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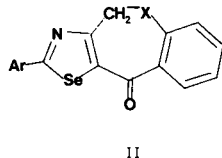
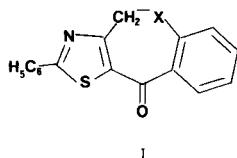
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Starting from the readily available ethyl 2-phenyl-4-methylthiazole-5-carboxylate (III), 2-phenyl-4-chloromethylthiazole (VIII) and 2-aryl-4-chloromethylselenazole (XIV), 2-phenyl-4,10-dihydro-10-oxo[1]benzoxepino[3,4-*d*]thiazole (Ia), 2-phenyl-4,10-dihydro-10-oxo[1]benzothiepine[3,4-*d*]thiazole (Ib), 2-aryl-4,10-dihydro-10-oxo[1]benzoxepino[3,4-*d*]selenazoles (IIa-IIe) and 2-aryl-4,10-dihydro-10-oxo[1]benzothiepine[3,4-*d*]selenazoles (IIf-IIj) were prepared.

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In continuation of the study on the chemistry of selenium heterocyclic compounds (1-8) and as a part of a program designed to expand the chemistry of [1]benzoxepin and [1]benzothiepin (9), it became necessary to synthesize substituted [1]benzoxepino[3,4-*d*]thiazole (I, X = O), [1]benzothiepine[3,4-*d*]thiazole (I, X = S), [1]benzoxepino[3,4-*d*]selenazole (II, X = O) and [1]benzothiepine[3,4-*d*]selenazole (II, X = S) for biological evaluation.



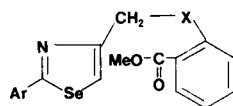
Compound I could be prepared starting from either ethyl 2-phenyl-4-bromomethylthiazole-5-carboxylate (IV) or 2-phenyl-4-chloromethylthiazole (VIII) (see Scheme I).

Reaction of ethyl 2-phenyl-4-methylthiazole-5-carboxylate (III) (10) with *N*-bromosuccinimide gave ethyl 2-phenyl-4-bromomethylthiazole-5-carboxylate (IV). Reaction of the latter with phenol according to the procedure reported previously (11) afforded ethyl 2-phenyl-4-phenoxyethylthiazole-5-carboxylate (Va). Alkaline hydrolysis of compound Va gave the acid VIa, which was cyclized according to the method reported previously (12) to give 2-phenyl-4,10-dihydro-10-oxo[1]benzoxepino[3,4-*d*]thiazole (Ia). The thia-analog of the latter (Ib) was prepared similarly (see Scheme I).

Compounds Ia and Ib could be prepared by another method. Reaction of methyl salicylate with 2-phenyl-4-chloromethylthiazole (VIII) (13) afforded methyl 2-(2-phenyl-4-thiazolylmethoxy)benzoate (Xa). Alkaline hydrolysis followed by cyclization afforded compound Ia.

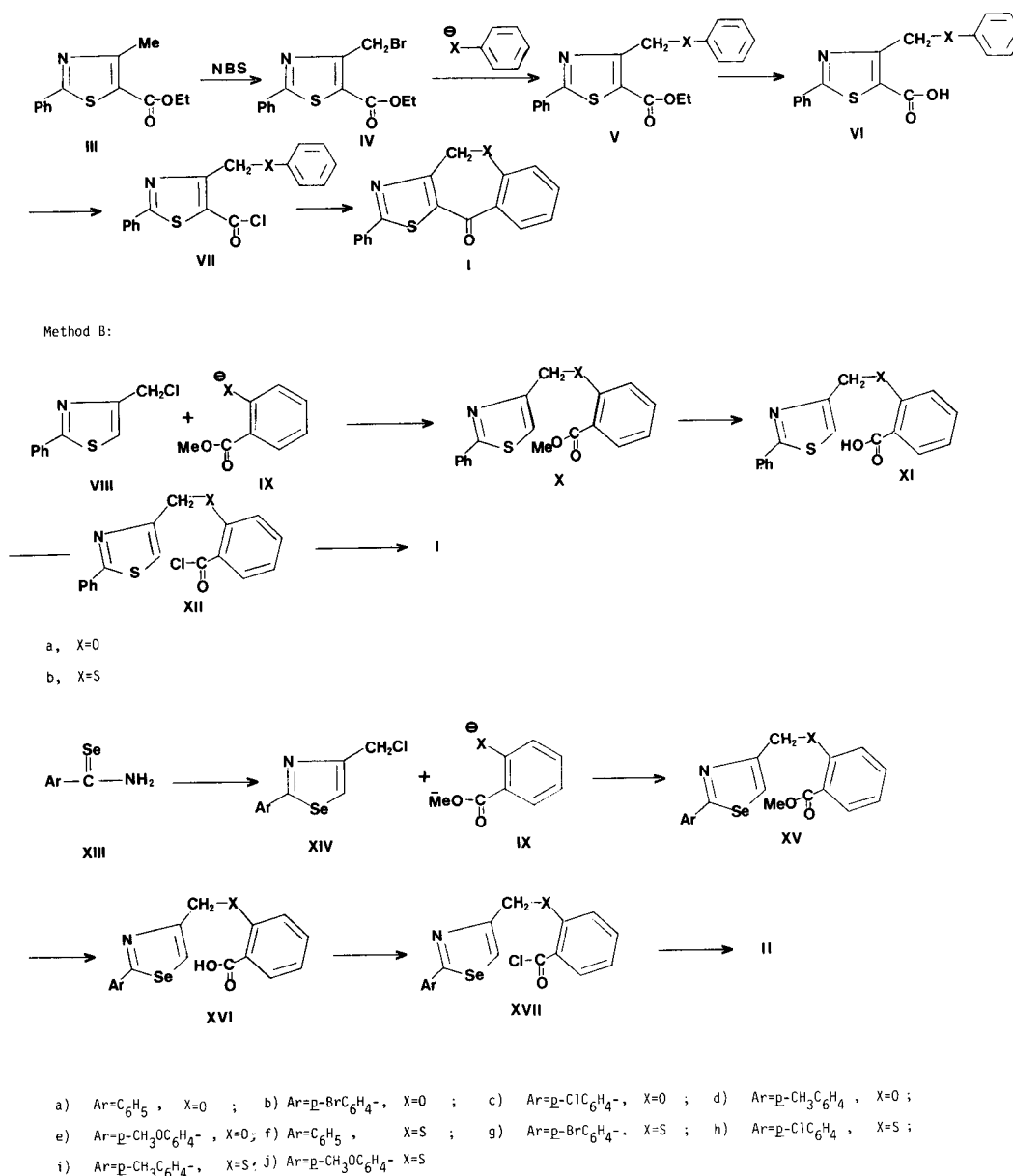
Starting from methyl *o*-mercaptobenzoate (IXb) and 2-phenyl-4-chloromethylthiazole (VIII), compound Ib was prepared similarly (see Scheme I).

Table I



Compound No.	Ar	X	Yield %	M.P. °C (a)	Formula	C		H		N	
						Calcd.	% Found	Calcd.	% Found	Calcd.	% Found
XVa	C <sub>6</sub> H <sub>5</sub> -	O	90	98-100	C <sub>18</sub> H <sub>15</sub> NO <sub>3</sub> Se	58.06	58.23	4.03	3.85	3.76	3.57
XVb	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> -	O	95	93-94	C <sub>18</sub> H <sub>14</sub> BrNO <sub>3</sub> Se	47.89	47.99	3.10	3.01	3.10	3.25
XVc	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> -	O	90	102-103	C <sub>18</sub> H <sub>14</sub> ClNO <sub>3</sub> Se	53.14	53.28	3.44	3.63	3.44	3.55
XVd	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> -	O	85	98-99	C <sub>19</sub> H <sub>17</sub> NO <sub>3</sub> Se	59.07	58.88	4.40	4.45	3.63	3.82
XVe	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> -	O	85	84-85	C <sub>19</sub> H <sub>17</sub> NO <sub>4</sub> Se	56.72	56.85	4.23	4.35	3.48	3.65
XVf	C <sub>6</sub> H <sub>5</sub> -	S	90	94-96	C <sub>18</sub> H <sub>15</sub> NO <sub>2</sub> SSe	55.67	55.49	3.87	3.98	3.61	3.80
XVg	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> -	S	95	82-84	C <sub>18</sub> H <sub>14</sub> BrNO <sub>2</sub> SSe	46.25	46.47	3.00	3.23	3.00	2.87
XVh	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> -	S	90	100-102	C <sub>18</sub> H <sub>14</sub> ClNO <sub>2</sub> SSe	51.12	51.31	3.31	3.16	3.31	3.45
XVi	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> -	S	85	109-110	C <sub>19</sub> H <sub>17</sub> ClNO <sub>2</sub> SSe	56.72	56.91	4.23	4.35	3.48	3.67
XVj	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> -	S	80	95-96	C <sub>19</sub> H <sub>17</sub> NO <sub>3</sub> SSe	54.55	54.36	4.07	4.18	3.35	3.59

(a) All compounds were crystallized from ether.



Scheme 1

Reaction of arylselenocarboxamide (XIII) with 1,3-dichloroacetone afforded 2-aryl-4-chloromethyl selenazole (XIV) (14). Reaction of methyl salicylate with XIV afforded methyl 2-(2-aryl-4-selenazolylmethoxy)benzoate (XV, X = O). Alkaline hydrolysis of the latter gave acid XVI (X = O) which was cyclized either with stannic chloride or polyphosphoric acid (see Experimental) to give IIa-IIe.

Starting from XIV and *o*-mercaptobenzoate, compounds II f-IIj were similarly prepared.

The physical constants of the compounds prepared are summarized in Tables I, II and III.

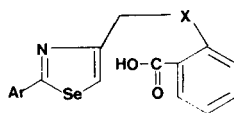
## EXPERIMENTAL

Melting points were taken on a Kofler hot stage microscope and were uncorrected. Nmr spectra were determined using a Varian T-60 spectrometer and chemical shifts ( $\delta$ ) are in ppm relative to internal tetramethylsilane. Mass spectra were run on a Varian MAT-311 spectrometer at 70 ev. Ir spectra were recorded on a Perkin-Elmer 267 spectrograph (potassium bromide).

Ethyl 2-Phenyl-4-bromoethylthiazole-5-carboxylate (IV).

A mixture of III (2.47 g., 0.01 mole) (10) and *N*-bromosuccinimide (1.96 g, 0.11 mole) in 30 ml. of carbon tetrachloride was irradiated with a 500 W (G. E. Photospot) lamp while heating and stirring at reflux temperature for 2.5 hours. The reaction mixture was cooled and filtered.

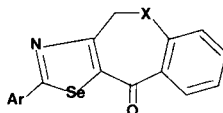
Table II



Compound No.	Ar	X	Yield %	M.p. °C (a)	Formula	C		H		N	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
XVIa	C <sub>6</sub> H <sub>5</sub> -	O	90	112-114	C <sub>17</sub> H <sub>13</sub> NO <sub>3</sub> Se	56.98	56.77	3.63	3.42	3.91	3.73
XVIb	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> -	O	95	145-147	C <sub>17</sub> H <sub>12</sub> BrNO <sub>3</sub> Se	46.68	46.85	2.75	2.65	3.20	3.35
XVIc	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> -	O	85	142-143	C <sub>17</sub> H <sub>12</sub> ClNO <sub>3</sub> Se	51.97	51.79	3.06	3.25	3.57	3.76
XVI d	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> -	O	90	125-126	C <sub>18</sub> H <sub>15</sub> NO <sub>3</sub> Se	58.06	58.21	4.03	4.18	3.76	3.93
XVI e	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> -	O	95	100-102	C <sub>18</sub> H <sub>15</sub> NO <sub>3</sub> Se	55.67	55.75	3.87	3.98	3.61	3.81
XVI f	C <sub>6</sub> H <sub>5</sub> -	S	90	120-122	C <sub>17</sub> H <sub>13</sub> NO <sub>2</sub> SSe	54.55	54.69	3.48	3.59	3.74	3.93
XVI g	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> -	S	95	156-158	C <sub>17</sub> H <sub>12</sub> BrNO <sub>2</sub> SSe	45.03	45.15	2.65	2.85	3.09	3.23
XVI h	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> -	S	85	157-159	C <sub>17</sub> H <sub>12</sub> ClNO <sub>2</sub> SSe	49.94	49.73	2.94	2.75	3.43	3.81
XVI i	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> -	S	85	208-210	C <sub>18</sub> H <sub>15</sub> NO <sub>2</sub> SSe	55.67	55.46	3.87	3.94	3.61	3.42
XVI j	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> -	S	90	153-155	C <sub>18</sub> H <sub>15</sub> NO <sub>2</sub> SSe	53.47	53.63	3.71	3.90	3.47	3.61

(a) All compounds were crystallized from ethanol-water.

Table III



Compound No.	Ar	X	Yield %	M.p. °C (a)	Formula	C		H		N	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
IIa	C <sub>6</sub> H <sub>5</sub> -	O	70	163-165	C <sub>17</sub> H <sub>11</sub> NO <sub>2</sub> Se	60.00	60.22	3.24	3.43	4.12	4.31
IIb	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> -	O	50	204-206	C <sub>17</sub> H <sub>10</sub> BrNO <sub>2</sub> Se	48.69	48.87	2.39	2.18	3.34	3.15
IIc	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> -	O	50	203-205	C <sub>17</sub> H <sub>10</sub> ClNO <sub>2</sub> Se	54.47	54.55	2.67	2.83	3.74	3.91
IId	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> -	O	70	171-174	C <sub>18</sub> H <sub>13</sub> NO <sub>2</sub> Se	61.02	61.21	3.67	3.85	3.95	3.98
IIe	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> -	O	35	116-118	C <sub>18</sub> H <sub>13</sub> NO <sub>2</sub> Se	58.38	58.19	3.51	3.70	3.78	3.59
II f	C <sub>6</sub> H <sub>5</sub> -	S	70	110-111	C <sub>17</sub> H <sub>11</sub> NOSSe	57.30	57.51	3.09	3.21	3.93	3.74
II g	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> -	S	60	216-218	C <sub>17</sub> H <sub>10</sub> BrNOSSe	46.90	47.12	2.30	2.14	3.22	3.01
II h	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> -	S	50	220-221	C <sub>17</sub> H <sub>10</sub> ClNOSSe	52.24	52.05	2.56	2.63	3.59	3.74
II i	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> -	S	60	180-182	C <sub>18</sub> H <sub>13</sub> NOSSe	58.38	58.19	3.51	3.70	3.78	3.94
II j	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> -	S	60	126-128	C <sub>18</sub> H <sub>13</sub> NO <sub>2</sub> SSe	55.96	55.78	3.37	3.56	3.63	3.45

(a) All compounds were crystallized from ether.

The solvent was evaporated and the residue was crystallized from carbon tetrachloride to give 2.93 g. (95%) of IV, m.p. 116-118°; nmr (deuteriochloroform): 8.10-7.77 (m, 2H, aromatic), 7.57-7.27 (m, 3H, aromatic), 4.77 (s, 2H, CH<sub>2</sub>), 4.37 (q, 2H, CH<sub>2</sub>) and 1.40 ppm (t, 3H, CH<sub>3</sub>).

Anal. Calcd. for C<sub>13</sub>H<sub>12</sub>BrNO<sub>2</sub>S: C, 47.85; H, 3.68; N, 4.29. Found: C, 47.98; H, 3.52; N, 4.02.

Ethyl 2-Phenyl-4-phenoxymethylthiazole-5-carboxylate (Va).

A mixture of IV (3.26 g., 0.01 mole), phenol (0.94 g., 0.01 mole), potassium carbonate (5.52 g., 0.04 mole), sodium iodide (100 mg.) and butanone (40 ml.) was stirred and refluxed overnight. The reaction mixture was cooled and filtered. The precipitate was washed with butanone (10 ml.). The solvent was evaporated. The residue was dissolved in ether, washed with water, 10% sodium bicarbonate, and water. The ether was dried, filtered and evaporated. The residue was purified by tlc (silica gel, chloroform) to give Va (oil, 2.71 g., 80%); nmr (deuteriochloroform): 8.17-7.90 (m, 2H, aromatic), 7.63-7.0 (m, 8H, aromatic), 5.57 (s, 2H, CH<sub>2</sub>), 4.40 (q, 2H, CH<sub>2</sub>) and 1.33 ppm (t, 3H, CH<sub>3</sub>).

Anal. Calcd. for C<sub>19</sub>H<sub>17</sub>NO<sub>3</sub>S: C, 67.26; H, 5.01; N, 4.13. Found: C, 67.49; H, 5.28; N, 4.31.

2-Phenyl-4-phenoxymethylthiazole-5-carboxylic Acid (VIa).

A solution of Va (3.39 g., 0.01 mole) and potassium hydroxide (0.67 g., 0.012 mole) in 20 ml. of ethanol and 3 ml. of water was refluxed for 3 hours. The solvent was evaporated and the residue was dissolved in water and acidified with hydrochloric acid. The precipitate was crystallized from ethanol-water to give 2.95 g. (95%) of VIa, m.p. 192-194°.

Anal. Calcd. for C<sub>17</sub>H<sub>13</sub>NO<sub>3</sub>S: C, 65.59; H, 4.18; N, 4.50. Found: C, 65.38; H, 4.35; N, 4.34.

2-Phenyl-4,10-dihydro-10-oxo[1]benzoxepino[3,4-*d*]thiazole (Ia).

Method A.

A mixture of VIa (311 mg., 1 mmole) and thionyl chloride (0.5 ml.) in 5 ml. of benzene was refluxed for 5 hours. The solvent was evaporated to give VIIa. To a stirring solution of the latter in 20 ml. of anhydrous methylene chloride stannic chloride (261 mg., 1 mmole) in 5 ml. of methylene chloride was added, stirring was continued at ambient temperature overnight and refluxed for an additional 2 hours. The solvent was evaporated. To the residue, ice-water was added, and the solution was neutralized with a solution of sodium bicarbonate and extracted

with chloroform. The chloroform was dried, filtered and evaporated. The residue was purified by tlc (silica gel, chloroform) and the desired compound was crystallized from ethanol to give 234 mg. (80%) of Ia, m.p. 154-155°; ir: 1620  $\text{cm}^{-1}$  (carbonyl); nmr (deuteriochloroform): 8.27-7.87 (m, 3H, aromatic), 7.67-7.0 (m, 6H, aromatic) and 5.37 ppm (s, 2H,  $\text{CH}_2$ ).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{13}\text{NO}_2\text{S}$ : C, 69.62; H, 3.75; N, 4.78. Found: C, 69.81; H, 3.56; N, 4.59.

#### Ethyl 2-Phenyl-4-phenylthiomethylthiazole-5-carboxylate (Vb).

A mixture of IV (3.26 g., 0.01 mole), thiophenol (1.1 g., 0.01 mole), potassium carbonate (5.52 g., 0.04 mole) sodium iodide (100 mg.) and butanone (40 ml.) was stirred and refluxed overnight and worked up similar to the preparation of Va to give 3.37 g. (95%) of Vb, m.p. 79-80° (ether); nmr (deuteriochloroform): 8.20-7.83 (m, 2H, aromatic), 7.66-7.26 (m, 8H, aromatic), 4.66 (s, 2H,  $\text{CH}_2$ ), 4.26 (q, 2H,  $\text{CH}_2$ ) and 1.30 ppm (t, 3H,  $\text{CH}_3$ ); ms: m/e (relative intensity) 355 ( $\text{M}^+$ , 100), 326 (38), 310 (35), 309 (48), 246 (95), 218 (95), 104 (52) and 71 (42).

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{17}\text{NO}_2\text{S}_2$ : C, 64.22; H, 4.79; N, 3.94. Found: C, 64.35; H, 4.58; N, 3.75.

#### 2-Phenyl-4,10-dihydro-10-oxo[1]benzothiepine[3,4-d]thiazole (Ib).

##### Method A.

A mixture of Vb (3.55 g., 0.01 mole) and potassium hydroxide (0.67 g., 0.012 mole) in 20 ml. of ethanol and 3 ml. of water was refluxed for 3 hours. The solvent was evaporated and the residue was dissolved in water and acidified with hydrochloric acid. The precipitate was filtered to give the acid Vb. A mixture of the latter and thionyl chloride (4 ml.) in 50 ml. of dry benzene was refluxed for 5 hours. The solvent was evaporated to give VIIb. To a stirring solution of the latter in 60 ml. of anhydrous methylene chloride, stannic chloride (2.61 g., 0.01 mole) in 20 ml. of methylene chloride was added and the procedure was continued as has been explained for Ia to give 2.16 g. (70%) of Ib, m.p. 151-152° (ethanol); ir: 1610  $\text{cm}^{-1}$  (carbonyl); nmr (deuteriochloroform): 8.26-7.83 (m, 3H, aromatic), 7.83-7.16 (m, 6H, aromatic) and 4.28 ppm (s, 2H,  $\text{CH}_2$ ); ms: m/e (relative intensity) 309 ( $\text{M}^+$ , 100), 275 (27), 206 (25), 178 (19), 177 (18), 174 (16), 136 (43) and 108 (27).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{11}\text{NOS}_2$ : C, 66.02; H, 3.56; N, 4.53. Found: C, 66.21; H, 3.39; N, 4.71.

#### Methyl 2-(2-Phenyl-4-thiazolylmethoxy)benzoate (Xa).

A mixture of 2-phenyl-4-chloromethylthiazole (VIII, 2.095 g., 0.01 mole), methyl salicylate (IXa, 1.52 g., 0.01 mole), potassium carbonate (5.52 g., 0.04 mole), sodium iodide (100 mg.) and butanone (40 ml.) was stirred and refluxed overnight and worked up similar to the work up of Va to give 2.76 g. (85%) of Xa, m.p. 59-60° (ether-petroleum ether); nmr (deuteriochloroform): 8.06-6.73 (m, 10H, aromatic), 5.33 (d, 2H,  $\text{CH}_2$ , J = 1.5 Hz), and 3.90 ppm (s, 3H,  $\text{CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{15}\text{NO}_3\text{S}$ : C, 66.46; H, 4.62; N, 4.31. Found: C, 66.27; H, 4.43; N, 4.50.

#### Methyl 2-(2-Phenyl-4-thiazolylmethylthio)benzoate (Xb).

This compound was prepared from VIII, *o*-mercaptobenzoate (IXb), potassium carbonate and sodium iodide in butanone as explained above in 85% yield, m.p. 69-71° (ether-petroleum ether); nmr (deuteriochloroform): 8.03-7.7 (m, 3H, aromatic), 7.77-7.0 (m, 7H, aromatic), 4.30 (s, 2H,  $\text{CH}_2$ ) and 3.90 ppm (s, 3H,  $\text{OCH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{15}\text{NO}_2\text{S}_2$ : C, 63.34; H, 4.40; N, 4.11. Found: C, 63.15; H, 4.25; N, 4.34.

#### 2-(2-Phenyl-4-thiazolylmethoxy)benzoic Acid (XIa).

To a stirring and refluxing solution of Xa (3.25 g., 0.01 mole) in 30 ml. of ethanol, a solution of sodium hydroxide (0.44 g., 0.011 mole) in 5 ml. of water was added dropwise. After addition was complete, the heating was continued for 15 minutes. The solvent was evaporated. The residue was dissolved in water and acidified with hydrochloric acid. The precipitate was crystallized from ethanol-water to give 2.25 g. (95%) of XIa, m.p.

121-123°.

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{13}\text{NO}_3\text{S}$ : C, 65.69; H, 4.18; N, 4.50. Found: C, 65.77; H, 4.01; N, 4.34.

#### 2-(2-Phenyl-4-thiazolylmethylthio)benzoic Acid (XIb).

Compound Xb was hydrolyzed as explained above to give XIb, m.p. 143-145° (ethanol-water); ir: 1690  $\text{cm}^{-1}$  (carbonyl).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{13}\text{NO}_2\text{S}_2$ : C, 62.39; H, 3.98; N, 4.28. Found: C, 62.67; H, 4.15; N, 4.09.

#### 2-Phenyl-4,10-dihydro-10-oxo[1]benzoxepino[3,4-d]thiazole (Ia).

##### Method B.

A mixture of XIa (311 mg., 1 mmole) and thionyl chloride (0.5 ml.) in 5 ml. of dry benzene was refluxed for 5 hours. The solvent was evaporated to give XIIa; ir: 1772  $\text{cm}^{-1}$  (carbonyl). To a stirring solution of the latter in 20 ml. of anhydrous methylene chloride, stannic chloride (261 mg., 1 mmole) in 5 ml. of methylene chloride was added and the procedure was continued in a manner similar to the preparation of Ia (Method A) to give 249 mg. (85%) of Ia, m.p. 154-155° (ethanol).

#### 2-Phenyl-4,10-dihydro-10-oxo[1]benzothiepine[3,4-d]thiazole (Ib).

A mixture of XIb (327 mg., 1 mmole), thionyl chloride (0.5 ml.) and 5 ml. of dry benzene was refluxed for 5 hours. The solvent was evaporated to give XIIb. To a stirring solution of the latter in 20 ml. of anhydrous methylene chloride, stannic chloride (261 mg., 1 mmole) in 5 ml. of methylene chloride was added and the procedure was continued as explained above to give 247 mg. (80%) of Ib, m.p. 151-152° (ethanol).

#### methyl 2-(2-Phenyl-4-selenazolylmethoxy)benzoate (XVa).

A mixture of 2-phenyl-4-chloromethylselenazole (XIVa, 2.565 g., 0.01 mole), methyl salicylate (IXa, 1.52 g., 0.01 mole), potassium carbonate (5.52 g., 0.04 mole), sodium iodide (100 mg.) and butanone (40 ml.) was stirred and refluxed overnight, and worked up in a manner similar to the preparation of Xa to give 3.35 g. (90%) of XVa, m.p. 98-100° (ether); nmr (deuteriochloroform): 8.0-6.60 (m, 10H, aromatic), 5.18 (d, 2H,  $\text{CH}_2$ , J = 1.2 Hz), and 3.82 ppm (s, 3H,  $\text{OCH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{15}\text{NO}_3\text{Se}$ : C, 58.06; H, 4.03; N, 3.76. Found: C, 58.23; H, 3.85; N, 3.57.

Compounds XVb-XVe were prepared similarly (see Table I)

#### Methyl 2-(2-Phenyl-4-selenazolylmethylthio)benzoate (XVf).

This compound was prepared from XIVa, *o*-mercaptobenzoate (IXb), potassium carbonate and sodium iodide in butanone as explained above in 90% yield, m.p. 94-96° (ether); nmr (deuteriochloroform): 8.03-7.67 (m, 4H, aromatic), 7.5-7.0 (m, 6H, aromatic), 4.27 (s, 2H,  $\text{CH}_2$ ) and 3.82 ppm (s, 3H,  $\text{OCH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{15}\text{NO}_2\text{SSe}$ : C, 55.67; H, 3.87; N, 3.61. Found: C, 55.49; H, 3.98; N, 3.80.

Compounds XVg-XVj were prepared similarly (see Table I).

#### 2-(2-Phenyl-4-selenazolylmethoxy)benzoic Acid (XVIa).

To a stirring and refluxing solution of XVa (3.72 g., 0.01 mole) in 30 ml. of ethanol, a solution of sodium hydroxide (0.44 g., 0.011 mole) in 5 ml. of water was added dropwise. After the addition was complete, the heating was continued for 15 minutes. The solvent was evaporated. The residue was dissolved in water and acidified with hydrochloric acid. The precipitate was crystallized from ethanol-water to give 3.22 g. (90%) of XVIa, m.p. 112-114°; ir: 1650  $\text{cm}^{-1}$  (carbonyl).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{13}\text{NO}_3\text{Se}$ : C, 56.98; H, 3.63; N, 3.91. Found: C, 56.77; H, 3.42; N, 3.73.

Compounds XVIb-XVIj were prepared similarly (see Table II).

#### 2-Phenyl-4,10-dihydro-10-oxo[1]benzoxepino[3,4-d]selenazole (IIa).

A mixture of XVIa (358 mg., 1 mmole) and thionyl chloride (0.5 ml.) in 5 ml. of dry benzene was refluxed for 5 hours. The solvent was evaporated to give XVIIa; ir: 1775  $\text{cm}^{-1}$  (carbonyl). To a stirring solution

of the latter in 20 ml. of anhydrous methylene chloride, stannic chloride (261 mg., 1 mmole) in 5 ml. of methylene chloride was added and the procedure was continued in a manner similar to the preparation of Ia (method A) to give 238 mg. (70%) of IIa, m.p. 163-165° (ether); ir: 1610  $\text{cm}^{-1}$  (carbonyl); nmr (deuteriochloroform): 8.30-7.90 (m, 3H, aromatic), 7.77-7.13 (m, 6H, aromatic) and 5.50 ppm (s, 2H,  $\text{CH}_2$ ); ms: m/e (relative intensity) 341 ( $\text{M}^+$ , 100), 261 (35), 238 (47), 210 (22), 158 (24), 121 (48), 120 (5), 104 (5) and 92 (5).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{11}\text{NO}_2\text{Se}$ : C, 60.00; H, 3.24; N, 4.12. Found: C, 60.22; H, 3.43; N, 4.31.

Compounds IIb-IId and IIe-IIi were prepared similarly (see Table III).

2-*p*-Methoxyphenyl-4,10-dihydro-10-oxo[1]benzoxepino[3,4-*d*]selenazole (IIe).

A mixture of XVIe (388 mg., 1 mmole) and polyphosphoric acid (3 ml.) was heated in an oil bath at 120° for 2 hours. After cooling, ice-water was added and the solution was neutralized with an aqueous solution of sodium bicarbonate and extracted with chloroform. The chloroform was dried, filtered and evaporated. The residue was purified by tlc (silica gel, chloroform) and the desired compound was crystallized from ether to give 129.5 mg. (35%) of IIe, m.p. 116-118°; nmr (deuteriochloroform): 8.16-7.1 (m, 8H, aromatic), 5.40 (s, 2H,  $\text{CH}_2$ ) and 3.92 ppm (s, 3H,  $\text{OCH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{13}\text{NO}_3\text{Se}$ : C, 58.38; H, 3.51; N, 3.78. Found: C, 58.19; H, 3.70; N, 3.59.

2-*p*-Methoxyphenyl-4,10-dihydro-10-oxo[1]benzothiepine[3,4-*d*]selenazole (IIj).

This compound was prepared similarly in 60% yield, m.p. 126-128° (ether); ir: 1590  $\text{cm}^{-1}$  (carbonyl); nmr (deuteriochloroform): 8.16-6.83 (m, 8H, aromatic), 4.20 ppm (s, 2H,  $\text{CH}_2$ ) and 3.90 ppm (s, 3H,  $\text{OCH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{13}\text{NO}_2\text{SSe}$ : C, 55.96; H, 3.37; N, 3.63. Found: C, 55.78; H, 3.56; N, 3.45.

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