

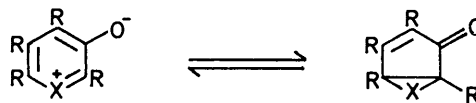
## Pyrylium Salts. Part VI.<sup>1</sup> Derivatives of 3,11-Dithiatricyclo[5.3.1.1<sup>2,6</sup>]-dodecane by Dimerisation of Thiopyrylium-3-olates

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Thiopyrylium-3-olate and its 5-methyl homologue have been synthesised from thiopyran-3-ones and isolated as perchloric acid salts. The thiopyrylium salts are readily dimerised to give stereoisomeric 3,11-dithiatricyclo[5.3.1.1<sup>2,6</sup>]dodecane derivatives with the *syn*-isomer as the major product. Spectroscopic and X-ray data for the isomers are discussed.

THE chemistry of thiopyrylium betaines has received little attention whereas their nitrogen analogues, the pyridinium-3-olates, have been widely investigated. The simple thiopyrylium-3-olates are expected to be more aromatically stabilized than the isoelectronic pyrylium analogues as reflected in the relative stabilities of their cations.<sup>2</sup> The low aromatic stabilisation of pyrylium betaines, even when aromatic substituents are present, is reflected in their ready isomerisation to the valence-isomeric 6-oxabicyclo[3.1.0]hex-3-en-2-ones (Scheme 1; X = O) and the ease with which these compounds react with dipolarophiles in 1,3-dipolar addition reactions.<sup>3,4</sup> We have described previously a synthesis of a benzo-homologue of thiopyrylium-3-olate (2-benzothiopyrylium-4-olate) and its ready dimerisation

to the *syn*- and *anti*-isomers of 5,6,12,13-tetrahydro-5,13:6,12-bisepithiodibenzo[*a,f*]cyclodecene-7,14-dione (11) (Scheme 3).<sup>1</sup> The corresponding oxygen analogues have also been prepared but the yields are lower owing



SCHEME 1

to the ready polymerisation of the benzopyrylium salt.<sup>5</sup> Here we describe a synthesis of the perchloric acid salt of the parent thiopyrylium-3-olate (5) (Scheme 2) and its 5-methyl homologue (6) and have studied their dimerisation. An almost equimolar isomeric mixture of

<sup>1</sup> Part V, K. Undheim and S. Baklien, *J.C.S. Perkin I*, 1975, 1366.

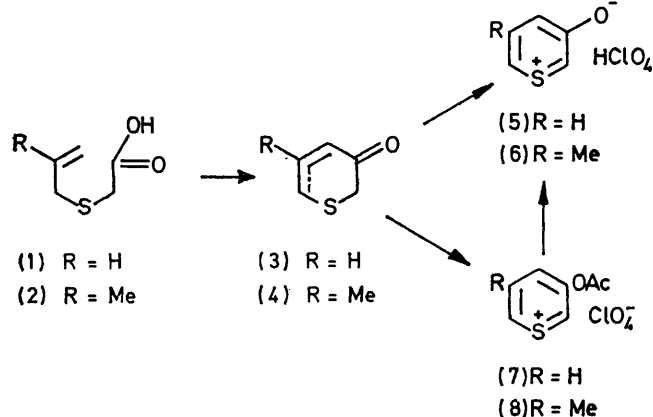
<sup>2</sup> J. Degani, R. Fochi, and C. Vincenzi, *Boll. sci. Fac. Chim. ind. Bologna*, 1965, **23**, 21.

<sup>3</sup> E. F. Ullman and W. A. Henderson, *J. Amer. Chem. Soc.*, 1966, **88**, 4942.

<sup>4</sup> J. M. Dunston and P. Yates, *Tetrahedron Letters*, 1964, 505.

<sup>5</sup> B. P. Nilsen and K. Undheim, unpublished data.

thiopyran-3(4*H*)-one and the -3(6*H*)-one (3) is formed on cyclisation of allylthioglycolyl chloride with aluminium chloride.<sup>6</sup> The 5-methyl homologue is similarly obtained as the -3(6*H*)-one (4);<sup>6</sup> variation in the cyclisation



SCHEME 2

conditions has been reported to give a mixture of the 4*H*- and 6*H*-isomers.<sup>7</sup> The yield in the cyclisation was improved over that reported<sup>6</sup> by slower addition of the acid chloride to the reaction medium. Treatment of the isomeric thiopyranones (3) or (4) with triphenylmethyl perchlorate in acetonitrile led to hydride abstraction and formation of the thiopyrylium betaines [(5) and (6)] in good yields as the perchloric acid salts. The use of a solution of acetic acid and acetic anhydride as solvent in the hydride abstraction furnished the 3-acetoxythiopyrylium perchlorates [(7) and (8)], which were readily deacetylated by trifluoroacetic acid in the cold.<sup>1</sup> The structural assignments for the products agree with the n.m.r. spectra (solvent CD<sub>3</sub>CN), which are characterised by low-field aromatic proton absorption. The chemical shifts for H-2 and H-6 in the acetate (8) overlap at  $\tau$  0.3, and the two low-field proton signals of (7) were at  $\tau$  0.1 and 0.0, in agreement with the chemical shift ( $\tau$  0.0) reported<sup>8</sup> for the  $\alpha$ -protons in the fluoroborate of the unsubstituted thiopyrylium cation. The chemical shifts for H-2 and H-6 in the hydroxy-analogues were  $\tau$  0.6 and 0.2 (5) and  $\tau$  1.0 and 0.7 (6). The assignment of chemical shifts follows from n.m.r. decoupling experiments or from deuteration experiments; thus 5-methylthiopyran-3(6*H*)-one (4) was deuterated selectively in the 2-position in alkaline deuterium oxide before the hydride abstraction reaction. The long-wave u.v. absorption band (solvent MeCN) for the hydroxy-derivatives is at *ca.* 325 nm and for the acetates at *ca.* 300 nm; these are comparable to the 288 nm band for the 3-hydroxy-*N*-methylpyridinium cation in aqueous solution.<sup>9</sup> The positional change in absorption maxima follows the expected direction for the interchange of sulphur and nitrogen heteroatoms.<sup>10</sup>

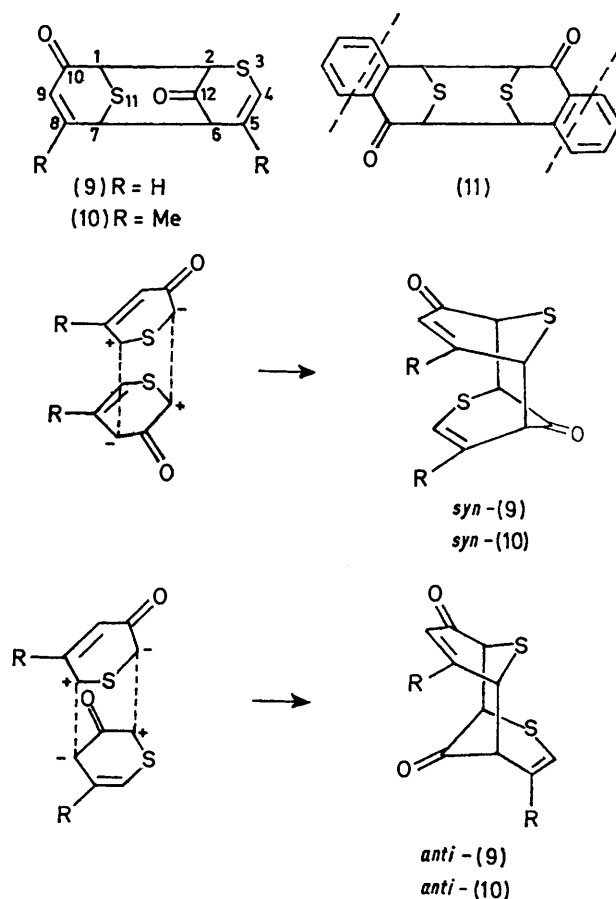
<sup>6</sup> K. Sato, S. Inoue, and K. Kondo, *J. Org. Chem.*, 1971, **36**, 2077.

<sup>7</sup> W. C. Lumma and G. A. Berchtold, *J. Org. Chem.*, 1969, **34**, 1566.

<sup>8</sup> K. Dimroth, W. Kinzebach, and M. Soyka, *Chem. Ber.*, 1966, **99**, 2351.

The thiopyrylium salts are fairly soluble in polar organic solvents, and are attacked by water. Treatment of the salts (5) and (6) in tetrahydrofuran with triethylamine gave a greenish-yellow colouration which quickly faded to give a solution of dimeric products. The ready dimerisation demonstrates that simple thiopyrylium betaines are highly reactive in the absence of strongly stabilising groups. Simple pyridinium analogues, however, do not show any pronounced tendency for dimerisation but possess 1,3-dipolar reactivity in cycloaddition reactions under forcing conditions.<sup>11</sup> Addition of triethylamine to the salts (5) and (6) in the presence of the usual dipolarophiles, however, resulted in selective dimerisation as observed for the benzo-homologue.<sup>1</sup>

The dimeric products were isolated in 70–80% yield. Two isomers were formed from the methyl derivative (6), in the ratio 12:1, whereas a homogenous product was isolated from the parent betaine (5). The i.r. spectra (KBr) for both dimers from (6) show unsaturated and



SCHEME 3

saturated carbonyl absorption at 1 655 and 1 705 cm<sup>-1</sup>, respectively; the corresponding bands of the dimer

<sup>9</sup> D. E. Metzler and E. E. Snell, *J. Amer. Chem. Soc.*, 1955, **77**, 2431.

<sup>10</sup> S. F. Mason, in 'Physical Methods in Heterocyclic Chemistry,' ed. A. R. Katritzky, Academic Press, New York and London, 1963, vol. 2, p. 1.

<sup>11</sup> A. R. Katritzky and Y. Takeuchi, *J. Chem. Soc. (C)*, 1971, 874.

from (5) were at 1 660 and 1 715  $\text{cm}^{-1}$ . The u.v. absorptions at 225–235 and 290–300 nm support the functional group deductions from the i.r. data, and the n.m.r. spectra (see later) show two differently substituted double bonds. The type of dimerisation observed for 2-benzothiopyrylium to form analogues of structure (11) is hence excluded.

The dimeric products were shown by X-ray analyses to have the structures (9) and (10), each of which can exist in an *anti*- or a *syn*-form; the dimer (9) and the major isomer (10) have the *syn*-configuration.<sup>12</sup> \* The carbon–sulphur bond distances correspond closely to the normal values for S–C( $sp^2$ ) and S–C( $sp^3$ ). The C(6)–C(7) bond length (1.58 Å) for the *syn*-isomers is *ca.* 0.01 Å shorter in *anti*-(10). The other interplanar bond [C(1)–C(2)] in *syn*-(9) (1.56 Å) and *syn*-(10) (1.55 Å) is also longer than the normal C–C bond (1.54 Å). The stretching of the C(6)–C(7) bond may in part be caused by repulsion between the  $\pi$ -electron clouds of the two double bonds; thus the vinylic carbon atoms C-5 and C-8 are 2.82 Å apart in *syn*-(10). The dimers can be regarded as 1-thian-4-one systems; the *syn*-isomer is locked in the boat conformation and the *anti*-isomer in the chair conformation. The torsion angles between H-1 and H-2 and between H-6 and H-7 in *syn*-(9) are  $1.5 \pm 2$  and  $12 \pm 2^\circ$ , in *syn*-(10)  $4.2 \pm 3.8$  and  $14.8 \pm 2.8$ , and in *anti*-(10)  $64.5 \pm 3.5$  and  $66.5 \pm 3.5^\circ$ , respectively. The coupling constants between the vicinal methine protons were *ca.* 10 Hz for the *syn*-form and *ca.* 4 Hz for the *anti*-form. Secondary coupling of *ca.* 2 Hz occurs over the sulphur bridge between H-1 and H-7, as observed for the benzo-analogue (11). The low-field proton signal ( $\tau$  2.7) in the spectrum of *syn*-(9) is assigned to H-8, which is a  $\beta$ -proton in an  $\alpha\beta$ -unsaturated carbonyl system. The chemical shifts for the other protons were assigned by means of scale expansions and decoupling experiments, and are very similar to those of the respective protons in thiopyran-3(4*H*)- and 3(6*H*)-one(3).<sup>6</sup> The methyl protons in the isomers (10) resonate as two singlets at  $\tau$  8.0 and 8.2; the former is ascribed to the 8-Me, which corresponds to the methyl group in the thiopyran (4).

Interconversion of the *syn*- and *anti*-isomers is not possible without cleavage and re-formation of bonds, which precludes isomerisation under the reaction conditions. The preferential formation of the *syn*-isomer may be associated with secondary orbital overlap from the olefinic  $\pi$ -orbitals in the transition state<sup>13</sup> and is related to the preferential formation of *syn*-(11) from 2-benzothiopyrylium-4-olate.<sup>1</sup> The formal charges in 1,3-dipole formation from the thiopyrylium betaine can be located on either side of the carbonyl group or on either side of the sulphur atom. The dimerisation may be stepwise or concerted in such a way that the two new  $\sigma$ -bonds are not developed to the same extent during the

reaction in order to allow for the different accommodation of the two double bonds.

#### EXPERIMENTAL

N.m.r. spectra were recorded with a Varian A-60A or A-100 instrument, u.v. spectra with a Cary 14 spectrophotometer, and mass spectra with an A.E.I. 902 spectrometer.

**5-Methylthiopyran-3(6*H*)-one (4).**—This was prepared as described previously.<sup>6</sup> The yield was increased from 49 to 70% by increasing the time from 3.5 to 7 h for addition of (2-methylallylthio)acetyl chloride to the aluminium chloride medium; the product showed  $\tau$  [( $\text{CD}_3$ )<sub>2</sub>SO] 8.0 (Me), 6.8 (2-H<sub>2</sub>), 6.7 (6-H<sub>2</sub>), and 4.2 (4-H).

**3-Hydroxythiopyrylium Perchlorate (5).**—A mixture (1 : 1) of thiopyran-3(4*H*)-one and -3(6*H*)-one<sup>6</sup> (2.28 g, 0.02 mol) was dissolved in anhydrous acetonitrile (20 ml), and triphenylmethyl perchlorate<sup>14</sup> (6.84 g, 0.02 mol) was added. The mixture was heated at 55–60 °C for 10 min and after cooling poured into anhydrous ether (200 ml). The precipitated *perchlorate* was washed with ether and methylene chloride before recrystallisation from chloroform; yield 2.50 g (60%), m.p. 70 °C (decomp.) (Found: C, 28.45; H, 2.6.  $\text{C}_8\text{H}_4\text{OS}, \text{HClO}_4$  requires C, 28.2; H, 2.4%);  $\tau$  [( $\text{CD}_3$ )<sub>2</sub>CO] 1.4 (H-4), 1.1 (H-5), 0.6 (H-2), and 0.2 (H-6);  $\lambda_{\text{max}}$  (MeCN) 277 (log  $\epsilon$  4.18), 248 (3.47), and 329 nm (3.53).

**3-Hydroxy-5-methylthiopyrylium Perchlorate (6).**—The *perchlorate* (6) was prepared as above from 5-methylthiopyran-3(6*H*)-one in 80% yield; m.p. 66 °C (decomp.) (from chloroform) (Found: C, 31.85; H, 3.1.  $\text{C}_9\text{H}_6\text{OS}, \text{HClO}_4$  requires C, 31.75; H, 3.1%);  $\tau$  ( $\text{CD}_3\text{CN}$ ) 7.3 (Me), 1.8 (H-4), 1.0 (H-2), and 0.7 (H-6);  $\lambda_{\text{max}}$  (MeCN), 223 (log  $\epsilon$  4.32), 252 (3.57), 272 (3.33), and 324 nm (3.71).

**3-Acetoxythiopyrylium Perchlorate (7).**—A mixture (1 : 1) of thiopyran-3(4*H*)-one and -3(6*H*)-one (2.28 g, 0.02 mol) was dissolved in acetic anhydride (10 ml) and acetic acid (10 ml), and triphenylmethyl perchlorate (6.84 g, 0.02 mol) was added. The resultant solution was heated at 55–60 °C for 5 min, cooled, and poured into anhydrous ether (200 ml). The precipitated *perchlorate* was washed with ether and methylene chloride before recrystallisation from acetic acid; yield 4.09 g (80%), m.p. 99 °C (decomp.) (Found: C, 32.9; H, 2.95.  $\text{C}_7\text{H}_7\text{ClO}_6\text{S}$  requires C, 32.95; H, 2.8%);  $\tau$  ( $\text{CD}_3\text{CN}$ ) 7.6 (Ac), 1.2 (H-4), 1.1 (H-5), 0.1 (H-2), and 0.0 (H-6);  $\lambda_{\text{max}}$  (MeCN) 211 (log  $\epsilon$  4.30), 252 (3.62), and 298 nm (3.60);  $\nu_{\text{max}}$  (KBr) 1 765  $\text{cm}^{-1}$  (CO).

**3-Acetoxy-5-methylthiopyrylium Perchlorate (8).**—The *perchlorate* (8) was prepared as above from 5-methylthiopyran-3(6*H*)-one in 90% yield; m.p. 105 °C (decomp.) (from acetic acid) (Found: C, 35.8; H, 3.6.  $\text{C}_8\text{H}_{10}\text{ClO}_6\text{S}$  requires C, 35.75; H, 3.4%);  $\tau$  ( $\text{CD}_3\text{CN}$ ) 7.6 (Ac), 7.2 (Me), 1.4 (H-4), and 0.3 (H-2 and -6);  $\lambda_{\text{max}}$  (MeCN) 209 (log  $\epsilon$  4.51), 260 (3.53), and 303 nm (3.61);  $\nu_{\text{max}}$  (KBr) 1 775  $\text{cm}^{-1}$  (CO).

**The Hydroxythiopyrylium Perchlorates (5) and (6) by Deacetylation.**—The 3-acetoxythiopyrylium perchlorate (7) or (8) (0.01 mol) was dissolved in trifluoroacetic acid and the solution left at room temperature for 5 h before evaporation. The hydroxy-compound was obtained in 70–80% yield on recrystallisation as above.

<sup>12</sup> P. Groth, *Acta Chem. Scand. (A)*, 1975, **29**, 453.

\* The X-ray data are available as Supplementary Publication No. SUP 21477 (10 pp.). For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

<sup>13</sup> J. W. Lown and K. Matsumoto, *Canad. J. Chem.*, 1971, **49**, 3446 and references therein.

<sup>14</sup> H. J. Dauben, L. R. Hönnen, and K. M. Harmon, *J. Org. Chem.*, 1960, **25**, 1442.

syn-3,11-Dithiatricyclo[5.3.1.1<sup>2,6</sup>]dodeca-4,8-diene-10,12-dione (9).—3-Hydroxythiopyrylium perchlorate (2.12 g, 0.01 mol) was dissolved in anhydrous tetrahydrofuran (200 ml) and a solution of triethylamine (1.01 g, 0.01 mol) in the same solvent (50 ml) was added dropwise with stirring over 1 h at 0 °C. The mixture was then washed with water, dried, and evaporated. The residue was dissolved in methylene chloride and chromatographed on silica gel (0.2–0.5 mm). The *title compound* was eluted with methylene chloride and recrystallised from chloroform; yield 0.80 g (70%), m.p. 185–186 °C. (Found: C, 53.45; H, 3.65. C<sub>10</sub>H<sub>8</sub>O<sub>2</sub>S requires C, 53.55; H, 3.6%);  $\tau$  [(CD<sub>3</sub>)<sub>2</sub>SO] 6.4 (H-6,  $J_{6,7}$  10,  $J_{5,6}$  8 Hz), 5.7 (H-1, -2, and -7), 4.2 (H-5,  $J_{4,5}$  10 Hz), 4.1 (H-9,  $J_{8,9}$  10 Hz), 3.7 (H-4), and 2.7 (H-8,  $J_{7,8}$  8 Hz);  $\lambda_{\max}$  (MeCN) 224 (log  $\epsilon$  3.90) and 300 nm (2.81);  $\nu_{\max}$  (KBr) 1 660 (unsat. CO) and 1 715 cm<sup>-1</sup> (sat. CO);  $m/e$  224 (86%,  $M^+$ ), 196(8), 191 (13), 163 (32), 113 (43), 112 (100), 96 (39), and 84 (74).

syn- and anti-5,8-Dimethyl-3,11-dithiatricyclo[5.3.1.1<sup>2,6</sup>]dodeca-4,8-diene-10,12-dione (10).—These were synthesised as above from 3-hydroxy-5-methylthiopyrylium perchlorate.

The crude product was dissolved in methylene chloride and chromatographed on a silica gel column (0.2–0.5 mm). The minor anti-*isomer* was eluted first with methylene chloride in 6% yield; m.p. 167–168 °C (from chloroform) (Found: C, 57.2; H, 4.75. C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>S<sub>2</sub> requires C, 57.1; H, 4.75%);  $\tau$  [(CD<sub>3</sub>)<sub>2</sub>SO] 8.2 (5-Me,  $J_{4,Me}$  1.5 Hz), 8.0 (8-Me,  $J_{9,Me}$  1.5 Hz), 6.8 (H-6,  $J_{6,7}$  4 Hz), 6.4 (H-2,  $J_{1,2}$  4 Hz), 6.2 (H-1,  $J_{1,7}$  2.5 Hz), 6.0 (H-7), 4.2 (H-9), and 3.8 (H-4);  $\lambda_{\max}$  (MeCN) 237 (log  $\epsilon$  4.10) and 293 nm (2.98);  $\nu_{\max}$  (KBr) 1 655 (unsat. CO) and 1 705 cm<sup>-1</sup> (sat. CO);  $m/e$  252 (100%,  $M^+$ ), 224(8), 219(23), 191(19), 127(31), 126(32), 110(23), 98(29), and 97(30). The major syn-*isomer* was eluted next in 75% yield; m.p. 185–186 °C (from chloroform) (Found: C, 57.2; H, 4.8%);  $\tau$  [(CD<sub>3</sub>)<sub>2</sub>SO] 8.2 (5-Me,  $J_{4,Me}$  1.5 Hz), 8.0 (8-Me,  $J_{9,Me}$  1.5 Hz), 6.5 (H-6,  $J_{6,7}$  10 Hz), 5.8 (H-1 and -2,  $J_{1,7}$  2 Hz), 5.6 (H-7), 4.2 (H-9), and 4.0 (H-4);  $\lambda_{\max}$  (MeCN) 233 (log  $\epsilon$  4.07) and 287sh nm (2.94);  $\nu_{\max}$  (KBr) 1 655 cm<sup>-1</sup> (unsat. CO) and 1 705 cm<sup>-1</sup> (sat. CO);  $m/e$  252 (35%,  $M^+$ ), 219(8), 209(12), 198(97), 191(14), 127(22), 126(82), 110(26), 98 (37), and 97(100).

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