

## 6. *The Dithiole Series. Part II.<sup>1</sup> Reactions of 1,2- and 1,3-Dithiolium Salts with Nucleophilic Reagents.*

By D. LEAVER, D. M. MCKINNON, and W. A. H. ROBERTSON.

The products formed from 1,2-dithiolium salts and nucleophilic reagents are in accord with a mechanism involving reaction at position 3 followed, in most instances, by ring-opening and loss of one atom of sulphur. Ammonia reacts with 1,2-dithiolium salts to give isothiazoles. The 2,4,5-triphenyl-1,3-dithiolium cation reacts with nucleophiles at position 2 to give relatively stable dithioles.

PREDICTIONS based on simple resonance theory, or on analogy with the reactions of azolium cations, suggest that 1,2- and 1,3-dithiolium cations will react with nucleophiles at positions 3 and 2, respectively. Molecular-orbital calculations<sup>2</sup> lead to the same result. It is also conceivable that nucleophilic attack could occur at a sulphur atom, either with participation of the sulphur *d*-orbitals (cf. reaction<sup>3</sup> of thiopyrylium cations with phenyl-lithium) or with ring fission.

Klingsberg and his co-workers<sup>4</sup> have shown that *NN*-dialkylanilines react with dithiolium salts (Ib, Ic, and IIa) to give, after oxidation, *p*-dialkylaminophenyldithiolium salts (Ie, If, and IIc, respectively) and that 1,2-dithiolium salts (Ib and Ic) react with hydrazines to give pyrazoles. Both observations are readily rationalised in terms of a nucleophilic attack at carbon atoms 3 and 2, respectively, of the cations (I) and (II).

During an investigation of the reactions of a selection of nucleophiles with dithiolium

<sup>1</sup> Part I, Leaver, Robertson, and McKinnon, *J.*, 1962, 5104.

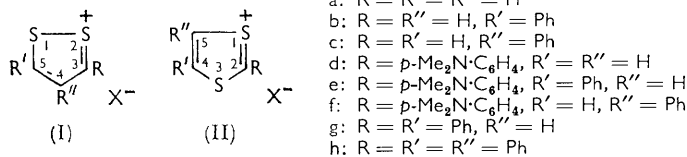
<sup>2</sup> Koutecky and Zahradnik, *Tetrahedron Letters*, 1961, 632.

<sup>3</sup> Suld and Price, *J. Amer. Chem. Soc.*, 1961, **83**, 1770; 1962, **84**, 2090, 2094.

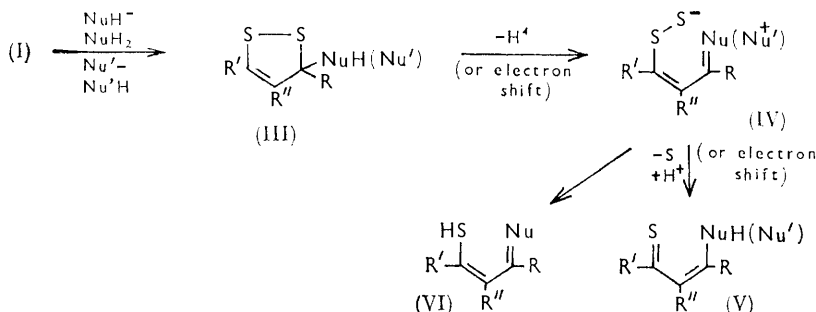
<sup>4</sup> (a) Klingsberg and Schreiber, *J. Amer. Chem. Soc.*, 1962, **84**, 2941; (b) Klingsberg, *ibid.*, p. 3410.

salts, we chose the symmetrical compounds (Ic), (Ig), and (IIh) for the most intensive study.

*Reaction with Reagents containing Nucleophilic Oxygen.*—Klingsberg<sup>5</sup> reported that the 3- and 4-phenyl-1,2-dithiolium cations are instantly decomposed, in presence of hydroxide ion, with liberation of sulphur, and he suggested that the reaction proceeds by way of an open-chain disulphide-aldehyde [conjugate acid of compound (IV; Nu = O, R = H)]



Scheme 1.



which would probably be very sensitive to alkali. We found that the 3,5-diphenyl compound (Ig) also reacted rapidly with an excess of potassium hydroxide to give sulphur and an orange-red solution which, on treatment with benzyl chloride, yielded  $\beta$ -(benzylthio)chalcone, identical with a specimen prepared by addition of toluene- $\alpha$ -thiol to benzoylphenylacetylene. These products are consistent with reaction according to scheme 1\* (NuH<sup>-</sup> = OH<sup>-</sup>) since the anion of compound (V; NuH = OH) would be expected to undergo S-benylation.

3,5-Diphenyl-1,2- and 2,4,5-triphenyl-1,3-dithiolium perchlorate reacted with ethoxide ion to give the colourless ethoxydithioles (VII) and (VIII; X = OEt), respectively, the structures of which follow from the fact that they are quantitatively reconverted into the original salts on treatment with perchloric acid. Compound (VII) decomposed during chromatography on alumina to give sulphur and a red compound which could not be obtained analytically pure, but was probably the thione (V; Nu' = OEt, R = R' = Ph, R'' = H) formed according to scheme 1 (Nu' = OEt<sup>-</sup>). No reagent other than activated alumina was effective in causing this transformation.

The 4-phenyl-1,2-dithiolium salt (Ic) was decomposed by ethoxide ion, and the only product isolated was 4-phenyl-1,2-dithiole-3-thione which has been shown<sup>6</sup> to be formed by the action of sulphur, under basic conditions, on the dithiolium salt.

*Reaction with Reagents containing Nucleophilic Nitrogen.*—Reaction of pyrylium<sup>7</sup> and thiopyrylium<sup>8</sup> salts with ammonia and primary amines occurs with replacement of

\* Four alternative types of nucleophile are shown and the one appropriate to the particular reaction under consideration will be designated in the discussion. Those reactions involving Nu' and Nu'H will give rise to intermediates and products containing the groups shown in parentheses in place of those shown alongside in the structural formulæ.

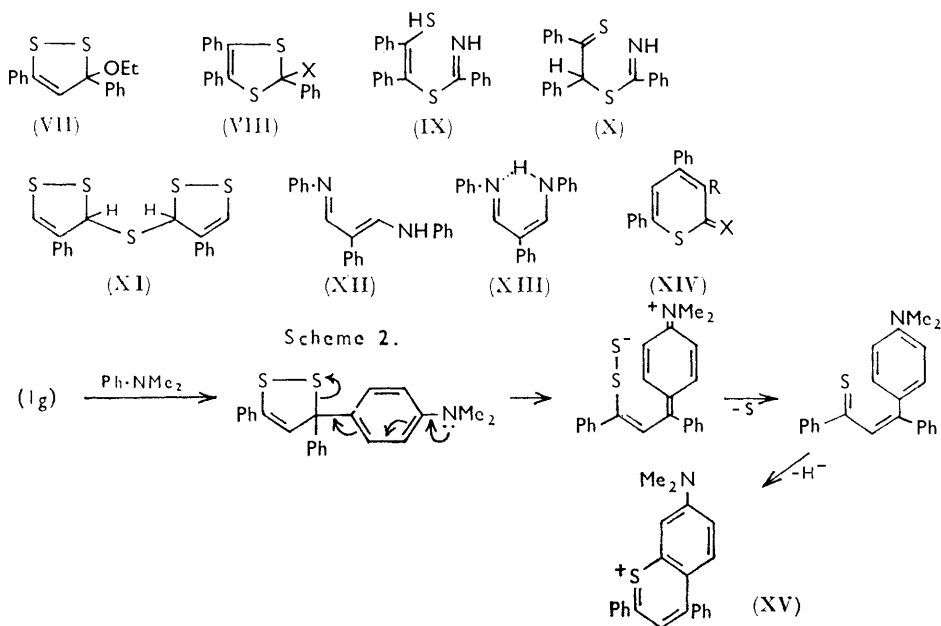
<sup>5</sup> Klingsberg, *J. Amer. Chem. Soc.*, 1961, **83**, 2934.

<sup>6</sup> Klingsberg, *J. Org. Chem.*, 1963, **28**, 529.

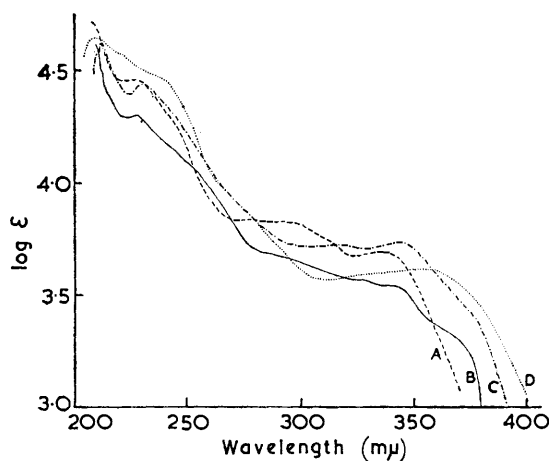
<sup>7</sup> Brody and Ruby, "Pyridine and its Derivatives," Part I, ed. Klingsberg, Interscience Publishers Inc., New York, 1960, p. 210.

<sup>8</sup> Wizinger and Ulrich, *Helv. Chim. Acta*, 1956, **39**, 207.

the heteroatom to form pyridines. It was therefore of interest to investigate the possibility of a related reaction with dithiolium salts.



Treatment of the triphenyl-1,3-dithiolium salt (IIh) with ammonia gas in dry benzene gave the aminodithiole (VIII;  $X = \text{NH}_2$ ) the structure of which follows from the similarity of its ultraviolet spectrum (Figure) to that of the ethoxydithiole (VIII;  $X = \text{OEt}$ ) and



Ultraviolet spectra, in ethanol, of 1,3-dithioles (VIII);

- A,  $X = \text{OEt}$ ;
- B,  $X = \text{H}$ ;
- C,  $X = \text{NH}_2$ ;
- D,  $X = \text{CN}$ .

from the fact that it was reconverted into the original salt by treatment with perchloric acid. When the aminodithiole was boiled in ethanol it decomposed, with evolution of hydrogen sulphide, to form a trace of sulphur, deoxybenzoin, thiobenzamide, triphenylthiazole, and 2,4,5-triphenyl-1,3-dithiole (VIII;  $X = \text{H}$ ). The constitution of the last compound follows from the similarity of its ultraviolet spectrum (Figure) to those of compounds (VIII;  $X = \text{NH}_2$  and  $X = \text{OEt}$ ) and from its conversion into the original

dithiolium salt by treatment with triphenylmethyl perchlorate, a reagent which is known<sup>9</sup> to abstract hydride ions, particularly when the reaction leads to a stable cation.

Tautomerisation (VIII;  $X = NH_2 \rightleftharpoons IX \rightleftharpoons X$ ) of the aminodithiole to an open-chain compound may be envisaged as the initial stage in the formation of these compounds. Compound (X) is the thione analogue of the ketonic intermediate in the synthesis of thiazoles from thioamides and  $\alpha$ -halogeno-ketones; it would be expected to cyclise readily, forming triphenylthiazole and hydrogen sulphide. It is easy to envisage the formation of thiobenzamide from compound (X) but the formation of deoxybenzoin implies that, at some stage, the alkyl-sulphur bond is broken with formation (complete or incipient) of a carbanion. A number of examples of this type of fission in  $\alpha$ -phenylphenacyl compounds (*e.g.*, the thiol), under basic conditions, have been reported<sup>10</sup> and attributed to nucleophilic attack at the sulphur atom. A similar cleavage of the mercaptodithiole (VIII;  $X = SH$ ), which might be formed by nucleophile exchange between the aminodithiole and hydrogen sulphide, could account for the formation of the triphenyldithiole (VIII;  $X = H$ ). Support for the last hypothesis was afforded by the observation that compound (VIII;  $X = H$ ) is formed, in good yield, when the dithiolium salt is treated with sodium hydrogen sulphide.

3,5-Diphenyl-1,2-dithiolium perchlorate (Ig) reacted with ammonia, in ethanol, to give 3,5-diphenylisothiazole.<sup>11</sup> This compound was previously unknown and all attempts to synthesise it by an unambiguous route have failed but its ultraviolet spectrum is consistent with the proposed structure. The 4-phenyl-1,2-dithiolium salt (Ic) failed to give an isothiazole with ammonia in ethanol but in dry benzene a low yield of the base was obtained. The main product (60% yield) in the latter solvent was a yellow compound, containing only carbon, hydrogen, and sulphur, which was converted into the original salt, with evolution of hydrogen sulphide, by treatment with perchloric acid. This behaviour, and the analytical results, suggest that the compound is the bisdithioly sulphide (XI). Its formation can be ascribed to a reaction of two dithiolium cations with one molecule of hydrogen sulphide which would be eliminated during formation of the isothiazole. The tropylium cation reacts in a similar way with hydrogen sulphide to give ditropyl sulphide.<sup>12</sup> A better yield of 4-phenylisothiazole was obtained by reaction of the dithiolium salt with ammonium acetate in acetic acid. Other workers<sup>13</sup> have also obtained isothiazoles from dithiolium salts and the method appears to be one of considerable utility. We failed, however, to obtain isothiazole from 1,2-dithiolium perchlorate (Ia).

The reaction of 1,3-dithiolium salts with amines was not investigated, but the 3,5-diphenyl-1,2-dithiolium salt (Ig) reacted with aniline to give a red compound, with elimination of elementary sulphur. It seemed probable that reaction was occurring according to scheme 1 ( $NuH_2 = Ph \cdot NH_2$ ) to give 3-anilino-1,3-diphenylpropene-1-thione (V;  $NuH = Ph \cdot NH$ ,  $R = R' = Ph$ ,  $R'' = H$ ). Confirmation of this structure was provided by an independent synthesis from the corresponding ketone<sup>14</sup> by treatment with phosphorus pentasulphide. The salt (Ig) reacted with piperidine, and 3-phenyl-1,2-dithiolium perchlorate (Ib) reacted with aniline and with *N*-methylaniline in the same way to give red compounds, all of which had closely similar ultraviolet and visible absorption spectra. The two anilino-compounds must, therefore, possess the thione structures, rather than the tautomeric mercapto-anil structures, since the spectrally similar compounds derived from secondary amines are incapable of tautomerism.

4-Phenyl-1,2-dithiolium perchlorate (Ic) reacted with two moles of aniline to give a yellow, sulphur-free perchlorate from which a yellow base could be liberated. It seemed

<sup>9</sup> Bonthron and Reid, *J.*, 1959, 2773.

<sup>10</sup> Iskander and Tewfik, *J.*, 1961, 2393.

<sup>11</sup> Preliminary communication, Leaver and Robertson, *Proc. Chem. Soc.*, 1960, 252.

<sup>12</sup> Doering and Knox, *J. Amer. Chem. Soc.*, 1957, **79**, 352.

<sup>13</sup> Dr. R. A. Olofson, personal communication.

<sup>14</sup> Roberts and Turner, *J.*, 1927, 1857.

probable that the reaction initially followed the same course as those of the other 1,2-dithiolium salts, but that the anilinothial (V; NuH = Ph·NH, R = R' = H, R'' = Ph) was sufficiently reactive to form phenylmalondialdehyde dianil with another molecule of aniline. The melting point (124°) of the yellow base, however, did not agree with that (138°) reported<sup>15</sup> by Rupe and Huber for phenylmalondialdehyde dianil. Repetition of their synthesis of the dianil gave, first the compound of m. p. 138°, and then, from the reaction mother-liquors, a second compound (m. p. 124°) identical with the one from the dithiolium salt. The two compounds were shown to be the *cis*- (m. p. 124°) and *trans*-isomers (m. p. 138°) of phenylmalondialdehyde dianil by examination of their proton magnetic resonance spectra. The most significant features (apart from the phenyl proton absorption centred at 2·7  $\tau$ ) in the spectrum of the *trans*-isomer (XII) were two equivalent one-proton doublets ( $J = 3\cdot6$  c./sec.) centred at 0·38 and 2·34  $\tau$ . The first of these doublets is attributed to the azomethine (aldehyde-like) proton, and the second to the proton attached to the  $\alpha$ -carbon atom of the enamine group. These doublets were absent in the spectrum of the *cis*-isomer (XIII) and were replaced by a two-proton singlet at 1·97  $\tau$ , the two methine protons being rendered spectroscopically equivalent by rapid tautomeric exchange of the internally hydrogen-bonded NH proton.

*Reaction with Reagents containing Nucleophilic Carbon.*—None of the dithiolium salts yielded characterisable products with phenylmagnesium bromide. Cyanide ion reacted with the triphenyl-1,3-dithiolium salt (IIh) to give a cyanodithiole (VIII; X = CN) the ultraviolet spectrum of which resembled the spectra of related dithioles (VIII) (Figure) but which was not reconverted into the original salt by treatment with perchloric acid. Treatment of the 1,2-dithiolium salts with sodium cyanide gave no characterisable products into which the cyano-group had been incorporated; a trace of the 3-thione was obtained from the 4-phenyl-compound (Ic).

Diethyl sodiomalonate reacted with 3,5-diphenyl-1,2-dithiolium perchlorate (Ig) to give a pale yellow compound, whose infrared spectrum showed one ester carbonyl absorption (1720  $\text{cm}^{-1}$ ) and another strong band at 1630  $\text{cm}^{-1}$  which was attributable to the thiopyrone carbonyl group in structure (XIV; R = CO<sub>2</sub>Et, X = O). Verification of this structure was provided by heating the compound with dilute sulphuric acid and treating the resulting thiopyrone (XIV; R = H, X = O) with phosphorus pentasulphide to give 4,6-diphenyl-2*H*-thiopyran-2-thione (XIV; R = H, X = S). The last compound was identical with a specimen prepared from the corresponding pyranthione<sup>16</sup> by treatment with potassium hydrogen sulphide, a reagent which is known<sup>17</sup> to convert pyranthiones into thiopyranthiones. The formation of compound (XIV; R = CO<sub>2</sub>Et, X = O) may be accounted for by scheme I [NuH<sup>-</sup> = CH(CO<sub>2</sub>Et)<sub>2</sub>; R = R' = Ph, R'' = H] followed by thiolactonisation of product [VI; Nu = C(CO<sub>2</sub>Et)<sub>2</sub>, R = R' = Ph, R'' = H].

The only products isolated from the reactions of 1,2-dithiolium perchlorate (Ia) and its 4-phenyl derivative (Ic) with diethyl sodiomalonate were the corresponding dithiolethiones.

Klingsberg and Schreiber showed<sup>4a</sup> that the *para*-position of the benzene ring acts as the nucleophilic centre in the reactions of *NN*-dialkylanilines with 1,2-dithiolium salts (*e.g.*, Ib, Ic) that lack substituents at the 3(5)-position. The resulting *p*-dialkylamino-phenyldithiolium salts (*e.g.*, Ie, If) were violet and we were surprised to find that 3,5-diphenyl-1,2-dithiolium perchlorate (Ig), in which an oxidative substitution of the above type is impossible owing to the absence of hydrogen atoms at positions 3 or 5, also yielded a violet salt on being boiled with *NN*-dimethylaniline. In this instance, however, the odour of hydrogen sulphide was apparent during the reaction and analysis indicated that an atom of sulphur had been lost. Although the constitution of the product requires final confirmation, its colour and elementary composition are in agreement with structure

<sup>15</sup> Rupe and Huber, *Helv. Chim. Acta*, 1927, **10**, 856.

<sup>16</sup> Arndt and Eistert, *Ber.*, 1925, **58**, 2318.

<sup>17</sup> Arndt and Aron, *Rev. Fac. Sci. Istanbul*, 1948, **13A**, 57 (*Chem. Abs.*, 1948, **42**, 4176); Mayer and Fischer, *Chem. Ber.*, 1962, **95**, 1307.

(XV). A plausible sequence of reactions leading to a compound of this structure is outlined in scheme 2. The first stage of this sequence is analogous to that established<sup>4a</sup> for the reactions between 3- and 4-phenyl-1,2-dithiolium salts and *NN*-dialkylanilines; the last stage is similar to the oxidative cyclisation of polymethoxychalcones to flavylum salts;<sup>18</sup> and the intermediate stages are similar to those of scheme 1.

## EXPERIMENTAL

Extracts were dried over anhydrous sodium sulphate and all solutions were evaporated under reduced pressure. Ultraviolet and visible spectra were measured for ethanol solutions. Infrared absorptions reported are for Nujol mulls. Nuclear magnetic resonance spectra were measured, for deuteriochloroform solutions, by means of a Perkin-Elmer 60 Mc./sec. spectrometer. Chromatographic separations were carried out on columns of alumina (Peter Spence, Type H). Light petroleum refers to the fraction of b. p. 40—60° unless otherwise stated.

*β*-(Benzylthio)chalcone.—(a) Toluene- $\alpha$ -thiol (0.12 g.) in ethanol (3 ml.) containing a catalytic quantity of sodium ethoxide was treated with benzoylphenylacetylene (0.2 g.) in ethanol (1 ml.). Separation of solid began after a few seconds and recrystallisation from ethanol yielded the *ketone* (0.27 g.), pale yellow plates, m. p. 134—135° (Found: C, 80.1; H, 5.3; S, 9.5.  $C_{22}H_{18}OS$  requires C, 80.1; H, 5.5; S, 9.7%).

(b) Aqueous 2*N*-potassium hydroxide (3 ml.) was added, dropwise with shaking, to 3,5-diphenyl-1,2-dithiolium perchlorate (0.7 g.) in dimethyl sulphoxide (20 ml.). The solution became green initially but rapidly changed to reddish-brown; it was diluted with water (80 ml.) and filtered to remove sulphur. The filtrate was shaken with benzyl chloride (1 ml.) for 1 hr. and the resulting yellow emulsion was extracted with ether. Evaporation of the extract and crystallisation of the residue yielded *β*-(benzylthio)chalcone (0.1 g.), m. p. and mixed m. p. 134—135°, infrared spectrum identical with that of an authentic specimen.

3-Ethoxy-3,5-diphenyl-1,2-dithiole.—3,5-Diphenyl-1,2-dithiolium perchlorate (1 g.) was boiled with ethanol (10 ml.) containing sodium ethoxide (from 0.07 g. sodium) until it dissolved. The solution was evaporated to dryness and the residue was extracted with light petroleum which, after concentration, deposited the *dithiole* (0.5 g.), needles, m. p. 68—69° (from light petroleum) (Found: C, 67.6; H, 5.1; S, 20.8.  $C_{17}H_{16}OS_2$  requires C, 68.0; H, 5.3; S, 21.3%). Treatment of the ethoxy-compound, in acetic acid, with perchloric acid caused precipitation of the original dithiolium perchlorate in almost quantitative yield.

The ethoxy-compound (0.5 g.), in benzene, was applied to a short column of alumina and, when the resulting red zone had reached its maximum intensity, the column was quickly stripped with acetone. Evaporation of the acetone and fractional crystallisation from light petroleum afforded a trace of sulphur and a red crystalline compound (0.14 g.), m. p. 73° (Found: C, 74.8; H, 5.3; S, 10.6. Calc. for  $C_{17}H_{16}OS$ : C, 76.3; H, 5.9; S, 11.9%). The latter is believed to be 3-ethoxy-1,3-diphenylpropene-1-thione [*β*-ethoxy(thiochalcone)], but further recrystallisation failed to improve the analytical results.

2-Ethoxy-2,4,5-triphenyl-1,3-dithiole.—2,4,5-Triphenyl-1,3-dithiolium perchlorate (2.15 g.) was boiled with ethanol (200 ml.) containing sodium ethoxide (from 0.115 g. of sodium) for 5 min. and the solution was evaporated to dryness. The residue was extracted with ether, and the extract was evaporated to yield the *dithiole* (1.1 g.), needles, m. p. 113° (from ethanol) (Found: C, 73.2; H, 5.5; S, 17.0.  $C_{23}H_{20}OS_2$  requires C, 73.4; H, 5.3; S, 17.1%). Treatment of the ethoxy-compound, in acetic acid, with perchloric acid caused precipitation of the original dithiolium perchlorate in almost quantitative yield.

2-Cyano-2,4,5-triphenyl-1,3-dithiole.—2,4,5-Triphenyl-1,3-dithiolium perchlorate (2.15 g.), in hot ethanol (100 ml.), was added to sodium cyanide (0.245 g.) in hot ethanol (30 ml.), and the mixture was boiled for 5 min. and then evaporated to dryness. Extraction of the residue with ether yielded the ethoxydithiole (0.5 g.), m. p. 113°, and further extraction with benzene gave the *cyanodithiole* (0.5 g.), pale yellow needles, m. p. 192—193° (from benzene) (Found: C, 73.9; H, 4.1; N, 3.9; S, 16.5.  $C_{22}H_{15}NS_2$  requires C, 73.9; H, 4.2; N, 3.9; S, 17.9%). Treatment of the latter, in boiling acetic acid, with perchloric acid caused no change.

2,4,5-Triphenyl-1,3-dithiole.—2,4,5-Triphenyl-1,3-dithiolium perchlorate (0.15 g.) was treated with a slight excess of sodium hydrogen sulphide in ethanol (10 ml.), and the solution

<sup>18</sup> Brown, Davidson, and Norman, *Chem. and Ind.*, 1962, 1237.

was boiled briefly. On being cooled, the solution deposited the *dithiole* (0.1 g.), pale yellow prisms, m. p. 242° (from *NN*-dimethylformamide) (Found: C, 75.3; H, 4.6; S, 19.7.  $C_{21}H_{16}S_2$  requires C, 75.7; H, 4.8; S, 19.3%). The *dithiole* (0.1 g.), in acetic acid, was boiled for 2 min. with a slight excess of triphenylmethyl perchlorate and the solution was filtered. Precipitation with ether and recrystallisation from acetic acid gave 2,4,5-triphenyl-1,3-dithiolium perchlorate, m. p. and mixed m. p. 254—255°.

*2-Amino-2,4,5-triphenyl-1,3-dithiole*.—A suspension of 2,4,5-triphenyl-1,3-dithiolium perchlorate (2.2 g.), in dry benzene (50 ml.), was treated with a stream of dry ammonia for 10 min. The resulting yellow solution was decanted from ammonium perchlorate and evaporated to give an orange solid which, after recrystallisation from benzene-light petroleum (b. p. 60—80°), afforded the *aminodithiole* (1.1 g.), colourless needles, m. p. 112—113° (Found: C, 72.8; H, 4.5; N, 4.2; S, 18.3.  $C_{21}H_{17}NS_2$  requires C, 72.6; H, 4.9; N, 4.0; S, 18.4%). Treatment of the amino-compound, in acetic acid, with perchloric acid caused precipitation of the original dithiolium perchlorate in almost quantitative yield.

*Decomposition of 2-Amino-2,4,5-triphenyl-1,3-dithiole*.—The *aminodithiole* (1 g.) was boiled in ethanol (50 ml.) for 30 min. Hydrogen sulphide was gradually evolved and a pale yellow precipitate formed. The latter was filtered off and yielded, after fractional crystallisation, a trace of sulphur and 2,4,5-triphenyl-1,3-dithiole (0.2 g.), m. p. 242°, whose infrared spectrum was identical with that of a specimen prepared as described above. The filtrate was evaporated to dryness and the residue was dissolved in light petroleum (10 ml.) and set aside to evaporate slowly. Recrystallisation of the solids that separated afforded, successively, thiobenzamide, 2,4,5-triphenylthiazole (0.45 g.), and deoxybenzoin, all of which were identified by comparison of their infrared spectra with those of authentic specimens.

*3,5-Diphenylisothiazole*.—3,5-Diphenyl-1,2-dithiolium perchlorate (0.6 g.) in boiling ethanol (40 ml.) was treated with a stream of ammonia. A dark red colour, produced initially, faded during 20 min. to pale orange. The passage of ammonia was then discontinued, the solution was concentrated to 2 ml., 2*N*-sodium hydroxide (50 ml.) was added, and the solution was extracted with ether. Evaporation of the extract and crystallisation from light petroleum yielded the *isothiazole* (0.2 g.), plates, m. p. 81° (Found: C, 76.05; H, 4.6; N, 5.5; S, 13.5.  $C_{15}H_{11}NS$  requires C, 75.95; H, 4.6; N, 5.9; S, 13.5%),  $\lambda_{max}$  207, 251, and 277  $m\mu$  (log  $\epsilon$  4.39, 4.43, and 4.34).

*4-Phenylisothiazole*.—A saturated solution (10 ml.) of ammonium acetate in acetic acid was added to 4-phenyl-1,2-dithiolium perchlorate (1.5 g.) in boiling acetic acid (50 ml.) and boiling was continued for 10 min. Evaporation of the filtered solution yielded an oily residue which was partitioned between ether and water. The material from the ether layer was treated, in acetic acid, with perchloric acid and then with ether to precipitate a perchlorate (0.6 g.) which, upon treatment with *N*-sodium hydroxide, extraction with ether, and crystallisation from light petroleum, afforded 4-phenylisothiazole (0.23 g.), m. p. 36° (lit.<sup>19</sup> m. p. 36—37°) (Found: C, 66.7; H, 4.1; N, 8.5; S, 20.0. Calc. for  $C_9H_7NS$ : C, 67.1; H, 4.3; N, 8.7; S, 19.9%),  $\lambda_{max}$  210, 242, and 269  $m\mu$  (log  $\epsilon$  4.21, 4.03, and 4.03).

*Di-(4-phenyl-1,2-dithiol-3-yl) Sulphide*.—A suspension of 4-phenyl-1,2-dithiolium perchlorate (2 g.), in dry boiling benzene (75 ml.), was treated with a stream of dry ammonia for 5 min. Evaporation of the filtered solution gave a solid which, after being washed with ether and crystallised from benzene, afforded the pale yellow *sulphide* (0.7 g.), m. p. 152° (Found: C, 55.35; H, 4.0; S, 40.7.  $C_{18}H_{14}S_5$  requires C, 55.3; H, 3.6; S, 41.0%),  $\lambda_{max}$  232 and 306  $m\mu$  (log  $\epsilon$  4.38 and 4.34). Evaporation of the ether washings gave a residue (0.2 g.) which, when crystallised from light petroleum, afforded 4-phenylisothiazole (0.1 g.). Treatment of the *sulphide*, in boiling acetic acid, with perchloric acid caused evolution of hydrogen sulphide, and the solution, after being cooled, deposited a good yield of the dithiolium perchlorate.

*3-Anilino-1,3-diphenylpropene-1-thione*.—(a)  $\beta$ -Anilinochalcone<sup>14</sup> (1 g.) and phosphorus pentasulphide (2 g.) were boiled in carbon disulphide (10 ml.) for 4 hr. Filtration, washing with water, and evaporation gave a red oil which was crystallised from ethanol, to yield the *thione* (0.23 g.), red plates, m. p. 158° (Found: C, 80.5; H, 5.1; N, 4.1; S, 10.8.  $C_{21}H_{17}NS$  requires C, 80.1; H, 5.4; N, 4.45; S, 10.9%),  $\lambda_{max}$  232, 313, and 435  $m\mu$  (log  $\epsilon$  4.13, 4.10, and 4.34).

(b) 3,5-Diphenyl-1,2-dithiolium perchlorate (0.5 g.) and aniline (0.5 g.) were boiled in ethanol (10 ml.) until the solution became homogeneous. The product that separated from the cooled

<sup>19</sup> Hübennett, Flock, Hansel, Heinze, and Hofmann, *Angew. Chem. (Internat. Ed.)*, 1963, **2**, 714.

solution was fractionally crystallised from ethanol to yield a trace of sulphur and the thione (0.3 g.), m. p. and mixed m. p. 158°.

**3-Piperidino-1,3-diphenylpropene-1-thione.**—3,5-Diphenyl-1,2-dithiolium perchlorate (0.5 g.) and piperidine (0.5 ml.) were boiled in methanol (6 ml.) until the solution became homogeneous and then deposited sulphur. Hot filtration and cooling of the filtrate afforded the *thione* (0.3 g.) purple-red plates, m. p. 146—147° (from methanol) (Found: C, 78.2; H, 6.75; N, 4.3; S, 10.8.  $C_{20}H_{21}NS$  requires C, 78.5; H, 6.9; N, 4.6; S, 10.4%).

**3-Anilino-1-phenylpropene-1-thione.**—3-Phenyl-1,2-dithiolium perchlorate (1 g.) and aniline (1 ml.) were heated gently in ethanol (5 ml.) until the solution became homogeneous. Cooling then caused deposition of the *thione* (0.2 g.), m. p. 105—106° (from methanol) (Found: C, 75.4; H, 5.0; N, 5.6; S, 13.6.  $C_{15}H_{13}NS$  requires C, 75.2; H, 5.45; N, 5.9; S, 13.4%),  $\lambda_{max}$ . 225, 236, 250, 324, and 440  $m\mu$  ( $\log \epsilon$  4.03, 4.04, 4.03, 4.07, and 4.39).

**3-N-Methylanilino-1-phenylpropene-1-thione.**—3-Phenyl-1,2-dithiolium perchlorate (0.5 g.) was triturated, in methanol (5 ml.), with *N*-methylaniline (0.5 ml.) for 10 min. at room temperature. The solution was then cooled, and the brown crystalline precipitate that formed was washed with light petroleum and purified by dissolution in benzene, filtration, and precipitation with light petroleum. The *thione* (0.16 g.), red-brown plates, had m. p. 93° (Found: C, 75.6; H, 5.8; N, 5.5; S, 12.6.  $C_{16}H_{15}NS$  requires C, 76.0; H, 5.9; N, 5.5; S, 12.6%),  $\lambda_{max}$ . 211, 255, 319, and 440  $m\mu$  ( $\log \epsilon$  4.24, 4.04, 4.07, and 4.24).

**cis- and trans-Phenylmalondialdehyde Dianil.**—Phenylmalondialdehyde (0.5 g.), in ether, was boiled with aniline (1 ml.) for 3 hr. and set aside for 7 days. The resulting yellow precipitate was recrystallised from ethanol to yield the *trans*-dianil (0.18 g.), m. p. 138° (lit.<sup>15</sup> m. p. 138°),  $\lambda_{max}$ . 225sh, 250, 310, and 370sh  $m\mu$  ( $\log \epsilon$  4.0, 3.86, 4.43, and 3.8). The ethereal mother-liquors were evaporated and the residue was crystallised from ethanol to yield the *cis*-dianil (0.21 g.), m. p. 123—124° (Found: C, 84.1; H, 6.2; N, 9.8.  $C_{21}H_{18}N_2$  requires C, 84.5; H, 6.0; N, 9.4%)  $\lambda_{max}$ . 211, 247, 287, and 404  $m\mu$  ( $\log \epsilon$  4.13, 4.10, 4.23, and 4.30).

**cis-Phenylmalondialdehyde Dianil.**—4-Phenyl-1,2-dithiolium perchlorate (0.4 g.) and aniline (3 ml.) were heated in benzene (3 ml.) for 5 min. and set aside to cool. The resulting precipitate was recrystallised from ethanol to yield *cis*-phenylmalondialdehyde dianil perchlorate monohydrate (0.42 g.), yellow needles, m. p. 204° (Found: C, 61.1; H, 5.1; Cl, 8.4; N, 6.6. ( $C_{21}H_{19}ClN_2O_4 \cdot H_2O$  requires C, 60.6; H, 5.1; Cl, 8.5; N, 6.7%) which, on treatment, in aqueous acetone, with sodium hydroxide gave the *cis*-dianil, m. p. and mixed m. p. 123—124°, infrared spectrum identical with that of an authentic specimen.

**3-Ethoxycarbonyl-4,6-diphenyl-2H-thiopyran-2-one.**—Diethyl malonate (0.23 g.) was added to sodium ethoxide (from 0.03 g. sodium) in dry ethanol (10 ml.) and the solution was evaporated to dryness. Ether (50 ml.) and 3,5-diphenyl-1,2-dithiolium perchlorate (0.5 g.) were added and the suspension was boiled for 1.5 hr. After filtration, the ethereal solution was evaporated to dryness and the residue was crystallised from light petroleum to yield the *thiopyrone* (0.35 g.) pale yellow needles, m. p. 77° (Found: C, 71.5; H, 5.0; S, 9.4.  $C_{20}H_{16}O_3S$  requires C, 71.4; H, 4.8; S, 9.5%).

**4,6-Diphenyl-2H-thiopyran-2-one.**—The ethoxycarbonylthiopyrone (0.55 g.) was boiled in acetic acid (20 ml.) containing 25% aqueous sulphuric acid (20 ml.) for 25 min. Dilution with water and extraction with ether then afforded the *thiopyrone* (0.4 g.), m. p. 97—98° (from ethanol) (Found: C, 76.7; H, 4.9; S, 12.35.  $C_{17}H_{12}OS$  requires C, 77.3; H, 4.5; S, 12.2%),  $\lambda_{max}$ . 212, 221sh, 265, 290sh, and 369  $m\mu$  ( $\log \epsilon$  4.33, 4.3, 4.36, 4.0, and 3.92),  $\nu_{max}$ . 1635  $cm^{-1}$ .

**4,6-Diphenyl-2H-thiopyran-2-thione.**—(a) 4,6-Diphenyl-2H-pyran-2-thione<sup>16</sup> (0.5 g.), in boiling ethanol (15 ml.), was treated with 1.25M-ethanolic potassium hydrogen sulphide (3 ml.) and boiling was continued for 7 min. Dilution with 0.15M-aqueous hydrochloric acid (70 ml.), extraction with ether, and evaporation of the extract gave a deep red solid which showed a weak infrared absorption at 1635  $cm^{-1}$  attributable to a small amount of the thiopyran-2-one. Accordingly, the crude product was boiled, in benzene (25 ml.), with phosphorus pentasulphide (1.5 g.) for 5 hr. and the solution was filtered and evaporated. Crystallisation of the residue from ethanol afforded the *thiopyranthione* (0.3 g.), deep red plates, m. p. 118—119° (Found: C, 72.8; H, 4.25; S, 22.5.  $C_{17}H_{12}S_2$  requires C, 72.8; H, 4.3; S, 22.8%),  $\lambda_{max}$ . 242, 309, and 480  $m\mu$  ( $\log \epsilon$  4.27, 4.44, and 3.85).

(b) 4,6-Diphenyl-2H-thiopyran-2-one (0.25 g.) and phosphorus pentasulphide (1 g.) were boiled, in carbon disulphide (25 ml.), for 5 hr. and the solution was filtered. The residue was washed thoroughly with benzene and the combined benzene and carbon disulphide solutions



were washed ( $\text{Na}_2\text{CO}_3$  then water), dried, and evaporated. The residual oil was crystallised from ethanol to yield the thiopyranthione (0.18 g.), m. p. and mixed m. p. 118—119°, infrared spectrum identical with that of an authentic specimen.

*Reaction of 3,5-Diphenyl-1,2-dithiolium Perchlorate with NN-Dimethylaniline.*—The perchlorate (0.36 g.) was boiled, in *NN*-dimethylaniline (1.5 ml.), for 5 min., during which time the odour of hydrogen sulphide was apparent. The cooled solution was diluted with ether (3.5 ml.) and the precipitated oil was dissolved in hot methanol (1 ml.) and treated with 70% perchloric acid (3 drops). The resulting perchlorate was recrystallised from ethanol containing a trace of perchloric acid to yield putative 7-dimethylamino-2,4-diphenylbenzo[b]thiopyrylium perchlorate (0.23 g.), deep purple needles, m. p. 236—238° (Found: C, 61.9; H, 4.8; Cl, 8.5; N, 3.0; S, 6.7.  $\text{C}_{23}\text{H}_{20}\text{ClNO}_4\text{S}$  requires C, 62.4; H, 4.5; Cl, 8.0; N, 3.2; S, 7.1%),  $\lambda_{\text{max}}$ . 220, 230, 262, 333, and 565  $\text{m}\mu$  ( $\log \epsilon$  4.50, 4.49, 4.64, 4.65, and 4.43).

The authors thank the D.S.I.R. for a Research Studentship (to D. M. M.) and Mr. E. G. Cummins of Perkin-Elmer Ltd., for n.m.r. spectra.

DEPARTMENT OF CHEMISTRY,  
WEST MAINS RD., EDINBURGH.

[Received, March 17th, 1964.]

---