, olefins based on *syn*-elimination were not formed.

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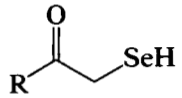
[20] Isomerization of *trans*-stilbene to *cis*-isomer was not observed under these reaction conditions. Further

studies on the mechanism of the reductive elimination of bromohydrins are in progress.

[21] In the case of α-halo ketones, the reaction may proceed either via the formation of enolate by the direct attack of HSe^- at the bromine atom or via the displacement of bromine atom by HSe^- to give α-selenol ketone (**8**) as the intermediate, followed by further attack of HSe^- on selenium atom of **8**. In fact, when an appropriate α-phenylselenoketone was reacted with Se, CO, and H_2O under the same reaction conditions, acetophenone was formed in 74% yield.



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