adjusted to allow complete reaction between 1–2 hr. in most cases.

The methanol was removed *in vacuo*, and the residue was taken up in chloroform. After washing the chloroform solution with dilute sodium carbonate and water, the solution was dried and evaporated, and the residue was recrystallized from the solvent indicated in Table I.

3-Methoxyoxindole (IIIa) was somewhat more difficult to purify than the other examples. After isolation of the majority of the product by recrystallization from aqueous methanol, the residue from the mother liquors was chromatographed on neutral alumina (Woelm grade III). The fractions obtained on elution with benzene containing 10% ethyl acetate were combined and recrystallized from aqueous methanol. Chromatography allowed the recovery of another 10–20% of 3-methoxyoxindole.

Thin layer chromatography of the crude product on silica gel (9:1 ether–chloroform) displayed 3-methoxyoxindole (R_f 0.33) as the major product and four minor products which were not investigated.

3-Ethoxyoxindole (IVa).—Similarly, 0.10 mole of IIa in ethanol yielded a dark red oil as the crude product. Trituration with three 250-ml. portions of hot water (charcoal), evaporation, and sublimation at 115° (5 μ) yielded 6.4 g. (36%) of 3-ethoxyoxindole. Recrystallization from 75 ml. of benzene–hexane (1:2 v./v.) produced a sample for analysis, m.p. 106–107.5°.

The n.m.r. spectrum displayed absorption at δ 9.37 (N–H, singlet), 4.95 (C-3–H, singlet), 3.79 (O–CH$_2$–, multiplet), and 1.27 (–CH$_3$, triplet).

Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.79; H, 6.32; N, 7.97.

3-*n*-Propoxyoxindole (IVb).—In an identical manner, 0.10 mole of IIa in 1-propanol yielded 7.0 g. (37%) of 3-*n*-propoxyoxindole. Recrystallization of the sublimate from hexane supplied a sample for analysis as colorless needles, m.p. 59–63°.

The n.m.r. spectrum displayed the following absorption: δ 9.20 (N–H, singlet), 4.92 (C-3–H, singlet), 3.62 (O–CH$_2$–, sextet), 1.68 (O–C–CH$_2$–, sextet), and 0.94 (O–C–C–CH$_3$, triplet).

Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.10; H, 6.85; N, 7.32. Found: C, 69.23; H, 7.10; N, 7.37.

3-Cyanoethyl-3-methoxyoxindole (V).—A mixture of 16.3 g. (0.10 mole) of IIIa and 1.0 g. of sodium methoxide in 200 ml. of dry benzene was warmed to 40°. The heat source was removed, and 6.4 g. (0.12 mole) of acrylonitrile was added at a rate so as to maintain a temperature of 40–45°. After stirring for 2 hr., the mixture was acidified with a small excess of acetic acid, washed with water, and dried. Removal of the solvent and distillation of the residue through a short-path apparatus yielded 20.7 g. (96%) of 3-cyanoethyl-3-methoxyoxindole, b.p. 164–169° (80 μ).

Anal. Calcd. for $C_{12}H_{12}N_2O_2$: C, 66.64; H, 5.59; N, 12.96. Found: C, 66.53; H, 5.49; N, 13.04.

3-Methoxy-3-pyrrolidinomethyloxindole (VI).—In a manner similar to that described by Hirai, Harvey, and Jensen,[17] a mixture of 10.0 g. (61.5 mmoles) of 3-methoxyoxindole, 3.7 g. (123 mmoles) of paraformaldehyde, and 31.2 g. (123 mmoles) of pyrrolidine hydrochloride in 200 ml. of dimethoxyethane was heated to reflux for 24 hr. The solvent was removed and the residue was stirred with 300 ml. of 3 *N* hydrochloric acid. After extraction with chloroform, the mixture was made basic with 10% sodium carbonate and extracted again with three 100-ml. portions of chloroform. The combined extracts were washed with water, dried, and evaporated. The residue provided 9.4 g. (62%) of VI on recrystallization from 125 ml. of 50% aqueous methanol. Repeated recrystallization from the same solvent provided a sample of analytical purity, m.p. 107–109°.

Anal. Calcd. for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.31; H, 7.00; N, 11.42.

1-Acetyl-3-methoxyoxindole (VII).—In a manner analogous to the preparation of 1-acetyloxindole,[19] a mixture of 16.3 g. (0.10 mole) of 3-methoxyoxindole and 41 g. (0.40 mole) of acetic anhydride was heated to reflux for 4 hr. To the cooled mixture was added cautiously 9.6 g. (0.30 mole) of anhydrous methanol. On standing, 15.6 g. (76%) of VI was deposited, m.p. 107–109°. Evaporation of the filtrate and recrystallization of the residue from 90% methanol provided another 3.8 g. (20%). The combined yield amounted to 19.4 g. (95%).

Further recrystallization from isopropyl ether supplied a sample of analytical purity, m.p. 108–110°.

Anal. Calcd. for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.82. Found: C, 64.52; H, 5.33; N, 6.84.

Acknowledgment.—The author is indebted to Dr. J. M. Vandenbelt, Messrs. R. B. Scott and E. Schoeb, and Mrs. C. Spurlock for spectral results, and to Mr. C. E. Childs and associates for microanalytical results.

Indolothiopyrylium Compounds. I. Benz[*b*]indolo[2,3-*d*]thiopyrylium Perchlorates. A Novel Heteroaromatic Ring System[1]

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Abstraction of a hydride ion from C-6 of 6,11-dihydrobenz[*b*]indolo[2,3-*d*]thiopyran (**3a**) with trityl perchlorate gave an 88% yield of benz[*b*]indolo[2,3-*d*]thiopyrylium perchlorate (**4a**), and the 2-chloro-, 2-nitro-, and 2-, 8-, and 11-methyl- analogs (**4b-f**, respectively) were similarly obtained in yields of 84–99%. The parent perchlorate salt **4a** underwent ready metathesis with potassium iodide to form the corresponding thiopyrylium iodide **6**. N.m.r. spectral evidence suggested that the positive charge in these cations is localized predominantly on the sulfur atom rather than on the conjugated nitrogen atom. Reaction of the N-methyl compound **4f** with phenylmagnesium bromide gave an adduct which was rearomatized with trityl perchlorate to 11-methyl-6-phenylbenz[*b*]indolo[2,3-*d*]thiopyrylium perchlorate (**8**).

Although salts of the thioxanthylium ion had long been known,[3] it remained for Wizinger and Ulrich[4] to spur renewed interest in thiopyrylium compounds with their synthesis of 2,4,6-triphenylthiopyrylium perchlorate in 1956. Since that time extensive studies by several groups have resulted in the synthesis of salts containing the unsubstituted parent,[5] in addition to the benzo[*b*]-,[6,7] benzo[*c*]-,[7] naphtho[2,1-*b*]-,[8] naphtho[1,2-*b*]-,[8] and dibenzo[*b,d*]thiopyrylium[9] ions. The resonance stabilization of these sulfur-containing cations has been compared with that of other aromatic cations (*e.g.*, tropylium) by both experimental[10] and

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[1] Abstracted from the Ph.D. Dissertation of P. H. Scott, Lehigh University, 1965.

[2] Warner-Lambert Research Fellow, 1963–1965.

[3] A. Werner, *Ber.*, **34**, 3311 (1901).

[4] R. Wizinger and P. Ulrich, *Helv. Chim. Acta*, **39**, 207 (1956).

[5] R. Pettit, *Tetrahedron Letters*, **No. 23**, 11 (1960).

[6] A. Luttringhaus and N. Engelhard, *Chem. Ber.*, **93**, 1525 (1960).

[7] W. Bonthrone and D. H. Reid, *Chem. Ind.* (London), 1192 (1960).

[8] N. Engelhard and A. Kolb, *Ann.*, **673**, 136 (1964).

[9] A. Luttringhaus and A. Kolb, *Z. Naturforsch.*, **16**, 762 (1961).

[10] R. G. Turnbo, D. L. Sullivan, and R. Pettit, *J. Am. Chem. Soc.*, **86**, 5630 (1964).

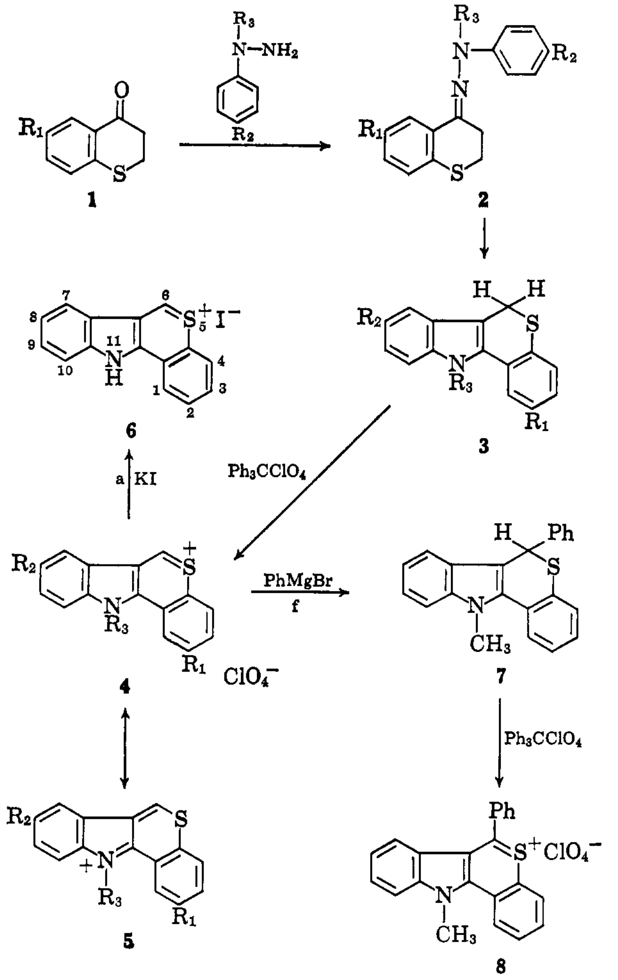
theoretical[11] means. Until now, however, no thiopyrylium compounds containing a second fused heteroaromatic nucleus have appeared in the literature. We, therefore, wish to report the synthesis (illustrated by formulas **1** to **4**) of benz[*b*]indolo[2,3-*d*]thiopyrylium perchlorate (**4a**) and several congeners, along with certain properties relevant to the structure of this novel ring system.

The precursor 6,11-dihydrobenz[*b*]indolo[2,3-*d*]thiopyrans (**3**)[12,13] were prepared by the Fischer method[14] from known thiochroman-4-ones (**1**) and the appropriate phenylhydrazine. Although Kiang and Mann[13] isolated the intermediate phenylhydrazone **2a** in their preparation of **3a**, we found that, except for the preparation of **3c**, improved yields of cyclized products (**3**) were obtained when isolation of the intermediates (**2**) was omitted.

Several attempts to prepare 8-nitro-6,11-dihydrobenz[*b*]indolo[2,3-*d*]thiopyran (**3**, $R_2 = NO_2$; R_1 and $R_3 = H$) from thiochroman-4-one *p*-nitrophenylhydrazone were unsuccessful. The phenylhydrazone was recovered unchanged from refluxing acetic acid, saturated ethanolic hydrogen chloride, or concentrated hydrochloric acid.[15] Polyphosphoric acid, which has previously been used to cyclize nitrophenylhydrazones,[16] yielded mainly tars, as did 85% phosphoric acid.

Benz[*b*]indolo[2,3-*d*]thiopyrylium perchlorate (**4a**) and its substituted analogs **4b–f**, were all obtained by abstraction of a hydride ion from the corresponding 6,11-dihydrobenz[*b*]indolo[2,3-*d*]thiopyrans **3a–f**, with trityl perchlorate[17] in hot glacial acetic acid solution[18] and under an atmosphere of dry nitrogen. The thiopyrylium salts **4**, which crystallized directly from the cooled reaction mixtures in high yields (84–99%) and purity, were stable yellow crystalline compounds having sharp, characteristic decomposition points. These decompositions were nonexplosive, although a gas was evolved, and the salts (**4**) could be safely oven-dried at 110° with no decomposition. During combustion analysis, however, mild explosions were frequently observed. These salts were best recrystallized from nitromethane, from which, except for the parent compound **4a**, they separated unsolvated. The parent salt **4a**, however, retained 0.5 mole of nitromethane of crystallization and on a small scale was best purified from glacial acetic acid.

The infrared spectra of the purified perchlorate salts **4**, taken in potassium bromide pellets, showed strong N-H stretching frequencies varying between 3077 cm.$^{-1}$ (broad) for the parent compound **4a** and 3460 cm.$^{-1}$ for the 2-methyl analog (**4d**), but were most significantly characterized by a very strong absorption band (1101–1111 cm.$^{-1}$) attributable to the perchlorate anion.[19] Ultraviolet absorption data and other pertinent properties of these compounds are summarized in Table I.



a, $R_1 = R_2 = R_3 = H$
b, $R_1 = Cl$; $R_2 = R_3 = H$
c, $R_1 = NO_2$; $R_2 = R_3 = H$
d, $R_1 = Me$; $R_2 = R_3 = H$
e, $R_1 = R_3 = H$; $R_2 = Me$
f, $R_1 = R_2 = H$; $R_3 = Me$

The parent perchlorate salt **4a** readily exchanged anions with potassium iodide in nitromethane solution to afford benz[*b*]indolo[2,3-*d*]thiopyrylium iodide (**6**, which also illustrates the numbering of the ring system). This orange crystalline iodide exhibited an infrared fingerprint comparable with that of the perchlorate **4a** (except for the absence of the strong 1101-cm.$^{-1}$ perchlorate absorption), did not, of course, explode during combustion analysis, but lacked a well-defined melting point, and otherwise offered no advantages over the perchlorate. Therefore, no other iodides were prepared.

Particular interest in the benz[*b*]indolo[2,3-*d*]thiopyrylium system centers on the question—to what extent do each of the forms **4** and **5** contribute to the ground state of the molecule? The n.m.r. spectra of **4a**, **d**, **e**, and **f** (*cf.* Table II) have provided a partial

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[11] R. Zharadnik and J. Koutecky [*Collection Czech. Chem. Commun.*, **28**, 1117 (1963)] have reported the results of HMO calculations for 15 heterocyclic sulfur compounds of contemporary interest.

[12] Compound **3a**, the only member of this group which was previously known,[13] was originally named as indolo(3′:2′-3:4)-1-thiochromene. We prefer the systematic name used in the text to maintain consistency with the nomenclature and position enumeration of the corresponding thiopyrylium compounds (**4**).

[13] A. K. Kiang and F. G. Mann, *J. Chem. Soc.*, 1909 (1951).

[14] *Cf.* B. Robinson, *Chem. Rev.*, **63**, 373 (1963), for a recent review of the Fischer indole synthesis.

[15] Z. A. Aksanova, N. F. Kucherova, and V. A. Zagorevskii [*Zh. Obshch. Khim.*, **33**, 213 (1963)], who recently prepared a number of analogs of structure **3**, also reported the failure of this particular ring closure using concentrated hydrochloric acid or hydrogen chloride in acetic acid.

[16] S. Parmeter, A. G. Cook, and W. Dixon, *J. Am. Chem. Soc.*, **80**, 4621 (1958).

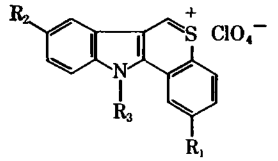
[17] Prepared by the method of K. A. Hoffman and H. Kimmreuther [*Ber.*, **42**, 4865 (1909)].

[18] Triphenylmethane could also be isolated; *cf.* Experimental Section. For other hydride abstractions with this reagent, see ref. 7 and W. Bonthrone and D. H. Reid, *J. Chem. Soc.*, 2773 (1959).

[19] F. A. Miller and C. H. Wilkens, *Anal. Chem.*, **24**, 1253 (1952).

Table I

Benz[*b*]indolo[2,3-*d*]thiopyrylium Perchlorates (4)

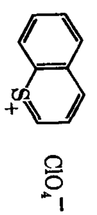


Compd.	R₁	R₂	R₃	M.p., °C. (dec.)	% yield	Formula	Calcd., % C	H	N	Found, % C	H	N	Ultraviolet-visible spectra,[a] λmax, mμ (log ε)		
4a	H	H	H	273–275	88	$C_{15}H_{10}ClNO_4S$	53.65	3.00	4.17	53.74	3.18	4.41	231 (4.21) sh, 292 (4.47),	234 (4.23), . . .,	269 (4.52), 400 (4.07)
4b	Cl	H	H	314	93	$C_{15}H_9Cl_2NO_4S$	48.66	2.45	3.78	48.74	2.69	3.82	. . ., 295 (4.55),	239 (4.28), . . .,	272 (4.56), 406 (4.12)
4c	NO₂	H	H	321–322	93	$C_{15}H_9ClN_2O_6S$	47.32	2.38	7.36	47.30	2.66	7.24	230 (4.40), 307 (4.41),	. . ., 324 (4.29) sh,	263 (4.68), 403 (4.08)
4d	Me	H	H	304–305	99	$C_{16}H_{12}ClNO_4S$	54.94	3.46	4.00	55.23	3.74	4.08	. . ., 293 (4.52),	237 (4.26), . . .,	273 (4.55), 404 (4.17)
4e	H	Me	H	324–326	84	$C_{16}H_{12}ClNO_4S$	54.94	3.46	4.00	54.95	3.43	4.05	231 (4.24), 300 (4.39) sh,	236 (4.16) sh, 322 (3.91) sh,	272 (4.59), 403 (4.07)
4f	H	H	Me	313	97	$C_{16}H_{12}ClNO_4S$	54.94	3.46	4.00	55.11	3.59	3.95	. . ., 296 (4.51),	237 (4.19), 323 (3.41) sh,	269 (4.47), 407 (4.14)

[a] Solvents: the spectrum of compound **4a** was run in acetonitrile containing 10% of 0.1 *M* sulfuric acid; the spectra of compounds **4b–f** were run in acetonitrile containing 1% of perchloric acid.

answer. The spectra of all four compounds revealed a unique singlet representing one proton at very low fields (δ 10.38–10.70). Snice only the protons at C-6 and N-H in the parent molecule (**4a**) should appear as singlets, and since **4f** contains an N-Me group, this low-field singlet is clearly assignable to the C-6 H. The unusually large δ value of this proton suggests a predominant contribution from the structure —CH=S⁺— in **4**, in which (in addition to normal ring-current deshielding effects) the high electronegativity[20] of the adjacent thionium center has caused a large downfield shift.

In corroboration, the n.m.r. spectrum of benzo[*b*]thiopyrylium perchlorate (**9**)[6,21] in dimethyl-d_6 sulfoxide also showed a sharp singlet (integration for one proton) at δ 12.12 as well as several multiplets extending from δ 9.0 through the normal aromatic region. Since published HMO calculations[11] indicate that C-2 is the center of lowest electron density in **9**, it is probable



9

that this low-field singlet can also be associated with the proton adjacent to the thionium center.[22] In any case, the low-field absorption appears to be characteristic of certain protons in these thiopyrylium ions, and, except for possible discrepancies due to solvent variation, are roughly comparable with chemical shifts reported for the readily exchangeable 2-position protons of 4-methyl-1,3-dithiolium[23] (δ 11.12 in CF_3COOD–D_2O) and 4-methylthiazolium[24] (δ 9.83 in CF_3COOH) cations.

Reported HMO calculations indicate that in the thiazolium cation the positive charge is distributed approximately 0.6 on sulfur and 0.4 on nitrogen.[24] In the indolothiopyrylium compounds (**4** ↔ **5**), in which the nitrogen–sulfur conjugation might be considered vinylogous with that in the thiazolium system, the nitrogen atom must also bear some of the positive charge since the N-methyl protons of **4f** are also unusually deshielded (δ 4.55) compared with the chemical shifts of the *bz*-methyl groups of **4d** (δ 2.63) and **4e** (δ 2.37). Although some of this difference can probably be attributed to additional ring-current deshielding by the angular benzo ring, the magnitude of the N-methyl group deshielding clearly suggests a significant contribution from the canonical azonium form **5**. It is apparent, however, that the thionium sulfur in **4** also transmits considerable positive charge into the angular benzo ring. The disappearance of one of the group-B protons and reduction of the other to a

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[20] For recent, detailed discussions of the relationship of charge densities in aromatic systems to proton n.m.r. shifts, see T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963); M. P. Schweizer, S. I. Chan, G. K. Helmkamp, and P. O. P. Ts'o, *J. Am. Chem. Soc.*, **86**, 696 (1964).

[21] We are indebted to Mr. C. J. Ohnmacht of Lehigh University for the preparation of this compound.

[22] Although a precise assignment is not essential to the comparisons being drawn here, this tentative assignment is being checked by further, more detailed n.m.r. studies of derivatives of **9**. The absence of splitting of the δ 12.12 absorption, which suggests rapid exchange similar to that reported for the dithiolium and thiazolium systems cited,[23,24] is also under further study.

[23] H. Berger and A. Lüttringhaus, *Angew. Chem. Intern. Ed. Engl.*, **4**, 435 (1965).

[24] P. Haake and W. B. Miller, *J. Am. Chem. Soc.*, **85**, 4044 (1963).

TABLE II

N.M.R. CHEMICAL SHIFTS OF BENZ[*b*]INDOLO[2,3-*d*]THIOPYRYLIUM PERCHLORATES (**4**)[a]

Group	Assignment	**4a**	**4d**	**4e**[b]	**4f**	**8**
A	C-6 H	10.70(1)s	10.62(1)s	10.38(1)s	10.70(1)s	...
B	Ar–H	8.75(2)m	8.60(1)d	8.58(2)m	9.27(1)m 8.72(1)m	9.41(1)m 8.74(1)m
C	Ar–H	8.22(3)m	8.35(2)m	8.10(2)m	8.25(4)m	8.27(3)m
D	N–H	7.72(1)s[c]	7.75(1)s[c]	7.80(1)s	...	...
E	Ar–H	7.67(3)m	7.75(4)m	7.37(2)m	7.70(2)m	7.85(5)s[d] 7.34(3)m
F	CH_3	...	2.63(3)s	2.37(3)s	4.55(3)s	4.69(3)s

[a] Spectra were determined on a Varian A-60 n.m.r. spectrometer in dimethyl-d_6 sulfoxide with tetramethylsilane as internal standard. Data are presented in the order: δ (number of protons) multiplicity, as s, d, and m for singlet, doublet, and multiplet, respectively. Values of δ (parts per million) are positive downfield from TMS and read at the centers of multiplets. [b] The number of protons indicated properly reflects the observed integral ratios. However, because of a high noise level the total integration was unsatisfactory, and one proton is unaccounted for in this example. [c] Although this band lay in the midst of a less intense multiplet (group E), the height, shape, and width (to the extent visible above the multiplet) were comparable with the singlet of group A. This band stood quite alone in **4e**, but was tenuously assigned to the indolic N–H, primarily because of its conspicuous absence from the spectrum of the N-methyl derivative **4f**. [d] Assigned to the phenyl substituent.

doublet by introduction of the 2-methyl group (*cf.* **4a** and **4b**, Table II) shows that these protons can be assigned to the angular benzo ring, their strongly deshielded δ values confirming distribution of positive charge into this ring.

Chemical evidence for the low electron density at C-6 in the benz[*b*]indolo[2,3-*d*]thiopyrylium system was obtained by reaction of the N-methyl compound **4f** with phenylmagnesium bromide. The intermediate adduct was immediately dissolved in glacial acetic acid and treated with trityl perchlorate to give 11-methyl-6-phenylbenz[*b*]indolo[2,3-*d*]thiopyrylium perchlorate (**8**) in 50% yield. The n.m.r. spectrum (Table II) of this easily purified product (**8**) was quite similar to that of the precursor (**4f**), but also showed five equivalent protons of the newly introduced phenyl group as a singlet at δ 7.85 and the striking absence of the δ 10.70 absorption present in **4f**, thus clearly confirming the assignment of the phenyl substituent to the 6-position. This result is also consistent with the reported[25] attack of phenylmagnesium bromide at the 2- and 4-positions of benzo[*b*]thiopyrylium ion.

Experimental Section[26]

Thiochroman-4-ones (1).—These compounds were prepared by cyclization of the corresponding β-arylmercaptopropionic acids with concentrated sulfuric acid as described in the literature.

Specific compounds prepared were as follows (substituent on **1**, per cent yield, melting point): none, 59, 27–30° (lit.[18] m.p. 29–30°); 6-methyl, 89, 38–40° (lit.[27] m.p. 41°); 6-chloro, 96, 66–69° (lit.[27] m.p. 67–69°); and 6-nitro, 83, 168–170° (lit.[28] m.p. 168–169°).

2-Chloro-6,11-dihydrobenz[*b*]indolo[2,3-*d*]thiopyran (3b).—To a solution of 40.8 g. (0.205 mole) of 6-chlorothiochroman-4-one in 200 ml. of methanol were added 20.5 ml. (0.205 mole) of phenylhydrazine and 0.5 ml. of glacial acetic acid. The solution was heated briefly at reflux temperature on a steam bath, after which it was allowed to stand until the phenylhydrazone had precipitated. The solution was again heated to reflux, and after the phenylhydrazone had partially redissolved, hydrogen chloride was bubbled through the well-stirred, refluxing solution for 30 min., during which time a precipitate began to form. The reaction mixture was then allowed to stand overnight, following which it was poured onto ice–water containing 65 ml. of 50% sodium hydroxide. The resulting mixture was stirred for several hours and permitted to stand overnight to assure complete hydrolysis. Finally, the precipitate was collected by filtration, washed thoroughly with water, and dried *in vacuo* over calcium chloride to give 53.21 g. of product, m.p. 140–160°, with prior softening.

Impurities were extracted from this precipitate by refluxing in 100 ml. of carbon tetrachloride. The portion insoluble in the carbon tetrachloride was then fractionally recrystallized from benzene to yield a total of 30.93 g. (56%) of light tan product, m.p. 159–163°. Recrystallization from benzene–cyclohexane yielded pure product (**3b**) as white crystals, m.p. 162–165°.

Anal. Calcd. for $C_{15}H_{10}ClNS$: C, 66.29; H, 3.71; Cl, 13.05; N, 5.16. Found: C, 66.46; H, 3.96; Cl, 12.89; N, 5.15.

6,11-Dihydrobenz[*b*]indolo[2,3-*d*]thiopyran (3a).—In a similar manner 20.73 g. (0.126 mole) of thiochroman-4-one and 13.64 g. (0.126 mole) of phenylhydrazine yielded 12.55 g. (42%) of crude product, m.p. 155–159°. Further recrystallization from benzene and final sublimation at 150° and 0.7 mm. gave pure **3a** as pale yellow crystals, m.p. 160.5–162° (lit.[18] m.p. 158–160°).

2-Methyl-6,11-dihydrobenz[*b*]indolo[2,3-*d*]thiopyran (3d).—Application of the foregoing procedure to 34.17 g. (0.192 mole) of 6-methylthiochroman-4-one and 19.4 ml. (0.194 mole) of phenylhydrazine gave a total of 15.63 g. (32% yield) of product, m.p. 173–177°. Recrystallization from benzene–cyclohexane afforded pale yellow crystals of pure **3d**, m.p. 173–175°.

Anal. Calcd. for $C_{16}H_{13}NS$: C, 76.45; H, 5.21; N, 5.57. Found: C, 76.67; H, 5.50; N, 5.52.

8-Methyl-6,11-dihydrobenz[*b*]indolo[2,3-*d*]thiopyran (3e).—A mixture of 13.53 g. (0.0825 mole) of thiochroman-4-one and 13.10 g. (0.0826 mole) of *p*-tolylhydrazine hydrochloride in 150 ml. of glacial acetic acid was refluxed with stirring overnight. The undissolved material was removed by hot filtration. The filtrate on cooling yielded 12.22 g. (59%) of yellow crystals, m.p. 178–188°. Successive recrystallization from chloroform, then from benzene–cyclohexane, gave analytically pure product as small pale yellow plates, m.p. 190–193°.

Anal. Calcd. for $C_{16}H_{13}NS$: C, 76.45; H, 5.21; N, 5.57. Found: C, 76.68; H, 5.47; N, 5.49.

11-Methyl-6,11-dihydrobenz[*b*]indolo]2,3-*d*]thiopyran (3f).—A solution of 21.9 g. (0.133 mole) of thiochroman-4-one and 16.25 g. (0.133 mole) of 1-methyl-1-phenylhydrazine in 100 ml. of glacial acetic acid was refluxed overnight. A precipitate of nearly white needles formed on cooling. This precipitate weighed 17.50 g. (52%) and had m.p. 95–99°. A portion recrystallized three times from cyclohexane had m.p. 97.5–99°.

Anal. Calcd. for $C_{16}H_{13}NS$: C, 76.45; H, 5.21; N, 5.57; S, 12.76. Found: C, 76.61; H, 5.46; N, 5.66; S, 12.68.

6-Nitrothiochroman-4-one Phenylhydrazone (2c).—To 5.84 g. (0.0279 mole) of 6-nitrothiochroman-4-one, stirred with 150 ml. of boiling methanol, was added 2.9 ml. (0.029 mole) of phenylhydrazine and 10 drops of glacial acetic acid. After 5 min., the

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[25] A. Lüttringhaus, N. Engelhard, and A. Kolb, *Ann.*, **654**, 189 (1962).

[26] Melting points were determined in capillary tubes using a Mel-Temp apparatus (Laboratory Devices, Cambridge, Mass.) and are corrected. Infrared spectra were recorded in potassium bromide disks on a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet spectra were recorded on a Beckman DK-2A spectrophotometer in solvents as specified with the reported spectra (*cf.* Table I).

[27] F. Arndt, W. Flemming, E. Scholz, and V. Lowensohn, *Ber.*, **56**, 1269 (1923).

[28] V. Bellavita, *Gazz. chim. ital.*, **70**, 599 (1940); *cf. Chem. Abstr.*, **35**, 1406 (1941).

mixture was cooled to room temperature, and on the next day the resulting red precipitate was collected by filtration. The yield was 7.55 g. (90%), m.p. 198–205°. Three recrystallizations from methanol gave an analytically pure sample, m.p. 204.5–206°.

Anal. Calcd. for $C_{15}H_{13}N_3O_2S$: C, 60.19; H, 4.37; N, 14.04; S, 10.71. Found: C, 60.19; H, 4.42; N, 13.97; S, 10.47.

2-Nitro-6,11-dihydrobenz[*b*]indolo[2,3-*d*]thiopyran (3c).—Hydrogen chloride gas was bubbled for 2 hr. through a slurry of 2.50 g. (8.36 mmoles) of 6-nitrothiochroman-4-one phenylhydrazone in 100 ml. of boiling methanol. The mixture was heated under reflux for 16 hr., after which it was poured into 1 l. of ice–water. The aqueous mixture was made basic with 50% sodium hydroxide, and the indole was collected by filtration. The rust-colored product, after being washed with water and air dried, weighed 2.22 g. (94%), melting with gradual darkening above 200°. Several recrystallizations from nitromethane afforded red needles, melting with gradual darkening above 250°.

Anal. Calcd. for $C_{15}H_{10}N_2O_2S$: C, 63.81; H, 3.57; N, 9.92; S, 11.36. Found: C, 63.63; H, 3.76; N, 9.72; S, 11.05.

Thiochroman-4-one *p*-Nitrophenylhydrazone.—A mixture of 3.00 g. of thiochroman-4-one, 2.88 g. of *p*-nitrophenylhydrazine, and 10 drops of acetic acid in 125 ml. of methanol was heated to boiling and then allowed to stand at ambient conditions for 4 hr. The resulting solution was refrigerated to give 3.65 g. (66%) of deep red crystals, m.p. 250–254° dec., which after recrystallization from 95% ethanol had m.p. 254–257° dec. (lit.[15] m.p. 242–244°).

Anal. Calcd. for $C_{15}H_{13}N_3O_2S$: C, 60.18; H, 4.38; N, 14.04. Found: C, 60.36; H, 4.43; N, 14.01.

Benz[*b*]indolo[2,3-*d*]thiopyrylium Perchlorates (4). General Procedure.—Into a 200-ml. three-neck round-bottom flask equipped with a stirrer was placed (0.0338 mole) of the appropriate 6,11-dihydrobenz[*b*]indolo[2,3-*d*]thiopyran (**3**) and 100 ml. of glacial acetic acid. A small erlenmeyer flask containing 11.5 g. (0.0338 mole) of trityl perchlorate was joined to the round-bottom flask by a short section of Gooch tubing and the entire system was charged with purified nitrogen, after which the acetic acid was warmed sufficiently to dissolve the thiopyran. As soon as the thiopyran has completely dissolved, the trityl perchlorate was added, in portions, to the acid solution. A yellow precipitate formed almost immediately, and when all the trityl perchlorate had been added, the solution was allowed to cool to room temperature with continued stirring. The stirrer was then shut off, and the reaction mixture was permitted to stand overnight.

On the following day, the precipitate was collected by filtration, washed with glacial acetic acid and then anhydrous ether, and dried *in vacuo* over potassium hydroxide. The filtrate on standing yielded a small amount of additional precipitate which was similarly treated and added to the original batch. The products at this stage (yield basis) were of high purity but usually required one recrystallization from nitromethane to furnish an analytical sample. Compounds **4b–f** were dried *in vacuo* at 78° prior to analysis. Compound **4a**, which retained 0.5 mole of nitromethane of crystallization, was oven dried at 110° prior to analysis.

After collection of the main products, the acetic acid filtrate was evaporated to dryness to leave a residue which was extracted with ether. Evaporation of the ethereal extract gave high yields (77% in the preparation of **4a**) of triphenylmethane, m.p. 92–93.5°, undepressed by admixture with an authentic sample.

Benz[*b*]indolo[2,3-*d*]thiopyrylium Iodide (6).—To a solution of 1.00 g. (2.98 mmoles) of benz[*b*]indolo[2,3-*d*]thiopyrylium perchlorate in 75 ml. of nitromethane was added 5.0 g. of potassium iodide, and the mixture was stirred for 15 min., after which it was heated to boiling and filtered while still hot. The cooled solution yielded 0.68 g. (63%) of orange needles which darkened above 205° and slowly decomposed above 245°. Three recrystallizations from nitromethane gave deep orange needles which had the same ill-defined decomposition point as the unrecrystallized product.

Anal. Calcd. for $C_{15}H_{10}INS$: C, 49.61; H, 2.78; I, 34.94. Found: C, 49.69; H, 2.79; I, 34.20.

6-Phenyl-11-methylbenz[*b*]indolo[2,3-*d*]thiopyrylium Perchlorate (8).—To a slurry of 900.7 mg. (2.58 mmoles) of **4f** in 6 ml. of anhydrous ether was added dropwise an ethereal solution of 2.9 mmoles of phenylmagnesium bromide. The exothermic reaction resulted in the formation of a dark tarry product which partially solidified when stirred for 1 hr. The mixture was then poured into an aqueous solution of ammonium sulfate, and the two liquid phases were separated. A yellow insoluble residue (*ca.* 100 mg.) was retained with the aqueous phase. The residue and water layer were extracted with 10 ml. of ether, which was then combined with the original ethereal solution. Evaporation of the dried ($MgSO_4$) ether phase on a rotary evaporator yielded 568.5 mg. of a yellow oil tentatively presumed to be **7** (1.74 mmoles). When cooled to room temperature, this oil solidified to a glass which crystallized. This solid was dissolved in 25 ml. of acetic acid at 60°, and to the stirred solution was added dropwise 604.5 mg. (1.76 mmoles) of trityl perchlorate in 10 ml. of nitromethane. When the addition was completed, the solution was refluxed for 8 min., after which it was allowed to stand overnight. The solvents were removed on a rotary evaporator, and the residue was triturated with ether. A yellow-green ether-insoluble solid (644.2 mg., m.p. 218–225° dec.) was collected by filtration. One recrystallization from acetic acid afforded 550.0 mg. (50% over-all yield) of **8**, m.p. 234–237° partial dec. A portion recrystallized several more times from acetic acid gave greenish yellow crystals, m.p. 237–241° partial dec.

Anal. Calcd. for $C_{22}H_{16}ClNO_4S$: C, 62.04; H, 3.79; Cl, 8.32; S, 7.53. Found: C, 61.77; H, 3.93; Cl, 8.41; S, 7.40.

The ether filtrate, after it had been washed with aqueous sodium hydroxide and with water, was dried and evaporated. The slightly oily residual solid (404.4 mg.) showed only one component by t.l.c. (Merck silica gel HF_{254}, 5% ethyl acetate in benzene), and that component had the same R_f value as authentic triphenylmethane. Recrystallization from 95% ethanol gave a pale yellow solid, m.p. 90–92°. A mixture with authentic triphenylmethane (m.p. 92–93°) had m.p. 90–93°, and the infrared spectrum of the compound was identical with that of triphenylmethane.

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