

Pyrylium Salts. Part V.¹ 5,6,12,13-Tetrahydro-5,13:6,12-bisepithiodibenzo[*a,f*]cyclodecene-7,14-diones by Dimerisation of 2-Benzothiopyrylium-4-olate

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2-Benzothiopyrylium-4-olate, synthesised from isothiochroman-4-one and isolated as the perchloric acid salt, is readily dimerised to give stereoisomeric 5,13:6,12-bisepithiodibenzo[*a,f*]cyclodecenes; the *syn*-isomer is the major product. Spectroscopic data for both isomers and *X*-ray data for the *syn*-form are discussed.

THREE-MEMBERED rings containing one heteroatom react with 1,3-dipolarophiles through an ylide intermediate.^{2,3} When such a three-membered ring is fused onto another ring of medium size, thermal conrotatory ring opening is not permitted by the geometry of the system, whereas disrotatory photochemical opening is allowed.⁴ In fused indeno-systems, however, both the formally disallowed and the allowed opening of the three-membered ring occur, as shown by 1,3-dipolar

addition reactions.⁴⁻⁶ In the absence of a suitable dipolarophile, dimerisation may take place.^{7,8} The first isomerisation reactions of this type were reported for phenyl-substituted indanone epoxides:^{7,9} these (1; X = O) are valence isomers of 2-benzopyrylium-4-olate (3; X = O). The 2,3-diphenyl epoxide (1; X = O) exists in an equilibrium with the mesoionic system (3); the equilibrium position is much in favour of the epoxide isomer.^{7,9} Presumably the reactive carbonyl

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⁴ J. W. Lown and K. Matsumoto, *J. Org. Chem.*, 1971, **36**, 1405.

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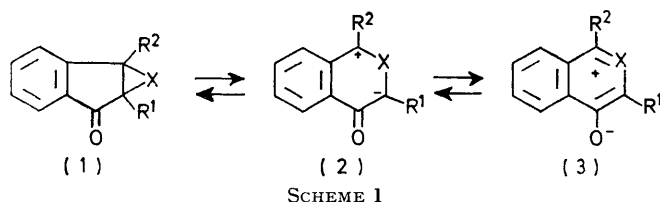
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⁷ E. F. Ullman and J. E. Milks, *J. Amer. Chem. Soc.*, 1964, **86**, 3814.

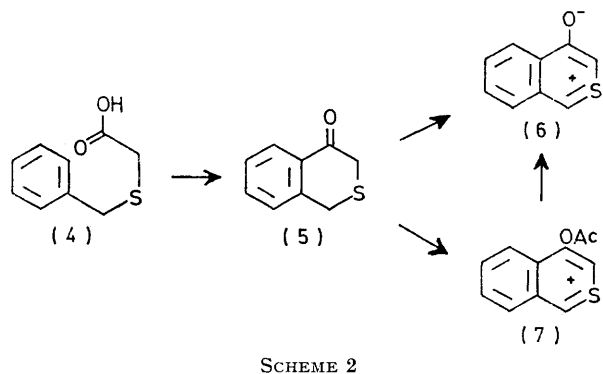
⁸ H. E. Zimmerman and R. D. Simkin, *Tetrahedron Letters*, 1964, 1847.

⁹ E. F. Ullman and W. A. Henderson, *J. Amer. Chem. Soc.*, 1966, **88**, 4942.

ylide (2) may arise from either of these forms. The related isomerisation of isoquinolinium-4-olates (3; X = NR) to 1a,6a-dihydroindeno[1,2-*b*]azirin-6(1*H*)-ones (1; X = NR) does not appear to have been reported; isomerisation in the opposite direction, however, constitutes a ready synthesis of isoquinolinium-4-olates.¹⁰ The azomethine ylide structure (2) explains the 1,3-dipolar character demonstrated by cycloadditions of *N*-methylisoquinolinium-4-olate;¹¹ 1,3-dipolar character has also been demonstrated for pyridinium-3-olates.¹² Pirylium-3-olate and its thio-analogue, however, have not been available for such studies.



The simple pyrylium- and thiopyrylium-3-olates are expected to be unstable, as reflected in the low stabilities of the pyrylium and thiopyrylium cations.¹³ We describe here a study of 2-benzothiopyrylium-4-olate (6). Synthesis of this compound from its valence isomeric episulphide (1; X = S) by analogy to the photolytic isomerisation of the aza-analogues to the isoquinolinium-4-olates¹⁰ was not attempted in view of the instability of activated episulphides; the synthesis was in fact carried out according to Scheme 2.



(Benzylthio)acetic acid (4) was cyclised to isothiochroman-4-one (5) by means of phosphorus pentoxide.¹⁴ Pirylium cations are readily generated from 4*H*-pyrans through hydride abstraction by triphenylmethyl perchlorate;¹⁵ the trityl reagent was also successful in the present case and 2-benzothiopyrylium-4-olate, as its perchloric acid salt, could be recrystallised from acetic acid. Preparation in the presence of acetic anhydride and acetic acid gave the 4-acetoxythiopyrylium cation

(7) in excellent yield. The acetoxy-derivative (7) in solution in trifluoroacetic acid (TFA) was completely deacetylated after a few hours at room temperature, and the mesoionic compound (6) was again obtained as the perchloric acid salt. The n.m.r. spectra of the thiopyrylium salts in CD₃CN are characterised by low field absorptions, especially for H-1 which resonates as a doublet at $\tau -0.5$ for (6) and at -0.9 for the acetate (7); in isoquinolinium analogues examined the chemical shift for H-1 is in the range $\tau 0.4-1.1$.^{10,16}

The thiopyrylium salt (6) is readily attacked by water and is thus less aromatically stabilised than its aza-analogues. Addition of triethylamine to a solution of the perchloric acid salt of (6) in acetonitrile and tetrahydrofuran resulted in a deeper yellowish-green colouring; the colour had faded after a few min. The colouring was sustained for a longer period at -60°C , but the same reaction took place as discussed below. Addition of the perchloric acid salt of (6) to a solution of potassium *t*-butoxide gave the same major product but the total product was more heterogeneous. U.v. absorptions recorded during the addition of triethylamine showed the disappearance of the long-wave 390 nm band of the perchloric acid salt (6) with the transient appearance of two new bands at 355 and 436 nm; λ_{max} for the final long-wave band was *ca.* 365 nm. The final spectrum was related to that of isothiochroman-4-one recorded in acetonitrile. The first shift in the u.v. maxima is attributed to the phenol-phenolate shift due to generation of the mesoionic system (6). The final product was composed of two substances without salt-like characteristics. These were separated by column chromatography on silica gel; both showed a molecular ion at *m/e* 324 and had related mass spectral fragmentation patterns, this implied that dimerisation of the thiopyrylium (6) had occurred. The isomer ratio was 1 : 7. The same product was obtained in attempted cycloaddition reactions with the usual 1,3-dipolarophiles during addition of the triethylamine; no cycloadducts were formed. Dimerisation in the analogous isoquinolinium series has not been reported. The equilibrium mixture of 1,3-diphenyl-2-benzopyrylium-4-olate (3; X = O) and its epoxide (1), however, is readily dimerised in such a way that the carbonyl group in one epoxide molecule (1) adds as a 1,3-dipolarophile to the carbonyl ylide (2).⁷ Spectroscopic data exclude such a dimerisation in the present case. Photolysis of the 2-methyl-3-phenyl epoxide (1) has yielded 6% of a dimeric material. The structure suggested⁸ from spectroscopic evidence is analogous to structure (9) described below for the thiopyrylium dimer; no further stereochemistry was discussed. The spectroscopic data for the thiopyrylium dimers suggest that both have the same carbon skeleton. They both have a strong carbonyl absorption band at

¹⁰ P. E. Hansen and K. Undheim, *J.C.S. Perkin I*, 1975, 305.
¹¹ N. Denis, A. R. Katritzky, and Y. Takeuchi, *J.C.S. Perkin I*, 1972, 2054.

¹² A. R. Katritzky and Y. Takeuchi, *J. Chem. Soc. (C)*, 1971, 874.

¹³ J. Degani, R. Fochi, and C. Vincenzi, *Boll. sci. Fac. Chim. ind. Bologna*, 1965, 23, 21.

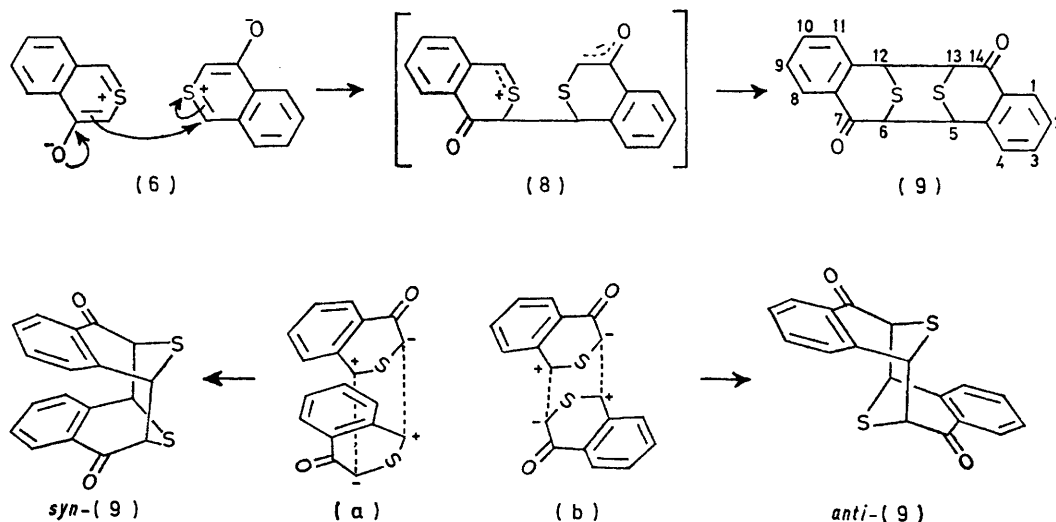
¹⁴ C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Amer. Chem. Soc.*, 1963, 85, 2278.

¹⁵ K. Undheim and E. T. Østensen, *Acta Chem. Scand.*, 1973, 27, 1385.

¹⁶ K. Undheim and P. E. Hansen, *Chemica Scripta*, 1973, 3, 113.

1670 cm^{-1} (KBr). The major isomer has u.v. bands (MeCN) at 292 and 371 nm and the minor isomer bands at 298, 350, and 365 nm. The n.m.r. spectra contain signals for two coupled methine protons besides the aromatic protons. The data are consistent with face-to-face dimerisation. A double-layer transition state in which the carbonyl groups lie above each other on the same side is unlikely because of directional polarisation in the monomers which results in dipolar or electrostatic repulsion. With the carbonyl groups arranged on opposite sides, however, attractive forces exist between the charge centres; the *syn*- (a) and the *anti*- (b) arrangements lead to the respective dimers shown (Scheme 3).

constant is 12 Hz. The methine protons show further secondary coupling (2 Hz). When *syn*-(9) is dissolved in $[\text{D}_6]\text{dimethyl sulphoxide}$ and dilute sodium deuterium oxide is added, the protons next to the carbonyl groups are rapidly exchanged; the benzyl methine protons are also easily exchanged. After exchange of the two protons next to the carbonyl groups (H-6 and -13) the singlet due to remaining two benzyl protons appeared broad, presumably because of long-range aromatic couplings. The secondary splitting of 2 Hz disappeared on deuteration and is therefore ascribed to coupling between the methine protons on either side of the sulphur bridge. A secondary coupling of about 2 Hz is also seen



SCHEME 3

From the n.m.r. spectra (see later) the major isomer was assigned the *syn*-structure, and this was confirmed by X-ray analysis.¹⁷ The molecule has a two-fold axis of symmetry. The faces are planar within 0.1 Å with the sulphur atom 1 Å out of the plane. The planes are tilted; the internal angle is 113° between the planes and the plane through the carbon atoms of the dithian ring. The distance between a carbonyl carbon (C-7) and the closest non-bonded aromatic carbon atom (C-4a) is 2.763 Å. The shortest interplanar distance between aromatic carbon atoms (C-4a and -11a) is 3.242 Å; the normal stacking distance for aromatic rings is 3.40 Å in crystals.¹⁸ In *syn*-(9) the benzene rings are displaced sideways relative to one another, which brings the π -electrons of the carbonyl groups near to the π -electrons of the benzene rings. The short interplanar distance implies repulsion between the π -systems; this is reflected in the C(5)–C(6) and C(12)–C(13) bond lengths (1.577 Å), which are significantly longer than the normal carbon–carbon single bond; the carbon–sulphur bonds, however, have normal values (1.811 and 1.815 Å).¹⁷ The sulphur atoms can be regarded as part of a 1,4-dithian ring locked in the boat conformation. Accordingly the torsion angle between the vicinal protons is small; the experimental value is $10.7 \pm 3^\circ$,¹⁷ and the vicinal coupling

in the spectrum of the *anti*-isomer, which is rigidly locked in a chair conformation of the 1,4-dithian ring; the vicinal coupling constant of the methine protons was 5.5 Hz. In both isomers the methine protons on either side of the sulphur atom are nearly synperiplanar; this may be the reason for the magnitude of the observed coupling. The resonances for the aromatic protons in the *syn*-isomer occur at higher field (τ 2.6–3.1) than in the *anti*-isomer (τ 1.8–2.7). The aromatic protons in isothiochroman-4-one (5) resonate in the region τ 2.0–2.8. The major shift difference occurs in the case of the aromatic proton *ortho* to the carbonyl group, which is responsible for the lowest-field aromatic signal in *anti*-(9) and (5). In the *syn*-isomer this proton lies above a benzene ring and is thus in the aromatic shielding zone which effectively counteracts the anisotropy effect from the carbonyl group.

The mass spectra of the dimers contain the same major fragments but differ in relative intensities. The base peak is at m/e 134 ($\text{C}_8\text{H}_6\text{S}$) and the relative intensities of the molecular ion are 15 and 30% for the *syn*- and *anti*-isomer, respectively. The spectrum from the perchloric

¹⁷ P. Groth, *Acta Chem. Scand.*, A, in the press.

¹⁸ D. J. Cram and J. M. Cram, *Accounts Chem. Res.*, 1971, 4, 204.

acid salt of the thiopyryliumolate (6) shows dominating pyrolytic dimerisation before evaporation and the spectrum resembles that of the *anti*-isomer in relative fragment intensities. Direct evaporation of the species (6) appears to be insignificant. This observation illustrates the difference in stabilisation by sulphur and nitrogen atoms of cationic aromatic systems: simple isoquinolinium-4-olates and pyridinium-3-olates are readily evaporated in the mass spectrometer without isomerisation.^{19,20}

The benzene rings in the dimer (9) are planar, not bent as in many highly strained cyclophane systems.¹⁸ The structure is rigid because of the sulphur cross-bonding preventing isomer interconversion; the *anti*-isomer is probably for steric reasons thermodynamically the more stable. The *syn*-isomer bears some resemblance to the symmetrical sandwich-like [2,2]orthocyclophane formed by intramolecular photodimerisation of 1,3-bis-(α -naphthyl)propane;²¹ the isomer formed is the one which has maximum overlap of the π -orbitals in the transition state.²¹ Preferential *endo*-adduct formation in 1,3-dipolar cycloadditions and in Diels-Alder reactions has been interpreted in terms of secondary orbital overlap in the transition state.⁵ Similar arguments may be advanced for the preferential formation of the *syn*-isomer of (9), although the dimerisation may be a two-step process *via* an intermediate zwitterion-like structure (8). Another possibility also exists for stereochemical direction in the dimerisation of (6): differential polarisation in the benzene rings, which is likely because of the charge separation in the hetero-rings, may result in weak dipolar attraction between the benzene rings when arranged as in (a). The stereochemistry of the final product is already determined by the first carbon-carbon bond formation in the absence of epimerisation. That the dimerisation reaction is fast and selective is shown by the failure of concerted 1,3-dipolar cycloadditions with all the dipolarophiles tried.

EXPERIMENTAL

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

Isothiochroman-4-one (5), prepared as described,¹⁴ had τ [(CD₃)₂SO] 6.4 (2 \times H-3), 6.0 (2 \times H-1), 2.0–2.2 (H-5), and 2.3–2.8 (3H, aromatic); λ_{\max} (MeCN) 248 (log ϵ 3.99), 291 (3.23), and 344 nm (2.36); *m/e* 164 (63%, M⁺), 118 (100), 90 (59), and 89 (17).

4-Hydroxy-2-benzothiopyrylium Perchlorate (6).—(a) Isothiochroman-4-one (3.28 g, 0.020 mol) was dissolved in anhydrous acetonitrile (20 ml) and triphenylmethyl perchlorate²² (6.50 g, 0.019 mol) was added. The reaction mixture was heated at 55–60 °C for 10 min. The cold solution was poured into anhydrous ether (250 ml) and the

precipitated greenish perchlorate collected. After washing with anhydrous ether and methylene chloride the *material* was recrystallised from acetic acid; yield 4.00 g (80%), m.p. 175–176° (decomp.) (Found: C, 41.3; H, 2.8. C₉H₆O₂S.HClO₄ requires C, 41.15; H, 2.7%); τ (CD₃CN) 1.2–1.9 (4H, aromatic and H-3) and –0.5 (H-1, d, *J* 3 Hz); λ_{\max} (MeCN) 230 (log ϵ 4.23), 258 (4.51), 310 (3.68), 319 (3.60), and 390 nm (3.74); *m/e* 324 (33%, M⁺), 291 (34), 162 (90), 149 (13), 147 (14), and 134 (100).

(b) 4-Acetoxy-2-benzothiopyrylium perchlorate (3.04 g, 0.01 mol) was dissolved in trifluoroacetic acid (50 ml) and left at room temperature for 5 h. The solution was then evaporated at reduced pressure and the residue (6) recrystallised from acetic acid; yield 1.83 g (70%).

4-Acetoxy-2-benzothiopyrylium Perchlorate (7).—Isothiochroman-4-one (1.64 g, 0.01 mol) was dissolved in acetic acid (10 ml) and acetic anhydride (10 ml), and triphenylmethyl perchlorate (3.42 g, 0.01 mol) was added. The mixture was heated at 60–70 °C for 5–10 min. The progress of the reaction was indicated by the dissolution of the perchlorate and the green colour of the resultant solution. The cold solution was poured into anhydrous ether (250 ml) and the precipitated *salt* washed with ether and methylene chloride before recrystallisation from acetic acid-acetonitrile; yield 2.50 g (95%), m.p. 150° (decomp.) (Found: C, 43.6; H, 3.25. C₁₁H₈O₂S.HClO₄ requires C, 43.35; H, 2.95%); τ (CD₃CN) 7.4 (Ac), 1.2–1.9 (4H, aromatic), 0.8 (d, *J*_{1,3} 3 Hz, H-3), and –0.9br (d, H-1); λ_{\max} (MeCN) 230 (log ϵ 4.23), 258 (4.51), 310 (3.68), 319 (3.60), and 390 nm (3.74).

syn- and anti-5,6,12,13-Tetrahydro-5,13:6,12-bisepithio-dibenzo[a,f]cyclodecene-7,14-dione (9).—4-Hydroxy-2-benzothiopyrylium perchlorate (2.62 g, 0.01 mol) was dissolved in anhydrous tetrahydrofuran (150 ml) and acetonitrile (50 ml). Triethylamine (1.01 g, 0.01 mol) in tetrahydrofuran (50 ml) was added dropwise with stirring over 1 h to the solution at room temperature. A deeper yellowish-green colour appeared during the addition and disappeared rapidly afterwards. The solution 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 *syn-dimer* (major isomer) was eluted with methylene chloride after the *anti-dimer*; yield 1.19 g (74%), m.p. 335° (subl.) (from chloroform) (Found: C, 66.55; H, 3.85. C₁₈H₁₂O₂S₂ requires C, 66.65; H, 3.7%); τ [(CD₃)₂SO] 5.6 (q, *J*_{5,6} = *J*_{12,13} = 12, *J*_{5,13} = *J*_{6,12} = 2 Hz, H-6 and -13), 5.0br (q, H-5 and -12), and 2.6–3.1 (8H, aromatic); λ_{\max} (MeCN) 221 (log ϵ 4.27), 241 (4.28), 292 (3.59), and 371 nm (2.77); *m/e* 324 (15%, M⁺) 291 (22), 162 (46), 149 (83), 147 (10), and 134 (100).

The yield of the *anti-isomer* was 0.16 g (10%); m.p. 242–243 °C (from chloroform) (Found: C, 66.4; H, 3.9%). τ [(CD₃)₂SO] 6.3 (q, *J*_{5,6} = *J*_{12,13} = 5.5, *J*_{5,13} = *J*_{6,12} = 2 Hz, H-6 and -13), 5.5br (q, H-5 and -12), 1.8–2.0 (2H, aromatic *ortho* to CO), and 2.3–2.7 (6H, aromatic); λ_{\max} (MeCN) 246 (log ϵ 4.34), 298 (3.80), 350 (2.94), and 365 nm (2.95); *m/e* 324 (32%, M⁺), 291 (43), 162 (94), 149 (14), 147 (19), and 134 (100).

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²¹ E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, 1970, **92**, 703.

²² H. J. Dauben, L. R. Hönnen, and K. M. Harmon, *J. Org. Chem.*, 1960, **25**, 1442.