The Dithiole Series. Part 6.[1] Intermediacy of Spirothiopyrans in Reactions of 3,5-Disubstituted 1,2-Dithiolylium Salts with Cationic Heterocycles containing Reactive Methyl Groups

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The self-condensation of 3-methyl-5-phenyl-1,2-dithiolylium perchlorate in the presence of base gives a 2-thiophenacylidene-2*H*-thiopyran. A mechanism involving the intermediacy of a spiro-[1,2-dithiole-3,2'-2*H*-thiopyran] is proposed, and evidence is presented that the related condensations of 4,6-diaryl-2-methylthiopyrylium salts with 3,5-diaryl-1,2-dithiolylium salts proceed *via* spirobi-2*H*-thiopyrans. A stable spirothiopyran is formed in the reaction of 2,3-dimethylbenzothiazolium perchlorate with 3,5-diphenyl-1,2-dithiolylium perchlorate. Spiro-1,2-dithioles, generated by the reactions of certain bidentate nucleophiles with 2-chloro- or 2-methylthio-5-phenyl-1,2-dithiolylium salts, lose one atom of sulphur to give thiophenacylidene heterocycles, thus providing further support for the mechanism proposed for the original self-condensation.

In Part 4,[2] we reported that treatment of 3-methyl-5-phenyl-1,2-dithiolylium perchlorate (1a) with pyridine yielded a purple compound (m.p. 218°). Elemental analysis and mass spectrometry (M^+ 320) showed that the compound had been formed from two cations of the dithiolylium salt with loss of two atoms of sulphur and two protons. It was reasonable to assume that the function of the pyridine was to convert a dithiolylium ion into its conjugate base (2) which could then attack another dithiolylium ion as shown in Scheme 1 [step (i)]. Further mechanistic speculation, based on our previous experience [2,3] of reactions in the 1,2-dithiole series, led us to suggest the remaining steps of Scheme 1 and to propose formula (5a) (or that with Me and Ph interchanged) as a possible structure for the purple compound. The ring fission and loss of sulphur shown in steps (iii) and (v)

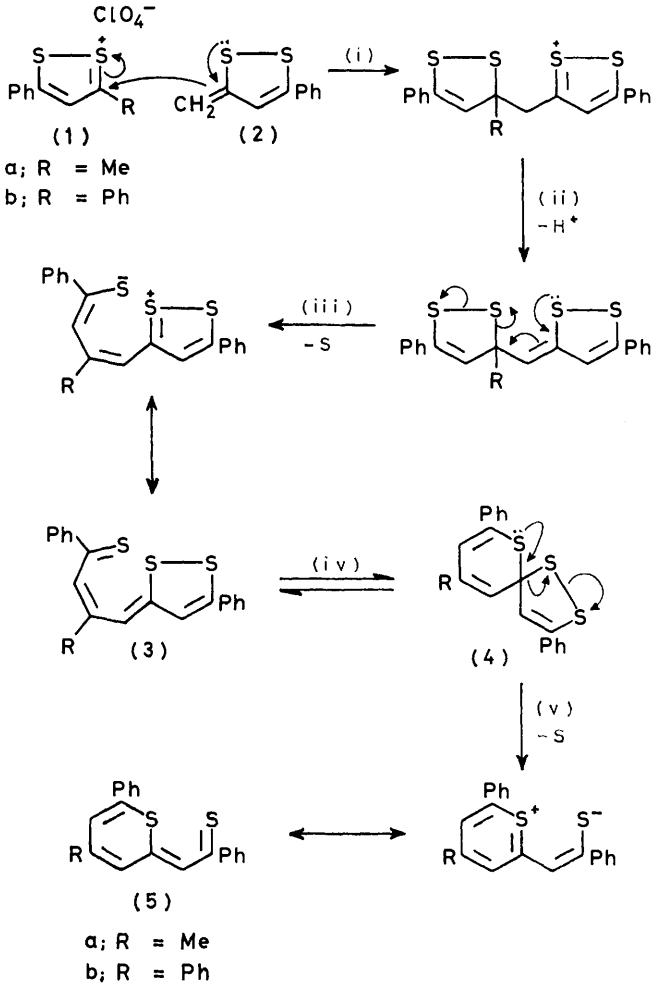
[1] Part 5, D. B. J. Easton, D. Leaver, and T. J. Rawlings, *J.C.S. Perkin I*, 1972, 41.

[2] (*a*) E. I. G. Brown, D. Leaver, and D. M. McKinnon, *J. Chem. Soc.* (*C*), 1970, 1202; (*b*) D. Leaver and D. M. McKinnon, *Chem. and Ind.*, 1964, 461.

[3] D. Leaver, D. M. McKinnon, and W. A. H. Robertson, *J. Chem. Soc.*, 1965, 32.

is a mode of reaction which has frequently been observed [3,4] after the attachment of a nucleophile to the 3-position of a 1,2-dithiolylium ion.

Evidence in support of structure (5) was obtained from the reaction of the 3-methyl-5-phenyldithiolylium salt (1a) with the 3,5-diphenyl compound (1b) in the presence of pyridine. This gave a purple compound closely resembling the product from the self-condensation of the

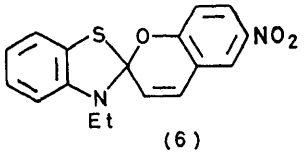


SCHEME 1

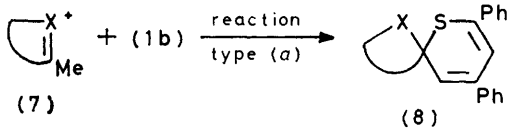
salt (1a) and identical with an authentic specimen [2] of the thiophenacylidenethiopyran (5b).

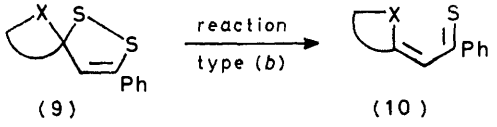
The key intermediates in Scheme 1 are the spirobiheterocycle (4) and its monocyclic precursor (3), which are partners in a valence-tautomeric equilibrium [step (iv)]. This pericyclic process is analogous to the well known [5] spiropyran–merocyanine interconversion which is responsible for thermo- and photo-chromism in compounds such as (6). In seeking analogies which might help to validate the proposed Scheme, we have therefore focussed our attention on the intermediate spiran and have carried out experiments of two types designed to show, respectively, (*a*) that spirothiopyrans (8) can indeed be formed [analogy for steps (i)—(iv)] in the base-promoted reactions of 3,5-diaryl-1,2-dithiolylium salts with cationic heterocycles containing a reactive methyl group, and (*b*) that spiro-1,2-dithioles of the type (9) can spontaneously extrude a sulphur atom [analogy for step (v)] to give thiophenacylidene heterocycles (10).

In the first experiments of type (*a*), the thiopyrylium salts (11) were chosen as reactive methyl compounds, and reaction with a dithiolylium salt (12) was expected



to give a spirobithiopyran (13). By making the aryl groups in the thiopyrylium salt different from those in the dithiolylium salt, two alternative routes to the same unsymmetrically substituted spiro-compound should thus be possible (Scheme 2). Initially, the reaction was carried out with phenyl groups in both reactants [*i.e.* (11a) and (12a)] and under the conditions (boiling in acetic acid–pyridine) which had yielded the thiophenacylidenethiopyran (5a) from the dithiolylium salt (1a). The product was not the expected spirobithiopyran (13a) but a purple salt (perchlorate), elemental analysis of which suggested $C_{33}H_{23}ClO_4S_2$ as the most probable empirical formula. It seemed likely that the salt had been





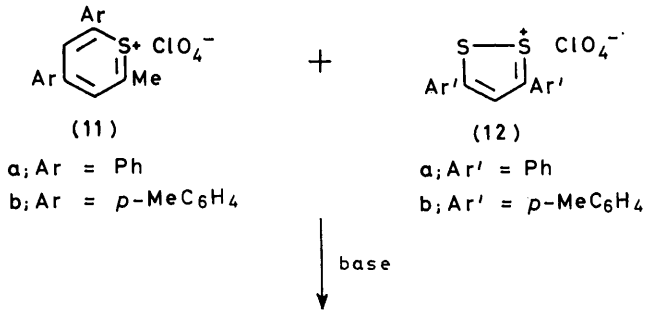
formed from the spirobithiopyran ($C_{33}H_{24}S_2$) by oxidation (formally, removal of H^-) and this suggested the structure (14a), confirmation of which was provided by synthesis of an identical product from 4,6-diphenyl-2*H*-thiopyran-2-thione (15) and 2,4-diphenylthiophen (16) by treatment with phosphoryl chloride and phosphorus pentachloride followed by perchloric acid.

A similar purple product was obtained when the reaction of a dithiolylium salt with a thiopyrylium salt was carried out with phenyl groups in one reactant and *p*-tolyl groups in the other; the product from the reaction of (11a) with (12b) was identical with

[4] E. Klingsberg, *J. Amer. Chem. Soc.*, 1961, **83**, 2934; R. Mayer and H. Hartmann, *Chem. Ber.*, 1964, **97**, 1886; C. Paulmier, Y. Mollier, and N. Lozac'h, *Bull. Soc. chim. France*, 1965, 2463; J. Bignebat, H. Quiniou, and N. Lozac'h, *ibid.*, 1966, 1699; 1969, 127; G. Le Coustumer and Y. Mollier, *ibid.*, 1970, 3076; 1971, 2958; D. M. McKinnon and E. A. Robak, *Canad. J. Chem.*, 1968, **46**, 1855.

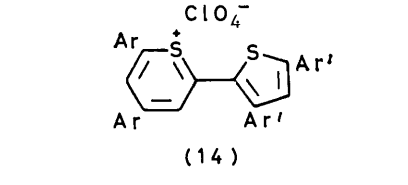
[5] R. C. Bertelson, ' Photochromism,' ed. G. H. Brown, Wiley–Interscience, New York, 1971, p. 49.

that from the reaction of (11b) with (12a). It was clear, moreover, that this product was a mixture since it had a relatively wide m.p. range and its ^1H n.m.r. spectrum showed two CMe signals in the intensity ratio 3 : 1. Since this pattern of signals cannot arise from a single compound containing two methyl groups, it follows that

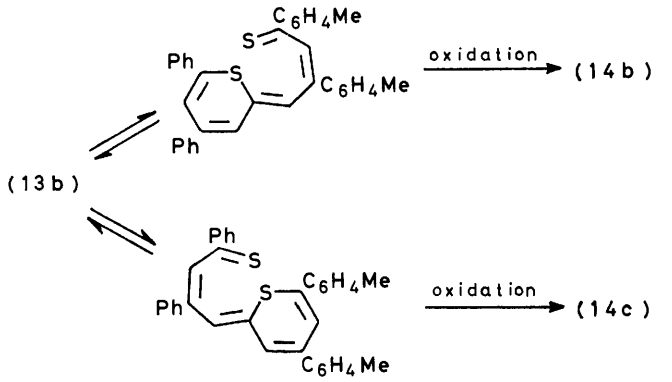


SCHEME 2

the product must consist of two compounds (14b and c) which together contain methyl groups in four different environments, three of which cause the same chemical shift. This result points clearly to a reaction intermediate, such as the spirobithiopyran (13b), in which the aryl substituents originally present in the dithiolylium salt have become equivalent, in their site occupancy, to those originally present in the thiopyrylium salt (Scheme 3).

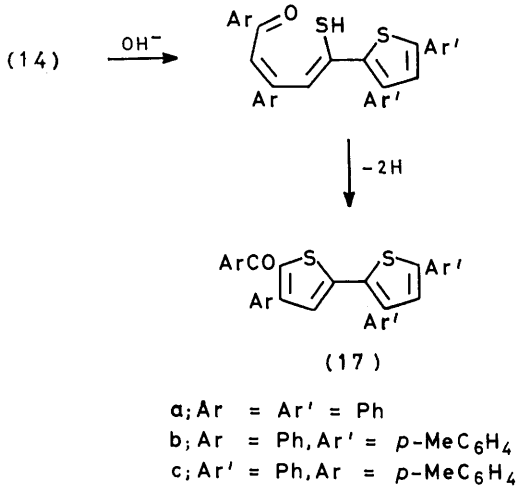


In an attempt to avoid oxidation of the intermediate spirobithiopyran, the reaction of the dithiolylium salt (11a) with the thiopyrylium salt (12a) was carried out at room temperature, in pyridine as the sole solvent. This procedure did not, in fact, prevent oxidation but gave a complex mixture of coloured products. These were separated by chromatography but only one, a yellow crystalline solid, was obtained pure. Its molecular formula ($C_{33}H_{22}OS_2$) suggested that it too could have been formed by oxidation of the spirobithiopyran, and



SCHEME 3

mass spectrometry showed that a benzoyl group was present [strong peaks at *m/e* 498 (M^+), 421 (M^+ — Ph), and 105 ($PhCO^+$)]. This evidence, and mechanistic considerations, led to formula (17a) as the probable structure of the yellow compound and to Scheme 4 as a likely mode of formation. Thus it was proposed that the purple salt (14a) was the immediate precursor of the yellow compound, that hydroxide ion (from water in the solvent) caused opening of the thiopyrylium ring, and that oxidative ring closure gave rise to a second thiophen ring. Either elemental sulphur (liberated during form-

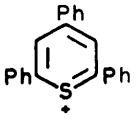


SCHEME 4

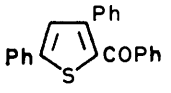
ation of the original spirobithiopyran) or oxygen (air) might have been responsible for the oxidation.

Support for the foregoing hypothesis was obtained from two experiments, the first of which confirmed that the yellow compound was formed from the purple salt (14a) when a solution of the latter and sulphur, in wet pyridine, was kept at room temperature. The second experiment was similar to the first but a less complex substrate, 2,4,6-triphenylthiopyrylium perchlorate (18), was chosen in order to provide a product which could more easily be identified by unambiguous synthesis. In this case, the expected thiophen (19) was obtained by boiling the pyrid-

ine solution for 30 min but it was not formed at room temperature. The product was identical with a specimen of 2-benzoyl-3,5-diphenylthiophen synthesised by benzoylation of 2,4-diphenylthiophen. Pedersen[6] has



(18)



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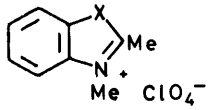
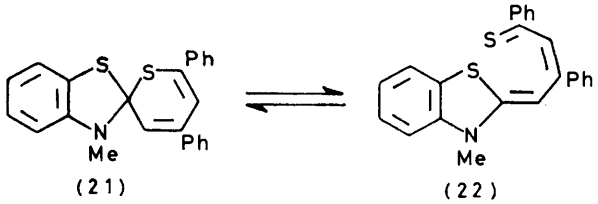


(20)

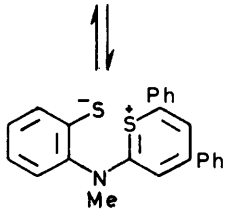
a; X = S
b; X = O

since obtained the same benzoylthiophen (19) by treatment of 2,4,6-triphenylpyrylium tetrafluoroborate with sodium sulphide followed by iodine.

When the di-*p*-tolyldithiolylium salt (12b) reacted with the diphenylthiopyrylium salt (11a) in cold pyridine, an analogous but non-crystalline yellow product was obtained and this was essentially identical with the product from the reaction of the diphenyldithiolyium salt (12a) with the di-*p*-tolylthiopyrylium salt (11b).



(21) (22)



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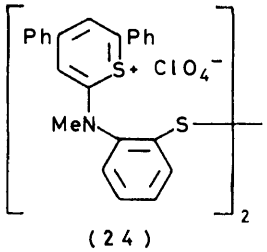

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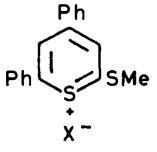
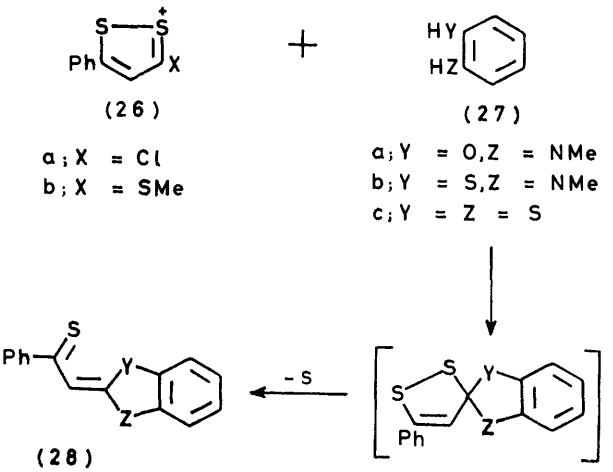


(25)

a; X = I
b; X = ClO_4

The product was evidently a mixture of the isomers (17b and c) since its ^1H n.m.r. spectrum showed four CMe signals of roughly equal intensity. This result is consistent with the mechanistic proposals embodied in Schemes 3 and 4 and thus provides further evidence pointing to spirobithiopyrans as reaction intermediates.

Conclusive evidence for a reaction of type (*a*) (paragraph 3) was finally obtained by using 2,3-dimethylbenzothiazolium perchlorate (20a) as the reactant of type (7). Reaction of this salt with the dithiolylium salt (1b), in pyridine, gave the spiro[benzothiazoline-2,2′-[2*H*]-thiopyran] (21) together with sulphur and a small amount of the thiopyrylium salt (24). The spiro-compound (21) was a pale yellow solid at room temperature but it became blue on being heated, gave a blue solution in ethanol, and formed a blue zone on chromatographic alumina. These colour changes, which are similar to those occurring in spirobenzopyrans such as (6), may be attributed to the formation of the coloured merocyanine tautomer (22) and are thus consistent with the proposed structure (21). Confirmation of this structure was provided by an alternative synthesis of the



(26) (27)

a; X = Cl
b; X = SMe

a; Y = O, Z = NMe
b; Y = S, Z = NMe
c; Y = Z = S

(28)

a; Y = O, Z = NMe
b; Y = S, Z = NMe
c; Y = Z = S

SCHEME 5

spiro-compound from 2-methylthio-4,6-diphenylthiopyrylium iodide (25a) and 2-(methylamino)benzenethiol.

The structure of the salt (24) was shown by its formation from the thiopyrylium salt (25b) and bis-2-(methylamino)phenyl disulphide; it was also formed (initially as an iodide) by oxidation of the spiro-compound (21) with iodine in ethanol, thus suggesting that the spiro-compound exists in equilibrium with a second monocyclic tautomer (23) as well as with the merocyanine (22).

In the experiments of type (*b*) (paragraph 3), representative spirobiheterocycles (9) were generated as transient intermediates by treating 3-chloro- or 3-methylthio-5-phenyl-1,2-dithiolylium perchlorate (26) with 2-(methylamino)phenol (27a), 2-(methylamino)benzenethiol (27b), or benzene-1,2-dithiol (27c) (Scheme 5). The expected thiophenacylidene heterocycles (28a—c), were isolated as major products and identified by comparison with authentic specimens. The thiophenacylidenebenzoxazoline (28a), which had not been reported previously, was synthesised by the reaction of 2,3-dimethylbenzoxazolium perchlorate (20b) with methyl dithiobenzoate in the presence of triethylamine.

Having now established the validity of reaction types

[6] C. L. Pedersen, *Acta Chem. Scand.*, 1975, **B29**, 791.

(*a*) and (*b*) (paragraph 3), we regard the mechanistic proposals shown in Scheme 1 for the self-condensation of 3-methyl-5-phenyl-1,2-dithiolylium perchlorate as resting on a sound foundation of analogy. Similar transformations of 1,2-dithioles and 1,2-dithiolylium salts into thiophenacylidenethiopyrans of type (5) have been reported briefly by other workers.[7]

EXPERIMENTAL

^{1}H N.m.r. data were obtained at 60 MHz with tetramethylsilane as internal standard. The adsorbents used for chromatography were Laporte alumina type H and Hopkin and Williams silica gel MFC. Light petroleum was the fraction of b.p. 40—60 °C. Extracts were dried over anhydrous sodium sulphate and evaporated under reduced pressure.

Self-condensation of 3-Methyl-5-phenyl-1,2-dithiolylium Perchlorate.—Pyridine (0.4 cm^3) was added to the dithiolylium salt (1 g) dissolved in acetic acid (5 cm^3) and the solution was boiled briefly and allowed to cool. The solid that crystallised was filtered off, washed with ether, water, and warm ethanol, and recrystallised from nitromethane to yield 4 (*or* 6)-*methyl*-6(*or* 4)-*phenyl*-2-*thiophenacylidene*-2H-*thiopyran* (0.42 g, 76%), dark purple needles, m.p. 218° (Found: C, 75.0; H, 4.5; S, 19.8%; M^+, 320. $C_{20}H_{16}S_2$ requires C, 75.0; H, 5.0; S, 20.0%; *M*, 320).

Condensation of 3-Methyl-5-phenyl-1,2-dithiolylium Perchlorate with 3,5-Diphenyl-1,2-dithiolylium Perchlorate.—A solution of the diphenyldithiolylium salt (0.35 g) in acetic acid (2 cm^3) and pyridine (0.5 cm^3) was added quickly to a hot solution of the methylphenyldithiolylium salt (0.29 g) in acetic acid (3 cm^3). The solution was boiled briefly and allowed to cool and the solid which had separated was filtered off and washed with ethanol and with hot water. Recrystallisation from nitromethane gave 4,6-diphenyl-2-thiophenacylidene-2*H*-thiopyran (0.22 g 58%), m.p. 194—196° (lit.,[2] 194—196°), identical (mixed m.p. and i.r. spectrum) with an authentic specimen.[2]

Condensation of 2-Methyl-4,6-diarylthiopyrylium Salts with 3,5-Diaryl-1,2-dithiolylium Salts in Acetic Acid–Pyridine.—(*a*) A solution of 2-methyl-4,6-diphenylthiopyrylium perchlorate (0.5 g) in boiling acetic acid (40 cm^3) was mixed with a solution of 3,5-diphenyl-1,2-dithiolylium perchlorate (0.49 g) in acetic acid (25 cm^3) and pyridine (25 cm^3). The combined solution was boiled for 20 min, cooled, and diluted with ether (100 cm^3), and the resulting precipitate was filtered off and washed with aqueous 10% perchloric acid (2 × 20 cm^3). Recrystallisation of the solid from acetic acid gave 4,6-*diphenyl*-2-(3,5-*diphenyl*-2-*thienyl*)*thiopyrylium perchlorate* (0.23 g, 29%), purple prisms, m.p. 246—247° (Found: C, 68.0; H, 3.9; Cl, 6.2; S, 11.3. $C_{33}H_{23}ClO_4S_2$ requires C, 68.2; H, 4.0; Cl, 6.1; S, 11.0%), identical (mixed m.p. and i.r. spectrum) with an authentic specimen.

(*b*) 2-Methyl-4,6-diphenylthiopyrylium perchlorate (0.6 g) was treated with 3,5-di-*p*-tolyl-1,2-dithiolylium perchlorate (0.57 g) as in (*a*). The product, after being filtered off and washed, was separated from starting materials by chromatography on silica gel in chloroform and obtained as a purple powder (0.16 g), m.p. 156—160°. Its ^{1}H n.m.r. spectrum (in $CDCl_3$) showed two regions of absorption at δ 2.3—2.4 (CH_3) and 7.0—8.5 (aromatic) in the intensity ratio 1 : 3.4 [structures (14b) and (14c) require 1 : 3.5], the high field signal consisting of two singlets (δ 2.4 and 2.3) in the intensity ratio 1 : 3.

(*c*) The reaction of 2-methyl-4,6-di-*p*-tolylthiopyrylium perchlorate (0.8 g) with 3,5-diphenyl-1,2-dithiolylium perchlorate (0.73 g) was carried out as in (*b*). The product, after purification, was a purple powder (0.24 g), m.p. 158—162°, i.r. spectrum identical with that of the product from (*b*). The ^{1}H n.m.r. spectrum showed the same features as that of the product from (*b*) though the signals were slightly less well resolved.

4,6-*Diphenyl*-2-(3,5-*diphenyl*-2-*thienyl*)*thiopyrylium Perchlorate* (14a).—A solution of 4,6-diphenylthiopyran-2-thione (0.28 g) and 2,4-diphenylthiophen (0.25 g) in phosphoryl chloride (10 cm^3) containing phosphorus pentachloride (0.2 g) was boiled under reflux for 30 min. Treatment with water (50 cm^3) gave a sticky solid which was dissolved in acetone (20 cm^3) and treated with 70% perchloric acid (0.5 cm^3). Addition of ether precipitated the thiopyrylium salt (0.28 g, 46%), purple prisms, m.p. 246—248° (from acetic acid).

Condensation of 2-Methyl-4,6-diarylthiopyrylium Salts with 3,5-Diaryl-1,2-dithiolylium Salts in Pyridine—(*a*) Solutions of 2-methyl-4,6-diphenylthiopyrylium perchlorate (0.5 g) in pyridine (25 cm^3) and of 3,5-diphenyl-1,2-dithiolylium perchlorate (0.49 g) in pyridine (25 cm^3) were mixed and kept at room temperature for 1 h. Ether (250 cm^3) was added, pyridinium perchlorate was filtered off, and the ethereal solution was washed with aqueous 2M-hydrochloric acid followed by water, dried, and evaporated. The residual oil was chromatographed on alumina. Elution with benzene gave several coloured bands, the two largest of which yielded (i) a red oil (0.25 g) and (ii) a yellow solid. More of the yellow solid was obtained by rechromatography of the red oil and the whole was recrystallised from ethanol to give 5′-*benzoyl*-3,4′,5-*triphenyl*-2,2′-*bithienyl* (0.08 g), yellow plates, m.p. 168—169° (Found: C, 79.2; H, 4.2; S, 12.75%; M^+, 498. $C_{33}H_{22}OS_2$ requires C, 79.5; H, 4.4; S, 12.8%; *M*, 498), $\nu_{max.}$ (Nujol) 1 650 cm^{-1} (C=O), δ(CS_2) 7.0—7.6 (complex m).

(*b*) Solutions of 2-methyl-4,6-diphenylthiopyrylium perchlorate (1.0 g) in pyridine (25 cm^3) and of 3,5-di-*p*-tolyl-1,2-dithiolylium perchlorate (1.05 g) in pyridine (25 cm^3) were mixed and treated as in (*a*). The chromatographic separation proceeded exactly as in (*a*) and the yellow product (0.12 g), which was non-crystalline, showed δ(CS_2) 2.20 (s, CH_3), 2.25 (s, CH_3), 2.34 (s, CH_3), 2.38 (s, CH_3), and 6.8—7.6 (m, aromatic). The methyl singlets were of almost equal intensity and the ratio of methyl to aromatic protons was *ca.* 1 : 3.5 [structures (17b) and (17c) require 1 : 3.3].

(*c*) 2-Methyl-4,6-di-*p*-tolylthiopyrylium perchlorate (1.0 g) and 3,5-diphenyl-1,2-dithiolylium perchlorate (0.91g) were treated as in (*b*) and the product chromatographed to yield a non-crystalline yellow product (0.14 g), the i.r. spectrum (CS_2) of which was essentially identical with that of the corresponding product from reaction (*b*). The ^{1}H n.m.r. spectrum showed the same features as that of the product from (*b*), though there were minor differences in the relative intensities of the four methyl signals.

Ring Contraction of Thiopyrylium Salts (with B. D. Baigrie).—(*a*) 4,6-Diphenyl-2-(3,5-diphenyl-2-thienyl)-thiopyrylium perchlorate (0.2 g) was dissolved in pyridine (15 cm^3) saturated with sulphur. The solution was kept in air overnight, then filtered, diluted with ether (100 cm^3), washed with water (5 × 50 cm^3), dried, and evaporated.

[7] G. Duguay, H. Quiniou, and N. Lozac'h, *Bull. Soc. chim. France*, 1967, 4485; G. Duguay and H. Quiniou, *ibid.*, 1970, 1918.

Chromatography of the residue on alumina in benzene gave (i) a trace of sulphur and (ii) 5′-benzoyl-3,4′,5-triphenyl-2,2′-bithienyl (0.05 g), greenish yellow plates, m.p. 167—168°: i.r. spectrum identical with that of the product obtained by reaction of the thiopyrylium salt (11a) with the dithiolylium salt (12a).

(*b*) 2,4,6-Triphenylthiopyrylium perchlorate (1 g) was dissolved in pyridine (50 cm³) containing water (5 drops) and sulphur (saturated solution) and the solution was boiled for 30 min. Ether (150 cm³) was added and the solution was washed with water (4 × 200 cm³), dried, and evaporated. The residual oil was chromatographed on alumina in benzene to yield (i) 2-benzoyl-3,5-diphenylthiophen, m.p. 97—98° (lit.,[8] 96.5—98°), $\nu_{max.}$ (Nujol) 1 630 cm^{-1} (C=O), identical (mixed m.p. and i.r. spectrum) with an authentic specimen, and (ii) a yellowish white solid, m.p. 112°, which did not contain sulphur and was identical with the product obtained by treating 2,4,6-triphenylpyrylium perchlorate with aqueous base (sodium acetate).

When the reaction was carried out at room temperature, as in (*a*), only the second product, m.p. 112°, was obtained.

Condensation of 2,3-*Dimethylbenzothiazolium Perchlorate with* 3,5-*Diphenyl*-1,2-*dithiolylium Perchlorate*.—Solutions of the benzothiazolium salt (0.5 g) in pyridine (25 cm³) and of the dithiolylium salt (0.67 g) in pyridine (25 cm³) were mixed and kept at room temperature for 2 h. Water (250 cm³) and ether (250 cm³) were added and, after thorough shaking, a yellow solid was filtered off. This was dissolved in acetone and reprecipitated with ether to yield the bis(thiopyrylium) salt (24) (0.015 g), m.p. 269—270°; i.r. spectrum identical with that of the specimen prepared as described below.

The ethereal portion of the filtrate was washed with water, dried, and evaporated and the residue was chromatographed on alumina. Elution with light petroleum gave a trace of sulphur and further elution with benzene gave a blue chromatographic zone from which a yellow solid was obtained. Recrystallisation from ethanol (blue solution) gave 3-*methyl*-4′,6′-*diphenylspiro*[*benzothiazoline*-2,2′-[2H]*thiopyran*] (0.66 g, 90%), yellow needles, m.p. 167—168° (turning blue at 150—160°) (Found: C, 74.6; H, 5.2; N, 3.4; S, 16.6. $C_{24}H_{19}NS_2$ requires C, 74.8; H, 5.0; N, 3.6; S, 16.6%), identical (mixed m.p. and i.r. spectrum) with the specimen obtained as described below.

3-*Methyl*-4′,6′-*diphenylspiro*[*benzothiazoline*-2,2′-[2H]*thiopyran*] (21).—A solution of 2-methylaminobenzenethiol (0.2 g) in ethanol (10 cm³) was added to a boiling solution of 2-methylthio-4,6-diphenylthiopyrylium iodide (0.2 g) in ethanol (100 cm³). The solution was kept for 1 h, diluted with water (200 cm³), and extracted with ether. The extract was washed with water, dried, and evaporated to yield the spiro-compound (0.08 g, 50%), yellow needles (from ethanol), m.p. 167—168° (turning blue at 150—160°).

4,4′,6,6′-*Tetraphenyl*-2,2′-[*dithiobis*-o-*phenylene*(*methylimino*)]*bisthiopyrylium Diperchlorate* (24).—(*a*) A solution of bis-2-(methylamino)phenyl disulphide (0.2 g) and 2-methylthio-4,6-diphenylthiopyrylium perchlorate (0.58 g) in 2-methoxyethanol (40 cm³) was heated under reflux for 1 h. Ether (150 cm³) was added to the cooled solution and the resulting precipitate was dissolved in boiling methanol. After treatment with charcoal, the solution was filtered and ether was added to reprecipitate the *diperchlorate* (0.46 g), a yellow powder, m.p. 269—270° (Found: C, 59.3; H, 3.8; Cl, 7.7; N, 3.0; S, 12.8. $C_{48}H_{38}Cl_2N_2O_8S_4$ requires C, 59.4; H, 3.9; Cl, 7.3; N, 2.9; S, 13.2%).

(*b*) A solution of the spiro-compound (21) (0.08 g) in ethanol (100 cm³) was titrated, at 30 °C, with ethanolic 0.025N-iodine until starch paper gave a positive reaction. The solution was heated until it became homogeneous and 70% perchloric acid (1 cm³) was added followed by ether (400 cm³). After 2 days, the yellow product (0.08 g), m.p. 269—270°, was filtered off. It was identical (mixed m.p. and i.r. spectrum) with the diperchlorate obtained in (*a*).

3-*Methyl*-2-*thiophenacylidenebenzoxazoline* (28a).—(*a*) A solution of 2,3-dimethylbenzoxazolium perchlorate (0.45 g), methyl dithiobenzoate (0.6 cm³), and triethylamine (2 cm³) in *NN*-dimethylformamide (20 cm³) was heated under reflux for 20 min, diluted with water, and extracted with chloroform. The extract was washed with aqueous 2M-hydrochloric acid (2 × 200 cm³) and with water, dried, and evaporated. The residual oil was chromatographed on alumina in ether–chloroform (1 : 1) to yield (i) methyl dithiobenzoate (0.44 g) and (ii) the *benzoxazoline* (0.1 g), red needles, m.p. 188—189° (from methanol) (Found: C, 71.7; H, 4.8; N, 5.4; S, 11.5. $C_{16}H_{13}NOS$ requires C, 71.9; H, 4.9; N, 5.2; S, 12.0%).

(*b*) 2-(Methylamino)phenol (0.2 g) in anhydrous acetone (10 cm³) was added to 3-chloro-5-phenyl-1,2-dithiolylium perchlorate (0.5 g) in anhydrous acetone (30 cm³) and the solution was kept at room temperature for 1 h. Ether (250 cm³) was added and the brown oil which precipitated was separated by decantation. Work-up of the ethereal solution gave 5-phenyl-1,2-dithiole-3-thione (0.04 g). The brown oil was dissolved in acetone and the solution was treated with aqueous sodium carbonate and extracted with ether. Evaporation of the extract yielded a red solid which was recrystallised from methanol to yield the benzoxazoline (0.25 g), m.p. 188—189°, identical (mixed m.p. and i.r. spectrum) with the product obtained in (a).

3-*Methyl*-2-*thiophenacylidenebenzothiazoline* (28b).—2-(Methylamino)benzenethiol (1 g) was added to a boiling solution of 3-methylthio-5-phenyl-1,2-dithiolylium iodide (0.5 g) in ethanol (100 cm³) and the solution was kept for 1 h, diluted with water, and extracted with ether. The extract was washed with water (5 ×), dried, and evaporated. Chromatography of the residual oil on alumina in light petroleum–benzene (1 : 1) gave several coloured bands, two of which yielded crystalline products: (i) 5-phenyl-1,2-dithiole-3-thione (0.02 g) and (ii) the benzothiazoline (0.22 g), orange-red needles, m.p. 179—181° (from benzene) (lit.,[9a] 176°), identical (mixed m.p. and i.r. spectrum) with a specimen prepared[9b] from 2,3-dimethylbenzothiazolium perchlorate.

2-*Thiophenacylidene*-1,3-*benzodithiole* (28c).—Benzene-1,2-dithiol (0.2 g) in anhydrous acetone (10 cm³) was added to a solution of 3-chloro-5-phenyl-1,2-dithiolylium perchlorate (0.44 g) in anhydrous acetone (30 cm³). After 2 h at room temperature, a brown solid had been deposited, and this was filtered off and recrystallised to yield the benzodithiole (0.32 g), greenish-brown plates, m.p. 185—186° (from acetone) (lit.,[1] 187—188°), identical (mixed m.p. and i.r. spectrum) with an authentic specimen.

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[8] M. Takaku, Y. Hayasi, and N. Nozaki, *Bull. Chem. Soc. Japan*, 1970, **43**, 1917.

[9] (*a*) P. De Smet and W. Mees, G.P. 740,773 (*Chem. Abs.*, 1946, **40**, 610); (*b*) P. De Smet and W. Mees, B.P. 592,482 (*Chem. Abs.*, 1948, **42**, 2444).