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REGIOSELECTIVE SYNTHESIS OF BICYCLIC DISELENIDES BY THE REACTION OF PHOSPHONIUM YLIDES WITH ELEMENTAL SELENIUM

Kentaro Okuma,* Isao Kaneko, Hiroshi Ohta, and Yoshinobu Yokomori†

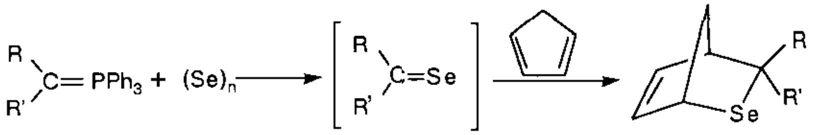
Department of Chemistry, Faculty of Science, Fukuoka University, Jonan-ku, Fukuoka 814-01, Japan

†Department of Chemistry, National Defence Academy, Hashirimizu, Yokosuka 239, Japan

Abstract - Selenabicyclo[2.2.1]heptenes reacted with elemental selenium to produce unusual bicyclic diselenides in 30-40% yield. The reaction of phosphonium ylides with excess of elemental selenium also afforded bicyclic diselenides in good yields. The reactions might proceed via biradical intermediates.

The chemistry of molecules having unstable carbon-heteroatom multiple bond is of great interest. Recently, many workers have reported the synthesis and reactions of selenoaldehydes and selenoketones.[1-4]

We have also described the formation of selenocarbonyl compounds (1) by the reaction of phosphonium ylides (2) with elemental selenium.[5] Because of the ease with which 1 could be converted into cyclic or bicyclic selenides (3) with dienes or cyclopentadiene, this reaction appears to have considerable synthetic potential.[3,4,6]



2 1 3

This consideration prompted us to investigate the further study of the reaction of phosphonium ylides with elemental selenium. In this communication, we would like to report the reaction of cyclic selenides with elemental selenium. When 3,3-diphenyl-2-selenabicyclo[2.2.1]hept-5-ene (**3a**) was treated with elemental selenium in toluene, we obtained bicyclic diselenide (**4a**) in 34% yield. Other bicyclic selenide (**3**) were successfully converted to **4** in moderate yields (Table 1). The reaction is regioselective; only one isomers of **4a-c** were obtained in this reaction.

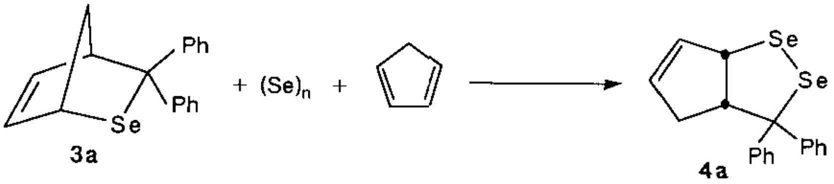


Table 1. Reaction of 3 with Elemental Selenium.

Compound 3			Conditions		Products	
	R	R'	Temperature	Solvent	4	Yield (%)
a	Ph	Ph	90 °C	benzene	a	34
a	Ph	Ph	reflux	toluene	a	38
b	p-MeC_6H_4	p-MeC_6H_4	90 °C	toluene	b	38
c	p-FC_6H_4	p-FC_6H_4	90 °C	toluene	c	40

Regiochemistry was determined by their ^{1}H- and ^{13}C-nmr spectra.[7] Additionally, X-ray crystallographic analysis was performed in the case of **4a**.[8]

Since 3 were prepared by the reaction of phosphonium ylides with selenium and cyclopentadiene, we further tried this reaction in the presence of excess of selenium. Treatment of diphenylmethyltriphenylphosphonium bromide with butyllithium (1.2 eq.) followed by the addition of elemental selenium (4 eq.) afforded a bright green solution of selenobenzophenone (**1a**). After treating this solution with 4 eq. of cyclopentadiene for 18 h at 90 °C, reddish orange crystals of bicyclic diselenide (**4a**) and triphenylphosphine selenide (**5**) were obtained in 42% and 75% yields, respectively. The reaction of other substituted 2 with elemental selenium was summarized in Table 2.

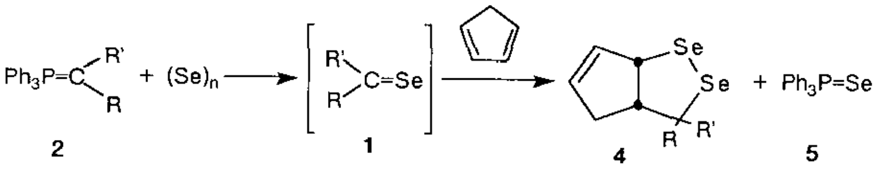
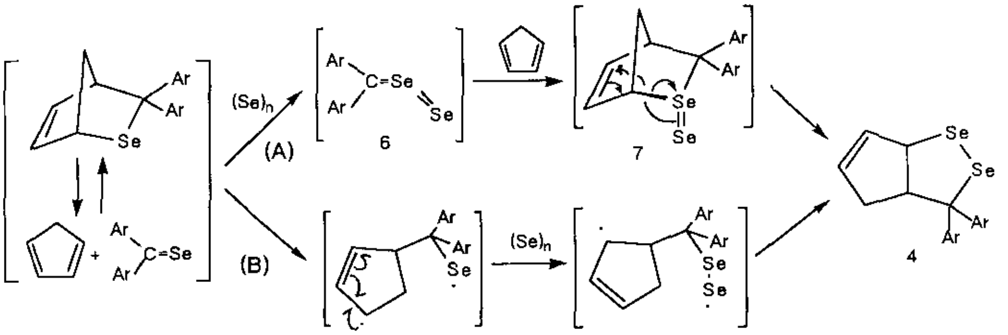


Table 2. Reaction of 2 with Selenium and Cyclopentadienes.

Ylide 2		Diene	Conditions		Products (Isolated Yield %)		
R	R'		Temperature	Solvent	4		5
Ph	Ph	Cp[a)]	reflux	benzene	a	42	75
Ph	Ph	Cp	90 °C	toluene	a	55	82
p-MeC_6H_4	p-MeC_6H_4	Cp	90 °C	toluene	b	71	80
p-FC_6H_4	p-FC_6H_4	Cp	90 °C	toluene	c	75	82
p-ClC_6H_4	p-ClC_6H_4	Cp	90 °C	toluene	d	62	78
Ph	Ph	MeCp	90 °C	toluene	e, f[b)]	63	76
H	COOEt	Cp	reflux	toluene	g	28	68

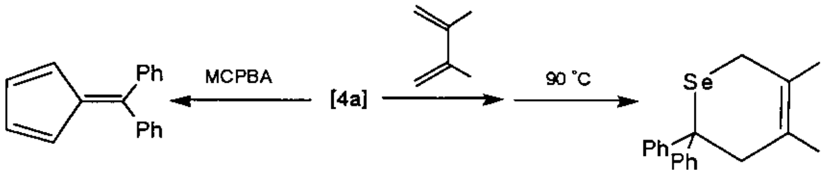
a) Cp=Cyclopentadiene, MeCp=Methylcyclopentadiene. b) A mixture of regioisomers of bicyclic diselenides (**4e** and **4f**) was obtained (ratio; **4e**:**4f**=4:1).

There are two possible mechanisms to explain the formation of **4**. First, **3** was decomposed to give selenobenzophenone via a retro-Diels-Alder reaction, which further reacted with elemental selenium to afford diarylselenoselenine (**6**). Compound (**6**) reacts with cyclopentadiene to give *endo*-selenoselenide (**7**) which rearranges to bicyclic diselenide (**4**) (Route A). Block *et al.* reported that bicyclic oxathiane was formed via an endo oxo-sulfide intermediate.[9] A radical mechanism is another explanation on the formation of bicyclic diselenides (**4**). The adducts (**3**) homolytically decompose to biradicals which further reacted with selenium followed by recombination to afford the bicyclic diselenide **4** (Route B).



To confirm which mechanism is operative, we then tried esr study in this reaction. When **2a** was treated with butyllithium, elemental selenium, followed by the addition of cyclopentadiene in toluene at 100 °C, a broad signal was observed in its esr spectrum (G value; 2.00). This result suggests that the reaction proceeds through a radical intermediate. At present, we think that Route B is plausible in the reaction.

Many methods have been reported on the preparation of acyclic diselenides. However, there is quite a few reports on the synthesis of cyclic diselenides. Only one example includes the cycloaddition of selenofluorenone, which acted as not only a dipolarophile but also a dipole.[10] This is the first convenient synthesis of cyclic diselenides. Diselenides (**4**) form a new class of compounds, and yet, their reactivity has not been known. In the case of cyclic selenides, many workers reported the *retro*Diels-Alder reaction.[4,11,12] We tried the reaction of **4a** with 2,3-dimethylbutadiene at 90 °C. The isolated product was a Diels-Alder adduct of selenobenzophenone (**8a**) as expected. Presumably, the thermal decomposition of **4a** afforded selenobenzophenone (**1a**), which reacted with 2,3-dimethylbutadiene to give **8a**. We also tried the oxidation of **4a**. Treatment of **4a** with 3-chloroperbenzoic acid (MCPBA) afforded diphenylfulvene in 48% yield.



8a

We are currently exploring the various possibilities offered by these preliminary results.

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7 **5a**; mp 159-160 °C, ^{1}H nmr ($CDCl_3$) δ 2.20 (m, 1 H), 2.35 (m, 1 H), 4.65 (q, J=7.0 Hz, 1 Hz), 5.10 (m, 1 H), 5.70 (m, 1 H), 5.85 (m, 1 H), 7.07-7.65 (m, 5 H), 7.15 (s, 5H), ^{13}C nmr ($CDCl_3$) δ 40.25, 57.15, 59.16, 83.21, 126.77, 126.94, 127.47, 128.23, 128.39, 130.40, 132.51, 132.94, 145.08, 146.70. **5b**; mp 118-119 °C. **5c**; mp 119-120 °C. **5d**; mp 122-124 °C. **5e**; mp 143-144 °C. **5f**; mp 141-142 °C.

8 Crystal data for **5a**: space group Pna2_1, a=10.694(1) Å, b=9.289(1) Å, c=15.340(2) Å, V=1523.8 Å^3, Z=4, d_{calc}=1.70 g cm^{-3}. Data collected at 25 °C on Rigaku AFC-III diffractometer with MoK radiation, m=47.9 cm^{-1}, 2q limits 3.0-50.0 , 182 variables refined with 1076 unique reflections F_o>3s (F_o) to R=0.067 (R_w=0.034).

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