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Photocyclization of the substituted 2-([1]benzothien-3-yl)-3-phenylpropenoic acids **3a-c** in the presence of iodine and air in a benzene-cyclohexane mixture afforded a separable mixture of three compounds, benzo[*b*]naphtho[2,1-*d*]thiophene-6-carboxylic acids **4a-c**, 6*H*-benzo[*b*]naphtho[2,3-*d*]thiopyran-6-ones **5a-c**, and 10-methoxy-2-methyl-6*H*-benzo[*b*]naphtho[2,3-*d*]pyran-6-one (**6**).

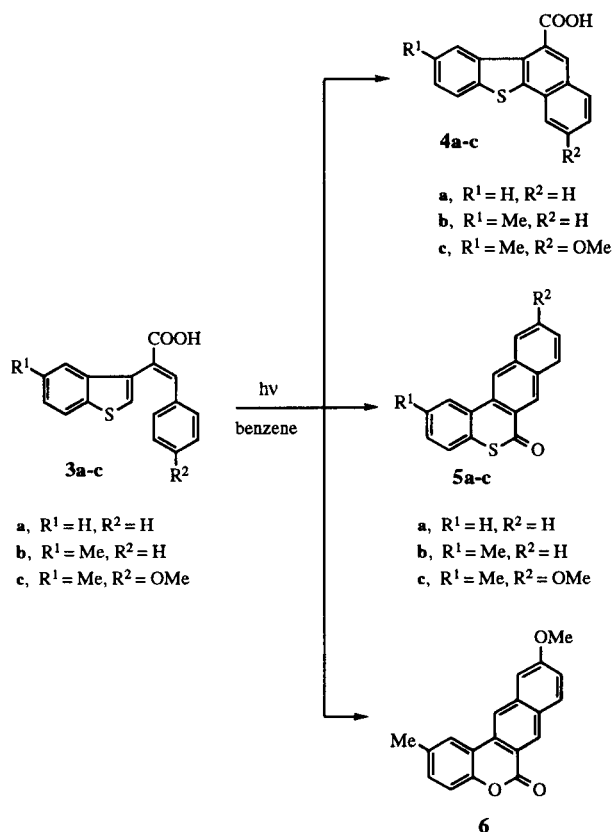
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During the past decade two reviews [1,2] indicate continuing interest in the production of polycyclic heterocycles *via* photocyclization reactions. More recently [3,4] improved methodology for the photocyclization of various stilbene-type compounds have been reported [5-11]. Thus we now report on the expansion of the photocyclization reaction of 2-([1]benzothienyl-3-yl)-3-phenylpropenoic acids [12, 13]

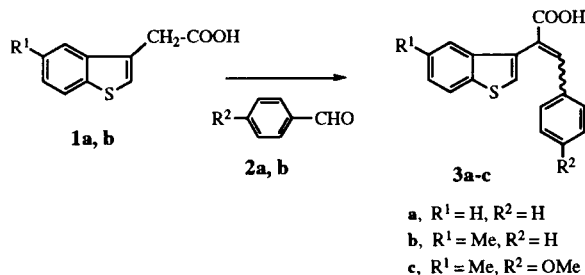
The reaction of [1]benzothienyl-3-ylacetic acids **1a,b** with aromatic aldehydes **2a,b** afforded the substituted 2-([1]benzothien-3-yl)-3-phenylpropenoic acids **3a-c** for photocyclization. Compounds **3a-c** upon irradiation in a benzene-cyclohexane mixture (3:2) in the presence of iodine and air afforded a separable mixture of two compounds **4a,b** in 63% and 48% yields, respectively [12] together with **5a** in 6% yield and **5b** in 15% yield. Photocyclization of **3c** under the same conditions provided a separable mixture of three compounds **4c**, in 73% yield, **5c** in 3% yield, and **6** in 4% yield. Compounds **4a-c** were the expected products and all crystallized from the reaction mixture in almost pure form. Compounds **5a-c** represent a novel polycyclic ring system and the three products are 6*H*-benzo[*b*]naphtho[2,3-*d*]thiopyran-6-one (**5a**), 2-methyl-6*H*-benzo[*b*]naphtho[2,3-*d*]thiopyran-6-one (**5b**) and 10-methoxy-2-methyl-6*H*-benzo[*b*]naphtho[2,3-*d*]thiopyran-6-one (**5c**) [14]. This ring system was characterized from COSY, HMQC, HMBC and NOE-difference spectroscopy of **5a** as well as ir, ms and elemental analysis. The third compound obtained is 10-methoxy-2-methyl-6*H*-benzo[*b*]naphtho[2,3-*d*]pyran-6-one (**6**) [15].

In order to explain the formation of compounds **4**, **5**, and **6** we propose the following reaction pathway. The photocyclization of **3** provides the unisolable proposed dihydro intermediate **A** which can either lose a hydrogen molecule to afford the main product **4** or suffers ring opening of the thiophene ring to give the intermediate **B** in which the mercapto group attacks the carboxy of the carbonyl group to afford species **C** which upon loss of a molecule of water provides the novel ring system **5**. Compound **6** can be formed by nucleophile displacement of the mercapto group with the hydroxy group of the hydroxycarbonyl group.

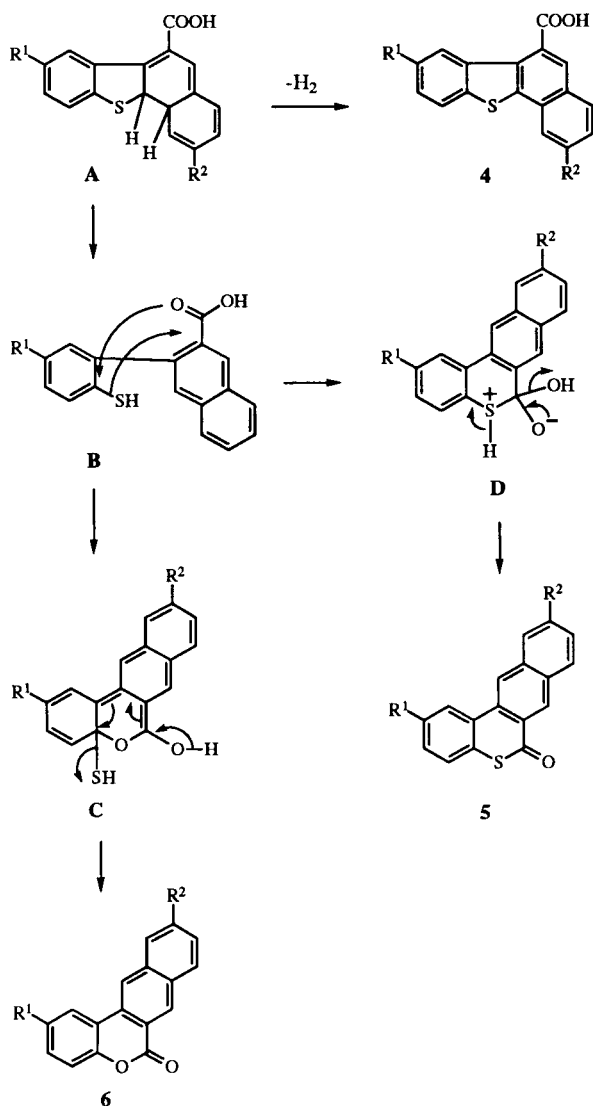
Scheme 2



Scheme 1



Scheme 3



EXPERIMENTAL

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. The ir spectra were recorded on a Beckman FT100 spectrometer as potassium bromide pellets and frequencies are expressed in cm⁻¹. The ¹H-nmr spectra were obtained on a JEOL FX90Q and a Bruker AMX 360 spectrometer in the solvent indicated with TMS as the internal standard and chemical shifts are reported in ppm (δ) and J values are in Hz. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona. The electron impact and high resolution ionization mass spectra were acquired by the Midwest Center for Mass spectroscopy.

2-([1]Benzothien-3-yl)-3-phenylpropenoic Acid (3a).

A mixture of 4.10 g (25 mmoles) of [1]benzothien-3-ylacetic acid (1a) 2.7 g (25.5 mmoles) of benzaldehyde, 10 ml of acetic anhydride, and 5 ml of triethylamine was refluxed for 4 hours. The reaction mixture was then poured into 100 ml of 10%

hydrochloric acid. The oily product was extracted with 200 ml of benzene. The benzene solution was extracted with 200 ml of a 5% sodium hydroxide solution. The aqueous solution and oily product that separated was acidified with 10% hydrochloric acid. The mixture was allowed to stand for 2 to 3 hours. The crystallized product was collected by filtration. After drying in air, the product was recrystallized from a mixture of hexane and benzene (3:1) to give 3.90 g (13.9 mmoles, 56%) of crystalline product. An analytical sample was recrystallized from a mixture of hexane and benzene (3:1) to give colorless prisms, mp 148-150°; ir (potassium bromide): 3091-2600 (broad, OH), 1676 (CO) cm⁻¹; ¹H nmr (deuteriochloroform): δ 7.09-7.55 (8H, m, 2,4,5-H, phenyl-H), 7.83-7.90 (1H, m, 7-H), 8.17 (1H, s, =CH).

Anal. Calcd. for C₁₇H₁₂O₂S₂: C, 72.83; H, 4.31; S, 11.43. Found: C, 72.85; H, 4.43; S, 11.29.

2-(5-Methyl[1]benzothien-3-yl)-3-phenylpropenoic Acid (3b).

Compound 3b (4.10 g, 13.9 mmoles) was synthesized from 2b (4.12 g, 20 mmoles) and benzaldehyde (2.70 g, 25.5 mmoles) in a manner similar to that described for the preparation of 3a and was obtained as tan crystals in 70% yield, mp 165-168° (lit [12] 168°); ir (potassium bromide): 3060-2300 (broad, OH), 1676 (CO) cm⁻¹; ¹H nmr (deuteriochloroform): δ 2.36 (3H, s, 5-Me), 7.12-7.35 (8H, m, 2,4,6-H, phenyl-H), 7.76 (1H, d, J = 8.3 Hz, 7-H), 8.16 (1H, s, =CH).

3-(4-Methoxyphenyl)-2-(5-methyl[1]benzothien-3-yl)-3-phenylpropenoic Acid (3c).

Compound 3c (3.92 g, 12.1 mmoles) was synthesized from 1c (4.12 g, 20 mmoles), *p*-anisaldehyde 3.26 g, 24 mmoles) in a manner similar to that described for the preparation of 3a and was obtained in 61% yield. An analytical sample was recrystallized from a mixture of benzene and hexane (2:1) to give colorless needles, mp 200-202°; ir (potassium bromide): 3060-2500 (broad, OH), 1676 (CO), 1599, 1509, 1422, 1257, 1180, 1028 cm⁻¹; ¹H nmr (deuteriochloroform): δ 2.36 (3H, s, 5-Me), 3.71 (3H, m, 2, 4, 6-H), 7.76 (1H, d, J = 8.0 Hz, 7-H), 8.11 (1H, s, =CH).

Anal. Calcd. for C₁₉H₁₆O₃S: C, 70.35; H, 4.97; S, 9.98. Found: C, 70.28; H, 5.07; S, 9.76.

Benzo[*b*]naphtho[2,1-*d*]thiophene-6-carboxylic Acid (4a) and 6*H*-Benzo[*b*]naphtho[2,3-*d*]thiopyran-6-one (5a).

A solution of 0.5 g (1.79 mmoles) of 2a and 50 mg of iodine in a mixture of 300 ml of benzene and 200 ml of cyclohexane was irradiated for 4 hours with a 450 Watt Hanovia medium pressure mercury lamp. During the course of the reaction, a slow stream of air was passed through the solution. The solvent was evaporated *in vacuo* and the residue was washed with 50 ml of benzene to give 0.33 g (1.19 mmoles, 63%) of 4a as tan needles. An analytical sample was recrystallized from benzene to give tan needles, mp 236-239°; ir (potassium bromide): 3400-2200 (broad, OH), 1689 (CO) cm⁻¹; ¹H nmr (deuteriochloroform + trifluoroacetic acid, 10:1): δ 7.36-8.25 (8H, m, aromatic-H), 8.47 (1H, s, 5-H).

Anal. Calcd. for C₁₇H₁₀O₂S: C, 73.90; H, 2.92; S, 11.60. Found: C, 73.92; H, 3.17; S, 11.49.

The above benzene solution was added to 70 ml of hexane. The mixture was chromatographed on a silica gel column (15 g) using a mixture hexane and benzene (1:1) as the eluent to give 30 mg (0.109 mmoles, 6%) of 5a as a yellow solid, which was recrystallized from methanol to give yellow needles, mp 170-

172°; ir (potassium bromide): 1640 (CO), 1617, 1165, 753, 723 cm^{-1} ; ^1H nmr (deuteriochloroform): δ 7.42-7.75 (5H, m, 2, 3, 8, 9, 10-H), 7.98-8.12 (2H, m, 1, 4-H), 8.42-8.53 (1H, m, 11-H), 8.79 (1H, s, 12 or 6-H), 8.96 (1H, s, 6 or 12-H); ms: m/z 264 (4.1), 263 (13), 262 (70), 236 (5), 235 (17), 234 (M^+ -32, 100), 189 (13); hrms: Calcd. for $\text{C}_{17}\text{H}_{10}\text{OS}^{32}$: 262.0452. Found: 262.0441. Calcd. for $\text{C}_{17}\text{H}_{10}\text{OS}^{34}$: 264.0410. Found: 264.0428.

Anal. Calcd. for $\text{C}_{17}\text{H}_{10}\text{OS}$: C, 77.81; H, 3.84; S, 12.22. Found: C, 77.79; H, 3.96; S, 11.96.

8-Methylbenzo[*b*]naphtho[2,1-*d*]thiophene-6-carboxylic Acid (**4b**) and 2-Methyl-6*H*-benzo[*b*]naphtho[2,3-*d*]thiopyran-6-one (**5b**).

These compounds were synthesized from **3b** (0.5 g, 1.5 mmole) in a manner similar to that described for the preparation of **4a** and **5a**. Compound **4b** was obtained as tan needles, mp 238-241 (lit [12] 240°) in 48% yield (0.21 g, 0.72 mmole); ir (potassium bromide): 3200-2200 (broad, OH); 1690 (CO) cm^{-1} .

Compound **5b** was purified by silica gel chromatography using a mixture of benzene and hexane (1:1) as the eluent to give 62 mg (0.225 mmole, 15%) of yellow needles. An analytical sample was recrystallized from a mixture of methanol and benzene (5:1) to give yellow needles, mp 194-195°; ir (potassium bromide): 1640 (CO), 1615, 951, 906, 800, 746 cm^{-1} ; ^1H nmr (deuteriochloroform): δ 2.51 (3H, s, 10-H), 7.25 (2H, s, 8, 9-H), 7.57-7.70 (2H, m, 2,3-H), 7.90-8.10 (2H, m, 14-H), 8.23 (1H, s, 11-H), 8.74 (1H, s, 5 or 12-H), 8.93 (1H, s, 12 or 5-H).

Anal. Calcd. for $\text{C}_{18}\text{H}_{12}\text{OS}$: C, 78.23; H, 4.38; S, 11.60. Found: C, 78.19; H, 4.50; S, 11.43.

2-Methoxy-8-methylbenzo[*b*]naphtho[2,1-*d*]thiophene-6-carboxylic Acid (**4c**), 10-Methoxy-2-methyl-6*H*-benzo[*b*]naphtho[2,3-*d*]thiopyran-6-one (**5c**), and 10-Methoxy-2-methyl-6*H*-benzo[*b*]naphtho[2,3-*d*]pyran-6-one (**6**).

A solution of 0.5 g (1.54 mmole) of **3c** and 50 mg of iodine in a mixture of 200 ml of benzene and 300 ml of cyclohexane was irradiated for 5 hours with a 450 watt Hanovia medium pressure mercury lamp. During the course of the reaction, a slow stream of air was passed through the solution. The solvent was evaporated *in vacuo* and the residue was washed with 50 ml of benzene to give 0.363 g (1.13 mmole, 73%) of tan crystals. The product was **4c** and recrystallized from benzene to give tan needles, mp 237-239°; ir (potassium bromide): 3100-2500 (broad, OH), 1697 (CO), 1622, 1470, 1221 cm^{-1} ; ^1H nmr (deuteriochloroform + trifluoroacetic acid [5:1]): δ 2.54 (3H, s, 8-Me), 4.04 (3H, s, OMe), 7.18-7.32 (2H, m, 9,10-H), 7.38 (1H, s, 9-H), 7.83 (1H, d, $J = 8.0$ Hz, 3 or 4-H), 7.92 (1H, d, $J = 8.0$ Hz, 4 or 3-H), 8.36 (1H, s, 1-H), 8.42 (1H, s, 5-H).

Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_3\text{S}$: C, 70.79; H, 4.38; S, 9.95. Found: C, 71.00; H, 4.59; S, 10.12.

The solvent of the above benzene solution was evaporated and the residue was chromatographed on a silica gel column (20 g) using a mixture of benzene and hexane (1:1) as the eluent to give a yellow

solid, which was recrystallized from methanol to give 15 mg (0.47 mmole, 3%) of yellow needles of **5c**, mp 194-198°; ir (potassium bromide): 1633 (CO), 1614, 1234, 1160 cm^{-1} ; ^1H nmr (deuteriochloroform): δ 2.52 (3H, s, 2-Me), 4.00 (3H, s, OMe), 7.17-7.28 (4H, m, 1, 4, 8, 9-H), 7.94 (1H, d, $J = 9.0$ Hz, 3-H), 8.25 (1H, bs, 11-H), 8.65 (1H, s, 12 or 5-H), 8.87 (1H, s, 5 or 12-H).

Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_3\text{S}$: C, 74.48; H, 4.61; S, 10.46. Found: C, 74.29; H, 4.78; S, 10.57.

Subsequent elution using a mixture of benzene and hexane (3:1) afforded a colorless crystalline substance which was recrystallized from methanol to give 20 mg (0.065 mmole, 49%) of **6** as colorless leaflets, mp 232-235°; ir (potassium bromide); 1723 (CO), 1628 cm^{-1} ; ^1H nmr (deuteriochloroform): δ 2.49 (3H, s, 3-Me), 3.99 (3H, s, OMe), 7.10-7.26 (1H, m, 1, 3, 7, 8-H), 7.93 (1H, d, $J = 9.0$ Hz, 4-H), 7.98 (1H, s, 10-H), 8.39 (1H, s, 11 or 5-H), 8.92 (1H, s, 5 or 11-H); ms: m/z 280 (M^+ , 100), 261 (3), 247 (1), 219 (15), 189 (9), 145 (5), 85 (16), 71 (24), 57 (33); hrms: Calcd. for $\text{H}_{19}\text{H}_{14}\text{O}_3$: 290.0943. Found: 290.0934.

Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_3$: C, 78.61; H, 4.86. Found: C, 78.82; H, 4.92.

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