Flash Pyrolysis of Selenides. Syntheses of Bibenzyls, Olefins, and Related Compounds

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Pyrolyses of a series of selenides and diselenides were studied. Selenides and diselenides bound with an active methylene group like benzyl gave a variety of substituted bibenzyls and related ethane derivatives in high yields. Other diselenides were easily caused to cleave to give various aromatic and aliphatic olefins in good yields together with elemental selenium. Lepidopterene, [2.2]paracyclophane, and benzocyclobutene were prepared by thermal cleavage of their corresponding phenylselenomethyl-substituted compounds as an application of the pyrolysis concerned.

Formation of carbon-carbon bond by sulfur extrusion is of importance as a synthetic method. For example, pyrolysis of cyclic sulfones made a significant contribution to the remarkable development of cyclophane chemistry.[1] In contrast, little attention has been paid to selenium extrusion of organoselenium compounds, partly because high oxidation states of selenium are usually unstable. Recently Chu and Lewicki[2] reported that bis(diphenylmethyl) diselenide thermally decomposed with loss of elemental selenium to give 1,1,2,2-tetraphenylethane. Couture *et al.*[3] studied pyrolysis of bis(9-anthrylmethyl) selenide and diselenide to 1,2-di(9-anthryl)ethane. We found that on gas-phase pyrolysis, dibenzyl selenide **1** gave bibenzyl in a high yield, in contrast to no reaction occurring with dibenzyl sulfide.[4] Several pieces of information on such labile C–Se bonds stimulated us to initiate an extensive study on thermal behaviors of various organoselenium compounds. Here we report on thermal decomposition of mono- and diselenides **2**—**13** and some applications to synthesis of related compounds.[5]

Results and Discussion

Selenides **2**—**13** were prepared by the conventional methods described in the experimental part. Selenium extrusion on them was carried out by the flash vacuum pyrolysis which had successfully been used for dibenzyl selenide **1**.[4] The reaction of **1** is capable of proceeding above 400 °C with the optimal yield at 600 °C under 20 mmHg (1 mmHg≈133.322 Pa). The best results obtained in the present study with almost the same conditions are summarized in Table 1. As seen from this table, pyrolysis products are significantly dependent on characters of selenium bonds, which are classified into four groups as follows:

1. Selenides **4**, **7**, and **9** were recovered because they possess no readily cleavable bonds. In spite of being highly susceptible to homolysis to phenylseleno radical, diphenyl diselenide **2** was exceptionally unreactive. Probably the fragment radical favors recombination to the original molecule over fragmentation.
2. Selenides **1** and **5**, both having labile bilateral bonds of selenium, readily underwent selenium extrusion to form C–C bonds.
3. Pyrolysis of benzyl phenyl selenide **3** gave a mixture of bibenzyl and diphenyl diselenide **2** in high yields. These two products were formed apparently by individual dimerizations of benzyl and phenylseleno radicals which had been generated by homolytic cleavage of the benzyl-Se bond of **3**.

$$\underset{\mathbf{3}}{PhCH_2SePh} \xrightarrow{\Delta} Ph\dot{C}H_2 + \dot{S}ePh$$

$$\longrightarrow PhCH_2CH_2Ph + \underset{\mathbf{2}}{PhSeSePh}$$

Table 1. Pyrolyses of organoselenides **1**—**13** at 600 °C under 20 mmHg

Selenide		Product (Yield/%)
$PhCH_2SeCH_2Ph$	**1**	$PhCH_2CH_2Ph(80)+Se$[b]
PhSeSePh	**2**	Recovery
$PhCH_2SePh$	**3**[a]	$PhCH_2CH_2Ph(92)+PhSeSePh(98)$
$PhCH_2CH_2SePh$	**4**	Recovery
$PhCH_2SeSeCH_2Ph$	**5**	$PhCH_2CH_2Ph(96)+Se$[b]
$PhCH_2SeCH_2CH_2Ph$	**6**	$PhCH{=}CH_2(96)+PhCH_2CH_2Ph(37)+PhCH_3(48)+Se$[b]
$PhCH_2CH_2SeCH_2CH_2Ph$	**7**	Recovery
$PhCH_2CH_2SeSeCH_2CH_2Ph$	**8**	$PhCH{=}CH_2(95)+Se$[b]
$n\text{-}C_6H_{13}Se\text{-}n\text{-}C_6H_{13}$	**9**	Recovery
$n\text{-}C_6H_{13}SeSe\text{-}n\text{-}C_6H_{13}$	**10**	$C_4H_9CH{=}CH_2(90)+C_{12}H_{26}(7)+Se$[b]
$PhSeCH_2CH{=}CH_2$	**11**	$CH_2{=}CHCH_2CH_2CH{=}CH_2(67)+PhSeSePh(88)$
$PhSeCH_2CN$	**12**	$NCCH_2CH_2CN(87)+PhSeSePh(90)$
$PhSeCH_2COCH_3$	**13**[a]	$CH_3COCH_2CH_2COCH_3(52)+PhSeSePh(93)$

a) Pyrolytic temperature, 650 °C. b) Almost quantitative yield.

Table 2. Yield and properties of $ArCH_2SePh$

Ar	Yield %	Mp °C	NMR data $CDCl_3$, δ	MS *m/e* M^+	Found (%)	Calcd (%)
p-$CH_3C_6H_4$	95	29—31 (30—31)[a]	2.30(s, CH_3), 4.08(s, CH_2), 7.08 (bs, ArH), 7.25—7.40(m, Ph)	262	C, 64.14 H, 5.31	64.37 5.36
p-ClC_6H_4	86	57.5—58.5	4.03(s, CH_2), 7.10, 7.17(A_2B_2m, ArH), 7.25—7.42(m, Ph)	282, 284	C, 55.16 H, 3.84 Cl, 12.72	55.41 3.91 12.61
o-ClC_6H_4	91	Oil	4.15(s, CH_2), 7.06—7.49(m, ArH, Ph)	282, 284	C, 55.52 H, 4.05 Cl, 12.64	55.41 3.91 12.61
p-BrC_6H_4	87	61—62	4.01(s, CH_2), 7.04, 7.45(A_2B_2m, ArH), 7.25—7.42(m, Ph)	326, 328	C, 47.62 H, 3.46 Br, 24.51	47.85 3.37 24.54
p-$NO_2C_6H_4$	67	59.5—60	4.09(s, CH_2), 7.22, 8.05(A_2B_2m, ArH), 7.26—7.37(m, Ph)	293	C, 53.23 H, 3.75 N, 4.79	53.42 3.77 4.79
p-$CH_3OC_6H_4$	90	74—75 (75—76)[a]	3.77(s, CH_3), 4.07(s, CH_2), 6.78, 7.11(A_2B_2m, ArH), 7.24—7.41(m, Ph)	278	C, 60.47 H, 5.26	60.65 5.05
p-$CH_3O_2CC_6H_4$	77	62.5—63	3.87(s, CH_3), 4.09(s, CH_2), 7.21, 7.88(A_2B_2m, ArH), 7.25—7.38(m, Ph)	306	C, 59.08 H, 4.68	59.01 4.59
p-NCC_6H_4	76	72—72.5	4.05(s, CH_2), 7.21, 7.47(A_2B_2m, ArH), 7.24—7.41(m, Ph)	273	C, 61.48 H, 4.14 N, 5.13	61.76 4.04 5.15
1-Naphthyl	83	Oil	4.54(s, CH_2), 7.21—8.08(m, ArH, Ph)	298	C, 68.41 H, 4.83	68.69 4.72
4-CH_3-1-Naphthyl	93	66—68	2.63(s, CH_3), 4.52(s, CH_2), 7.24—8.08(m, ArH, Ph)	312	C, 69.45 H, 5.23	69.45 5.44
2-Thienyl	88	Oil	4.29(s, CH_2), 6.79—7.51(m, ArH, Ph)	254	C, 51.99 H, 3.97	52.17 3.95
2-Pyridyl	78	Oil	4.22(s, CH_2), 7.15—7.47(m, ArH, Ph)	249	C, 58.23 H, 4.53 N, 5.78	58.06 4.43 5.65

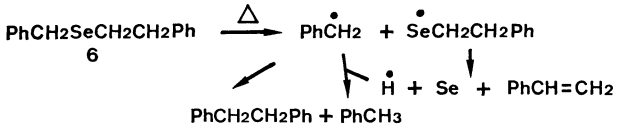
a) Ref. 19.

Allyl phenyl selenide **11**, phenylselenoacetonitrile **12**, and phenylselenoacetone **13** underwent analogous cleavages to give biallyl, succinonitrile, and 2,5-hexanedione, respectively, together with diphenyl diselenide.

4. Diphenethyl diselenide **8** was caused to cleave to yield styrene and elemental selenium but no 1,4-diphenylbutane, as expected on the simple selenium extrusion sequence. Dihexyl diselenide **10** showed a similar behavior in yielding 1-hexene with a minute amount of dodecane. Pyrolyses of dioctyl diselenide **14** and dioctyl disulfide **15** were examined for comparison of reactivities between both the organochalcogen compounds. 1-Octene was obtained in a high yield (93%) from **14**, while in a low yield (18%) from **15**.

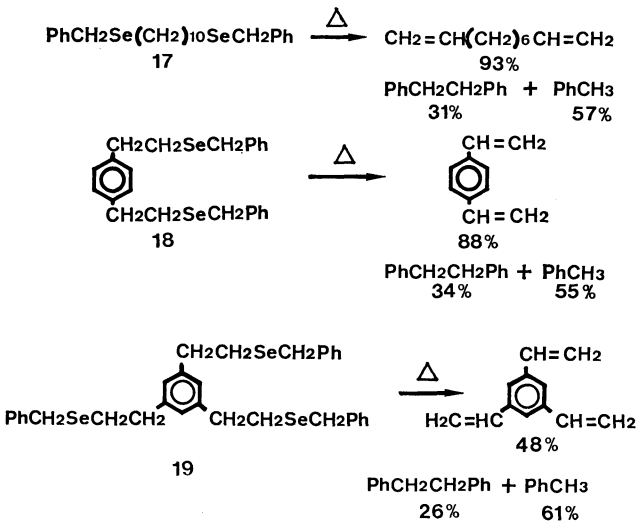
$$\underset{\mathbf{14}}{C_8H_{17}SeSeC_8H_{17}} \xrightarrow{\Delta} \underset{93\%}{C_6H_{13}CH{=}CH_2} \xleftarrow{\Delta} \underset{18\%}{C_8H_{17}SSC_8H_{17}}\ \mathbf{15}$$

Benzyl phenethyl selenide **6** is particularly interesting, for it can combine with functional groups of types 3 and 4 specified above. In fact, it gave four products, bibenzyl, styrene, toluene, and elemental selenium, in a high total yield. As seen from the scheme, the formation of a considerable amount of toluene indicates that part of benzyl radicals are possibly quenched by H· radicals derived from phenethylseleno radicals.

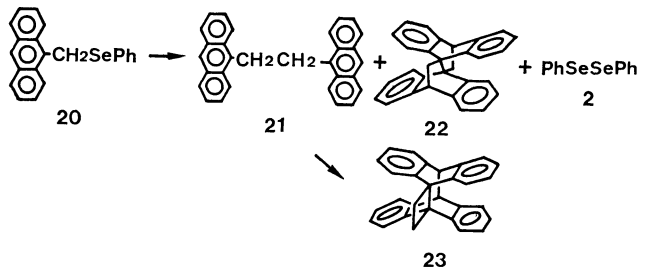


In the case of sulfur derivatives, on the other hand, benzyl phenethyl sulfide failed to undergo any pyrolytic reactions, while its sulfone **16** decomposed to give a mixture of bibenzyl, styrene, and 1,3-diphenylpropane. The pyrolysis of **6** and **16** indicates that the pyrolytic mechanism of selenide is somewhat different from that of sulfone. Analogous pyrolytic reactions were observed with polyfunctional compounds **17**, **18**, and **19** which yield polyolefins.

$$\underset{\mathbf{16}}{PhCH_2SO_2CH_2CH_2Ph} \xrightarrow{\Delta} \underset{56\%}{PhCH_2CH_2Ph} + \underset{34\%}{PhCH{=}CH_2}$$
$$PhCH_2CH_2CH_2Ph + SO_2$$
$$28\%$$



Of many synthetic methods for bibenzyls the most convenient ones utilize the Grignard reaction and the Wurtz reaction on benzyl halides. However, some functional groups have a reactivity so variable with reaction conditions as to make it difficult to synthesize their related bibenzyls by these methods. Extrusion reactions of dibenzyl sulfone,[6] dibenzyl oxalate,[7] and dibenzyl selenide[4] have been useful for preparation of some bibenzyls. Benzyl phenyl selenide **3** also can be utilized as a starting material for synthesis of bibenzyls. Thus, pyrolyses of derivatives of **3**, which are readily prepared by treatment of the corresponding benzyl halides with benzeneselenolate (Table 2), gave various bibenzyls and 1,2-diarylethanes in high yields (Table 3). It is noticeable that diphenyl diselenide **2** concomitantly formed in such reactions is reusable to generate benzeneselenolate. Accordingly, the present method surpasses the extrusion methods with regard to yield and wide applicability, as described below. Vapor pressures of sulfones, oxalates, and selenides with bifunctional polar groups are very low and hence they are often subject to undesirable decomposition before being vaporized for extrusion. For example, 4,4′-dimethoxybibenzyl could be obtained by the present method, but not by pyrolysis of its corresponding dibenzyl oxalate.[7]



A flash vacuum pyrolysis of 9-anthrylmethyl phenyl selenide **20** gave 1,2-di(9-anthryl)ethane **21** as expected (see Table 4). On the other hand, a thermal reaction of **20** in solid state or in toluene solution at 150—170 °C provided in a high yield a unique structure compound, lepidopterene **22** which had previously been synthesized by reaction of 9-(chloromethyl)-anthracene with methylmagnesium iodide[8] or photolysis of 9-anthrylmethyl sulfide or selenide.[3] The yields of **22** by the present method are much higher than those by the previous methods. Photolysis of **20** also led to **22** as well as a photodimer biplanene **23**. In every case, diphenyl diselenide **2** was a concomitant product with almost a quantitative yield.

The ring contraction accompanying the extrusion of sulfur dioxide from cyclic sulfones is very suitable for synthesis of cyclic hydrocarbons. For example, a heating of cyclic disulfone **24** gave [2.2]paracyclophane **25** in 15—18% yield.[9] In contrast, no synthesis of cyclophanes by organoselenium has yet been known, because no cyclic selenides have so far been made available.[10] One may expect that heating of 1,4-bis(phenylselenomethyl)benzene **27** would generate, with elimination of diphenyl diselenide **2**, biradical **28** which, in equilibrium with quinodimethane **29**, is dimerized to form [2.2]paracyclophane **25**.[11] In fact, acyclic diselenide **27** was readily prepared in 85% yield from 1,4-bis(chloromethyl)benzene **26** and gave [2.2]paracyclophane **25** (23% yield) and diphenyl di-

Table 3. Pyrolyses of $ArCH_2SePh$ to $ArCH_2CH_2Ar$

Ar	Yield/% of $ArCH_2CH_2Ar$	Mp/°C of $ArCH_2CH_2Ar$(lit)
p-$CH_3C_6H_4$	87	80—81(81—81.5)[a]
p-ClC_6H_4	73	98—99(100—101)[b]
o-ClC_6H_4	72	57—58.5(59—61)[b]
p-BrC_6H_4	83	113—114(112—114)[b]
p-$NO_2C_6H_4$	73	177—178.5(179—180)[c]
p-$CH_3OC_6H_4$	66	124—125(126.4—126.8)[a]
p-$CH_3O_2CC_6H_4$	90	120—121(119)[e]
p-NCC_6H_4	73	197.5—198(198)[d]
1-Naphthyl	76	161—162(163.5—164.5)[f]
4-CH_3-1-Naphthyl	90	157—158(154—155)[i]
2-Thienyl	92	64—64.5(64—65)[g]
2-Pyridyl	68	48.5—50(49.5—50.5)[h]

a) G. H. Coleman, W. H. Holst, and R. D. Maxwell, *J. Am. Chem. Soc.*, **58**, 2310 (1936). b) W. S. Trahanovsky, C. C. Ong, and J. A. Lawson, *J. Am. Chem. Soc.*, **90**, 2839 (1968). c) W. Leppert, *Ber.*, **9**, 15 (1876). d) P. Kattwinkel and R. Wolffenstein, *Ber.*, **34**, 2423 (1901). e) C. Fischer and R. Wolffenstein, *Ber.*, **37**, 3216 (1904). f) E. A. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, **92**, 3586 (1970). g) F. F. Blicke and J. H. Burckhalter, *J. Am. Chem. Soc.*, **64**, 477 (1964). h) P. G. Campbell and P. C. Teague, *J. Am. Chem. Soc.*, **76**, 1371 (1954). i) Ref. 6.

Table 4. Thermal and photochemical reactions of 9-AnthCH_2SePh **20**

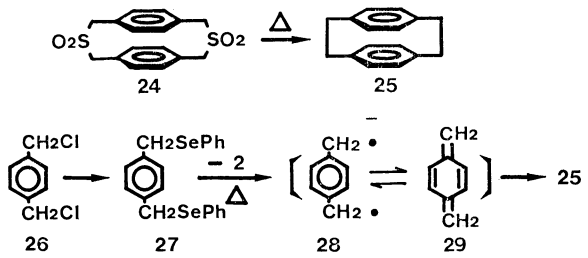
System(Conditions)	**2**	**21**	**22**	**23**
Flash vacuum pyrolysis(600 °C, 20 mmHg)	94	91	0	0
Pyrolysis in sealed tube(150 °C, 5 min)	96	14	82	0
Pyrolysis in toluene(170 °C, 735 min)[a]	95	24	68	0
Photolysis in benzene(r. t., 4 h)[b]	95	0	66	25

a) In a sealed tube, a second order reaction with a_0 9×10^{-3} mol dm^{-3} and $\tau_{1/2}=8$ min. b) Wtih a high pressure mercury lamp in nitrogen.

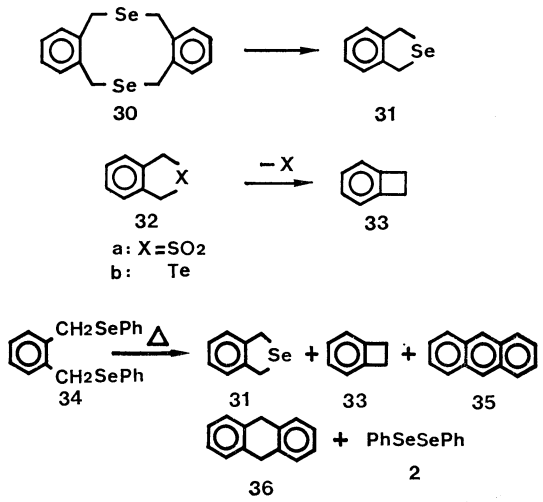
Table 5. Flash vacuum pyrolysis of 1,2-bis(phenylselenomethyl)benzene **34**

Conditions	Yield/%					
	2	**31**	**33**	**34**	**35**	**36**
600 °C, 3 mmHg	10	0	5	83	0	0
600 °C, 8 mmHg	42	13	40	34	0	0
600 °C, 20 mmHg	47	38	7	0	16	8

selenide **2** (69%) on pyrolysis at 650 °C under 7 mmHg.



In connection with the formation of bibenzyl from dibenzyl selenide, it is expected that pyrolysis of 2,11-diselena[3.3]orthocyclophane **30** would give 1,2:5,6-dibenzo-1,5-cyclooctadiene. However, **30** gave 1,3-dihydro-2-benzoselenophene **31**[14] in 92% yield instead of 1,2:5,6-dibenzo-1,5-cyclooctadiene. Selenophene **31** is thermally stable in contrast to the fact that similarly constructed compounds **32a**[12] and **32b**[13] can easily afford 1,2-dihydrobenzocyclobutene **33** on pyrolysis. On the other hand, **33** was obtained by pyrolysis of 1,2-bis(phenylselenomethyl)benzene **34**. As shown in Table 5, the reaction conditions available are critical and the products are dependent on the vacuum pressure of the pyrolytic system. The best yield (40%) of **33** was attained under 8 mmHg. Under higher vacuum (3 mmHg), most of **34** was recovered and under lower vacuum (20 mmHg) other products, 1,3-dihydro-2-benzoselenophene **31**, anthracene **35**, and 9,10-dihydroanthracene **36**, were favored. In the present stage, the formation mechanism for **35** and **36** is equivocal.



In conclusion, pyrolyses of organoseleniums are capable of providing a new method for the preparation of olefins, bibenzyls, and related compounds.

Experimental

Melting points were not corrected. All the solvents were of reagent grade. NMR spectra were recorded on a JEOL FX-100 (100 MHz) spectrometer using deuterochloroform as the solvent and tetramethylsilane as the internal standard. MS spectra were recorded on a Hitachi RMU-7 spectrometer (70 eV) using the direct injection technique. MS spectra of organoseleniums are characteristic of isotope patterns with respect to selenium atoms and description of molecular ion peaks is based on ^{80}Se only. IR spectra were recorded on a Hitachi EPI-G2 spectrometer for neat or nujol mull.

General Synthetic Method of Selenides ***3***, ***4***, ***6***, ***7***, ***9***, ***11***, ***12***, ***13***, ***20***, *and Bis- and Tris-selenides* ***17***, ***18***, ***19***, ***27***, *and* ***34***. Alkyl phenyl selenides **3**, **4**, **11**, **12**, **13**, **20**, **27**, and **34** were prepared by treatment of their corresponding alkyl halides with sodium benzeneselenolate which had been generated by reduction of diphenyl diselenide **2**[15] or phenyl selenocyanate[16] with sodium borohydride. The substitutional derivatives of **3** shown in Table 2 were prepared in the same way. The other selenides were similarly prepared by using phenethyl selenocyanate[17] for **6** and **7**, hexyl selenocyanate[18] for **9**, and benzyl selenocyanate[4] for **17**, **18**, and **19** as precursors for the above selenolates.

The general procedure will be illustrated below by using the synthesis of benzyl phenyl selenide **3** as an example. Sodium borohydride (0.32 g, 8.4 mmol) was carefully added with ice-cooling to a solution of phenyl selenocyanate (1.5 g, 8.2 mmol) in ethanol (50 ml), with nitrogen being bubbled through the solution. After the solution was allowed to stand at room temperature, a solution of benzyl chloride (1.1 g, 8.6 mmol) in ethanol (20 ml) was added dropwise over a period of 30 min. The mixture was refluxed for 5 h and cooled to room temperature. Water (100 ml) and benzene (200 ml) were successively added. The organic layer was separated, washed with saturated aq sodium chloride solution, and dried over anhyd magnesium sulfate. After evaporation, the residue was chromatographed on silica gel (Wako gel C-200) with hexane and a recrystallization of the first eluate from benzene–hexane gave colorless plates of **3** in 92% yield: mp 33.5—34 °C (lit,[19] 34—35 °C); NMR δ=4.08 (s, CH_2), 7.19 (bs, ArH), and 7.23—7.41 (m, SePhH); MS, *m/e*, 248 (M^+).

4: yield 95%; colorless oil; NMR δ=3.02, 3.12 (A_2B_2m, CH_2), and 7.02—7.47 (m, ArH); MS, *m/e*, 262 (M^+). Found: C, 64.23; H, 5.47%. Calcd for $C_{14}H_{14}Se$: C, 64.36; H, 5.36%.

6: yield 95%; colorless oil; NMR δ=2.70, 2.81 (A_2B_2m, CH_2CH_2), 3.72 (s, CH_2), and 7.21 (m, ArH); MS, *m/e*, 276 (M^+). Found: C, 65.21; H, 5.89%. Calcd for $C_{15}H_{16}Se$: C, 65.46; H, 5.82%.

7: yield 83%; pale yellow oil; NMR δ=2.81, 2.91 (A_2B_2m, CH_2), and 7.20 (m, ArH); MS, *m/e*, 290 (M^+). Found: C, 66.28; H, 6.28%. Calcd for $C_{16}H_{18}Se$: C, 66.44; H, 6.23%.

9: yield 88%; pale yellow oil; NMR δ=0.89 (t, CH_3), 1.32—1.66 (m, CH_2), and 2.55 (t, $SeCH_2$); MS, *m/e*, 250 (M^+). Found: C, 57.68; H, 10.64%. Calcd for $C_{12}H_{26}Se$: C, 57.83; H, 10.44%.

11:[20] yield 93%; pale yellow oil; NMR δ=3.50 (d, CH_2), 4.87, 5.02, 5.88 (ABXm, $CH{=}CH_2$), and 7.23—7.49 (m, ArH); MS, *m/e*, 198 (M^+); IR 1630 cm^{-1} ($\nu_{C=C}$).

12: yield 94%; colorless oil; NMR δ=3.34 (s, CH_2) and

7.34—7.65 (m, ArH); MS, *m/e*, 197 (M^+); IR 2250 cm^{-1} ($\nu_{C\equiv N}$). Found: C, 48.79; H, 3.62; N, 7.30%. Calcd for C_8H_7NSe: C, 48.98; H, 3.57; N, 7.14%.

13: yield 94%; pale yellow oil; NMR δ=2.25 (s, CH_3), 3.57 (s, CH_2), and 7.27—7.51 (m, ArH); MS ,*m/e*, 214 (M^+); IR 1715 cm^{-1} ($\nu_{C=O}$). Found: C, 50.58; H, 4.90%. Calcd for $C_9H_{10}OSe$: C, 50.70; H, 4.69%.

17: yield 89%; colorless oil; NMR δ=1.24, 1.56 (m, CH_2), 2.49 (t, $SeCH_2$), 3.76 (s, $PhCH_2$), and 7.26 (m, ArH); MS, *m/e*, 482 (M^+). Found: C, 59.73; H, 7.11%. Calcd for $C_{24}H_{34}Se_2$: C, 60.00; H, 7.08%.

18: yield 87%; colorless oil; NMR δ=2.73, 2.80 (A_2B_2m, CH_2CH_2), 3.74 (s, CH_2Se), 7.04 (s, ArH), and 7.25 (m, ArH); MS, *m/e*, 474 (M^+). Found: C, 60.95; H, 5.57%. Calcd for $C_{24}H_{26}Se_2$: C, 61.02; H, 5.51%.

19: yield 78%; colorless oil; NMR δ=2.72, 2.82 (A_2B_2m, CH_2CH_2), 3.75 (s, CH_2Se), 6.75 (s, ArH), and 7.26 (m, ArH); MS, *m/e*, 672 (M^+). Found: C, 58.94; H, 5.33%. Calcd for $C_{33}H_{36}Se_3$: C, 59.19; H, 5.38%.

20: yield 94%; pale yellow prisms from hexane–benzene; mp 124.5—126.0 °C; NMR δ=5.15 (s, CH_2), 7.25, 7.46 (m, PhH), 7.94, 8.22 (m, AnthH), and 8.37 (s, AnthH); MS, *m/e*, 348 (M^+). Found: C, 72.75; H, 4.58%. Calcd for $C_{21}H_{16}Se$: C, 72.62; H, 4.61%.

27: yield 85%; colorless plates from hexane–benzene; mp 137—138 °C; NMR δ=4.06 (s, CH_2), 7.06 (s, ArH), and 7.25—7.42 (m, PhH); MS, *m/e*, 418 (M^+). Found: C, 57.53; H, 4.34%. Calcd for $C_{20}H_{18}Se_2$: C, 57.69; H, 4.33%.

34: yield 87%; colorless plates from hexane–benzene; mp 30.5—31.5 °C; NMR δ=4.18 (s, CH_2), 7.05 (s, ArH), and 7.23—7.43 (m, PhH); MS, *m/e*, 418 (M^+). Found: C, 57.96; H, 4.44%. Calcd for $C_{20}H_{18}Se_2$: C, 57.69; H, 4.33%.

*General Synthetic Method of Diselenides **5**, **8**, **10**, and **14**.* Diselenides **5**, **8**, **10**, and **14** were prepared by alkaline hydrolysis of benzyl selenocyanate,[4] phenethyl selenocyanate,[17] hexyl selenocyanate,[18] and octyl selenocyanate,[21] respectively. The general procedure will be illustrated below by using the synthesis of dibenzyl diselenide **5** as an example.

A solution of benzyl selenocyanate (3.88 g, 19.8 mmol) in methanol (30 ml) was added dropwise to methanol (30 ml) containing potassium hydroxide (0.6 g, 23.2 mmol) at room temperature. After stirring for 3 h, water (100 ml) and benzene (200 ml) were added. The organic layer was separated, washed with saturated aq sodium chloride solution, and dried over anhyd magnesium sulfate. After evaporation, the residue was chromatographed on silica gel (Wako gel C-200) with hexane and a recrystallization of the first eluate gave **5** in 95% yield: pale yellow needles from hexane–benzene; mp 91—92 °C (lit,[22] 92—93 °C); NMR δ=3.84 (s, CH_2) and 7.25 (bs, ArH); MS, *m/e*, 342 (M^+). Found: C, 49.64; H, 4.22%. Calcd for $C_{14}H_{14}Se_2$: C, 49.41; H, 4.11%.

8: yield 98%; colorless oil; NMR δ=3.03, 3.11 (A_2B_2m, CH_2), and 7.22 (m, ArH); MS, *m/e*, 370 (M^+). Found: C, 52.42; H, 5.12%. Calcd for $C_{16}H_{18}Se_2$: C, 52.17; H, 4.89%.

10: yield 96%; pale yellow oil; NMR δ=0.89 (t, CH_3), 1.34—1.73 (m, CH_2), and 2.29 (t, CH_2Se); MS, *m/e*, 330 (M^+). Found: C, 43.76; H, 7.97%. Calcd for $C_{12}H_{26}Se_2$: C, 43.90; H, 7.93%.

14: yield 97%; colorless oil; NMR δ=0.88 (t, CH_3), 1.30—1.76 (m, CH_2), and 2.91 (t, CH_2Se); MS, *m/e*, 386 (M^+). Found: C, 50.00; H, 9.07%. Calcd for $C_{16}H_{34}Se_2$: C, 50.00; H, 8.85%.

Dioctyl disulfide **15** was prepared according to the procedure of Yiannios and Karabinos.[23] Benzyl phenethyl sulfide and sulfone **16** were prepared according to the procedure of Böhme *et al.*[24]

*2,11-Diselena[3.3]orthocyclophane **30** and 1,3-Dihydro-2-benzoselenophene **31**.* A solution of 1,2-bis(bromomethyl)benzene (2.3 g, 8.0 mmol) in benzene (30 ml) and a solution of sodium selenide (1.12 g, 8.9 mmol) in 60% ethanol (100 ml) were added simultaneously and dropwise to a stirred ethanol (150 ml) at room temperature under a nitrogen atmosphere. The addition took 1.5 h. After an additional stirring for 2 h, benzene (300 ml) was added and the mixture was washed with saturated aq NaCl solution and dried over anhyd $MgSO_4$. After evaporation of the solvent, the residue was triturated with 1:1 benzene–hexane and the insoluble solid was recrystallized from dichloromethane–benzene to give colorless needles of **30** in 25% yield: mp 201—202 °C; NMR δ=3.66 (s, CH_2), 7.21, and 7.29 (A_2B_2m, ArH); MS, *m/e*, 368 (M^+). Found: C, 52.74; H, 4.37%. Calcd for $C_{16}H_{16}Se_2$: C, 52.46; H, 4.37%.

The benzene–hexane solution was chromatographed on silica gel (Wako gel C-100) with hexane to give a minute amount of **31** from the first eluate: mp 31—33 °C. The spectral data of this specimen were identical with those of product **31** obtained by pyrolysis of **30**. **31**: NMR δ=4.30 (s, CH_2), 7.14, and 7.20 (A_2B_2m, ArH); MS, *m/e*, 184 (M^+); mol wt 191 (vapor pressure osmometry, CH_2Cl_2). Found: C, 52.60; H, 4.29%. Calcd for C_8H_8Se: C, 52.46; H, 4.37%.

General Method for Flash Vacuum Pyrolysis. A Pyrex tube closed at one end, 40 cm long and 1 cm in diameter, was used for pyrolysis. The sample (50—300 mg) of organoselenium was placed at the closed end of the tube. The other open end was connected to a vacuum system and cooled with Dry Ice or liq. nitrogen. The middle part was enclosed within an electric furnace (25 cm long) preheated at 600 °C. After heating for *ca.* 2 min, the sample part was slidden into the furnace. Pyrolysis immediately occurred and the pyrolysates condensed at the cool part. The organic products were extracted with dichloromethane and isolated by preparative gel-permeation liquid chromatography (Nihon Bunseki Kogyo LC-08) with chloroform as eluent. All of them were identified by comparison of their melting points and spectral data with those of authentic samples or reported data.[25]

*Pyrolysis of 9-Anthrylmethyl Phenyl Selenide **20**.* *a) In Solid State*: Selenide **20** (20 mg) was heated in an oil bath at 150 °C for 5 min. A gel-permeation liquid chromatography of the pyrolysates gave 1,2-di(9-anthryl)ethane **21** (1.3 mg, 14%), lepidopterene **22** (7.8 mg, 82%), and diphenyl diselenide **2** (9.2 mg, 96%), successively.

21: pale yellow plates from toluene; mp 318.5—320.5 °C (lit,[8] 320 °C); NMR δ=4.07 (s, CH_2), 7.53, 8.03, and 8.39 (m, ArH); MS, *m/e*, 382 (M^+).

22: colorless columns from toluene; mp 298—299 °C (lit,[8] 298 °C); NMR δ=2.89 (d, J=3 Hz, CH_2), 4.63 (t, J=3 Hz, CH), 6.76, 6.81, 6.98, and 7.30 (m, ArH).

b) In Solution: Selenide **20** (20 mg) was placed in an NMR tube and dissolved in 0.7 ml of toluene-d_8. The tube was degassed by the freeze-pump-thaw method and sealed. The reaction at 170 °C was followed by NMR measurement. After *ca.* 12 h, the signals of **20** completely disappeared. A gel-permeation liquid chromatography of the products gave **21** (2.2 mg, 24%), **22** (6.5 mg, 68%), and **2** (95%).

*Photolysis of 9-Anthrylmethyl Phenyl Selenide **20**.* Selenide **20** (20 mg) was dissolved in benzene (20 ml) and irradiated with a high pressure mercury lamp in a nitrogen atmosphere. After evaporation, a gel-permeation liquid chro-

matography of the residue gave **22** (6.4 mg, 66%), biplanene **23** (2.3 mg, 25%), and **2** (9.1 mg, 95%).

23: colorless columns from benzene–toluene; mp 329 °C dec (lit,[8] 320 °C); NMR δ=3.01 (s, CH_2), 4.5 (s, CH), and 6.82—7.13 (m, ArH); MS, *m/e*, 382 (M^+).

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