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Facile C-Se and C-S Bond Cleavages in Diorganyl Selenides and Sulfides by Iodine

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The C-Se and C-S bonds in $ArSeCH_2SeAr$, $PhCH_2SeCH_2SeCH_2Ph$, $(p\text{-}t\text{-}BuC_6H_4SeCH_2)_2$, 1,8-$(MeSe)_2C_{10}H_6$, $PhCH_2SeMe$, $PhSCH_2SPh$, and $PhCH_2SCH_2SCH_2Ph$ are easily cleaved by iodine, while those of $PhSe(CH_2)_3SePh$, 1-$MeSeC_{10}H_7$, $PhSeCH_2I$, and $PhCH_2SMe$ are not. The driving force of the reaction is also discussed.

The σ^*-orbital of iodine has been well established to accept the n-electrons of ethers, sulfides, and selenides to yield molecular complexes (MC's),$^{1)}$ however, the chemistry of MC's has received less attention. During the course of the investigation into the reaction of iodine with diorganyl chalcogenides, I have encountered a facile C-Se bond cleavage in bis(phenylseleno)methane (**1**) by iodine (eq 1). Here I wish to report the scope of the facile carbon-chalcogen bond cleavages in diorganyl chalcogenides by iodine and the driving force of the reaction.

Table 1 shows the scope of the reaction.$^{2)}$ The C-Se bonds in $(p\text{-}YC_6H_4Se)_2CH_2$ (**2a**: Y = MeO, **2b**: Y = Me, **2c**: Y = Cl), bis(benzylseleno)methane (**3**), $(p\text{-}t\text{-}BuC_6H_4SeCH_2)_2$ (**4**), 1,8-bis(methylseleno)naphthalene (**5**), and benzyl methyl selenide (**6**) were easily cleaved by iodine, together with that of **1**, while those of 1,3-bis(phenylseleno)propane (**7**), 1-(methylseleno)naphthalene (**8**), $PhSeCH_2I$, and PhSeMe did not react with iodine under the conditions ($[S]_o = 0.015$ mol/l and $[I_2]_o = n[S]_o$ ($n \geq 3.0$) in $CDCl_3$ at ca. 27 °C or higher temperatures). The reaction of **5** with iodine was very fast to yield naphtho[1,8-*c*,*d*]-1,2-diselenole and methyl iodide. The C-S bond cleavage was also observed in bis(phenylthio)methane (**9**) and bis(benzylthio)methane (**10**), whereas those in $PhCH_2SMe$ and PhSMe did not react with iodine under the conditions. Though the benzyl-S bond was not cleaved in **10**, the benzyl-Se bond was cleaved in **3**. The C-O bonds of ethers such as bis(phenoxy)methane (**11**), $PhCH_2OMe$, and PhOMe were not cleaved by iodine.

$$PhSeCH_2SePh\,(\mathbf{1}) + I_2 \longrightarrow PhSeCH_2I + PhSeI \qquad (1)$$

$$R\text{-}Z\text{-}R' + I_2 \rightleftharpoons R\text{-}ZI_2\text{-}R'\,(MC) \xrightarrow{I_2} R\text{-}Z^+I\text{-}R' + I_3^- \xrightarrow{-I_2} R\text{-}Z\text{-}I + R'\text{-}I \qquad (2)$$

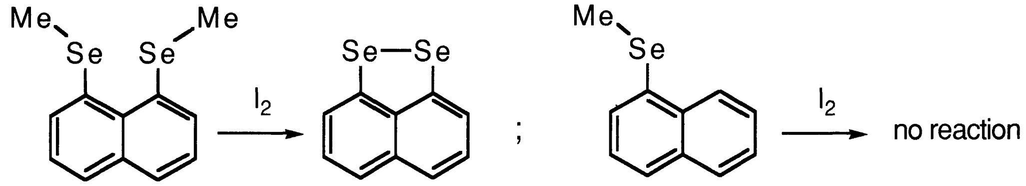
A chalcogenide (R-Z-R') is in rapid equilibrium with $R\text{-}ZI_2\text{-}R'$ under the conditions (eq 2).$^{1b)}$ An iodochalcogenium ion ($R\text{-}Z^+I\text{-}R'$) and an I_3^- ion would form when $R\text{-}ZI_2\text{-}R'$ is attacked by an iodine molecule. The C-Z bond is suggested to be cleaved by the following S_N2 type reaction of the two species (eq 2).$^{3)}$

In the case of the monoselenide **6**, the small dissociation energy of the benzyl-Se bond would be the driving force of the reaction, while the benzyl-S bond in $PhCH_2SMe$ may not be weak enough for the reaction.$^{4)}$ The C-Se and C-S bonds in **8**, $PhSeCH_2I$, PhSeMe, and PhSMe may also be too strong to be cleaved. The benzyl-Se bond cleavage in **3** in contrast to the methylene-S scission in **10** must be the reflection of the weak benzyl-Se

Table 1. C-Se and C-S Bond Cleavages by Iodine

Compound[a]	Rate of the reaction[b]	Compound[a]	Rate of the reaction[b]
ArSeCH$_2$-SeAr (**1**, **2**)[c]	++	PhSeCH$_2$CH$_2$CH$_2$SePh (**7**)	-
PhCH$_2$SeCH$_2$Se-CH$_2$Ph (**3**)	++	1-MeSeC$_{10}$H$_7$ (**8**)	-
ArSeCH$_2$CH$_2$-SeAr (**4**)[d]	++	PhOCH$_2$OPh (**11**)	-
1,8-(Me-Se)$_2$C$_{10}$H$_6$ (**5**)	+++	PhCH$_2$SMe	-
PhCH$_2$-SeMe (**6**)	++	PhCH$_2$OMe	-
PhSCH$_2$-SPh (**9**)	++	PhSeCH$_2$I	-
PhCH$_2$SCH$_2$-SCH$_2$Ph (**10**)	++	PhZMe (Z = O, S, Se)	-

a) Bonds being cleaved are shown as -. b) ++: Fairly fast (half-lives are a few hours), +++: Very fast to measure the rate, -: No sign of the reaction or very slow. c) **1** (Ar = Ph), **2a** (Ar = *p*-MeOC$_6$H$_4$), **2b** (Ar = *p*-MeC$_6$H$_4$), **2c** (Ar = *p*-ClC$_6$H$_4$). d) Ar = *p*-*t*-BuC$_6$H$_4$.



5 **8**

bond relative to the benzyl-S bond: the benzyl-Se bond must be more reactive than the methylene-Se bond in **3** under the conditions, whereas the benzyl-S bond would be less reactive than the methylene-S bond in **10**.

The fact that the facile C-Se and C-S bond cleavages were observed in bis-selenides **1**-**5** and bis-sulfides **9** and **10** shows that those bonds react with iodine for such selenides or sulfides that contain two selenium or two sulfur atoms placed in proximity in space.[5] The very facile C-Se bond cleavage in **5**[6] supports the conclusion, although the reactivity of the compounds in Table 1 is not thoroughly explained yet.[5] The details of the reaction containing the role of the second seleno- and thio-groups are in progress.

References

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3) The C-Se bond cleavage by bromine has been reported: O. J. K. Edwards, W. R. Gaythwaite, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, **1928**, 2293; J. Gosselck, *Chem. Ber.*, **91**, 2345 (1958).
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6) See also, H. Fujihara, R. Saito, M. Yabe, and N. Furukawa, *Chem. Lett.*, **1992**, 1437.

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