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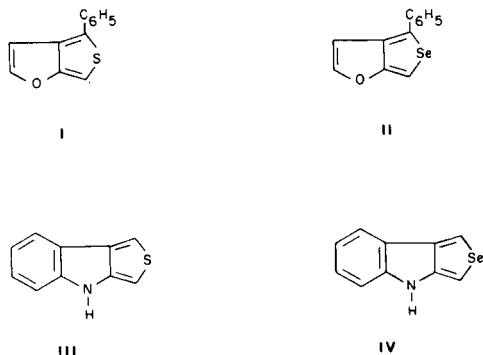
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Starting from the readily available 2-methyl-3-benzoylfuran, 1-phenylthieno[3,4-*b*]furan and 1-phenyl-seleno[3,4-*b*]furan were prepared. Also, starting from phenyl 3-methylindol-2-yl ketone and aryl 2-methylindole-3-yl ketones a series of substituted thieno[3,4-*b*]indoles and substituted seleno[3,4-*b*]indoles were prepared.

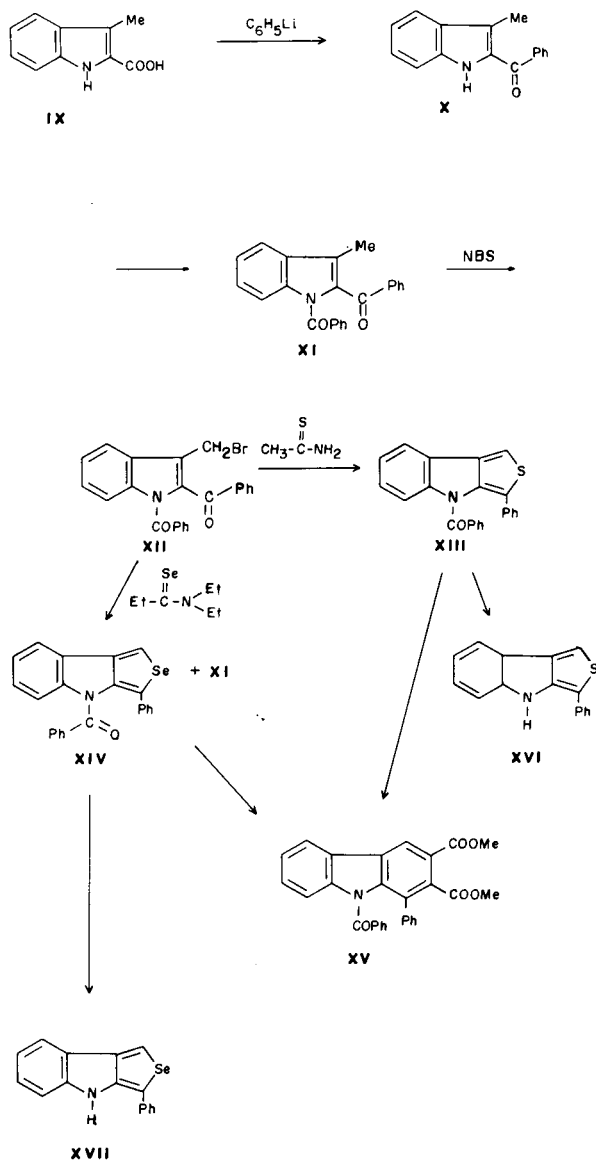
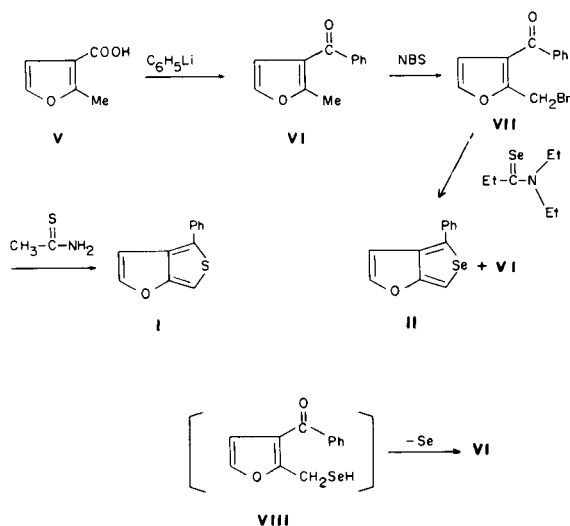
J. Heterocyclic Chem., **19**, 227 (1982).

In continuation of the study on the chemistry of selenium heterocyclic compounds (2-8) and as a part of a program designed to expand the chemistry of fused thiophene and selenophene heterocycles (9), it became necessary to synthesize thieno[3,4-*b*]furan (I), selenolo[3,4-*b*]furan (II), thieno[3,4-*b*]indole (III) and selenolo[3,4-*b*]indole (IV) for biological evaluation.



The starting material, 2-methyl-3-benzoylfuran (VI), could be prepared from the reaction of phenyl lithium with 2-methyl-3-furancarboxylic acid (V) (10). Reaction of

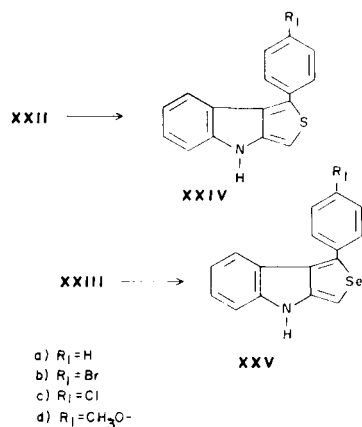
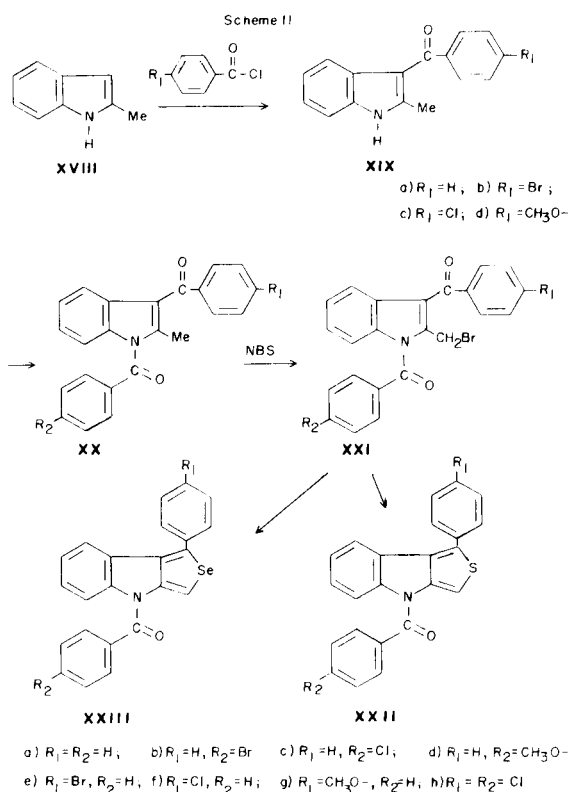
Scheme 1



N-bromosuccinimide with compound VI afforded 2-bromomethyl-3-benzoylfuran (VII). Reaction of thioacetamide with the latter, according to our procedure

reported previously (11), gave the desired compound I. The reaction of *N,N*-diethylselenopropionamide (12) with compound VII afforded compound VI in addition to the desired compound II. Debromination of compound VII probably occurred through the intermediate VIII.

The nmr spectrum of compound II was in agreement with the suggested structure. In the nmr spectrum of this compound the proton which is *geminal* to the selenium appears as a strong doublet (long range coupling with H-6) and a weak quartet centered around the doublet. This quartet is assigned to the splitting caused by the presence of the selenium isotope ^{77}Se with a natural abundance of 7.5%. The selenium splitting constant was found to be 45 cps. This splitting was similar with the one reported for the fused selenophene (11).



Reaction of 3-methylindole-2-carboxylic acid (IX) (13) with phenyllithium afforded phenyl 3-methylindol-2-yl ketone (X) (14). Reaction of *n*-butyllithium with compound X and subsequent addition of benzoic anhydride afforded 1,2-dibenzoyl-3-methylindole (XI). Reaction of *N*-bromosuccinimide with compound XI gave 1,2-dibenzoyl-3-bromomethylindole (XII). Reaction of thioacetamide with the latter afforded 3-phenyl-4-benzoylthieno[3,4-*b*]indole (XIII). The reaction of *N,N*-diethylselenopropionamide with compound XII afforded compound XI in addition to the desired compound XIV.

The reaction of compound XIII or XIV with dimethyl acetylenedicarboxylate afforded 5-benzoyl-4-phenyl-2,3-dicarbomethoxycarbazole (XV), in support of the structures XIII and XIV.

The nmr spectrum of compound XIV was also in agreement with the suggested structure. In the nmr spectrum of this compound the proton which is *geminal* to the selenium atom appears as a strong singlet and a weak doublet centered around the singlet with the splitting constant of 44 Hz (^{77}Se coupling).

Alkaline hydrolysis of compounds XIII and XIV afforded the parent compounds 3-phenyl-thieno[3,4-*b*]indole (XVI) and 3-phenylselenolo[3,4-*b*]indole (XVII) respectively (See Scheme I).

Reaction of 2-methylindole (XVIII) with ethylmagnesium bromide and subsequent addition of aryl chloride afforded aryl 2-methylindole-3-yl ketones (XIX) (15). The latter was transformed to the desired compounds 1-arylthieno[2,3-*b*]indole (XXIII) and 1-arylselenolo[2,3-*b*]indole (XXV) as it is shown in Scheme II.

The physical constant of the compounds prepared are summarized in Tables I and II.

EXPERIMENTAL

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. The ir spectra were obtained using a Perkin-Elmer model 267 spectrograph (potassium bromide discs). The nmr spectra were recorded on a Varian T-60 spectrometer and chemical shifts (δ) are in ppm relative to internal tetramethylsilane. Mass spectra were run on a Varian MAT MS-311 spectrometer at 70 eV.

2-Methyl-3-benzoylfuran (VI).

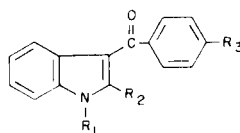
To a stirring solution of phenyl lithium, which was prepared from bromobenzene (15.2 g, 0.1 mole) and lithium (1.4 g) in dry ether (100 ml) (16), was added 2-methyl-3-furancarboxylic acid (V, 2.52 g, 0.02 mole) at ice-water temperature. The mixture was stirred under nitrogen overnight at room temperature. Ice-water was added to the mixture followed by extraction with ether. The ether was dried, filtered and evaporated. The residue was distilled under reduced pressure to give 2.58 g (75%) of VI, bp 80-84° (4 mm Hg); ir (film): 1652 cm^{-1} (carbonyl), nmr (deuteriochloroform): 7.83-7.63 (m, 2H, aromatic), 7.57-7.27 (m, 3H, aromatic), 7.20 (d, 1H, H-5, $J_{4,5} = 2$ Hz), 6.47 (d, 1H, H-4) and 2.47 ppm (s, 3H, CH_3).

Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{O}_2$: C, 77.42; H, 5.38. Found: C, 77.61; H, 5.19.

2-Bromomethyl-3-benzoylfuran (VII).

A mixture of VI (1.86 g, 0.01 mole) and *N*-bromosuccinimide (1.96 g, 0.011 mole) in 30 ml of carbon tetrachloride was irradiated with a 500 W

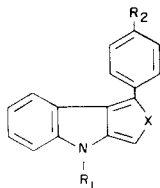
Table I



Compound No.	R ₁	R ₂	R ₃	Mp °C (a)	Yield	Formula	C%		H%		N%	
							Calcd.	Found	Calcd.	Found	Calcd.	Found
XIXb	H	CH ₃	Br	185-187 (c)	70	C ₁₆ H ₁₂ BrNO	61.15	61.02	3.82	3.98	4.46	4.35
(b)												
XIXc	H	CH ₃	Cl	190-193 (c)	63	C ₁₆ H ₁₂ ClNO	71.24	71.03	4.45	4.26	5.19	5.01
XIXd	H	CH ₃	CH ₃ O	218-220 (c)	58	C ₁₇ H ₁₅ NO ₂	76.98	77.19	5.66	5.85	5.28	5.12
XXa	C ₆ H ₅ CO-	CH ₃	H	118-119	90	C ₂₃ H ₁₇ NO ₂	81.40	81.61	5.05	5.22	4.13	3.92
XXb	<i>p</i> -BrC ₆ H ₄ CO-	CH ₃	H	110-112	85	C ₂₃ H ₁₆ BrNO ₂	66.03	65.85	3.83	4.01	3.35	3.53
XXc	<i>p</i> -ClC ₆ H ₄ CO-	CH ₃	H	114-116	95	C ₂₃ H ₁₆ ClNO ₂	73.90	73.75	4.28	4.09	3.75	3.56
XXd	<i>p</i> -MeOC ₆ H ₄ CO-	CH ₃	H	120-122	85	C ₂₄ H ₁₈ NO ₃	78.05	78.24	5.15	5.34	3.79	3.98
XXe	C ₆ H ₅ CO-	CH ₃	Br	154-155	85	C ₂₃ H ₁₆ BrNO ₂	66.03	65.85	3.83	4.01	3.35	3.53
XXf	C ₆ H ₅ CO-	CH ₃	Cl	120-121	76	C ₂₃ H ₁₆ ClNO ₂	73.90	73.74	4.28	4.19	3.75	3.66
XXg	C ₆ H ₅ CO-	CH ₃	CH ₃ O	168-170	67	C ₂₄ H ₁₉ NO ₃	78.05	78.24	5.15	5.33	3.79	3.94
XXh	<i>p</i> -ClC ₆ H ₄ CO-	CH ₃	Cl	123-125	95	C ₂₃ H ₁₅ Cl ₂ NO ₂	67.65	67.83	3.68	3.74	3.43	3.62
XXIa	C ₆ H ₅ CO-	CH ₂ Br	H	145-147	95	C ₂₃ H ₁₆ BrNO ₂	66.03	66.21	3.83	4.01	3.35	3.52
XXIb	<i>p</i> -BrC ₆ H ₄ CO-	CH ₂ Br	H	210-212 (d)	95	C ₂₃ H ₁₅ Br ₂ NO ₂	55.53	55.37	3.02	3.21	2.82	2.98
XXIc	<i>p</i> -ClC ₆ H ₄ CO-	CH ₂ Br	H	184-186	95	C ₂₃ H ₁₅ BrClNO ₂	60.99	61.12	3.31	3.14	3.09	3.24
XXId	<i>p</i> -MeOC ₆ H ₄ CO-	CH ₂ Br	H	135-137 (d)	95	C ₂₄ H ₁₈ BrNO ₃	64.29	64.45	4.02	4.21	3.13	3.32
XXIe	C ₆ H ₅ CO-	CH ₂ Br	Br	175-176 (d)	90	C ₂₃ H ₁₅ Br ₂ NO ₂	55.53	55.38	3.02	3.11	2.82	2.65
XXIf	C ₆ H ₅ CO-	CH ₂ Br	Cl	163-165 (d)	95	C ₂₃ H ₁₅ BrClNO ₂	60.99	61.15	3.31	3.52	3.09	3.26
XXIg	C ₆ H ₅ CO-	CH ₂ Br	CH ₃ O	174-175 (d)	95	C ₂₄ H ₁₈ BrNO ₃	64.29	64.44	4.02	4.18	3.13	3.21
XXIh	<i>p</i> -ClC ₆ H ₄ CO-	CH ₂ Br	Cl	158-160	95	C ₂₃ H ₁₄ BrCl ₂ NO ₂	56.67	56.85	2.87	2.94	2.87	2.96

(a) Unless otherwise mentioned the compound was crystallized from ether. (b) Compound XIXa was prepared according to reference (15). (c) This compound was crystallized from methanol. (d) This compound was crystallized from ethanol.

Table II



Compound No.	R ₁	R ₂	R ₃	Mp °C (a)	Yield	Formula	C%		H%		N%	
							Calcd.	Found	Calcd.	Found	Calcd.	Found
XXIIa	C ₆ H ₅ CO-	H	S	144-145	50	C ₂₃ H ₁₅ NOS	78.19	78.01	4.25	4.12	3.97	3.75
XXIIb	C ₆ H ₅ CO-	Br	S	159-160	45	C ₂₃ H ₁₄ BrNOS	68.89	63.74	3.24	3.05	3.24	3.12
XXIIc	C ₆ H ₅ CO-	Cl	S	153-155	50	C ₂₃ H ₁₄ ClNOS	71.23	71.05	3.61	3.80	3.61	3.45
XXIId	C ₆ H ₅ CO-	CH ₃ O	S	102-104	45	C ₂₄ H ₁₇ NO ₂ S	75.20	75.06	4.44	4.63	3.66	3.45
XXIIe	<i>p</i> -BrC ₆ H ₄ CO-	H	S	148-149	45	C ₂₃ H ₁₄ BrNOS	63.89	63.71	3.24	3.06	3.24	3.12
XXIIIf	<i>p</i> -ClC ₆ H ₄ CO-	H	S	143-144	55	C ₂₃ H ₁₄ ClNOS	71.23	71.07	3.61	3.45	3.61	3.79
XXIIg	<i>p</i> -MeOC ₆ H ₄ CO-	H	S	125-126	45	C ₂₄ H ₁₇ NO ₂ S	75.20	75.06	4.44	4.29	3.66	3.78
XXIIh	<i>p</i> -ClC ₆ H ₄ CO-	Cl	S	127-129	45	C ₂₃ H ₁₃ Cl ₂ NOS	65.40	65.26	3.08	2.91	3.32	3.51
XXIIIa	C ₆ H ₅ CO-	H	Se	145-147	35	C ₂₃ H ₁₅ NOSe	69.00	69.18	3.75	3.56	3.50	3.36
XXIIIb	C ₆ H ₅ CO-	Br	Se	138-140	35	C ₂₃ H ₁₄ BrNOSe	57.62	57.81	2.92	2.74	2.92	3.11
XXIIIc	C ₆ H ₅ CO-	Cl	Se	131-133	40	C ₂₃ H ₁₄ ClNOSe	63.52	63.71	3.22	3.04	3.22	3.11
XXIIId	C ₆ H ₅ CO-	CH ₃ O	Se	117-119	30	C ₂₄ H ₁₇ NO ₂ Se	66.98	67.15	3.95	4.14	3.26	3.45
XXIIIe	<i>p</i> -BrC ₆ H ₄ CO-	H	Se	128-130	35	C ₂₃ H ₁₄ BrNOSe	57.62	57.80	2.92	2.74	2.92	2.76
XXIIIIf	<i>p</i> -ClC ₆ H ₄ CO-	H	Se	135-136	35	C ₂₃ H ₁₄ ClNOSe	63.52	63.65	3.22	3.09	3.22	3.02
XXIIIg	<i>p</i> -MeOC ₆ H ₄ CO-	H	Se	103-105	35	C ₂₄ H ₁₇ NO ₂ Se	66.98	66.79	3.95	3.78	3.26	3.87
XXIIIh	<i>p</i> -ClC ₆ H ₄ CO-	Cl	Se	125-127	40	C ₂₃ H ₁₃ Cl ₂ NOSe	58.85	59.04	2.77	2.91	2.98	3.16
XXIVa	H	H	S	118-120	90	C ₁₆ H ₁₁ NS	77.11	76.94	4.42	4.27	5.62	5.81
XXIVb	H	Br	S	164-165	90	C ₁₆ H ₁₀ BrNS	58.54	58.63	3.05	2.89	4.27	4.45
XXIVc	H	Cl	S	156-158	95	C ₁₆ H ₁₀ ClNS	67.72	67.91	3.53	3.71	4.94	4.81
XXIVd	H	CH ₃ O	S	115-117	90	C ₁₇ H ₁₃ NOS	73.12	72.94	4.66	4.47	5.02	4.85
XXVa	H	H	Se	115-117	75	C ₁₆ H ₁₁ NSe	64.86	64.99	3.72	3.88	4.73	4.55
XXVb	H	Br	Se	168-169	80	C ₁₆ H ₁₀ BrNSe	51.20	51.37	2.67	2.85	3.73	3.57
XXVc	H	Cl	Se	174-175	85	C ₁₆ H ₁₀ ClNSe	58.09	57.92	3.03	3.21	4.24	4.34
XXVd	H	CH ₃ O	Se	115-117	85	C ₁₇ H ₁₃ NOSe	62.58	62.75	3.99	4.15	4.29	4.44

(a) All compounds were crystallized from ether.

(G. E. Photospot) lamp while heating and stirring at reflux temperature for 4 hours. The reaction mixture was cooled and filtered. The solvent was evaporated and the residue was distilled under the reduced pressure to give 2.40 g (90%) of VII, bp 118-120° (4 mm Hg); nmr (deuteriochloroform): 8.02-7.7 (m, 2H, aromatic), 7.67-7.33 (m, 4H, aromatic), 6.63 (d, 1H, H-4, $J_{4,5} = 2$ Hz) and 4.78 ppm (s, 2H, CH₂).

Anal. Calcd. for C₁₂H₉BrO₂: C, 54.34; H, 3.40. Found: C, 54.56; H, 3.58.

1-Phenylthieno[3,4-*b*]furan (I).

A solution of VII (265 mg, 1 mmole) and thioacetamide (82.5 mg, 1.1 mmoles) in 10 ml of ethanol was refluxed for 5 hours. The solvent was evaporated and the residue was purified by tlc (silica gel, chloroform-petroleum ether, 1:1). The desired compound was crystallized from ether to give 90 mg (45%) of I, mp 75-77°; nmr (deuteriochloroform): 7.83-7.06 (m, 7H, aromatic) and 6.70 ppm (d, 1H, H-6); ms: *m/e* (%) 200 (M⁺, 67), 171 (100), 155 (10), 139 (17), 121 (30), 77 (31) and 51 (19).

Anal. Calcd. for C₁₂H₁₀OS: C, 72.00; H, 4.00. Found: C, 71.84; H, 4.21.

1-Phenylselenolo[3,4-*b*]furan (II).

A solution of VII (265 mg, 1 mmole) and *N,N*-diethylselenopropionamide (211 mg, 1.1 mmoles) (12) in 10 ml of ethanol was refluxed for 4 hours. The solvent was evaporated and the residue was purified by tlc (silica gel, chloroform-petroleum ether, 1:1). The fast moving fraction was crystallized from ether to give 87 mg (35%) of II, mp 80-82°; nmr (deuteriochloroform): 7.67 (d, 1H, H-5, $J_{5,6} = 2.2$ Hz), 7.60-7.23 (m, 5H, aromatic), 7.20 [d, 1H, H-3, $J_{3,6} = 1$ Hz; this hydrogen was split into a quartet with $J = 45$ Hz (⁷⁷Se coupling)] and 6.58 ppm (q, 1H, H-6, $J_{5,6} = 2.2$ Hz, $J_{3,6} = 1$ Hz); ms: *m/e* (%) 248 (M⁺, 100), 219 (30), 168 (26), 139 (63), 77 (20) and 51 (20).

Anal. Calcd. for C₁₂H₈OSe: 58.30; H, 3.24. Found: C, 58.12; H, 3.02.

The slow moving fraction gave 37 mg (20%) of VI (oil) with the similar physical data of an authentic sample.

Phenyl 3-Methylindol-2-yl Ketone (X).

To a stirring solution of phenyllithium, which was prepared from bromobenzene (15.2 g, 0.1 mole), lithium (1.4 g) in dry ether (100 ml) (16), was added 3-methylindole-2-carboxylic acid (IX, 3.5 g, 0.02 mole) (13) at ice-water temperature. The mixture was stirred overnight under nitrogen at room temperature. Ice-water was added to the mixture followed by extraction with ether. The ether was dried, filtered and evaporated. The residue was crystallized from ether to give 4.2 g (89%) of X, mp 145-146° [lit (14), mp 140-140.5]; ir: 1600 cm⁻¹ (carbonyl); nmr (deuteriochloroform): 9.90 (bs, 1H, NH), 8.0-7.0 (m, 5H, aromatic) and 2.27 ppm (s, 3H, CH₃).

Anal. Calcd. for C₁₆H₁₃NO: C, 81.70; H, 5.53; N, 5.96. Found: C, 81.92; H, 5.37; N, 6.10.

1,2-Dibenzoyl-3-methylindole (XI).

To a stirring solution of X (2.35, 0.1 mole) in 100 ml of dry ether was added dropwise 5.5 ml of a solution of 12.5% *n*-butyllithium in *n*-hexane. After addition was complete the mixture was stirred 10 minutes and a solution of benzoic anhydride (2.26 g, 0.1 mole) in 50 ml of dry ether was added. The mixture was stirred one hour at room temperature and filtered. The solvent was evaporated and the residue was crystallized from ether-petroleum ether to give 2.90 g (85%) of XI, mp 102-104°; ir: 1680 cm⁻¹ (ketone); nmr (deuteriochloroform): 8.0-7.0 (m, 14H, aromatic) and 2.33 ppm (s, 3H, CH₃).

Anal. Calcd. for C₂₃H₁₇NO₂: C, 81.42; H, 5.01; N, 4.13. Found: C, 81.60; H, 5.19; N, 4.31.

1,2-Dibenzoyl-3-bromomethylindole (XII).

This compound was prepared similar to VII in 90% yield, mp 125-127° (ether) nmr (deuteriochloroform): 8.17-7.73 (m, 2H, aromatic), 7.71-7.17 (m, 12H, aromatic) and 4.72 ppm (s, 2H, CH₂).

Anal. Calcd. for C₂₃H₁₆BrNO₂: C, 66.03; H, 3.83; N, 3.35. Found: C, 66.24; H, 3.98; N, 3.16.

3-Phenyl-4-benzoylthieno[3,4-*b*]indole (XIII).

This compound was prepared from XII and thioacetamide similar to I

in 70% yield, mp 111-112° (ethanol); nmr (deuteriochloroform): 7.90-7.63 (m, 2H, aromatic), 7.42 (s, 1H, H-1), 7.55-7.13 (m, 7H, aromatic) and 7.07 (s, 5H, aromatic).

Anal. Calcd. for C₂₂H₁₃NOS: C, 78.19; H, 4.25; N, 3.97. Found: C, 78.01; H, 4.44; N, 4.18.

3-Phenyl-4-benzoylseleno[3,4-*b*]indole (XIV).

This compound was prepared from XII and *N,N*-diethylselenopropionamide similar to II in 50% yield, mp 127-128° (ethanol); nmr (deuteriochloroform): 8.05 (s, 1H, H-1, this hydrogen was split into a doublet with $J = 44$ Hz (⁷⁷Se coupling)), 7.87-7.53 (m, 2H, aromatic), 7.47-7.07 (m, 7H, aromatic) and 7.05 ppm (s, 5H, aromatic).

Anal. Calcd. for C₂₃H₁₅NOSe: C, 69.00; H, 3.75; N, 3.50. Found: C, 68.82; H, 3.56; N, 3.36.

5-Benzoyl-4-phenyl-2,3-dicarboxymethoxycarbazole (XV).

A solution of XIII (176.5 mg, 0.5 mmole) and dimethyl acetylenedicarboxylate (71 mg, 0.5 mmole) in 10 ml of xylene was refluxed for 72 hours. The solvent was evaporated and the residue was purified by tlc (silica gel, chloroform) to give 58 mg (25%) of XV, mp 182-184 (ether); ir: 1722 (ester), 1680 cm⁻¹ (amide); nmr (deuteriochloroform): 8.87 (s, 1H, H-1), 8.27-7.97 (m, 2H, aromatic), 7.95-6.62 (m, 12H, aromatic), 3.95 (s, 3H, OCH₃) and 3.47 ppm (s, 3H, OCH₃); ms: *m/e* (%) 463 (M⁺, 8), 462 (21), 326 (14), 240 (17), 106 (30), 105 (92), 77 (100) and 51 (15).

Anal. Calcd. for C₂₅H₂₁NO₅: C, 75.16; H, 4.54; N, 3.02. Found: C, 75.34; H, 4.73; N, 3.21.

Compound XV was also obtained in 20% yield from the reaction of XIV and dimethylacetylenedicarboxylate.

3-Phenylthieno[3,4-*b*]indole (XVI).

A solution of XIII (176.5 mg, 0.5 mmole) and sodium hydroxide (400 mg, 10 mmoles) in 50 ml of ethanol and 3 ml of water was refluxed for 3 hours. The solvent was evaporated and the residue was purified by tlc (silica gel, chloroform-petroleum ether, 1:1). The desired compound was crystallized from ethanol to give 100 mg (80%) of XVI, mp 162-163° (ethanol); ms: *m/e* (%) 249 (M⁺, 100), 248 (20), 247 (12), 217 (17), 204 (31), 124 (20), 121 (11), 102 (10) and 77 (10).

Anal. Calcd. for C₁₆H₁₁NS: C, 77.11; H, 4.42; N, 5.62. Found: C, 77.30; H, 4.25; N, 5.47.

3-Phenylselenolo[3,4-*b*]indole (XVII).

This compound was prepared similar to XVI, in 70% yield, mp 170-171° (ethanol); nmr (deuteriochloroform): 8.07 (s, 1H, H-1), and 7.97-7.0 ppm (m, 10H, aromatic and NH).

Anal. Calcd. for C₁₆H₁₁NSe: C, 64.86; H, 3.72; N, 4.73. Found: C, 64.65; H, 3.91; N, 4.92.

3-Aroyl-2-methylindole (XIX).

These compounds were prepared as reported previously (15) (See Table I).

1,3-Dibenzoyl-2-methylindole (XXa).

This compound was prepared from 3-benzoyl-2-methylindole (XIXa) similar to XI in 90% yield, mp 118-119°; ir: 1680 (amide), 1622 cm⁻¹ (ketone); nmr (deuteriochloroform): 8.16-7.16 (m, 14H, aromatic) and 2.53 ppm (s, 3H, CH₃).

Anal. Calcd. for C₂₃H₁₇NO₂: C, 81.40; H, 5.05; N, 4.13. Found: C, 81.61; H, 5.22; N, 3.92.

Compounds XXe-XXg were prepared similarly (See Table I).

1-*p*-Bromobenzoyl-3-benzoyl-2-methylindole (XXb).

To a stirred solution of 3-benzoyl-2-methylindole (2.35 g, 0.01 mole) in dry benzene (70 ml), thallous ethoxide (0.92 ml, 0.013 mole) was added. With exclusion of moisture, the solvent was slowly distilled off and continuously replaced with fresh anhydrous benzene. After distilling a total of 50 ml of solvent, the solution was cooled in ice-water and *p*-bromobenzoyl chloride (2.85 g, 0.013 mole) was added dropwise. The reaction mixture was refluxed under nitrogen for 5 hours, the mixture was filtered

and evaporated. The residue was crystallized from ether to give 3.55 g 85% of XXb, mp 110-112°; ir: 1680 (amide), 1610 cm^{-1} (ketone); nmr (deuteriochloroform): 8.16-6.93 (m, 13H, aromatic) and 2.45 ppm (s, 3H, CH_3).

Anal. Calcd. for $\text{C}_{23}\text{H}_{16}\text{BrNO}_2$: C, 66.03; H, 3.83; N, 3.35. Found: C, 65.85; H, 4.01; N, 3.53.

Compound XXc, XXd and XXh were prepared similarly (See Table I).
1,3-Dibenzoyl-2-bromomethylindole (XXIa).

This compound was prepared from 1,3-Dibenzoyl-2-methylindole (XXa) similar to VII in 95% yield; mp 145-147° (ether); ir: 1690 (amide), 1633 cm^{-1} (ketone); nmr (deuteriochloroform): 8.33-6.83 (m, 14H, aromatic) and 5.17 ppm (s, 2H, CH_2).

Anal. Calcd. for $\text{C}_{22}\text{H}_{16}\text{BrNO}_2$: C, 66.03; H, 3.83; N, 3.35. Found: C, 66.21; H, 4.01; N, 3.52.

Compounds XXIb-XXIh were prepared similarly (Table I).

1-Phenyl-4-benzoylthieno[3,4-*b*]indole (XXIIa).

This compound was prepared from XXIa and thioacetamide similar to I in 50% yield, mp 144-145° (ethanol); ir: 1658 cm^{-1} (carbonyl); nmr (deuteriochloroform): 8.33-7.03 (m, 14H, aromatic) and 6.25 ppm (s, 1H, H-3).

Anal. Calcd. for $\text{C}_{23}\text{H}_{15}\text{NOS}$: C, 78.19; H, 4.25; N, 3.97. Found: C, 78.01; H, 4.12; N, 3.75.

Compounds XXIIb-XXIIh were prepared similarly (See Table II).

1-Phenyl-4-benzoylselenolo[3,4-*b*]indole (XXIIIa).

This compound was prepared from XXIa and *N,N*-diethylseleno-propionamide similar to II in 35% yield, mp 145-147° (ethanol); ir: 1653 cm^{-1} (carbonyl); nmr (deuteriochloroform): 8.01-7.10 (m, 14H, aromatic) and 7.03 ppm [(s, 1H, H-3); this hydrogen was split into a doublet with $J = 47$ Hz (^{77}Se coupling)].

Anal. Calcd. for $\text{C}_{23}\text{H}_{15}\text{NOSe}$: C, 69.00; H, 3.75; N, 3.50. Found: C, 69.18; H, 3.56; N, 3.36.

Compounds XXIIIb-XXIIIh were prepared similarly (See Table II).

1-Phenylthieno[3,4-*b*]indole (XXIVa).

This compound was prepared similar to XVI in 90% yield; mp 118-120°; nmr (deuteriochloroform): 8.23-6.83 (m, 10H, aromatic and NH) and 6.36 ppm (s, 1H, H-3).

Anal. Calcd. for $\text{C}_{16}\text{H}_{11}\text{NS}$: C, 77.11; H, 4.42; N, 5.62. Found: C, 76.94; H, 4.27; N, 5.81.

Compounds XXIVb-XXIVd and XXVa-XXVd were prepared similarly (See Table II).

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