which was recrystallized from benzene, giving **13** (0.30 g., 0.19 mmole, 19%), m.p. 204–205° (lit.[34] m.p. 203–204°).

Triethyl N-(*o*-Ethylphenyl)phosphorimidate (23) and Diethyl N-(*o*-Ethylphenyl)phosphoramidate (24).—A solution of *o*-nitroethylbenzene (3.02 g., 20 mmoles) in triethyl phosphite (13.4 g., 81 mmoles) was refluxed for 14 hr. and then vacuum distilled, giving first unreacted triethyl phosphite and then triethyl phosphate (7.0 g., 38 mmoles, 96%), b.p. 52–54° (0.4 mm.). The cooled distillation residue was diluted with ether (30 ml.) and extracted successively with dilute hydrochloric acid (two 20-ml. portions) and 1% sodium hydroxide (two 20-ml. portions). The ether layer was dried over magnesium sulfate, filtered, and concentrated, leaving a brown oil. The oil crystallized from hexane, giving **24** (0.13 g., 0.51 mmole, 2.5%), m.p. 105°. Recrystallization from hexane gave the analytical sample: m.p. 105°; ν_{NH} 3200 cm.$^{-1}$, ν_{C-O} 1240 cm.$^{-1}$, ν_{POC} 1025, 980 cm.$^{-1}$. The n.m.r. spectrum showed two overlapping triplets, the weaker one at 1.23 p.p.m. (CH_3) and a stronger triplet at 1.29 p.p.m. (CH_3), a quartet at 2.60 p.p.m. (CH_2), a five-line pattern (overlapping quartets) at 4.15 p.p.m. (OCH_2), a broad doublet at 5.2 p.p.m. (NH?), and the aromatic multiplet at 6.9–7.4 p.p.m.

Anal. Calcd. for $C_{12}H_{20}NO_3P$ (257.26): C, 56.02; H, 7.84. Found: C, 55.85; H, 7.55.

When the acidic extract of the distillation residue was made alkaline with solid sodium hydroxide, a dark oil separated. The oil was dissolved in ether and the solution was dried over sodium sulfate, filtered, and concentrated. Simple vacuum distillation gave **23** (2.236 g., 8.8 mmoles, 44%), b.p. 110–130° (0.45 mm.). Redistillation through a short Vigreux column gave the product as a yellow oil: b.p. 108–111° (0.6 mm.); ν_{NH} none, ν_{POC} 1035, 970 cm.$^{-1}$. The n.m.r. spectrum (CCl_4) showed overlapping triplets at 1.20 p.p.m. (weaker, ethyl CH_3) and 1.32 p.p.m. (stronger, ethoxy CH_3), an irregular quintet apparently containing a quartet from the benzyl CH_2 at 2.63 p.p.m., a quintet at 4.20 p.p.m. (OCH_2), and a multiplet at 6.7–7.2 p.p.m.

Anal. Calcd. for $C_{14}H_{24}NO_3P$ (285.31): C, 58.93; H, 8.48; P, 10.86. Found: C, 58.93; H, 8.30; P, 10.74.

Conversion of Triethyl N-(*o*-Ethylphenyl)phosphorimidate (23) into Diethyl N-(*o*-Ethylphenyl)phosphoramidate (24).—A solution of **23** (1.00 g., 3.5 mmoles) in hexane (~10 ml.) was placed on a column of silicic acid (30 g.) and kept at room temperature for 16 hr. Elution with ether, evaporation, and crystallization of the residue from hexane gave **24** (0.67 g., 2.6 mmoles, 87%), m.p. 103–104°. A similar transformation was effected in lower yield using alumina and a 3-day reaction period

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research through a PRF Type-G Grant. This work was also supported in part by funds from a National Science Foundation Institutional Grant to the University of Virginia. The author gratefully acknowledges the contribution of Mr. J. A. Johnson, who determined most of the n.m.r. spectra reported herein. The triethyl phosphite was a generous gift of the Virginia-Carolina Corporation.

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Alkoxyoxindoles. A Convenient Method for the Reduction of Isatins

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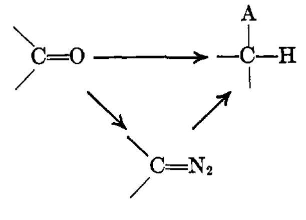
Received May 25, 1965

The treatment of 3-diazooxindoles in methanol solution with a suitable Lewis acid provided a preparative source of 3-methoxyoxindoles. Alcohols other than methanol yielded 3-alkoxyoxindoles. This sequence constitutes a useful technique for the reduction of isatins from which the 3-diazooxindoles were derived.

Most conventional methods for the preparation of dioxindoles from readily available isatins lack convenience or satisfactory yields or both.[1,2] Attempts to employ several selective metal hydrides for this reduction resulted in the formation of complexes or bimolecular products from which no dioxindole could be isolated when isatin was used as starting material.[3] As an alternative, several reactions were explored which involve over-all a change in hybridization and thus result in reduction (eq. 1). This communication reports the preparation of 3-alkoxyoxindoles from intermediate 3-diazooxindoles derived in turn from isatins. While the reaction of diazo compounds with acids in the presence of various nucleophiles is familiar,[4,5] this sequence has been used less frequently as a specific method for the reduction of carbonyl groups from which the diazo function was generated.[6–8] The sequence possesses synthetic utility in this special example because the 3-diazooxindoles are relatively stable and easily prepared.



(1)

3-Diazooxindole (IIa) has been prepared by mercuric oxide oxidation of isatin hydrazone[9] and by treatment of isatin *p*-toluenesulfonylhydrazone (Ia) with aqueous base.[10] More recently 1-methyl-3-diazooxindole has been prepared by treatment of the corresponding isatoxime with chloramine in addition to preparation from 1-methylisatin hydrazone and 1-methylisatin *p*-toluenesulfonylhydrazone.[11] Few reactions of 3-diazooxindole have been recorded other than to observe its decomposition on treatment with sulfuric acid[9] and to observe the formation of an isomeric indigo

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TABLE I

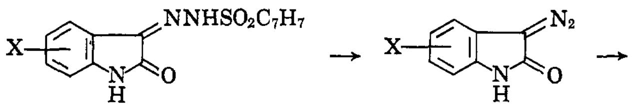
Compd.	Yield, % (recrystn. solvent[a])	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Ia[b]	90–95 (A)	210–212 dec.	57.13	57.26	4.16	4.19	13.33	13.33 13.53
Ib[c]	89 (B)	205–206 dec.	58.34	58.19	4.59	4.51	12.76	12.88
Ic[d]	90 (C)	217 dec.	45.69	45.92	3.07	3.25	10.66	10.65
Id[e]	90 (B)	196–198 dec.	46.88	46.66	2.89	2.98	10.94	10.92
Ie[f]	91 (D)	214–215 dec.	49.99	50.03	3.36	3.28	15.55	14.83
IIa	90–95 (A)	175–176 dec.	60.39	60.33	3.17	3.23	26.41	26.50
IIb	98 (E)	193–195 dec.	62.41	62.43	4.08	3.83	24.27	24.12
IIc[g]	95 (A)	218–219 dec.	40.37	40.23	1.69	1.85	17.66	17.56
IId[h]	100 (E)	219–220 dec.	42.14	41.89	1.33	1.42	18.43	18.52
IIe[i]	98 (A)	238–240 dec.	47.07	46.71	1.98	2.50	27.45	25.69
IIIa	79–84 (F)	129–130	66.23	66.21	5.56	5.29	8.58	8.47
IIIb	44 (F)	125–129	67.77	67.86	6.25	6.21	7.90	7.91
IIIc[j]	59 (G)	151–153	44.65	44.78	3.33	3.41	5.79	5.74
IIId[k]	81 (H)	185–186[l] 267–270	46.57	46.38	3.04	3.25	6.04	6.14
IIIe	69 (F)	194–197	51.92	52.15	3.88	3.74	13.46	13.48
IVc	81 (A, I)	56–57	69.10	69.34	6.85	7.04	7.32	7.41
IVd	85 (E)	141–143[l] 151–152	54.29	54.05	4.10	4.57	12.67	12.46

[a] A, ethanol–water; B, acetic acid; C, dimethylformamide; D, acetone–ethanol; E, ethanol; F, methanol–water; G, benzene–heptane; H, benzene; and I, hexane. [b] *Anal.* Calcd.: S, 10.7. Found: S, 10.06. [c] *Anal.* Calcd.: S, 9.74. Found: S, 9.65. [d] *Anal.* Calcd.: Br, 20.27; S, 8.14. Found: Br, 20.38; S, 7.97. [e] *Anal.* Calcd.: Cl, 18.46; S, 8.35. Found: Cl, 18.14; S, 8.31. [f] *Anal.* Calcd.: S, 8.90. Found: S, 9.04. [g] *Anal.* Calcd.: Br, 33.58. Found: Br, 33.27. [h] *Anal.* Calcd.: Cl, 31.10. Found: Cl, 31.36. [i] The product is photosensitive and attempts to improve the analytical results were unsuccessful. [j] *Anal.* Calcd.: Br, 33.01. Found: Br, 32.80. [k] *Anal.* Calcd.: Cl, 30.56. Found: Cl, 30.41. [l] Double melting point.

when a benzene solution was heated.[12] More recently contributions have been made to reactions of 3-diazooxindoles proceeding through carbenic intermediates.[11] In the current investigation several substituted 3-diazooxindoles (IIa–e, Table I) were prepared according to Cava, Litle, and Napier[10] from the substituted isatin *p*-toluenesulfonylhydrazones (Ia–e, Table I). The yields of the isatin *p*-toluenesulfonylhydrazones averaged 90% and those of the 3-diazooxindoles averaged about 95%. It is a matter of considerable preparative convenience that the 3-diazooxindoles are stable and that purification of either the *p*-toluenesulfonylhydrazones or diazooxindoles is unnecessary.

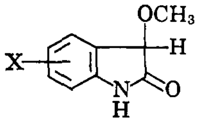
The stability of 3-diazooxindoles can be attributed to resonance delocalization which is enhanced by electron-withdrawing substituents as observed by Warren[13] in the case of 9-diazofluorenes. Mechanistically, the reaction of diazo compounds in the presence of acids involves pre-equilibrium protonation, rate-determining loss of nitrogen, and finally capture of a nucleophile or anion.[14] In order to observe normal reaction, the acid used must be capable of protonating the diazo compound. Acetic acid failed to react with 3-diazooxindole unless heated and, although other carboxylic acids (formic, chloroacetic, or trifluoroacetic acids) reacted spontaneously at room temperature or below, none of the acyloxyoxindoles could be isolated under the conditions employed.

3-Methoxyoxindole (IIIa) was obtained when a methanol solution of IIa was treated with mineral acids or boron trifluoride. Modest, erratic yields were obtained unless the temperature was carefully regulated. The negatively substituted 3-diazooxindoles proved to be less reactive, in agreement with Warren,[13]

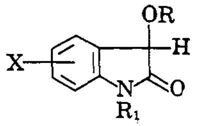


Ia, X = H
b, X = 5-CH$_3$
c, X = 5-Br
d, X = 5,7-Cl
e, X = 5-NO$_2$

IIa, X = H
b, X = 5-CH$_3$
c, X = 5-Br
d, X = 5,7-Cl
e, X = 5-NO$_2$



IIIa, X = H
b, X = 5-CH$_3$
c, X = 5-Br
d, X = 5,7-Cl
e, X = 5-NO$_2$



IVa, R = C$_2$H$_5$; R$_1$, X = H
b, R = *n*-C$_3$H$_7$; R$_1$, X = H
c, R = C$_2$H$_5$; R$_1$ = CH$_3$; X = H
d, R = C$_2$H$_5$; R$_1$ = H; X = 5-NO$_2$

and heating was required to establish a suitable rate of reaction. When solutions of 3-diazooxindole in ethanol or 1-propanol were similarly treated, modest yields of 3-ethoxy and 3-*n*-propoxyoxindole were obtained.[15]

3-Methoxyoxindole (IIIa) displays reactions characteristic of its activated C-3 position. Treatment of IIIa with acrylonitrile in the presence of sodium methoxide resulted in the formation of 3-cyanoethyl-3-methoxyoxindole (V) in 96% yield. A similar reaction with methyl methacrylate was unsuccessful. In a manner analogous to related examples,[16] IIIa yielded a Mannich product, 3-methoxy-3-pyrrolidinomethyloxindole (VI), under conditions described by Hirai, Harvey, and Jensen.[17]

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TABLE II

Compound	Infrared spectra, cm.$^{-1}$ $\nu_{C=O}$[a]	Ultraviolet spectra, λ_{max}, mμ (log ϵ)[b]			N.m.r. spectra, p.p.m.[c]		
					N–H	C-3–H	–OCH$_3$
IIIa	1728 (1734)[d] (1693)	293 (3.13)	251 (3.77)		9.37	4.92	3.57
IIIb	1725	301 (3.14)	257 (3.95)		9.57	4.87	3.50
IIIc	1725	302 (3.17)	259 (4.03)		9.21	4.85	3.50
IIId	1740	308 (3.30)	258 (3.99)	214 (4.40)	12.45[e]	5.08[e]	3.58[e]
IIIe	. . . (1767)[d] (1725)	322 (4.19)	. . .		10.5[e]	5.13[e]	3.67[e]
IVa	1724	291 (3.12)	250 (3.93)		9.37	4.95	. . .
IVb	1724	292 (3.30)	250 (3.89)		9.20	4.92	. . .
IVc	1717, 1707[d]	291 (3.08)	258 (3.79)		. . .	4.85	. . .
IVd	. . . 1724[d]	323 (4.07)	. . .		9.3	4.95	. . .
V	1740 1728	292 (3.16)	248 (3.82)		9.4	. . .	3.02
VI	1737	292 (3.16)	250 (3.76)		9.4	. . .	3.03

[a] Chloroform solutions unless otherwise specified. [b] Methanol solutions. [c] Deuteriochloroform solutions unless otherwise specified. [d] Potassium bromide disk. [e] Pyridine solutions.

Isatin yields 3-alkyl(aryl)dioxindoles in moderate to low yields on treatment with organometallic reagents.[16b,18] The yields are particularly low and the isolation is tedious when alkyl organometallic agents are employed. As an alternative, alkylation of the activated C-3 position of IIIa was attempted. 1-Acetyl-3-methoxyoxindole (VII) was obtained in high yield when 3-methoxyoxindole (IIa) was treated with acetic anhydride according to Suida,[19] but attempted alkylation with methyl iodide in aprotic solvents resulted in a complex mixture, probably by loss or exchange of the N-acetyl blocking group.

The n.m.r. spectra of 3-ethoxy- (IVa) and 3-*n*-propoxyoxindole (IVb) displayed multiple splitting of the protons on the methylene group attached to the ether oxygen which is induced by the asymmetric center represented by C-3 of the oxindole nucleus (molecular asymmetry).[20–22] The normal quartet for the methylene protons in an ethyl group is instead a 12-fold multiplet (gross appearance) in IVa centered at δ 3.79. In detail, the multiplet is almost identical with the spectra of cyclopropylmethylcarbinyl ethyl ether[22a] and acetaldehyde ethyl acetal.[23] The normal triplet–sextet–triplet array for the methylene–methylene–methyl protons in a *n*-propyl grouping is a sextet–sextet–triplet combination (gross appearance) in IVb with the low-field sextet centered at δ 3.62. Less well-resolved multiple splitting patterns are also observed for the methylene groups attached to C-3 in V and VI. Additional n.m.r. spectral data are presented in Table II.

The positions of absorption of C-3–*H* and –OC*H*$_3$, as well as the amide protons, are solvent dependent. Solvent dependence is also encountered in the multiplicity of the geminal methylene absorption of the O-alkyl substituents of IVa–d. In these examples, it is more difficult to rationalize conformational preference as contributing to the nonequivalence of the geminal protons.[22b] Little solvent dependence has been previously observed for aliphatic groups attached to the methylene group of asymmetric ethers.[22b]

The ultraviolet spectra in Table II, measured in methanol solutions, show a close correspondence with the spectrum reported for 3-hydroxyoxindole in 0.1 *N* hydrochloric acid.[24] The spectrum of IIIe (Table II) deviates significantly and resembles *p*-nitroacetanilide[25] more closely than 3-hydroxyoxindole. In order to establish the structure assigned with greater certainty, IVd was prepared and the existence of an asymmetric center at C-3 was demonstrated by the multiple splitting pattern in the n.m.r. spectrum. The infrared spectra in the $\nu_{C=O}$ region are summarized in Table II.

Experimental Section[26]

Isatin *p*-toluenesulfonylhydrazones (Ia–e) were prepared essentially as described by Cava, Litle, and Napier.[10]

3-Diazooxindoles (IIa–e).—To a solution of 0.25 mole of sodium hydroxide in 0.75–1.0 l. of water was added in one lot 0.10 mole of the appropriate isatin *p*-toluenesulfonylhydrazone. The mixture was warmed to 50–55°, then the heat source was removed, and the mixture was stirred for 18–24 hr. overnight. In some cases a heterogeneous mixture was obtained throughout the reaction period. Carbon dioxide was passed through the solution to pH 7; the solid was collected, washed, dried, and recrystallized from the solvent indicated in Table I. Crude yields are reported.

3-Methoxyoxindoles (IIIa–e).—The appropriate 3-diazooxindole was dissolved or suspended in 50 ml. of methanol/g. of diazooxindole. The temperature was adjusted to 15° and 10 mole % of 70% perchloric acid in methanol was injected with stirring. The temperature was then raised until a wet-test meter attached to the apparatus through the reflux condenser indicated a moderate reaction rate. In this investigation, the rate was

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(24) J. W. Cornforth, C. E. Dalgliesh, and A. Neuberger, *Biochem. J.*, **48**, 598 (1951).

(25) H. E. Ungnade, *J. Am. Chem. Soc.*, **76**, 5133 (1954).

(26) Melting points are corrected. The n.m.r. spectra were measured in deuteriochloroform solution. The spectra were obtained on a Varian A-60 spectrometer and are reported as recorded in parts per million from tetramethylsilane. The infrared spectra were obtained on a Beckman IR-7 spectrometer, and the ultraviolet spectra were measured with a Cary Model 11 instrument.

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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Received June 28, 1965

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.

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