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Reactions of Benzeneselenyl and Benzenesulfenyl Chlorides with *syn*- and *anti*-9,9′-Bibenzonorbornenylidenes

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ABSTRACT: *Reaction of* syn-*9,9′-bibenzonorbornenylidene* **(1a)** *with benzeneselenyl chloride produced* vic-*dichloride* **(4)** *exclusively, which corresponds to the* cis-*addition product of* **1a** *with molecular chlorine, with retention of the original alkene configuration. Moreover, the reaction of* anti-*9,9′-bibenzonorbornenylidene* **(1b)** *with benzeneselenyl chloride gave the same* vic-*dichloride* **(4)** *exclusively with inversion of the original alkene configuration. No expected benzeneselenyl chloride adducts were formed in both cases. On the other hand, reactions of* **1a** *and* **1b** *with benzenesulfenyl chloride only resulted in the* syn–anti *isomerization of the alkenes without any adduct formation. Mechanisms of these reactions are discussed in some detail.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:625–629, 2001

INTRODUCTION

Quite recently, we have synthesized *syn*-9,9′-bibenzonorbornenylidene **(1a)** and *anti*-9,9′-bibenzonorbornenylidene **(1b)** [1]. The use of a pair of these alkenes as the substrate enabled us to carry out not only a stereochemical study of many reactions at the double bond but also a study of the neighboring group participation by the benzene rings. Thus, the sulfuration of **1a** by elemental sulfur resulted in the exclusive formation of episulfides **2a** and **2a′** with retention of the original stereochemistry of **1a** [2] (Scheme 1). The sulfuration of **1b** also gave the episulfide **2b** exclusively with retention of the stereochemistry. Trithiolane and pentathiepane derivatives, which often form in the sulfuration of cyclic alkenes, were not formed. On the other hand, molecular bromine underwent an exclusive *cis*-addition to **1a** to give *vic*-dibromide **(3)** with retention of the original stereochemistry, while it underwent an exclusive *trans*-addition to **1b** to give the same bromide **3** with inversion of the original stereochemisrty [3] (Scheme 1). These results prompted us to investigate the reactions of **1a** and **1b** with benzeneselenyl chloride and benzenesulfenyl chloride, which are known to undergo generally stereospecific *trans*-additions to alkenes [4].

RESULTS AND DISCUSSION

Reactions of 1a and 1b with Benzeneselenyl Chloride

The reaction of the *syn*-alkene **1a** with an equimolar amount of benzeneselenyl chloride at −78°C in $CDCl_3$ did not form the expected benzeneselenyl chloride adduct even in a trace amount, but furnished a 50% yield of the *vic*-dichloride **(4)**, which

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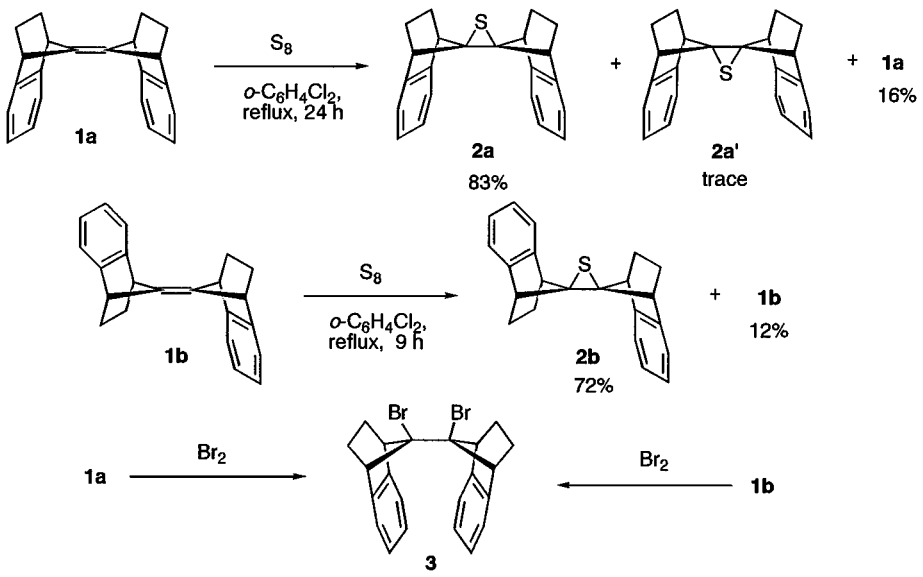


SCHEME 1

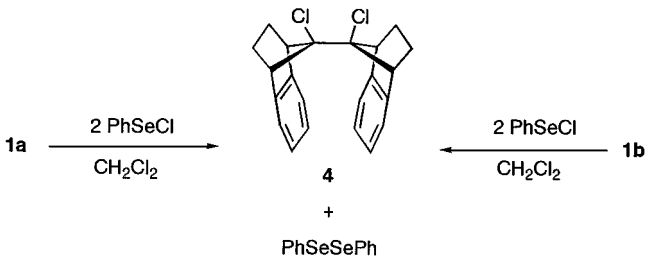
corresponds to the *cis*-addition product of **1a** with molecular chlorine (Table 1, run 1) (Scheme 2). The *syn*-alkene **1a** was recovered in 50% yield, without any isomerization to the *anti*-alkene **1b**. In addition, diphenyl diselenide was formed quantitatively. The formation of **4** by addition of molecular chlorine to **1a** was previously reported and its structure was determined unambiguously [3]. The reaction of the *anti*-alkene **1b** with benzeneselenyl chloride under the same conditions also furnished the same chlorine adduct **4** in 50% yield (Table 1, run 3) with quantitative formation of diphenyl diselenide (Scheme 2). The *syn*-alkene **1b** was recovered in 50% yield without any isomerization to **1a**. The same products were also obtained in similar yields by reactions carried out at room temperature (Table 1, runs 2,4). The use of two equimolar amounts of benzeneselenyl chloride furnished the adduct **4** quantitatively (Table 1, runs 5,6). Thus, the net results of the reaction of **1a** with benzeneselenyl chloride involve an exclusive *cis*-addition of molecular chlorine to **1a** with retention of the configuration, the addition thereby taking place at the more sterically crowded ethylene chain side; the X-ray crystallographic analysis of **1a** revealed that the ethylene chain side is more crowded than the benzene ring side [1]. On the other hand, the reaction of **1b** with benzeneselenyl chloride shows that the chlorine addition now proceeded by inversion of the configuration of **1b** with exclusive *trans*-addition.

The following are the probable mechanisms that can best accommodate the experimental observations. Initially, benzeneselnyl chloride adds to **1a** in the usual manner from the ethylene chain side to produce the episelenonium ion **5a**. The episelenonium ion **5a**, thus formed, should come to equilibrium with the ring-opened form, carbocation **6a**. Both **5a** and **6a** would be stabilized by the anchimeric

TABLE 1 Reactions of Alkenes **1a** and **1b** with Benzeneslenyl Chloride in $CDCl_3$

		Conditions		*Products; yield (%)*[b]		
Runs	*Alkenes*	*PhSecl*[a]	*Temperature*	**4**	**1a**	**1b**
1	**1a**	1	−78°C	50	50	
2	**1a**	1	RT[c]	50	50	
3	**1b**	1	−78°C	50		50
4	**1b**	1	RT	50		50
5	**1a**	2	−78°C	100		
6	**1b**	2	−78°C	100		

[a]Equimolar amounts of PhSeCl used.
[b]Yields were determined by ^{1}H NMR spectrum analyses.
[c]RT stands for room temperature.



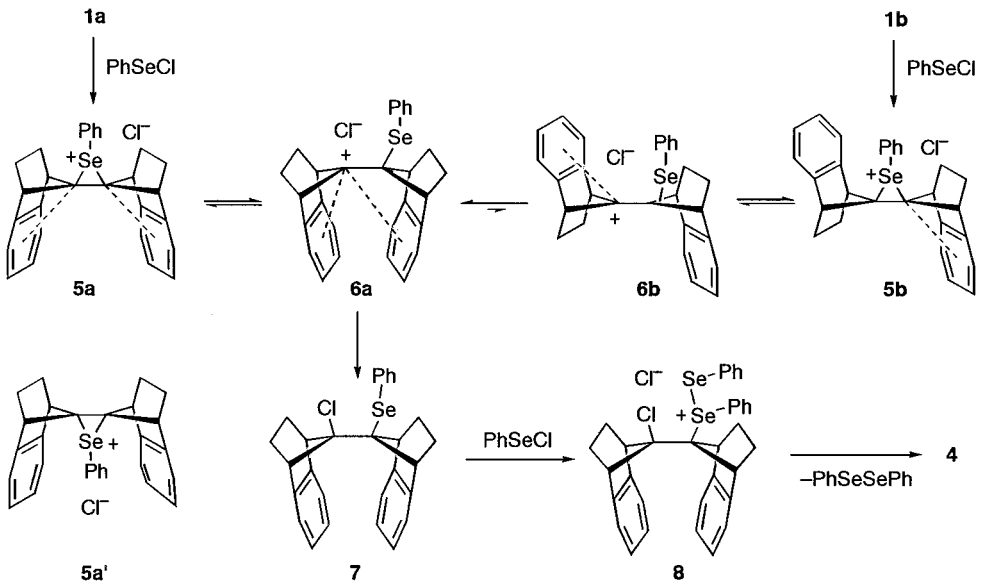
SCHEME 2

assistance of the two benzene rings. Moreover, the episelenonium ion intermediate **5a**′, formed by the addition from the benzene ring side, cannot enjoy such stabilization. This would explain the addition of benzeneselenyl chloride from the ethylene chain side. Next, the covalent bond formation of **6a** with the chloride ion takes place at the ethylene chain side to give the *cis*-adduct **7** because the benzene ring side is blocked by the anchimeric assistance of the benzene rings. The reaction of **7** with benzeneselenyl chloride then produces the selenonium ion **8**. Elimination of diphenyl diselenide from **8**, followed by the addition of the chloride ion from the same side, would explain the final formation of the *cis*-addition product **4** (Scheme 3). Reportedly, the reaction of 1-phenylcyclohexene with two molar amounts of benzeneselenyl chloride afforded a 77:23 cis–trans mixture of 1,2-dichloro-1-phenylcyclohexane quantitatively [5].

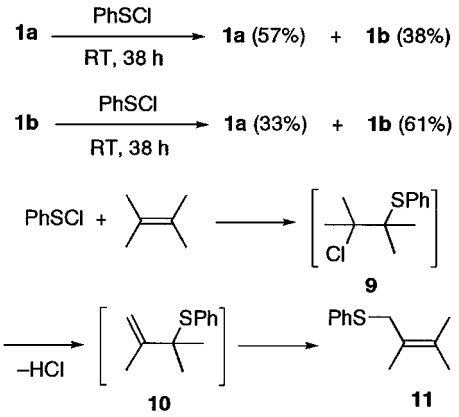
On the other hand, the addition of benzeneselenyl chloride to **1b** produces the episelenonium ion **5b**, which would also come to equilibrium with the ring-opened form, carbocation **6b**. The carbocation **6b**, which is stabilized by anchimeric assistance of only the one benzene ring, would be less stable than **6a**, and thus undergoes a conformational change to **6a** by free rotation about the cabon–carbon bond to give **4** as the final product. In this way, the same product **4** would be formed, both from **1a** and **1b**. The recovery of **1a** and **1b** without any isomerization indicates that additions of benzeneselenyl chloride to both **1a** and **1b** are irreversible.

Reactions of 1a and 1b with Benzenesulfenyl Chloride

In contrast to the reactions of benzeneselenyl chloride with **1a** and **1b**, those of benzenesulfenyl chloride gave neither benzenesulfenyl chloride adducts nor chlorine adducts; benzenesulfenyl chloride only worked as the catalyst of the mutual isomerization of **1a** and **1b**. Thus, treatment of **1a** with an equimolar amount of benzenesulfenyl chloride at room temperature for 38 h gave a mixture of **1a** (57%) and **1b** (38%), while treatment of **1b** with benzenesulfenyl chloride gave **1a** (33%) and **1b** (61%) (Scheme 4). For these reactions, prior to the product isolation procedure, excess tetramethylethylene was added to the reaction mixtures to scavenge the benzenesulfenyl chloride, which remained unchanged. Otherwise addition of the molecular chlorine, produced by decomposition of the benzenesulfenyl chloride, to **1a** and **1b** takes place to give **4**. Thus, 2,3-dimethyl-1-phenylthio-2-butene **(11)** [6], which is a secondary



SCHEME 3



SCHEME 4

product, produced from the initial adduct **9** during workup by silica-gel column chromatography, was isolated in about 40% yield in both cases (Scheme 4). A separate reaction of tetramethylethylene with benzenesulfenyl chloride gave **11** in a better yield of 60%.

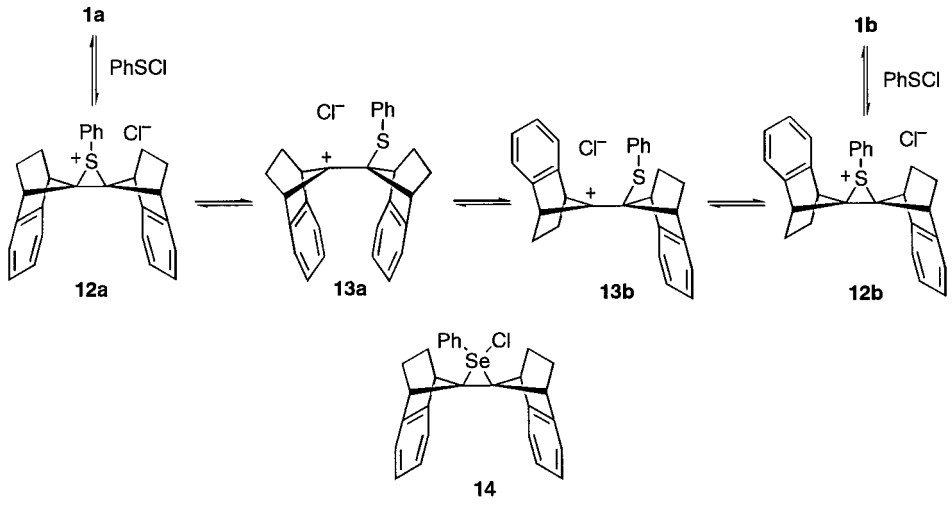
The isomerization, discussed earlier, might be explained as follows. Benzenesulfenyl chloride reacts with **1a** and **1b** to reversibly form episulfonium ions **12a** and **12b**. These sulfonium ions would then come to equilibrium with the ring-opened carbocations **13a** and **13b**, respectively, which are interconvertible through bond rotation (Scheme 5). The whole process would result in the isomerization between **1a** and **1b**. These considerations mean that the chloride ion does not undergo covalent bond formation with the carbocations **13a** and **13b**, unlike the selenium case. One of plausible explanations is that in the selenium case the episelenium ion is in an equilibrium with a selenurane intermediate **14**, thus placing the chloride ion closer to the carbocation center to favor the covalent bond formation, whereas in the sulfur case the ion pairs are solvent-separated and disfavor the bond formation.

EXPERIMENTAL

Solvents were purified and dried in the usual manner. All of the reactions were carried out under argon. Silica-gel column chromatography was performed on silica gel 7734 (Merck, 70-230 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX400 or a Bruker AM400 spectrometer using $CDCl_3$ as the solvent with TMS as the internal standard.

*Reaction of the Alkene **1a** with Benzeneselenyl Chloride*

A solution of 68 mg (0.35 mmol) of benzeneselenyl chloride in 2 ml. of dichloromethane was added to a solution of 100 mg (0.35 mmol) of **1a** in 80 ml. of dichloromethane at −78°C. The reaction mixture, which turned from red to yellow after 10 min, was warmed to −18°C and evaporated under reduced pressure. The residue was chromatographed on a column of silica gel. Elution of the column with hexane/chloroform (4:1) gave 57 mg (57%) of **1a** and a mixture of the dichloride **4** and diphenyl diselenide. The mixture part was further purified by GPC (gel permeation chromatography) to give 54 mg (43%) of **4** and 49 mg (89%) of diphenyl diselenide. The structure of **4** was determined by comparison with an authentic sample that was obtained by addition of molecular chlorine to **1a** [3].



SCHEME 5

The data given in Table 1 were obtained by carrying out the reactions in an **NMR** tube, with $CDCl_3$ as the solvent.

*Reaction of the Alkene **1b** with Benzeneselenyl Chloride*

A solution of 68 mg (0.35 mmol) of benzeneselenyl chloride in 2 ml. of dichloromethane was added to a solution of 100 mg (0.35 mmol) of **1b** in 80 ml. of dichloromethane at −78°C. The reaction mixture, which turned from red to yellow after 10 min, was warmed to −18°C and evaporated under reduced pressure. The residue was purified as described previously to give 61 mg (61%) of **1b**, 50 mg (39%) of **4**, and 47 mg (86%) of diphenyl diselenide.

The data given in Table 1 were obtained by carrying out the reactions in an **NMR** tube, with $CDCl_3$ as the solvent.

*Reaction of the Alkene **1a** with Benzenesulfenyl Chloride*

Benzenesulfenyl chloride was prepared from thiophenol and sulfuryl chloride and used immediately after purification by distillation (54°C;2 mm Hg). A dichloromethane solution containing 26 mg (0.18 mmol) of benzenesulfenyl chloride was added to a solution of 50 mg (0.18 mmol) of **1a** in 10 ml. of dichloromethane at room temperature. After the mixture had been stirred for 38 h at room temperature, ca. 100 mg (1.2 mmol) of tetramethylethylene was added, which brought about disappearance of the yellow color of benzenesulfenyl chloride. The mixture was evaporated and the residue was purified by silica-gel column chromatography and then by GPC to give 47 mg (95%) of a mixture of **1a** and **1b** in the ratio 65:35 and 13 mg (40%) of 2,3-dimethyl-1-phenylthio-2-butene **(11)** [6].

*Reaction of the Alkene **1b** with Benzenesulfenyl Chloride*

The reaction was carried out under the same conditions as that described earlier. The mixture was also purified in the same way as described previously to give 47 mg (95%) of a mixture of **1a** and **1b** in the ratio 40:60 and 14 mg (40%) of 2,3-dimethyl-1-phenylthio-2-butene **(11)**.

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