August, 1980] © 1980 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 53, 2415—2416 (1980) 2415

# Synthesis of 1-Benzothiopyrylium Perchlorates and Related Compounds

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(Received February 5, 1980)

**Synopsis.** The blue colored 1-benzothiopyrylium perchlorates were synthesized by the reduction of thiocoumarins with lithium aluminium hydride followed by the treatment with acid. A number of new thiocarbonyl derivatives of thiocoumarins and thiochromones were also synthesized, the spectral characterization of which has been described.

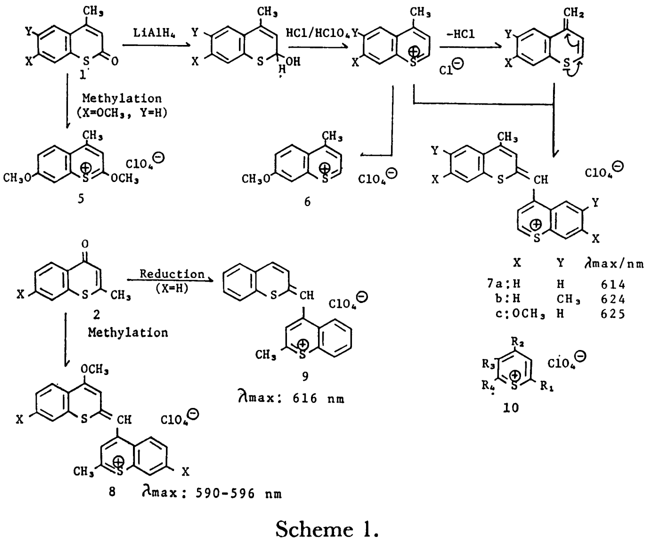
In our previous papers, we have reported the syntheses and methylation of 2*H*-1-benzothiopyran-2-ones (thiocoumarins) (**1**) and 4*H*-1-benzothiopyran-4-ones (thiochromones) (**2**), an isomer of **1**.[1,2]

In this paper, we wish to report (i) the reduction of thiocoumarins (**1**) with lithium aluminium hydride ($LiAlH_4$) and synthesis of 2*H*-1-benzothiopyran-2-thiones (**3**) and 4*H*-1-benzothiopyran-4-thiones (**4**) as reactants to prepare 1-benzothiopyrylium salts, and (ii) spectral characterization of **3** and **4** to distinguish them.

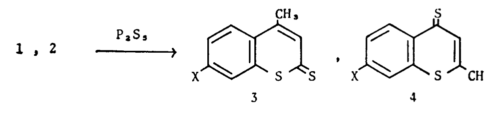
## Results and Discussion

*Preparation of 1-Benzothiopyrylium Perchlorates (7).* In the previous paper,[2] we reported that the methylation of **2** with dimethyl sulfate gave the dimerized product **8**, while in the case of isomeric thiocoumarin **1** ($X=OCH_3$), none of the dimerized product but *O*-methylated product **5** was isolated by the same reaction.

We now found that a blue colored 1-benzothiopyrylium perchlorate **7** could be obtained in yields of 22—72%, by the reduction of thiocoumarin **1** with $LiAlH_4$ followed by the treatment with acid. Similar reduction of **2** with aluminium hydride or $LiAlH_4$ also gave an isomeric blue colored 1-benzothiopyrylium salt **9**.[2] Mckinnon[3] has already reported that some of thiopyrylium salts (**10**) were obtained from 2*H*(or 4*H*)-thiopyran-2(or 4)-ones under the same conditions. In the case of **1c** ($X=OCH_3$), both of 1-benzothiopyrylium salts **7c** and **6**, as the precursor of **7c**, were isolated in yields of 30 and 39%, respectively. Compounds **7a** and **6** also could be obtained by the cyclization of 4-(phenylthio)-2-butanones with PPA or perchloric acid.[4] A possible mechanism for the formation of **7** is given in a similar manner as described in the case of thiochromones (Scheme 1). It is shown that the condensation takes place between 4-methyl group of **1** and 2-carbon atom of the other molecule in this reaction.



Scheme 1.

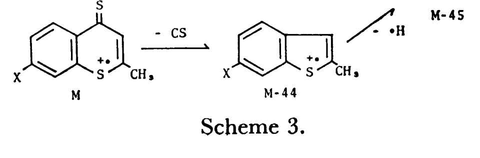


Scheme 2.

On the other hand, it is also known that the oxidation of 2*H*(or 4*H*)-thiopyran-2(or 4)-thiones give thiopyrylium salts (**10**). Then, we synthesized a number of new thiocarbonyl derivatives **3** and **4** as reagents to prepare **7** and **9**. Compounds **3** and **4** were obtained by the usual reaction of **1** and **2** with $P_2S_5$, respectively (Scheme 2), but an attempt to prepare **7** from **3** was failed. That is, the oxidation of **3a** with hydrogen peroxide gave an undetermined product, which showed the two $\lambda_{max}$'s of 579 and 626 nm in acetone solution and complex peaks in the NMR spectra.

*Spectral Characteristics.* The spectral data of **3** and **4** are summarized in Table 1. We proposed some spectral characterization of **1** and **2** to distinguish. From **3** and **4**, the additional distinction between thiocoumarin and thiochromone nuclei became possible as follows. In the NMR spectra, the characteristic deshielding effect of benzenoid proton at the 5-position of **4** was observed similar to that of thiochromones (**2**). The proton showed the chemical shift at *ca.* 9.00 ppm. In the series of thiocoumarin **3**, however, such a proton showed the chemical shift at *ca.* 7.80 ppm. This difference may be utilized to distinguish them as well as that of **1** and **2**. The proton at the 3-position of both derivatives **3** and **4** showed the chemical shift in the aromatic region (above 7.00 ppm), compared to that of **1** and **2** in the range of 6.48—6.75 ppm, except for **3c** and **4c**.

In the mass spectra, the major fragmentation pathway for each of **3** and **4** was elimination of C=S, followed by the loss of a hydrogen atom leading to the formation of 1-benzothiopyrylium ion (Scheme 3). The series of



Scheme 3.

TABLE 1. THE SPECTRAL DATA OF 1-BENZOTHIOPYRAN-THIONE DERIVATIVES

| No. | X | NMR in $CDCl_3$ $\delta$/ppm | $m/e$ (rel. intensity) | $\lambda_{max}$/nm[a] ($\varepsilon \times 10^{-4}$) |
|---|---|---|---|---|
| **3a** | H | 2.45(3H, s)<br>7.38—7.85(5H, m) | 192 (M, 100), 191 (12)<br>177 (20), 148(M−44, 100)<br>147 (M−45, 73) | 234(3.9)<br>302(1.7)<br>420(1.1) |
| **3b** | 7-$CH_3$ | 2.40 (6H, s)<br>7.15—7.30(3H, m)<br>7.70 (1H, d, $J$=10 Hz) | 206 (M, 82), 205 (10)<br>191 (17), 162 (M−44, 92)<br>161 (M−45, 50) | 238(2.7)<br>303(1.1)<br>425(1.0) |
| **3c** | 7-$OCH_3$ | 2.42 (3H, s)<br>3.88 (3H, s)<br>6.88 (1H, s)<br>7.05—7.30 (2H, m)<br>7.77 (1H, d, $J$=10 Hz) | 222 (M, 82), 221 (6)<br>207 (8), 178 (M−44, 100)<br>177 (M−45, 9), 163 (45) | 245(4.5)<br>272(1.2)<br>278(1.2)<br>309(0.82)<br>432(1.5) |
| **4a** | H | 2.40 (3H, s)<br>7.43—7.70 (3H, m)<br>7.96 (1H, s)<br>9.01 (1H, m) | 192 (M, 100), 191 (M−1, 58)<br>177 (18), 148 (M−44, 20)<br>147 (M−45, 57) | 236(1.6)<br>244(2.3)<br>293(0.75)<br>412(2.1) |
| **4b** | 7-$CH_3$ | 2.38 (3H, s)<br>2.40 (3H, s)<br>7.20—7.40 (2H, m)<br>7.85 (1H, s)<br>8.85 (1H, d, $J$=10 Hz) | 206 (M, 100), 205 (M−1, 54)<br>191 (39), 162 (M−44, 13)<br>161 (M−45, 34) | 238(1.3)<br>247(2.4)<br>296(0.84)<br>412(1.8) |
| **4c** | 7-$OCH_3$ | 2.36 (3H, s)<br>3.90 (3H, s)<br>6.96 (1H, s)<br>7.15—7.84 (2H, m)<br>8.96 (1H, d, $J$=10 Hz) | 222 (M, 100), 221 (M−1, 41)<br>207 (23), 178 (M−44, 13)<br>177 (M−45, 13), 163 (15) | 253(1.9)<br>289(1.1)<br>343(0.74)<br>409(2.2) |

a) In EtOH.

thiochromone **4** were characterized by abundant molecular ion as the base peak and the M−1 fragment ion, formula of which was not assigned. In the case of **3**, such an M−1 fragment ion was very small (below 12 (rel. intensity)). It was observed that in the case of **3** the M−44 fragment ion was much stronger than that of M−45. The M−40 fragment ion was not observed in **4**, which was found characteristically in the mass spectra of **2**.[1]

The absorption maxima of the longest wavelength of **3** were longer by *ca.* 10 nm than those of **4**.

## Experimental

All the melting points are uncorrected. $^1$H-NMR spectra were taken on a Hitachi R-24A spectrometer with tetramethylsilane as an internal standard. Absorption spectra were obtained with a Hitachi EPS-3T spectrometer. Mass spectra were taken on a Hitachi RMU-6E mass spectrometer operating at 80 eV. Elemental analyses were performed on a Yanaco CHN recorder MT-2.

*The Reduction of 1 with Lithium Aluminium Hydride.* Powdered $LiAlH_4$ (0.1 g) was added to a stirred solution of **1a** (1.0 g) in anhydrous diethyl ether (100 ml) at room temperature. After 1 h, ethyl acetate (2 ml) was added, and after 10 min, addition of 10% dilute HCl (10 ml) gave a blue colored mixture. After 30 min, diethyl ether was evaporated below 30 °C. The residue was dissolved in glacial acetic acid (30 ml) and 60% perchloric acid (0.5 ml) was added. After standing for 20 h at room temperature, the mixture was diluted with diethyl ether, and the resulting solid was separated and washed with a mixture of acetone and benzene (1: 2) and EtOH. The crude product was recrystallized from glacial acetic acid (80 ml) containing a small amount of perchloric acid to give **7a** (X=H, Y=H). **7a**:[4] 72%, NMR ($CF_3COOH$): $\delta$=3.30 (3H, s), 5.95 (2H, s), and 7.50—9.10 (≈10H, m). Found: C, 57.01; H, 3.77%. Calcd for $C_{20}H_{15}O_4ClS_2$: C, 57.35; H, 3.58%. $\lambda_{max}$ (acetone): 614 nm ($\varepsilon$ 8.30×10$^4$); **7b** (X=H, Y=$CH_3$): 22%, NMR ($CF_3COOH$): $\delta$=2.83 (6H, s), 3.30 (3H, s), 5.88 (2H, s), and 8.0—8.8 (≈8H, m). Found: C, 58.61; H, 4.28%. Calcd for $C_{22}H_{19}O_4ClS_2$: C, 59.13; H, 4.26%. $\lambda_{max}$ (acetone): 624 nm ($\varepsilon$ 4.3×10$^4$). In the case of **1c** (X=$OCH_3$), the residue from diethyl ether was washed with glacial acetic acid (50 ml) containing perchloric acid and dissolved in glacial acetic acid (100 ml) at 70 °C. After cooling, diethyl ether was added to this solution, and then **7c** was isolated in 30% yield. The other 1-benzothiopyrylium salt **6** was isolated in 39% yield from the filtrate (washed with AcOH). **7c**: NMR ($CF_3COOH$): $\delta$=3.20 (3H, s), 4.12 (3H, s), 4.22 (3H, s), 5.65 (2H, s), and 7.50—9.00 (≈8H, m). Found: C, 55.13; H, 4.03%. Calcd for $C_{22}H_{19}O_6ClS_2$: C, 55.17; H, 3.97%. $\lambda_{max}$ (acetone): 625 nm ($\varepsilon$ 6.2×10$^4$); **6**:[4] dec 200 °C (lit, 205 °C), NMR ($CF_3COOH$): $\delta$=3.25 (3H, s), 4.20 (3H, s), 7.50—8.00 (2H, m), 8.35 (1H, d, $J$=10 Hz), 8.70 (1H, d, $J$=10 Hz), and 9.60 (1H, d, $J$=10 Hz). Found: C, 45.52; H, 3.85%. Calcd for $C_{11}H_{11}O_5SCl$: C, 45.44; H, 3.79%. $\lambda_{max}$ (acetone): 415 nm ($\varepsilon$ 6.4×10$^3$).

*Oxidation of* **3a** *with Hydrogen Peroxide.* 30% Hydrogen peroxide (0.7 ml) was added to a suspended solution of **3a** (0.5 g) in acetic acid (27 ml), and the mixture was stirred at 30 °C. After 2 h, perchloric acid (0.8 ml) was added to the solution. Dilution with diethyl ether gave a crude product, which was recrystallized from acetic acid. Found: C, 56.35; H, 3.06%. NMR ($CF_3COOH$): $\delta$=2.40—3.40 (m) and 7.50—9.50 (m).

*2H-1-Benzothiopyran-2-thiones (3) and 4H-1-Benzothiopyran-4-thiones (4).* 4-Methyl (thiocoumarin) **1a**[5] (1.35 g, 7.7 mmol) and $P_2S_5$ (7.5 g, 34 mmol) were added to benzene (50 ml). The mixture was heated under reflux for 7 h and was filtered. The filtrate was evaporated, and the residue was extracted with diethyl ether. The extract was evaporated, and the resulting solid was recrystallized from EtOH to give **3a** (1.1 g, 74%). The other **3** and **4** were obtained similarly. **3a**:[6] mp 111—112 °C, Found: 62.86; H, 4.26%. Calcd for $C_{10}H_8S_2$: C, 62.50; H, 4.17%. **3b**: 67%, mp 136—137 °C, Found: C, 64.03; H, 4.94%. Calcd for $C_{11}H_{10}S_2$: C, 64.08; H, 4.85%. **3c**: 42%, mp 150—151 °C. Found: C, 59.10; H, 4.57%. Calcd for $C_{11}H_{10}OS_2$: C, 59.46; H, 4.50%. **4a**:[7] 40%, mp 107—108 °C, Found: C, 62.57; H, 4.26%. Calcd for $C_{10}H_8S_2$: C, 62.50; H, 4.17%. **4b**: 15%, mp 134—136 °C, Found: C, 63.87; H, 4.76%. Calcd for $C_{11}H_{10}S_2$: C, 64.08; H, 4.85%. **4c**: 21%, mp 138—140 °C, Found: C, 58.97; H, 4.56%. Calcd for $C_{11}H_{10}OS_2$: C, 59.46; H, 4.50%.

The authors wish to acknowledge the assistance of N. Yoshikawa and M. Hirano.

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