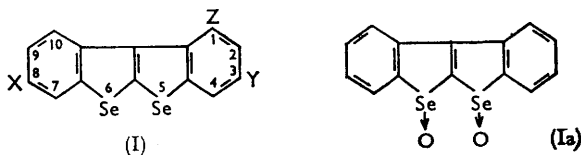


<sup>4</sup> Frick, *J. Amer. Chem. Soc.*, 1923, **45**, 1795.

In a preliminary communication<sup>5</sup> we reported the formation of benzoselenopheno-[2,3-*b*]benzoselenophens (I) from 1,1-diarylethylenes and selenium oxychloride. In the present paper we detail the synthesis of a number of such derivatives of (I) and some of the by-products formed in the reaction.



Addition of selenium oxychloride to a solution of a diarylethylene in dry ether causes exothermic reaction, the solution usually soon becomes green (probably owing to formation of a carbonium ion from the ethylene as the same colour appears in sulphuric acid), and later red or brown, and the product crystallizes. Reaction occurs also in other solvents, such as pyridine, dimethylformamide, and propan-2-ol.

The stability of the polycyclic system (I) is indicated qualitatively by its stability to oxidizing agents such as neutral or alkaline potassium permanganate and to Raney nickel and by the easy formation of coloured molecular compounds with picric acid, trinitrobenzene and styphnic acid. Elementary analyses and molecular weight determination in the series, and *X*-ray data and infrared spectra of compound (I; *X* = *Y* = *Z* = H) also fit the structure proposed. There is a strong peak in the spectrum of this parent compound at 763  $\text{cm}^{-1}$  (four adjacent hydrogen atoms); its 3,8-dichloro-derivative shows peaks at 810 and 865  $\text{cm}^{-1}$ , corresponding to a trisubstituted benzene ring, and similar assignments could be made with other derivatives. Additional proof<sup>15</sup> is that bromination of compounds (I; *X* = *Y* = Me or Bu<sup>t</sup>) gives only monobromo-derivatives (*Z* = Br). A model shows strong steric interference between 1- and 10-substituents which allows only monosubstitution and seems to make the introduction of a substituent at the second of these positions impossible.

The parent compound (I) was also obtained by two independent syntheses, one being reaction of 1,1-diphenylethylene with selenium dioxide at high temperatures and the second reaction of the compound formed from 3-hydroxybenzoselenophen<sup>6</sup> and phenylmagnesium bromide (*i.e.*, presumably 3-phenylbenzoselenophen) with selenium oxychloride.

The essential condition for the reaction seems to be the presence of an  $\text{Ar}_2\text{C}:\text{C}$  grouping, with or without electron-donating substituents. Electron-attracting groups, (*e.g.*, nitro) inhibit the reaction. We propose the following mechanism: The terminal methylene group of the 1,1-diarylethylene is attacked by two molecules of selenium oxychloride, substituting (possibly by addition to the double bond, followed by elimination of hydrogen chloride) both hydrogen atoms by the  $-\text{SeOCl}$  group. Ring closure at the *ortho*-position of the aryl group takes place subsequently with elimination of hydrogen chloride. This ring closure probably involves electrophilic attack of the  $-\text{SeO}^+$  group on the ring, but the site of attack is determined by steric considerations only, as in similar cyclizations. Electron-donating substituents promote, and electron-withdrawing groups inhibit, both the initial attack and the cyclization. We cannot yet decide whether attack by the second molecule of oxychloride occurs before or after the first cyclization. The product of the cyclization should be the appropriate diselenoxide (Ia). As we could not isolate a product of this type we believe that the thermodynamic stability of the completely aromatic system (I) is a sufficiently strong factor to make the reduction of the oxide extremely easy or perhaps spontaneous.

Owing to the steric interference (see above) between 1- and 10-substituents, large groups

<sup>5</sup> Patai, Sokolovsky, and Friedlander, *Proc. Chem. Soc.*, 1960, 181.

<sup>6</sup> Lesser and Weiss, *Ber.*, 1912, **45**, 1835.

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at these positions make co-planarity of the molecule impossible and therefore its formation difficult. This is borne out by the fact that 1,1-di-1'-naphthylethylene does not give the expected product while 1,1-di-2'-naphthylethylene does.

Products (I) (see Table I) were obtained from 1,1-diphenylethylene and its derivatives with methyl, *t*-butyl, chloro-, bromo-, methoxy-, and cyclohexyl groups in the *para*-position of one or both of the phenyl groups, as well as from 1-phenyl-1-*o*-tolyl- and 1-1'-naphthyl-1-phenyl-ethylene (see II), 1-2'-naphthyl-1-phenylethylene (IIIa or b), 1,1-di-2'-naphthylethylene (see IV or isomer) and 1-1'-naphthyl-1-2'-naphthyl-ethylene (see V or isomer).

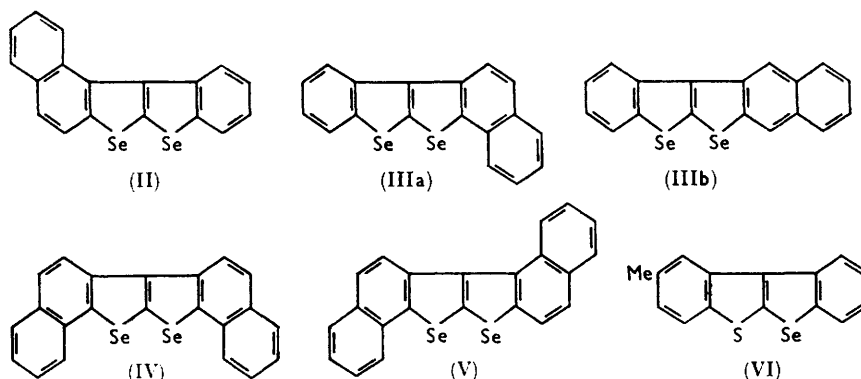
No "normal" reaction took place with styrene,  $\alpha$ -methylstyrene, ethyl  $\beta\beta$ -diphenylacrylate, 2-chloro-1,1-diphenylethylene, 1,1-diphenylpropene, stilbene, triphenylethylene, 1,1-di-*p*-nitrophenyl-, 1,1-di-1'-naphthyl-, or 1,1-di-*p*-dimethylaminophenyl-ethylene, or dibenzofulvene.

When one of the aryl groups was 2-naphthyl, several isomers might have been produced (cf. IIIa and b). Although the structures of these products were not proved, we prefer in all cases the isomer in which the cyclization is assumed to take place to the 1-position of the naphthyl group in analogy with other cyclizations such as the Elbs reaction.<sup>7</sup>

5-Methyl-3-phenylthionaphthen also gave the "normal" reaction; the product (VI) gave the correct analysis and coloured molecular compounds with picric acid and trinitrobenzene, and its infrared spectrum was very similar to that of the diselena-compound (I).

In some cases by-products were isolated but their structures were not proved. Reaction of 1,1-di-*p*-*t*-butylphenylethylene gave a substance  $C_{44}H_{56}Cl_2Se$ , possibly  $[(p\text{-Bu}^t\text{-C}_6\text{H}_4)_2\text{CCl-CH}_2]_2\text{Se}$ , formed by a reaction similar to (5). A by-product,  $C_{22}H_{15}Cl$ , from the reaction of 1,1-di-2'-naphthylethylene is possibly 1,1-di-2'-naphthylvinyl chloride, analogous to the vinyl chloride derivatives obtained from diarylethylenes and thionyl chloride.

Chlorination and bromination of the parent (I) gave the dihalogeno-derivatives ( $X = Y = \text{Cl}$  or  $\text{Br}$ ), the former product being also obtained by chlorination of the 3-monochloro-compound. These products were identical (mixed m. p. and spectrum) with those obtained by cyclization from the substituted diarylethylenes. Hence it can be seen that electrophilic substitution is directed to positions 3 and 8, *i.e.*, *meta* to the selenium



atom, in distinction from the results obtained with dibenzoselenophen, in which nitration<sup>8</sup> and acylation<sup>9</sup> take place *para* to the selenium atom. Although no such direct proof

<sup>7</sup> Pullman and Pullman in "Progress in Organic Chemistry," ed. J. W. Cook, Butterworths Scientific Publns., London, 1958, Vol. IV, p. 31.

<sup>8</sup> Sawicki and Ray, *J. Amer. Chem. Soc.*, 1952, **74**, 4120.

<sup>9</sup> Ng Ph. Buu-Hoi and Ng Hoan, *J.*, 1952, 3745; *J. Org. Chem.*, 1952, **17**, 643.

exists, we assume, by analogy, that nitration takes place in positions 3 and 8. If these positions are occupied, only monobromination takes place, at the 1-position. This is again *meta* to the hetero-atom and the fact that only monosubstitution occurs is due to the steric hindrance between the 1- and the 10-position. This can also be taken as a proof of the position of the entering halogen as at any other position disubstitution would have to be expected in the asymmetrical compounds (I; X = Me or Bu<sup>t</sup>, Y = Z = H).

## EXPERIMENTAL

**Materials.**—Solvents were purified by distillation. Commercial selenium oxychloride (B.D.H.) was used. The following diarylethylenes were prepared by procedures described in the literature: diphenyl;<sup>10</sup> di-*p*-tolyl;<sup>11</sup> di-*p*-bromophenyl;<sup>12</sup> di-*p*-chlorophenyl;<sup>11</sup> di-*p*-methoxyphenyl;<sup>13</sup> 1-*p*-methoxyphenyl-1-phenyl;<sup>14</sup> 1-*p*-chlorophenyl-1-phenyl;<sup>15</sup> di-*p*-*t*-butylphenyl;<sup>16</sup> 1-*p*-cyclohexylphenyl-1-phenyl;<sup>1</sup> 1-1'-naphthyl- and 1-2'-naphthyl-1-phenyl;<sup>3</sup> di-2'-naphthyl;<sup>17</sup> 1-1'-naphthyl-1-2'-naphthyl;<sup>17</sup> di-1'-naphthyl;<sup>18</sup> 1-phenyl-1-*o*-tolyl.<sup>3</sup>

5-Methyl-3-phenylthionaphthen was prepared by Krollpfeiffer's method.<sup>19</sup>

The following procedures were used for the syntheses and gave the *products* listed in the Table.

(A) To a solution of the ethylene (0.01 mole) in dry ether (5–10 ml.), selenium oxychloride (0.03 mole, 2 ml.) was added and the mixture was left at room temperature until no more solid separated. Alternatively the mixture was refluxed for 15–30 min. The solid was filtered off and recrystallized.

(B) The ethylene (0.01 mole), pyridine (10–20 ml.), and selenium oxychloride (0.03 mole, 2 ml.) were refluxed for 0.5–4 hr., then the mixture was poured into water (200 ml.). If a solid separated it was filtered off and recrystallized; if the crude product was an oil it was extracted with chloroform, washed with dilute hydrochloric acid and then with water and dried (Na<sub>2</sub>SO<sub>4</sub>); most of the solvent was removed and the product precipitated by ethanol or light petroleum.

(C) Procedure was as in (B) but with dimethylformamide as solvent.

(D) If an oil was obtained on addition of ethanol or light petroleum to the chloroform extract (cf. B), the product was isolated as the complex with trinitrobenzene. The complex was decomposed by refluxing it with tin and aqueous hydrochloric acid, and the pure product extracted with chloroform and precipitated by ethanol or light petroleum.

(E) Procedure was as in (A) with propan-2-ol as solvent.

The molecular weight of the parent (I) was determined by Rast's method (Found, mean of three determinations: *M*, 320. C<sub>14</sub>H<sub>8</sub>Se<sub>2</sub> requires *M*, 334).

Nitration of the parent (I) was carried out in boiling concentrated nitric acid.

**Independent Syntheses of Compound (I).**—(a)<sup>20</sup> 1,1-Diphenylethylene (2 g.) and selenium dioxide (4 g.) were heated at 240–250° for 1 hr., then extracted with benzene, and the product was precipitated as picrate in 8% yield. The picrate and the parent were identified by m. p.s. and mixed m. p.s.

(b) Phenylmagnesium bromide (from 0.25 g. of magnesium and 1.6 g. of bromobenzene in 10 ml. of ether) was added to a suspension of 3-hydroxyselenonaphthen<sup>6</sup> (1.05 g.) in refluxing tetrahydrofuran (30 ml.). Working up as usual gave an oil, b. p. 110°/0.02 mm. (0.76 g.). Attempts to crystallize this or to purify it by distillation were unsuccessful, as shown by unsatisfactory analyses. Nevertheless, the crude oil on reaction with selenium oxychloride

<sup>10</sup> Allen and Converse, *Org. Synth.*, 1941, **1**, 226.

<sup>11</sup> Bergmann and Szmuskowicz, *J. Amer. Chem. Soc.*, 1948, **70**, 2748.

<sup>12</sup> Coates and Sutton, *J.*, 1942, 567.

<sup>13</sup> Pfeiffer and Wizinger, *Annalen*, 1928, **461**, 144.

<sup>14</sup> Stoermer and Simon, *Ber.*, 1904, **37**, 4163.

<sup>15</sup> Bergmann and Bondi, *Ber.*, 1931, **64**, 1468.

<sup>16</sup> Patai and Dayagi, *J.*, 1958, 3059.

<sup>17</sup> Wolf, *J. Amer. Chem. Soc.*, 1953, **75**, 2673.

<sup>18</sup> Pfeiffer and Schnieder, *J. prakt. Chem.*, 1931, **129**, 129.

<sup>19</sup> Krollpfeiffer, *Annalen*, 1949, **563**, 15; 1950, **566**, 139.

<sup>20</sup> Cf. Yurev, Mezantsova, Melenteva, and Treshehova, *Zhur. obshchei Khim.*, 1957, **27**, 2260.

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(method A) gave, after working up with water, extraction by chloroform, and addition of picric acid a low yield (~30 mg.) of the picrate, m. p. and mixed m. p. 166°, of compound (I).

*Infrared Spectra.*—These spectra were obtained on a Baird-Atomic Inc. spectrophotometer and refer to potassium bromide discs. Numerals identify the substances as in Table 1.

- 1, 720s, 763s, 1000m, 1400m, 1460m.
- 2, 730m, 763m, 840m, 870m, 900w, 1120s, 1330s, 1450w, 1520m, 1570m.
- 4, 733s, 810s, 850m, 865m, 912m, 1080m, 1190w, 1290w, 1370m, 1470m.
- 5, 720w, 762s, 810s, 867s, 907m, 1100m, 1370m, 1450m, 1570m.
- 7, 717s, 730s, 758s, 790s, 835s, 910w, 995—1040m, 1180—1300m, 1360—1470m.
- 9, 720s, 755s, 865w, 1000w, 1380m.
- 10, 650s, 728m, 752w, 843s, 855m, 870m, 917w, 1120w, 1160w, 1210w, 1260m, 1370m, 1450m, 1600m, 2800s.
- 13, 635s, 720s, 742s, 762s, 807s, 880m, 917m, 1010m, 1030m, 1270m, 1400m, 1460s, 1600w, 2800s.
- (II) 680w, 728m, 752s, 780m, 805s, 1000w, 1160w, 1390m, 1460w, 1630w.
- (III) 660m, 675m, 725s, 745s, 775m, 808s, 840w, 860w, 960w, 1020m, 1200m, 1340s, 1410, 1440, 1470m, 1520, 1550w, 1600w.
- (IV) 658s, 695m, 750s, 775m, 815s, 862s, 905s, 980w, 1030m, 1090w, 1140w, 1160w, 1220m, 1260m, 1330s, 1390, 1440, 1450, 1515, 1550, 1600, 1620 (all m).
- (V) 658s, 695m, 750s, 775m, 815s, 862s, 905s, 980w, 1030m, 1090w, 1140w, 1160w, 1220m, 1260m, 1330s, 1390, 1440, 1450, 1515, 1550, 1600, 1620 (all m).
- (VI) 655w, 718w, 735s, 762s, 802s, 860m, 1027m, 1160m, 1410s, 1470m, 1600m, 3000m.

## Benzoselenopheno[2,3-b]benzoselenophens (I).

No.*	X	Y	Z	M. p.	Solvent for recryst.	Yield (%)	Method and temp.
1	H	H	H	190—191°	BuOH	33	A, E, room
P				166	C <sub>6</sub> H <sub>6</sub>	—	—
T				192—193	"	—	—
2	NO <sub>2</sub>	NO <sub>2</sub>	H	340	PhNO <sub>2</sub>	—	—
3	Me	Me	H	156—157	BuOH	29	A, room
P				126	C <sub>6</sub> H <sub>6</sub>	—	—
T				223—224	C <sub>6</sub> H <sub>6</sub>	—	—
4	Br	Br	H	306	THF <sup>c</sup>	30	A, b. p. <sup>d</sup>
5	Cl	Cl	H	280—281	"	31	A, room <sup>e</sup>
6	MeO	MeO	H	159—160	BuOH	24	A, b. p.
7.	MeO	H	H	143—144	BuOH or CHCl <sub>3</sub>	27, 13, 3	A, B, C, b. p.
P				148	CHCl <sub>3</sub>	—	—
T				152	"	—	—
8	Cl	H	H	200	C <sub>6</sub> H <sub>6</sub> or CHCl <sub>3</sub> -C <sub>6</sub> H <sub>14</sub>	30, 21	A (room), B (b. p.)
9	H	H	Me	99—101	EtOH	1	D, b. p.
T				163	EtOH-CHCl <sub>3</sub>	—	—
10	Bu <sup>t</sup>	Bu <sup>t</sup>	H	172.5	"	15, 30	B, C, b. p.
P				207—218	"	—	—
T				220—230	"	—	—
11	Bu <sup>t</sup>	Bu <sup>t</sup>	Br	137—141	"	—	f
12	Me	Me	Br	208—210	"	30	g
13	C <sub>6</sub> H <sub>11</sub> <sup>h</sup>	H	H	144	"	13	D, b. p.
T				170	CHCl <sub>3</sub>	—	—
14	[(p-Bu <sup>t</sup> -C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CCl-CH <sub>2</sub> ] <sub>2</sub> Se			87	CHCl <sub>3</sub> -EtOH	—	i
II				154	"	5	D, b. p.
T				158	"	—	—
III				219—221	"	3, 25	A, B, b. p.
DP				158	CHCl <sub>3</sub>	—	—
T				184	"	—	—
IV				346	C <sub>6</sub> H <sub>5</sub> N	39	B, b. p.
TP				250	Decalin	—	—
15	(2-C <sub>10</sub> H <sub>7</sub> ) <sub>2</sub> C:CHCl			150—153	CHCl <sub>3</sub> -EtOH	—	j
V				337	C <sub>6</sub> H <sub>5</sub> N	11.5	B, b. p.
TP				252—255	Decalin	—	—
BT				200 <sup>k</sup>	"	—	—
VI				122	C <sub>6</sub> H <sub>5</sub> -EtOH	66	B, b. p.
T				193	CHCl <sub>3</sub>	—	—
P				165	"	—	—

TABLE. (Continued).

No.	Required (%)					Formula	Found (%)				
	C	H	Hal	N	Se		C	H	Hal	N	Se
P	50.3	2.4	—	—	47.3	C <sub>14</sub> H <sub>8</sub> Se <sub>2</sub>	50.2	2.4	—	—	45.6
I	—	—	—	7.4	—	C <sub>20</sub> H <sub>11</sub> N <sub>3</sub> O <sub>7</sub> Se <sub>2</sub>	—	—	—	7.1	—
T	—	—	—	7.7	—	C <sub>20</sub> H <sub>11</sub> N <sub>3</sub> O <sub>8</sub> Se <sub>2</sub>	—	—	—	7.85	—
2	39.6	1.4	—	6.7	37.2	C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub> Se <sub>2</sub>	40.4	1.4	—	6.8	35.2
3	53.1	3.3	—	—	43.6	C <sub>16</sub> H <sub>12</sub> Se <sub>2</sub>	53.0	3.5	—	—	41.6
P	—	—	—	7.1	—	C <sub>22</sub> H <sub>15</sub> N <sub>3</sub> O <sub>7</sub> Se <sub>2</sub>	—	—	—	7.0	—
T	—	—	—	7.3	—	C <sub>22</sub> H <sub>15</sub> N <sub>3</sub> O <sub>8</sub> Se <sub>2</sub>	—	—	—	7.3	—
4	34.2	1.2	32.5	—	32.1	C <sub>14</sub> H <sub>8</sub> Br <sub>2</sub> Se <sub>2</sub>	34.7	1.5	32.1	—	29.9
5	—	—	17.6	—	39.2	C <sub>14</sub> H <sub>8</sub> Cl <sub>2</sub> Se <sub>2</sub>	—	—	17.9	—	37.2
6	48.7	3.05	—	—	—	C <sub>16</sub> H <sub>12</sub> O <sub>2</sub> Se <sub>2</sub>	48.4	3.2	—	—	—
7	49.5	2.8	—	—	43.4	C <sub>15</sub> H <sub>10</sub> OSe <sub>2</sub>	49.4	2.7	—	—	43.2
P	—	—	—	7.1	—	C <sub>21</sub> H <sub>13</sub> N <sub>3</sub> O <sub>7</sub> Se <sub>2</sub>	—	—	—	8.6	—
T	—	—	—	7.3	—	C <sub>21</sub> H <sub>13</sub> N <sub>3</sub> O <sub>8</sub> Se <sub>2</sub>	—	—	—	7.9	—
8	45.6	1.9	9.6	—	—	C <sub>14</sub> H <sub>8</sub> ClSe <sub>2</sub>	46.0	2.24	11.2	—	—
9	51.6	2.9	—	—	—	C <sub>15</sub> H <sub>10</sub> Se <sub>2</sub>	50.7	2.9	—	—	—
T	44.8	2.5	—	7.5	28.1	C <sub>21</sub> H <sub>13</sub> N <sub>3</sub> O <sub>6</sub> Se <sub>2</sub>	44.9	2.5	—	7.3	30.25
10	59.2	5.42	—	—	35.4	C <sub>23</sub> H <sub>14</sub> Se <sub>2</sub>	59.2	5.2	—	—	35.25
P	—	—	—	6.2	—	C <sub>28</sub> H <sub>27</sub> N <sub>3</sub> O <sub>7</sub> Se <sub>2</sub>	—	—	—	6.8	—
T	—	—	—	6.4	—	C <sub>28</sub> H <sub>27</sub> N <sub>3</sub> O <sub>8</sub> Se <sub>2</sub>	—	—	—	6.9	—
11	50.3	4.1	15.2	—	30.0	C <sub>22</sub> H <sub>23</sub> BrSe <sub>2</sub>	51.0	4.2	15.1	—	30.8
12	—	—	18.1	—	—	C <sub>16</sub> H <sub>11</sub> BrSe <sub>2</sub>	—	—	19.7	—	—
13	57.3	4.3	—	—	37.9	C <sub>20</sub> H <sub>18</sub> Se <sub>2</sub>	57.45	4.5	—	—	38.4
T	49.7	3.3	—	6.6	25.0	C <sub>26</sub> H <sub>21</sub> N <sub>3</sub> O <sub>6</sub> Se <sub>2</sub>	48.1	3.2	—	6.9	24.6
14	71.9	7.7	9.65	—	10.7	C <sub>44</sub> H <sub>58</sub> Cl <sub>2</sub> Se	72.5	7.3	8.6	—	11.3
II	56.3	2.6	—	—	41.1	C <sub>18</sub> H <sub>10</sub> Se <sub>2</sub>	55.6	3.1	—	—	40.4
T	58.3	2.2	—	7.0	26.4	C <sub>24</sub> H <sub>13</sub> N <sub>3</sub> O <sub>6</sub> Se <sub>2</sub>	58.1	2.1	—	7.3	26.85
III	56.3	2.6	—	—	41.1	C <sub>18</sub> H <sub>10</sub> Se <sub>2</sub>	56.3	2.5	—	—	41.25
DP	—	—	—	10.0	—	C <sub>30</sub> H <sub>18</sub> N <sub>3</sub> O <sub>14</sub> Se <sub>2</sub>	—	—	—	11.2	—
T	—	—	—	7.0	—	C <sub>34</sub> H <sub>13</sub> N <sub>3</sub> O <sub>6</sub> Se <sub>2</sub>	—	—	—	7.9	—
IV	60.8	2.8	—	—	36.4	C <sub>22</sub> H <sub>12</sub> Se <sub>2</sub>	61.1	2.8	—	—	36.6
TP	—	—	—	11.2	—	C <sub>40</sub> H <sub>21</sub> N <sub>3</sub> O <sub>21</sub> Se <sub>2</sub>	—	—	—	11.1	—
15	83.9	4.8	11.3	—	—	C <sub>22</sub> H <sub>15</sub> Cl	83.1	4.3	11.2	—	—
V	60.8	2.8	—	—	36.4	C <sub>22</sub> H <sub>12</sub> Se <sub>2</sub>	62.1	2.9	—	—	36.4
TP	—	—	—	11.2	—	C <sub>40</sub> H <sub>21</sub> N <sub>3</sub> O <sub>21</sub> Se <sub>2</sub>	—	—	—	11.1	—
BT	—	—	—	9.8	—	C <sub>34</sub> H <sub>18</sub> N <sub>3</sub> O <sub>13</sub> Se <sub>2</sub>	—	—	—	10.6	—
VI	59.8	3.3	—	—	—	C <sub>15</sub> H <sub>10</sub> SSe <sup>m</sup>	59.6	3.5	—	—	—
T	49.0	2.5	—	8.2	—	C <sub>21</sub> H <sub>13</sub> N <sub>3</sub> O <sub>6</sub> SSe <sup>m</sup>	49.0	2.7	—	8.1	—
P	47.55	2.5	—	7.6	—	C <sub>31</sub> H <sub>13</sub> N <sub>3</sub> O <sub>7</sub> SSe <sup>m</sup>	47.2	2.6	—	7.7	—

<sup>a</sup> P = Picrate, T = trinitrobenzene complex, DP = dipicrate, TP = tripicrate, BT = bistrinitrobenzene complex of preceding parent. <sup>b</sup> Prep. by nitration of no. 1 at the b. p. <sup>c</sup> Tetrahydrofuran. <sup>d</sup> Prep. also by bromination of no. 1 in AcOH-Ac<sub>2</sub>O. <sup>e</sup> Prep. also by chlorination of no. 1 (45% yield) or no. 8 in AcOH. <sup>f</sup> Prep. by bromination of no. 10. <sup>g</sup> Prep. by bromination of no. 3. <sup>h</sup> Cyclohexyl. <sup>i</sup> By-product of no. 10. <sup>j</sup> By-product of compound (IV). <sup>k</sup> Decomp. <sup>l</sup> Selenium analyses gave consistently low results (Dr. E. Meier, Weizmann Institute, Rehovoth). <sup>m</sup> Sulphur analyses were erratic owing to presence of selenium.

Compounds: (II) *benzo[b]naphtho[2,1-e]selenopheno[2,3-b]selenophen*. (III) *Benzo[b]naphtho[2,1(or 2,3)-e]selenopheno[2,3-b]selenophen*. (IV) *Dinaphtho[1,2-b : 2',1'-e]selenopheno[2,3-b]selenophen*. (V) *Dinaphtho[1,2-b : 1,2-e]selenopheno[2,3-b]selenophen*. (VI) *2-Methylbenzoseleno[2,3-b]benzoselenophen*. 14, *Bis-(2-chloro-2,2-di-p-t-butylphenylethyl) selenide*.

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