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NEW SYNTHETIC METHOD OF [2.2]PARACYCLOPHANE, BENZOCYCLOBUTENE, AND LEPIDOPTERENE: PYROLYSIS OF ARYLMETHYL PHENYL SELENIDES

Hiroyuki HIGUCHI, Yoshiteru SAKATA, and Soichi MISUMI*
The Institute of Scientific and Industrial Research, Osaka University
Suita, Osaka 565
Tetsuo OTSUBO, Fumio OGURA, and Hachiro YAMAGUCHI
Department of Applied Chemistry, Faculty of Engineering,
Hiroshima University, Sendamachi, Hiroshima 730

The flash vacuum pyrolysis of benzyl phenyl selenides gave bibenzyls and diphenyl diselenide in excellent yields. This type of reaction was successfully applied to the synthesis of the title compounds.

It is well known that the chemistry of cyclophanes bearing unusual geometrical features has been drastically developed by the emergence of the synthetic method via desulfurization of dithia cyclophanes.1) Organoseleniums have been recently appreciated to be very useful for organic syntheses,2) and are also expected to be applicable to the synthesis of cyclophanes. Mitchell reported that the conversion of diselena[3.3]metacyclophane to [2.2]metacyclophane-diene was failed.3) Here we report on the syntheses of [2.2]paracyclophane and the other title aromatic hydrocarbons by utilizing the pyrolytic reactions of acyclic organoseleniums.

We previously described that the flash vacuum pyrolysis of dibenzyl selenide at 600 °C under 20 mmHg resulted in ready extrusion of elemental selenium to give bibenzyl in high yield.4) The thermal lability of benzylic C-Se bond was also found in the case of benzyl phenyl selenide 1. Thus, similar pyrolysis of 1 led to a mixture of bibenzyl 2 (92%) and diphenyl diselenide 3 (98%). Diphenyl diselenide 3 was treated with benzyl chloride or bromide in ethanol in the presence of sodium borohydride to give the starting material 1 in over 90% yield.5)

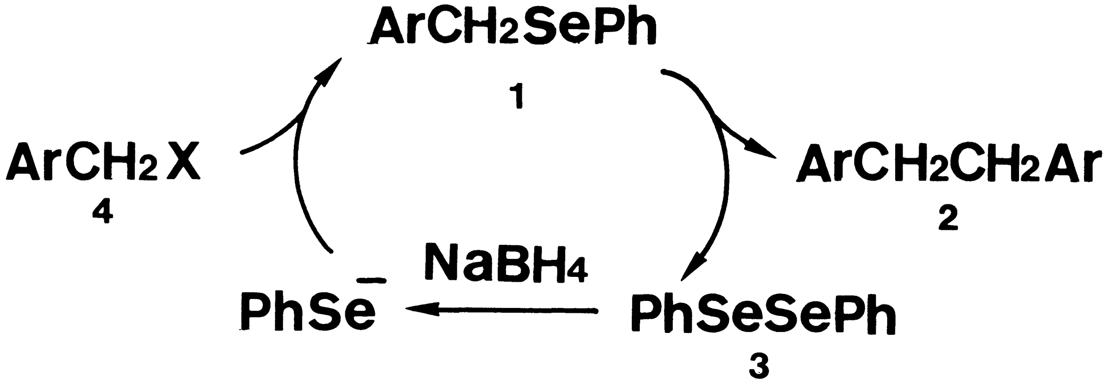
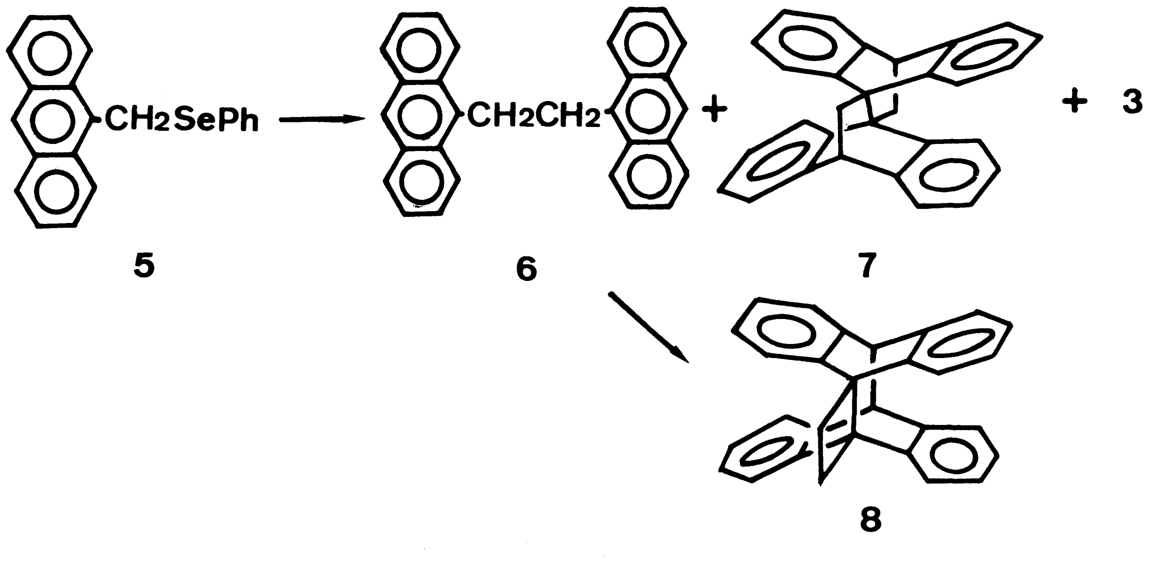


Table 1. Pyrolyses of $ArCH_2SePh$ to $ArCH_2CH_2Ar$

Ar	$ArCH_2CH_2Ar$ Yield %	Ar	$ArCH_2CH_2Ar$ Yield %
$p-CH_3C_6H_4$	87	$p-NCC_6H_4$	73
$p-ClC_6H_4$	73	$p-CH_3O_2CC_6H_4$	90
$o-ClC_6H_4$	72	1-Naphthyl	76
$p-BrC_6H_4$	83	4-Me-1-Naphthyl	90
$p-NO_2C_6H_4$	73	2-Thienyl	92
$p-CH_3OC_6H_4$	66	2-Pyridyl	68

Accordingly, this reaction cycle provides a new method for the preparation of bibenzyl **2** from benzyl halide **4**. Pyrolyses of various derivatives of **1**, which were readily prepared by treatment of the corresponding benzyl halides with benzene selenoates, gave a series of bibenzyl derivatives and 1,2-diarylethanes in high yields, as shown in Table 1. This pyrolytic method surpasses the other pyrolyses of dibenzyl sulfones, oxalates, and selenides with regard to the yields of bibenzyl derivatives bearing polar functional groups, because the latter three methods are often subject to undesirable decomposition due to low vapor pressure of the starting compounds. For example, p,p'-dimethoxybibenzyl can not be obtained by pyrolysis of the corresponding oxalate.6)



1-Naphthylmethyl phenyl selenide underwent the similar reaction to 1,2-di(1-naphthyl)ethane in 76% yield and 9-anthrylmethyl phenyl selenide **5**5) to 1,2-di(9-anthryl)ethane **6** in 91% yield. On the other hand, the thermal reaction of **5** in solid state or in a toluene solution at 150-170 °C gave a polycyclic compound **7** of unique structure as a main product (Table 2).7) The novel compound **7** was recently synthesized by the reaction of 9-chloromethylanthracene with methylmagnesium iodide8) or photolysis of 9-anthrylmethyl sulfide or selenide,9) and named lepidopterene. The irradiation of **5** with a high pressure mercury lamp in benzene solu-

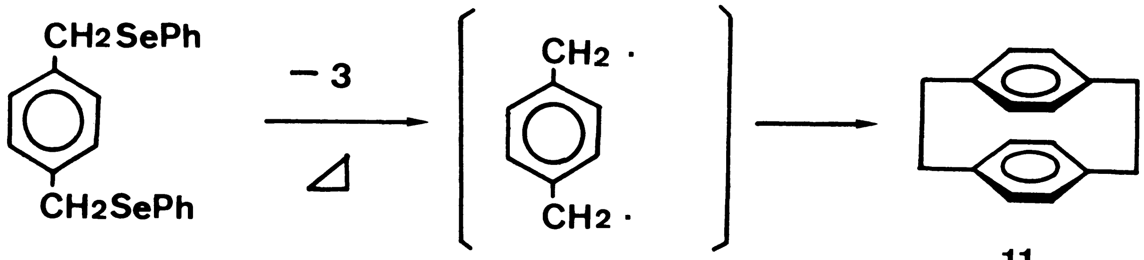
Table 2. Thermal and Photochemical Reactions of 9-AnthCH_2SePh 5.

	3	6	7	8
flash vacuum pyrolysis(600 °C, 20 mmHg)	94	91	0	0
pyrolysis in sealed tube(150 °C, 5 min)	96	14	82	0
pyrolysis in toluene(170 °C, 735 min)[a]	95	24	68	0
photolysis in benzene(r.t., 4 h)[b]	95	0	66	25

a) in a sealed tube. b) with a high pressure mercury lamp under N_2.

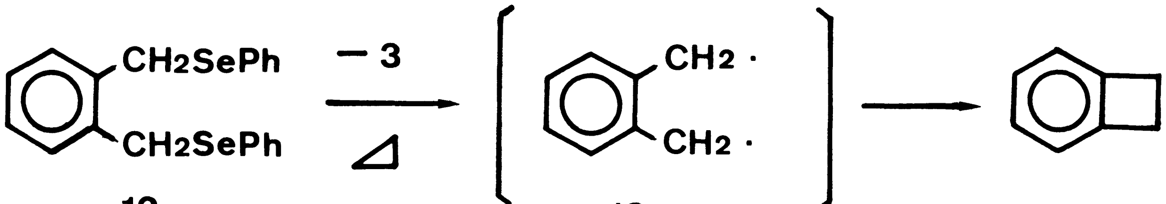
tion also gave rise to lepidopterene in good yield. In this case, a photoisomer **8** (biplanene) was isolated in the place of dianthrylethane **6**.[7)]

The analogous reaction of bifunctional benzene is expected to provide a method for the synthesis of cyclophane. Thus, the thermal elimination of diphenyl diselenide **3** from 1,4-bis(phenylselenomethyl)benzene **9**[5)] may generate biradical **10** which dimerizes to yield [2.2]paracyclophane **11**.[10)] In fact, pyrolysis of **9** at 650 °C under 7 mmHg gave **11** (23% yield) and diphenyl diselenide (69%). The yield of **11** is relatively low due to competition with polymerization, but fairly higher than those of other pyrolytic methods via cyclic[11)] or acyclic[12)] bis-sulfones.



9 10 11

A similar pyrolysis of 1,2-bis(phenylselenomethyl)benzene **12**[5)] gave rise to benzocyclobutene **14**[1c)] via intramolecular ring closure of biradical **13**. As shown in Table 3, the yield was very dependent on the vacuum pressure of the pyrolytic



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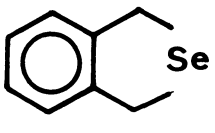

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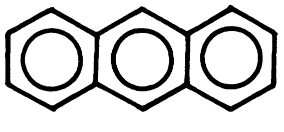

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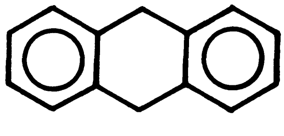

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system. Under lower vacuum, some side reactions occurred to form 1,3-dihydrobenzo[c]selenophene **15**$^{13)}$ and two incomprehensible products, anthracene **16** and dihydroanthracene **17**.

Table 3. Flash Vacuum Pyrolysis of 1,2-Bis(phenylselenomethyl)benzene **12**.

Conditions	Yield %				
	3	**14**	**15**	**16**	**17**
600 °C, 3 mmHg	10	5	0	0	0
600 °C, 8 mmHg	40	40	13	0	0
600 °C, 20 mmHg	47	7	38	18	8

References and Notes

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5) All the selenides were prepared in the same way as described for **1**. **1**, mp 33.5-34 °C; **5**, mp 124.5-126 °C; **9**, mp 137-138 °C; **12**, mp 30.5-31.5 °C.

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