(m), 2.8 (m). ^{13}C NMR ($CDCl_3$) δ 31.5, 32.8, 47.9, 208.7. IR ($CHCl_3$) 2920, 1723, 1716, 1330, 1100 cm^{-1}.

2,6-Bis(methoxycarbonyl)phenol (5). 1,1,3,3-Tetramethoxypropane (16.4 g, 0.10 mol) was stirred with 100 mL of 1.0 M HCl for 2 h, 2.76 g (0.02 mol) of $NaH_2PO_4 \cdot H_2O$ was added, and the solution was titrated to pH 3 with 12 mL of 10 M NaOH. Dimethyl 3-oxoglutarate (17.4 g, 0.10 mol) was added, followed by 100 mL of methanol, and the pH was adjusted to 5.0 with 2 M NaOH (~8 mL). After an hour, the pH was readjusted to 5.0 with 2 M HCl, which was repeated after the mixture had stirred overnight. After 3 days it was acidified to pH 3 with 2 mL of 10 M HCl. Filtration gave 7.4 g (19%) of a sticky solid that was proved to be mainly **3** by ^1H NMR. The filtrate was extracted with three 75-mL portions of dichloromethane, dried over sodium sulfate, and evaporated to 14 g of brown oil. This material was treated with 50 mL of 2 M NaOH, and the precipitate was filtered to give 3.17 g of tan solid. An additional 0.15 g of this solid was obtained by acidifying the filtrate, extracting it with dichloromethane, counter-extracting the dichloromethane with saturated bicarbonate, evaporating the organic layer, and treating the residual oil with 10 mL of 2 M NaOH. The combined sodium salts were acidified by stirring with 10 mL of 2 M HCl; the solid present after 30 min was filtered off and dried under vacuum to give 2.88 g (14%) of **5**, mp 64–67 °C. Anal. Found: C, 59.96; H, 4.93. Calcd for $C_{10}H_{10}C_5$: C, 57.14; H, 4.80. Recrystallization from 10 mL of hot methanol gave 2.10 g (10%), mp 68–70 °C (lit.[56] 71 °C). ^1H NMR ($CDCl_3$) δ 3.97 (s, 6 H), 6.95 (t, J = 8 Hz, 1 H), 8.08 (d, J = 8 Hz, 2 H), 11.8 (s, 1 H). ^{13}C NMR ($CDCl_3$) δ 52.5, 116.6, 118.5, 136.3, 161.6, 168.1. IR ($CHCl_3$) 3600–2700, 2940, 1720, 1700, 1680, 1610, 1465, 1325, 1300, 1145, 995 cm^{-1}.

Study of the pH Dependence of the Formation of 3 and 5. Sodiomalondialdehyde[8] (1.12 g, 10.0 mmol) and $NaH_2PO_4 \cdot H_2O$ (0.69 g, 5.0 mmol) were added to each to eight 50-mL round-bottom flasks, followed by 5 mL of water and 5 mL of methanol. The pH was adjusted to the value in Table I with either 2 M HCl or 2 M NaOH. Dimethyl 3-oxoglutarate (1.50 mL, 1.80 g, 10.3 mmol) was added, followed by another 5 mL of methanol. The pH was readjusted to the desired value with acid or base as necessary, and finally the total amount of water added was brought to 10 mL. The septum-capped flasks were stirred at 25 °C for 7 days, during which time the pH was periodically readjusted to its nominal value (initially every hour, later once a day). The reaction mixtures were then acidified to pH 3 and immediately extracted with two 30-mL portions of dichloromethane. Drying over sodium sulfate and evaporation under reduced pressure followed by removal of the last traces of solvent in vacuum gave the amounts of crude products listed in Table I. The 0.10-g quantity of insoluble material present in the pH 9 reaction mixture was removed by filtration. The products were transferred with $CDCl_3$ (1% Me_4Si) to 5-mL volumetric flasks, which were brought to volume and inverted several times to homogenize the contents. The ^1H NMR spectrum of each solution was measured and integrated under identical conditions. Since one of the reaction mixtures (pH 8) contained only **3** and **5**, it was possible to calculate the yield of each. The yields of these two products in the other reaction mixtures were then determined by using the ratios of their integrals to those of the pH 8 mixture and the ratio of the weights of the crude extracts to the pH 8 weight. Allowing the $CDCl_3$ solution from the pH 9 reaction mixture to evaporate gave 1.3 g of **3** (33% based on sodio-**2**, 63% based on **1**).

Other Small Scale Reactions. 1,1,3,3-Tetramethoxypropane (2.2 g, 13 mmol) was stirred with 5.0 mL of 2.0 M HCl for 1.5 h, 0.69 g (5.0 mmol) of $NaH_2PO_4 \cdot H_2O$ was added, and the pH was adjusted to 6.5 with 3.5 mL of 5.0 M NaOH. Dimethyl 3-oxoglutarate (1.5 mL, 1.8 g, 10.3 mmol) was added followed immediately by 10 mL of methanol and 1.5 mL of water. The pH was held at 7.0 ± 0.1 by adding a few drops of 2 M HCl or 2 M NaOH as necessary. After stirring at room temperature (~25 °C) for a week, the workup was the same as for the reaction mixtures in the pH study, except that it was not acidified. The ^1H NMR spectrum of the crude product showed significantly more peaks other than those due to **3** and **5**. Trituration with methanol and filtration gave 0.46 g (12%) of **3**.

A mixture of 1.64 g (10 mmol) of **6** and 5.0 mL of 2.0 M HCl was stirred for 1.5 h, and 9.0 mL of 2.0 M NaOH was added, followed by 3.5 g (20 mmol) of dimethyl 3-oxoglutarate and then 10 mL of methanol (pH 7.0). After 3 days at 25 °C, the reaction mixture was acidified from pH 8 to pH 4, and the white solid was collected. The weight of vacuum-dried product was 2.29 g (60%).

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Registry No. 1, 1830-54-2; **2**, 542-78-9; **3**, 77589-54-9; **4**, 770-15-0; **5**, 36669-06-4; **5**·Na, 97732-36-0; **6**, 102-52-3; glyoxal, 107-22-2; sodiomalondialdehyde, 24382-04-5.

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Thiopyranothiopyran Chemistry. 5. Synthesis of Dibenzo[*b*,*g*]thiopyrano[3,2-*b*]thiopyran-6,12-dione (Thioepindolidione)

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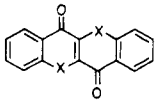
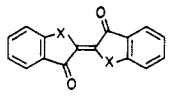
The novel thioepindolidione, a derivative of a thiopyrano[3,2-*b*]thiopyran, was synthesized from thiochroman-4-one. The absorption and fluorescence characteristics of thioepindolidione are compared with those of thioindigo and epindolidione.

Epindolidione (**1**) is a well-known yellow electrophoretic pigment.[1] The hitherto unknown thio analogue dibenzo[*b*,*g*]thiopyrano[3,2-*b*]thiopyran-6,12-dione (thioepindolidione, **2**) can be regarded as a derivative of the novel class of thiopyrano[3,2-*b*]thiopyrans (**3**),[2] of which few examples are known.[3] Furthermore, although thioepindolidione (**2**) is isomeric to thioindigo (**5**),[4] the differences in absorption characteristics and pigment properties between epindolidione (**1**)[5] and indigo (**4**)[6] are quite dra-



1, X = NH
2, X = S

3



4, X = NH
5, X = S

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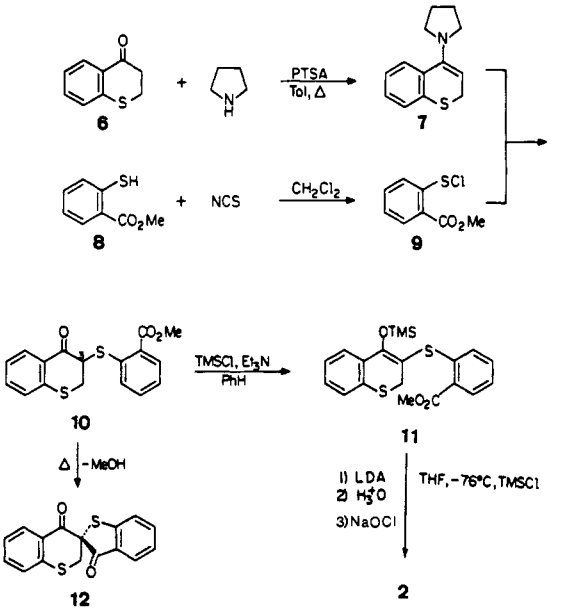
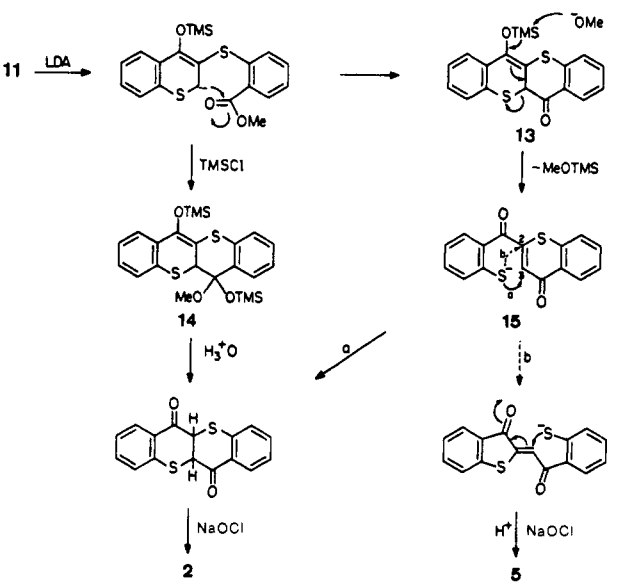
Scheme I



Scheme II



matic and have been, for some time, a topic of theoretical interests.[7,8] As part of a project to synthesize various novel thiopyranothiopyrans[9] and to provide further understanding of the "H-chromophore" in epindolidinoid dyes, we have synthesized thioepindolidione (**2**) and compared its chromogenic properties with those of thioindigo (**5**) and epindolidione (**1**).

Results and Discussion

As shown in Scheme I, the enol of **6** was activated through the formation of the enamine **7** in the usual manner; pyrrolidine was much better than morpholine in this reaction. To form the C–S bond at C-3, it was necessary to convert the nucleophilic mercaptan **8** to the electrophilic sulfenyl chloride **9** by treating **8** with 1 equiv of *N*-chlorosuccinimide (NCS) in methylene chloride at room temperature. Since both **7** and **9** were sensitive to aqueous workup, they were generated in situ and used immediately to produce the desired product **10** in 72% overall yield. Selective oxidation of **10** in attempts to prepare the corresponding monosulfoxide derivative of thiochroman produced a mixture, which, expectedly, is due to the lack of discrimination between the two sulfide functions in the molecule. Attempts to prepare the same sulfoxide derivative of **10** by nucleophilic displacement of 3-bromothiochroman-4-one 1-oxide[10] with either the sodium or thallous salt of methyl 2-mercaptobenzoate (**8**)[11] were also unsuccessful. Thermolysis of **10** under vacuum, >200 °C, produced the novel spiro diketone **12**, which presumably was derived from the enol of **10** via a heat-promoted intramolecular Claisen condensation at C-3 by elimination of methanol. We found later that this reaction was best run in refluxing diphenyl ether/biphenyl eutectic mixture (bp 253 °C) under N_2, from which pure **12** crystallized directly from the reaction mixture on cooling, in 50% yield. The characterization of **12** was routine. The spiro nature of the structure was confirmed by the appearance of the unique quaternary carbon in its ^{13}C NMR spectrum as a singlet (off-resonance decoupling) at δ 67.34.

To prevent the elimination of the thiophenolate at C-3 during the cyclization of **10** with base, **10** was converted to the trimethylsilyl ether **11**. At this stage, the oxidation state of **11** was $2e^-$ lower than that of the desired seco intermediate. Cyclization of **11** would therefore produce a dihydro derivative of **2**, which, as an enediol,[12] should be readily oxidizable to the desired thioepindolidione (**2**). Indeed, when **11** was deprotonated with LDA at −76 °C in THF, equilibrated to room temperature, and treated with aqueous ammonium chloride and Clorox bleach, a dark red solid was separated in 64% yield. Further analysis of this solid showed it was composed of two products in ~2:1 ratio. The major product in this mixture was a fluorescent yellow-orange solid, which was characterized by spectral and TLC analyses as the desired thioepindolidione (**2**). The minor component was a deep red solid, which was readily identified as *trans*-thioindigo (**5**)[4] by comparison with an authentic sample. The formation of thioindigo (**5**) from the base cyclization of **11** was interesting. A plausible mechanism is shown in Scheme II. The skeletal rearrangement was most likely induced by the methoxide released in situ during the cyclization. Cleavage of the trimethylsilyl ether in **13** eliminated a seco thiophenolate **15**, which could Michael add at either C-2 or C-3 to give eventually either **2** or **5**, as shown in pathways a and b in Scheme II.

To circumvent the problem of separating **2** and **5**, we lithiated **11** at −76 °C in the presence of excess trimethylsilyl chloride as a trapping agent. We reasoned that the methoxide as well as the cyclized alkoxide intermediate might be trapped instantaneously as the inert methyl trimethylsilyl ether and **14**, shown in Scheme II, so that further skeletal rearrangement would be avoided. Indeed, when the reaction was repeated in the presence of a fourfold excess of trimethylsilyl chloride and subsequently worked up by consecutive addition of aqueous NH_4Cl and NaOCl (1 equiv), it was possible to obtain **2** free of thioindigo. The yield of **2**[13] was about 31% on the basis of

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(13) No attempt was made to isolate the labile intermediate **14**. When hydrolysis was carried out in the absence of NaOCl, only **2** was isolated in low yield. Presumably, the dihydro derivative of **2**, which has an "enediol" structure, was easily oxidized during workup to give the more stable thioepindolidione (**2**).

Table I. Spectral Properties of Thioepindolidione (2), *trans*-Thioindigo (5), and Epindolidione (1)

spectrum	2	5	1[a]
UV–vis λ_{max} (ϵ), nm	445 (11 680),[b] 420 (9070)[b]	544 (15 100),[b] 510 (shoulder)[b]	444 (20 200),[c] 419 (13 200),[c] 398 (5200)[c]
emission λ_{max} (ϵ), nm	487[b]	600[b]	*d*
quantum efficiency (Φ)	0.2	0.47	
IR (KBr), cm^{-1}			
C=O	1630	1655	1640
C=C	1600	1590	1570 (br)
EIMS, *m/e* (rel intensity)	296 (100), 268 (5), 252 (6), 240 (15), 208 (3), 195 (3), 164 (3), 148 (5), 132 (3), 120 (11)	296 (100), 240 (13), 208 (3), 192 (5), 164 (5), 148 (4), 120 (18)	
^1H NMR ($CDCl_3$) δ	7.63 (ddd, J = 7, 7, 1.5 Hz); 7.75 (ddd, J = 7, 7, 1.5 Hz); 7.84 (dd, J = 7, 1.5 Hz);[f] 8.64 (dd, J = 7, 1.5 Hz)[f]	7.35 (ddd, J = 7, 7, 1.5 Hz); 7.56 (dd, J = 7, 1.5 Hz);[f] 7.63 (ddd, (J = 7, 7, 1.5 Hz); 7.95 (dd, J = 7, 1.5 Hz)[f]	*e*

[a] Reference 5. [b] In CH_2Cl_2. [c] In DMF. [d] Not fluorescent at ambient temperature. [e] Insoluble. [f] Additional $J_{para-para}$ <1 Hz was also recorded.

thiochroman-4-one derivative **10**.

Structure and Properties of Thioepindolidione (2). Pure thioepindolidione (**2**) synthesized according to Scheme I is an orange-yellow powdery solid that fluoresces orange in the solid form under UV excitation at 355 nm. It is very stable and does not melt or decompose up to 380 °C. Thioepindolidione (**2**), lacking the strong intermolecular hydrogen bonding between the carbonyl oxygen and the NH hydrogen atoms, is slightly more soluble in common organic solvents (e.g., CH_2Cl_2, $CDCl_3$) than epindolidione (**1**). Table I compares the spectral characteristics of **2**, thioindigo (**5**), and epindolidione (**1**).

Klessinger and Luttke,[7] in attempts to explain the unusually bathochromic color of indigoids, defined their chromogens as H-chromophores, where two merocyanine conjugations are crossed via a common ethylenic bridge. From a structural point of view, this crossing also appears to be present in the epindolidionoid chromogen, except that the central double bond is confined in two fused six-membered rings. Yet the blue indigo (**4**, λ_{max} 605 nm) is about 160-nm bathochromic of the yellow epindolidione (**1**, λ_{max} 444 nm). Further calculations[8] have shown that ground-state configurations, conformations, and dipole moments of the H-chromophores apparently have a significant influence on the electronic transitions of these systems. In support of Klessinger's MO calculations,[7,8] *trans*-thioindigo (**5**), having a trans-s-cis ground-state H-chromophoric configuration, is ~100-nm bathochromic of thioepindolidione (**2**), which has a trans-s-trans configuration. Thioepindolidione, having a lower extinction coefficient (ϵ), is not as good a dye pigment as thioindigo. Both **2** and **5** are fluorescent in solution and in the solid state. In methylene chloride solution, thioindigo, which fluoresces red (600 nm), has a slightly larger Stokes shift (55 nm) and a much higher quantum efficiency (Φ = 0.47) than thioepindolidione, a yellow-orange fluorescer (487 nm), which has a Stokes shift of 39 nm and a quantum efficiency Φ = 0.2. Strikingly different is epindolidione (**1**), which is not fluorescent at room temperature, presumably because of quenching by intermolecular hydrogen bonding.[5]

Experimental Section

Melting points, obtained on a Thomas-Hoover melting-point apparatus, are uncorrected. ^1H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded on Varian EM-390 and Bruker WH-270 spectrometers, with Me_4Si as the internal standard. Mass spectra were obtained on an AEI MS-30 mass spectrometer. Field-desorption mass spectra were recorded on a Varian MAT-731 spectrometer. IR spectra were obtained on a Beckman IR 4250 spectrophotometer. Elemental analyses were done by the Analytical Sciences Division, Kodak Research Laboratories. Absorption and fluorescence spectra were obtained on Perkin-Elmer 330 and LS-5 spectrophotometers.

3-[(2-(Methoxycarbonyl)phenyl)thio]thiochroman-4-one (10). The pyrrolidinyl enamine **7** was prepared by azeotropic refluxing with a 4-in. Vigreux column for 24 h a solution of 4.92 g (0.03 M) of thiochroman-4-one (**6**), 2.4 g (1.1 equiv) of pyrrolidine, and 350 mg of *p*-toluenesulfonic acid in 50 mL of toluene. The crude, dark red solution of enamine **7** was immediately added dropwise to an ice-cooled solution of 2-(methoxycarbonyl)-benzenesulfenyl chloride (**9**) in CH_2Cl_2. The latter was prepared in situ by adding 4.4 g (0.033 M) of NCS slowly to a solution of 5 g (0.03 M) of methyl 2-mercaptobenzoate (**8**) in 50 mL of CH_2Cl_2 (reaction temperature was kept below 30 °C by occasional cooling with tap water) and stirring overnight at room temperature.

The reaction mixture of **7** and **9** was stirred at room temperature overnight and poured into water. The organic phase was separated, washed with H_2O until neutral, dried ($MgSO_4$), and concentrated on a rotary evaporator to give 12 g of crude **10** as a dark viscous oil. Half of this material (6 g) was flash chromatographed over silica gel with CH_2Cl_2/cyclohexane (4:1) as developing solvent, giving 3.6 g (72%) of pure **10**: mp 95–96 °C; field-desorption mass spectrum, *m/e* 330 (M^+); ^1H NMR ($CDCl_3$) δ 3.47 (dd, 1 H, J = 13.8, 7.4 Hz), 3.65 (dd, 1 H, J = 13.5, 3.1 Hz), 3.85 (s, 3 H, Me), 4.45 (dd, 1 H, J = 7.5, 3.3 Hz, methine), 7.1–7.5 (m, 5 H, Ar H), 7.66 (dd, 1 H, Ar H), 7.86 (dd, 1 H; Ar H), 8.1 (dd, 1 H, Ar H). Anal. Calcd for $C_{17}H_{14}O_3S_2$: C, 61.8; H, 4.3; S, 19.4. Found: C, 61.6; H, 4.1; S, 19.3.

2,3:8,9-Dibenzo-1,7-dithiaspiro[4.5]decane-4,10-dione (12). A solution of 0.5 g (1.5 mmol) of **10** in 4 mL of diphenyl ether/biphenyl eutectic mixture (bp 253 °C) was refluxed under N_2 for 2.5 h. On cooling to room temperature, a white solid precipitated, which was collected by filtration and washed thoroughly with ether to give 225 mg (50%) of pure **12**: mp 191–192 °C; field-desorption mass spectrum, *m/e* 298 (M^+), 162, 136; IR (KBr) $\nu_{C=O}$ 1705, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.15 (d, 1 H, J_{gem} = 14 Hz, H-6), 4.37 (d, 1 H, J_{gem} = 14 Hz, H-6), 7.18–7.62 (m, 6 H, Ar H), 7.84 (d, 1 H, Ar H), 8.13 (dd, 1 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 34.64 (t, C-6), 67.34 (s, C-5 quaternary), 124.41, 125.57, 125.87, 127.06, 127.49, 129.24, 130.43, 131.43, 133.92, 136.30, 140.65, 149.43, 188.61 (C=O), 199.18 (C=O). Anal. Calcd for $C_{16}H_{10}O_2S_2$: C, 64.4; H, 3.4; S, 21.5. Found: C, 64.4; H, 3.3; S, 21.1.

3-[(2-(Methoxycarbonyl)phenyl)thio]-4-(trimethylsiloxy)-2*H*-thiochromene (11). To a solution of 1.5 g (4.5 mmol) of **10** and 0.93 g (9.2 mmol) of triethylamine in 25 mL of benzene (cooled with tap water) was added by syringe 1.25 mL (d = 0.856 g mL^{-1}, 2.2 equiv) of freshly distilled (over CaH_2) trimethylsilyl chloride under N_2. The mixture was stirred overnight at room temperature, and ice-cold aqueous NH_4Cl was added to the precooled reaction mixture. The reaction mixture was quickly extracted with ether, and the organic phase was separated, dried ($MgSO_4$) immediately, and concentrated on a rotary evaporator to give 1.8 g (100%) of crude **11**: field-desorption mass spectrum, *m/e* 402 (M^+), 328 ($M^+ - Me_3SiH$); ^1H NMR ($CDCl_3$) δ 0.15 (s, 9 H, Me_3Si), 3.5 (s, 2 H, CH_2), 3.85 (s, 3 H, CH_3), 7–7.6 (m, 6 H, Ar H), 7.73 (d, 1 H, Ar H), 7.97 (dd, 1 H, Ar H).

This material was used immediately without further purification.

Dibenzo[*b*,*g*]thiopyrano[3,2-*b*]thiopyran-6,12-dione (Thioepindolidione) (2). To a solution of 0.91 g (2.25 mmol) of crude **11** and 1.2 mL (9.5 mmol) of freshly distilled (over CaH_2) trimethylsilyl chloride in 30 mL of dry THF at −76 °C was added dropwise by syringe 1.3 equiv of lithium diisopropylamide (LDA) (freshly prepared from 0.41 mL of diisopropylamine and 1.2 mL of 2.5 M of *n*-BuLi in 1.5 mL of THF) under argon. The reaction mixture was kept at −75 °C for 30 min, equilibrated to ~3 °C (ice cooling), and stirred for 2 h. The brown solution was cooled with ice, and 35 mL of aqueous NH_4Cl was added dropwise (pot temperature was kept below 17 °C), followed by 3.2 mL (1 equiv) of 5.25% aqueous NaOCl bleach (Jones Chemicals, Inc., New York), and the mixture was stirred overnight under a nitrogen flush. The precipitated brownish yellow solid was filtered and washed with water and ether to give 245 mg of a light brown solid, which was shown by TLC to contain no thioindigo. The crude product was purified by boiling it in 50 mL of ethyl acetate. After cooling, the insoluble light brown solid was filtered and washed with ethyl acetate to give 205 mg (31%) of thioepindolidione (**2**): mp ~380 °C; electron-impact mass spectrum, *m/e* 296 (M^+), 268 ($M^+ - CO$), 240 ($M^+ - 2CO$); IR (KBr) and ^1H NMR ($CDCl_3$) (see Table I). Anal. Calcd. for $C_{16}H_8O_2S_2$: C, 64.8; H, 2.7; S, 21.6. Found: C, 64.7; H, 2.6; S, 21.7.

Thioepindolidione (2) and *trans*-Thioindigo (5). To a solution of 525 mg (1.3 mmol) of trimethylsilyl ether **11** in 60 mL of dry THF cooled to −76 °C was added by syringe 1.2 equiv of LDA (freshly prepared from 336 μL of diisopropylamine and 0.96 mL of 2.5 M *n*-BuLi in 2 mL of THF) under argon. The dark red reaction mixture was allowed to equilibrate to room temperature overnight and poured into a beaker containing aqueous NH_4Cl and Clorox. The precipitated red solid was filtered and washed thoroughly with water and ether, giving 250 mg (64%) of a dark red powder. TLC (silica gel, CH_2Cl_2) of this material showed only two spots corresponding to *trans*-thioindigo (**5**) (R_f 0.66) and thioepindolidione (**2**) (R_f 0.43). Electron-impact mass spectrum of this mixture showed the following: *m/e* 296 (M^+), 268 ($M^+ - CO$), 252 ($M^+ - CO_2$), 240 ($M^+ - 2CO$), 120. By integration over the ^1H NMR region where the peri H's adjacent to the carbonyl resonate (δ 7.95 for **5** and δ 8.62 for **2**), the ratio of **5** to **2** in this mixture was estimated as ~1:2.

Acknowledgment. We thank Dr. Joe L. Lippert and Karen E. Maskasky of the Analytical Sciences Division for obtaining the fluorescence spectra of thioepindolidione and thioindigo and Frank M. Michaels and Sandra M. Finn for helping on the high-field NMR spectra.

Registry No. **1**, 17352-37-3; **2**, 97634-87-2; **5**, 3844-31-3; **6**, 3528-17-4; **7**, 67220-30-8; **8**, 4892-02-8; **9**, 78880-71-4; **10**, 97634-84-9; **11**, 97634-86-1; **12**, 97634-85-0; pyrrolidine, 123-75-1.

Nonlinear Brønsted-Type Plot in the Pyridinolysis of 2,4-Dinitrophenyl Benzoate in Aqueous Ethanol

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From the kinetics of the title reaction in 44 wt% aqueous ethanol at 25 °C, ionic strength 0.2 M (KCl), a curved Brønsted-type plot is obtained. The curve is interpreted in terms of a zwitterionic tetrahedral intermediate in the reaction path and a change in the rate-determining step from breakdown to products of this intermediate to its formation as the pyridine becomes more basic. A semiempirical equation based on this hypothesis accounts for the experimental results. The center of the Brønsted-type curvature ($pK_a°$) is located at $pK_a = 9.5$, lower than the value found in the pyridinolysis of 2,4-dinitrophenyl *p*-nitrobenzoate in the same solvent, showing that electron withdrawal from the acyl group of the substrate favors amine expulsion relative to phenoxide from the tetrahedral intermediate. It is claimed that the influence of the acyl group of the substrate on the value of $pK_a°$ cannot be quantified when comparing similar reactions in water and aqueous ethanol since the $pK_a°$ value for a given reaction should be larger in the latter solvent. The activation parameters obtained support the hypothesis that for the title reactions, $pK_a° > 9$.

Structure–reactivity correlations for nucleophilic reactions have usually been expressed through Brønsted-type plots, log k_N against basicity of the nucleophile, where k_N is the second-order rate constant for the reaction of the nucleophile with a common substrate (electrophile).

The nucleophilic reactions of series of structurally similar amines with aryl acetate esters exhibit linear Brønsted-type plots when the leaving group of the substrate is moderately basic, but the plots are curved when the basicity of the leaving group decreases.[1] Primary and secondary amines also show curved Brønsted-type plots in their reactions with other reactive carboxylic acid derivatives.[2]

The nucleophilic reactions of quinuclidines with aryl phenyl carbonates show linear Brønsted-type plots for the substrates with more basic leaving groups; however the plots become nonlinear as the leaving ability of the aryl oxide group increases.[3]

The above picture is also obtained in the pyridinolysis of methoxycarbonyl and acetyl derivatives. The Brønsted-type plots are straight for leaving groups such as phenoxide[1,4] and *p*-nitrophenoxide[5,6] ions and curved for 2,4-dinitrophenoxide[4,7] and chloride[5,8] anions.

The nonlinear Brønsted-type plots described above have been explained through a tetrahedral intermediate along the reaction path (eq 1, N and L represent the substituted amine and the leaving group, respectively) and a change in the rate-determining step, from the second to the first one, as the nucleophile becomes more basic.[3-9] The slope

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