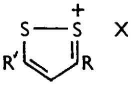
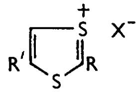
984. *The Dithiole Series. Part I.*[1] *Synthesis of* 1,2- *and* 1,3-*Dithiolium Salts.*

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

Reaction of hydrogen disulphide with β-diketones in presence of a strong acid yields 1,2-dithiolium salts. *S*-α-Oxoalkyl thio- and dithio-carboxylates are cyclised by treatment with hydrogen sulphide and a strong acid, yielding 1,3-dithiolium salts. Suitably placed methyl groups in both types of dithiolium salt condense with *p*-dimethylaminobenzaldehyde. *O*-Ethyl *S*-α-oxoalkyl dithiocarbonates with phosphorus pentasulphide afford 1,3-dithiole-2-thiones which are oxidised to dithiolium salts by peracetic acid.

THE chemistry of the heterocyclic cations (I) and (II) (dithiolium salts) has received little attention and, until recently, few general methods for the synthesis of such compounds were known. We have developed routes to diaryl- and alkylaryl-1,2- and -1,3-dithiolium salts, and Klingsberg[2] has reported a synthesis of 1,2-dithiolium salts (including the parent compound) by treatment of 1,2-dithiole-3-thiones with peracetic acid.


(I)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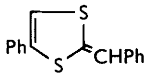
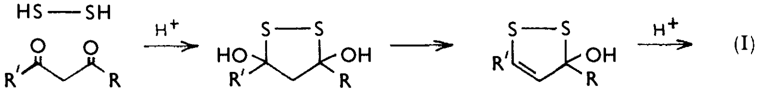

(III)

a : R = R′ = Ph ; b : R = Me, R′ = Ph;
c : R = Ph, R′ = Me; d : R = CH_2Ph, R′ = Ph
e : R = R′ = H ; f : R = H, R′ = Ph
g : R = p-$Me_2N{\cdot}C_6H_4{\cdot}CH{:}CH$, R′ = Ph

The observation by Bloch and his co-workers[3] that hydrogen disulphide adds readily to the carbonyl group of aromatic aldehydes suggested that reaction of the disulphide with β-diketones might afford a route to 1,2-dithiolium salts according to Scheme 1.

Scheme I.



Accordingly, dibenzoylmethane, benzoylacetone, and acetylacetone were allowed to react with hydrogen disulphide in benzene saturated with hydrogen chloride. The first two compounds yielded crystalline chlorides which were converted into the more stable perchlorates (Ia and b; X = ClO_4); benzoylacetone reacted the more rapidly and gave the better yield. Acetylacetone, however, gave only a syrup which, although insoluble in benzene, showed no salt-like properties and did not yield a perchlorate.

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[1] Preliminary communication, Leaver and Robertson, *Proc. Chem. Soc.*, 1960, 252.

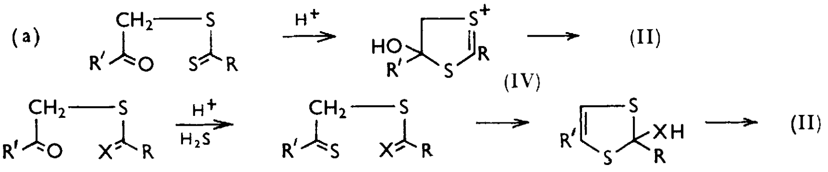
[2] Klingsberg, (*a*) *Chem. and Ind.*, 1960, 1568; (*b*) *J. Amer. Chem. Soc.*, 1961, **83**, 2934.

[3] Bloch, Höhn, and Bugge, *J. prakt. Chem.*, 1910, **82**, 473; Höhn and Bloch, *ibid.*, p. 486; Bugge and Bloch, *ibid.*, p. 512.

Consideration of the methods employed for synthesis of azoles and of thiopyrylium salts[4] led us to suppose that 1,3-dithiolium salts might be formed by acid-catalysed cyclisation of α-oxoalkyl dithiocarboxylates, R·CO·CH_2·S·CS·R′. Phenacyl dithiobenzoate gave a 40% yield of the chloride (IIa) during three weeks in ether saturated with hydrogen chloride, but when the solution was also saturated with hydrogen sulphide (method A), a better yield (98%) was obtained in a shorter time (4 days). α-Phenylphenacyl dithiobenzoate did not cyclise in ether but, with hydrogen sulphide and perchloric acid in boiling acetic acid (method B), it afforded a good yield of triphenyl-1,3-dithiolium perchlorate. Acetonyl dithiobenzoate and phenacyl dithioacetate and phenyl(dithioacetate) yielded dithiolium salts by method A. The last two compounds gave a better yield when boron trifluoride was used instead of hydrogen chloride, but the effect of boron trifluoride on the yields of other dithiolium salts was not investigated. The cation (perchlorate salt), and its conjugate base, obtained from phenacyl phenyl(dithioacetate) corresponded in melting points and ultraviolet spectra to the known 2-benzyl-4-phenyl-1,3-dithiolium perchlorate (IId) and 2-benzylidene-4-phenyl-1,3-dithiole (III) which were obtained[5] as photolysis products of 4-phenyl-1,2,3-thiadiazole.

The function of hydrogen sulphide in these cyclisations is probably to convert the carbonyl group of the ester into a thiocarbonyl group, so allowing the reaction to take place according to scheme 2(b) (X = S) rather than 2(a) which involves a less probable intermediate (IV). If the necessary hydrogen sulphide is not added, it may be formed by decomposition of half of the starting material, so that yields of the salt cannot then exceed 50%. It follows from this hypothesis that dithiolium salts might also be formed according to Scheme 2(b) (X = O). When method A was used, *S*-phenacyl thiobenzoate

Scheme 2.



slowly gave the chloride (IIa), but *S*-phenacyl thioacetate failed to cyclise; both esters, however, readily gave the dithiolium perchlorates (IIa) and (IIb) by method B and this is the most convenient route to these particular salts. *S*-α-Phenylphenacyl thiobenzoate gave only a very low yield of a dithiolium salt by method B. The main product, tetraphenylthiophen, which was also produced in the absence of hydrogen sulphide, is thought to arise by hydrolysis to α-mercaptodeoxybenzoin, self-condensation of this to tetraphenyl-1,4-dithiin, and extrusion of a sulphur atom. The last reaction is known to occur readily.[5]

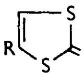
Methyl phenacyl trithiocarbonate and *O*-ethyl *S*-phenacyl dithiocarbonate failed to yield dithiolium salts but, with phosphorus pentasulphide in boiling tetralin, both esters yielded 4-phenyl-1,3-dithiole-2-thione (V; R = Ph). Similar reactions afforded 1,3-dithiole-2-thione (V; R = H) and its 4-methyl derivative (V; R = Me). Treatment of the thiones (V; R = H and Ph) in acetic acid with hydrogen peroxide (conditions similar to those described by Klingsberg[2] for the 1,2-dithiole-3-thiones) yielded 1,3-dithiolium perchlorate (IIe) and its 4-phenyl derivative (IIf). 5-Thio-1,2-dithiole-3-carboxylic acid was previously[2a] used as the source of the unsubstituted 1,2-dithiolium cation (Ie) but we found that the unsubstituted thione also yields this cation on treatment with peracetic acid.

The methyldithiolium perchlorates (Ib) and (IIb) with *p*-dimethylaminobenzaldehyde

[4] Wizinger and Ulrich, *Helv. Chim. Acta*, 1956, **39**, 207.

[5] Kirmse and Horner, *Annalen*, 1958, **614**, 4.

in boiling acetic acid rapidly gave the *p*-dimethylaminostyryl compounds, and they are, therefore, comparable in reactivity with 2-methylbenzo-1,3-dithiolium salts.[6] The perchlorate (IIc), however, failed to react in acetic acid or acetic anhydride, even in the presence of pyridine or triethylamine; evidently the conjugate bases of 4-methyl-1,3-dithiolium cations are not effectively stabilised by *d*-orbital resonance (VIA ←→ VIB).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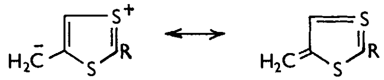
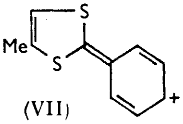


(VIA) (VIB)

The ultraviolet absorption spectra of the dithiolium salts are given in Table 2. When the structure permits positive charge delocalisation over one or more phenyl groups [as, *e.g.*, in (VII)] there is strong absorption in the region 350—400 mμ, but 4-phenyl- and 2-methyl-4-phenyl-1,3-dithiolium perchlorate (IIf and IIb), in which interannular conjugation of this type is impossible without participation (VIII) of sulphur *d*-orbitals, absorb at lower wavelengths (305—310 mμ). Klingsberg[2b] observed similar differences between the spectra of 3- and 4-phenyl-1,2-dithiolium salts.

An unexpected reaction occurred when phenacyl bromide was allowed to react with sodium phenyl(dithioacetate) in boiling ethanol; analysis suggested that the product had been formed from the expected dithioester (IX) by loss of water, and was possibly, therefore, the thiophenthiol (X) or one of its thione tautomers. Evidence in support of such a structure was provided by hydrogenolysis with Raney nickel to *meso*-2,3-diphenylbutane. Subsequent preparations of the ester (IX) were conducted below room temperature and with neutralisation of the excess of alkali in the sodium phenyl(dithioacetate) solution.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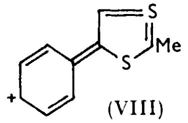
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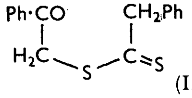

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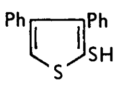

(X)

Experimental

1,2-Dithiolium Salts from Hydrogen Disulphide.—Hydrogen disulphide was prepared by the method of Fehér, Laue, and Winkhaus.[7] Dibenzoylmethane (3 g.), in dry benzene (100 ml.) saturated with hydrogen chloride, was treated with the disulphide (2 ml.) and left at room temperature for 3 days. The solution deposited a chloride (1·5 g.), pale yellow needles, m. p. 137°, which yielded unsatisfactory analytical results. Treatment of this, in acetic acid, with perchloric acid gave 3,5-*diphenyl*-1,2-*dithiolium perchlorate* (1·1 g.), pale yellow needles, m. p. 258—259° (Found: C, 50·9; H, 3·0; Cl, 9·4; S, 17·95. $C_{15}H_{11}ClO_4S_2$ requires C, 50·8; H, 3·1; Cl, 10·0; S, 18·0%).

Benzoylacetone (4 g.), treated similarly, yielded a chloride, m. p. 46—48°, which was converted into 3-*methyl*-5-*phenyl*-1,3-*dithiolium perchlorate* (7·2 g.), needles, m. p. 114—115° (from acetic acid–butyl acetate) (Found: C, 41·3; H, 3·2; Cl, 12·1; S, 21·95. $C_{10}H_9ClO_4S_2$ requires C, 41·0; H, 3·1; Cl, 12·1; S, 21·9%).

Thioesters and Dithioesters.—Dithioacids were prepared from Grignard reagents and carbon disulphide, and aqueous solutions of the sodium salts were purified as described by Bost and Shealy.[8] Addition of the halogeno-ketone (1 mol.; phenacyl bromide, α-phenylphenacyl chloride, or bromoacetone) in an equal volume of ethanol, and heating at 75—80° for a minute, gave the dithioesters which were isolated by filtration or extraction with ether. Thioesters were prepared similarly from the commercially available thioacids.

Conditions for the preparation of phenacyl phenyl(dithioacetate) were more critical: an

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[6] Soder and Wizinger, *Helv. Chim. Acta*, 1959, **42**, 1733, 1779.

[7] Fehér, Laue, and Winkhaus, *Z. anorg. Chem.*, 1956, **288**, 113.

[8] Bost and Shealy, *J. Amer. Chem. Soc.*, 1951, **73**, 24.

aqueous 1·25M-solution (35 ml.; freed from alkali by titration with hydrochloric acid until dithioacid began to separate) of sodium phenyl(dithioacetate) was added slowly to phenacyl bromide (7·2 g.) in ethanol (200 ml.), and more ethanol was added to give a clear solution. The solution, after being left at 0° for 1 hr., diluted with water until cloudy, and set aside for 15 hr., deposited the dithioester (52%).

M. p.s and analyses of the esters are in Table 1. Acetonyl dithiobenzoate was a red oil that was not purified.

TABLE 1.

Thioesters and dithioesters.

			Found (%)				Required (%)		
Phenacyl ester	M. p.	Form	C	H	S	Formula	C	H	S
Thioacetate	42—43°	Colourless plates *	62·1	5·4	16·5	$C_{10}H_{10}O_2S$	61·9	5·2	16·5
Dithioacetate	48—49	Yellow needles †	56·4	4·5	30·6	$C_{10}H_{10}OS_2$	57·1	4·8	30·5
Dithiobenzoate	75—76	Red ,, ‡	65·7	4·3	23·6	$C_{15}H_{12}OS_2$	66·2	4·4	23·5
Phenyl(dithioacetate)	48	Yellow ,, †	67·1	4·9	22·3	$C_{16}H_{14}OS_2$	66·75	4·9	22·4
(α-Phenylphenacyl dithiobenzoate) ...	102—103	Red plates §	72·5	4·9	17·9	$C_{21}H_{16}OS_2$	72·4	4·6	18·4

* From ether. † From light petroleum (b. p. 40—60°). ‡ From acetic acid. § From light petroleum (b. p. 80—100°).

1,3-*Dithiolium Salts by Cyclisation of Esters*.—(*a*) *Without hydrogen sulphide*. Ether (100 ml.) containing phenacyl dithiobenzoate (5 g.) was saturated with hydrogen chloride and left at room temperature for 3 weeks. The solution slowly deposited a chloride (2·1 g., 40%), yellow prisms, which yielded unsatisfactory analytical results. Treatment of this, in acetic acid, with perchloric acid gave 2,4-*diphenyl*-1,3-*dithiolium perchlorate*, yellow plates, m. p. 209—210° (Found: C, 50·0; H, 3·0; Cl, 10·2; S, 18·4%).

After 4 days at room temperature, phenacyl dithioacetate (0·5 g.) in ether (25 ml.) containing boron trifluoride (2 ml.; BF_3,Et_2O), yielded a salt which was converted into 2-*methyl*-4-*phenyl*-1,3-*dithiolium perchlorate* (0·23 g., 37%), plates, m. p. 160—161° (from acetic acid containing a little perchloric acid) (Found: C, 40·75; H, 2·9; Cl, 12·05; S, 21·9%).

(*b*) *Method A*. Solutions of the esters in ether (20 ml. per g. of ester) were saturated with hydrogen chloride and hydrogen sulphide and left at room temperature. The salts which crystallised were, in most instances, converted in acetic acid into the perchlorates.

Phenacyl dithiobenzoate gave (after 4 days) 2,4-diphenyl-1,3-dithiolium perchlorate (98%), m. p. 209—210°.

S-Phenacyl thiobenzoate[9] gave (after 6 weeks) a salt (*ca*. 95%), m. p. 144—145°, intermediate in composition between 2,4-diphenyl-1,3-dithiolium chloride and the dithiolium hydrogen dichloride (Found: C, 56·7; H, 3·75; Cl, 17·4; S, 20·2. Calc. for $C_{15}H_{11}ClS_2$: C, 62·0; H, 3·8; Cl, 12·2; S, 22·0. Calc. for $C_{15}H_{12}Cl_2S_2$: C, 55·0; H, 3·7; Cl, 21·7; S, 19·6%).

Acetonyl dithiobenzoate gave (after 3 days) 4-*methyl*-2-*phenyl*-1,3-*dithiolium perchlorate* (46%), pale yellow plates, m. p. 102—103° (from acetic acid) (Found: C, 41·35; H, 3·2; Cl, 12·2; S, 21·8%).

Phenacyl dithioacetate gave (after 3 weeks) 2-methyl-4-phenyl-1,3-dithiolium perchlorate (79%), m. p. 160—161°; use of boron trifluoride instead of hydrogen chloride gave 85% after 4 days.

Phenacyl phenyl(dithioacetate) (with boron trifluoride instead of hydrogen chloride) gave (after 24 hr.) 2-benzyl-4-phenyl-1,3-dithiolium perchlorate (74%), m. p. 113° (lit.,[5] m. p. 113°), which with aqueous sodium carbonate afforded 2-benzylidene-4-phenyl-1,3-dithiole, m. p. 204° (lit.,[5] m. p. 205—207°), $\lambda_{max.}$ 354 mμ (log ε 4·34) in dioxan [lit.,[5] 354 (4·33) in tetrahydrofuran].

(*c*) *Method B*. Hydrogen sulphide was passed for 1·5—3 hr. through boiling solutions of the esters in acetic acid (15 ml. per g. of ester) containing 70% perchloric acid (1 ml. per g. of ester). The dithiolium perchlorates crystallised from the cooled solutions and further crops were obtained by addition of ether to the mother-liquors.

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[9] Groth, *Arkiv Kemi, Min., Geol.*, 1924, **9**, 50.

α-Phenylphenacyl dithiobenzoate gave 2,4,5-*triphenyl*-1,3-*dithiolium perchlorate* (60%), yellow needles, m. p. 254—255° (from acetic acid) (Found: C, 58·2; H, 3·5; Cl, 8·5; S, 14·8. $C_{21}H_{15}ClO_4S_2$ requires C, 58·5; H, 3·5; Cl, 8·2; S, 14·9%).

S-Phenacyl thiobenzoate gave 2,4-diphenyl-1,3-dithiolium perchlorate (43%), m. p. 209—210°.

S-Phenacyl thioacetate gave 2-methyl-4-phenyl-1,3-dithiolium perchlorate (33%), m. p. 160—161°.

S-α-Phenylphenacyl thiobenzoate [10] (2 g.) gave tetraphenylthiophen (1 g.), m. p. 184—185° (lit.,[11] m. p. 184°), shown by its infrared spectrum to be identical with an authentic specimen. Dilution of the mother-liquors with ether yielded 2,4,5-triphenyl-1,3-dithiolium perchlorate (0·3 g.). Under the same conditions, but without hydrogen sulphide, the thioester gave tetraphenylthiophen in the same yield.

Methyl Phenacyl Trithiocarbonate.—Methanethiol (12 ml.) and, afterwards, carbon disulphide (17·4 g.) were added, below 0°, to ethanol (200 ml.) containing sodium ethoxide (from 5·3 g. of sodium). Phenacyl bromide (45 g.) in ethanol (200 ml.) was then added and the solution was left at room temperature for 1 hr. and poured into water (1·5 l.). The product which separated recrystallised from light petroleum (b. p. 60—80°), to yield *methyl phenacyl trithiocarbonate* (41·8 g.), yellow needles, m. p. 40—41° (Found: C, 49·3; H, 4·2; S, 39·7. $C_{10}H_{10}OS_3$ requires C, 49·6; H, 4·1; S, 39·9%). Attempted cyclisations by methods A and B failed.

O-*Ethyl* S-*Acetonyl and* O-*Ethyl* S-2′-*Oxoethyl Dithiocarbonate.*—Bromoacetone and chloroacetaldehyde were allowed to react with potassium *O*-ethyl dithiocarbonate in ethanol for 1 hr. at 0°. The solutions were then poured into water, and the oils which separated were dried ($CaCl_2$) in ether and used without purification.

1,3-*Dithiole*-2-*thiones.*—The di- and tri-thiocarbonates were heated with phosphorus pentasulphide (2—3 mol.) in boiling tetralin (10—20 ml. per g. of ester) for 20 min. The cooled solutions were decanted into twice their volume of ether, washed successively with water, 10% sodium hydroxide solution, and water, and dried ($CaCl_2$). The thione–mercuric chloride complexes were then precipitated by pouring the solutions into saturated methanolic mercuric chloride and were decomposed by shaking them with saturated aqueous sodium sulphide. The thiones were recovered by extraction of the resulting mixed solids with hot ethanol or acetone (and, in the case of the unsubstituted compound, by extraction of the sodium sulphide solution with ether).

Methyl phenacyl trithiocarbonate and *O*-ethyl *S*-phenacyl dithiocarbonate gave 4-phenyl-1,3-dithiole-2-thione (35%), reddish-brown needles, m. p. 117—118° (from ethanol) (lit.,[12] m. p. 116°) (Found: C, 51·4; H, 2·4; S, 45·85. Calc. for $C_9H_6S_3$: C, 51·4; H, 2·9; S, 45·7%).

O-Ethyl *S*-acetonyl dithiocarbonate gave 4-*methyl*-1,3-*dithiole*-2-*thione* (23%), yellow plates, m. p. 30° after chromatography (in benzene) on alumina and recrystallisation from light petroleum (b. p. 40—60°) (Found: C, 32·8; H, 3·0; S, 64·2. $C_4H_4S_3$ requires C, 32·4; H, 2·7; S, 64·9%).

O-Ethyl *S*-2′-oxoethyl dithiocarbonate gave 1,3-dithiole-2-thione (8%), m. p. and mixed m. p. 49—50° (lit.,[13] m. p. 50°) after chromatography (in benzene) on alumina and recrystallisation from light petroleum (b. p. 40—60°).

Dithiolium Salts by Oxidation of Dithiolethiones.—(*a*) 1,2-*Dithiolium perchlorate.* 1,2-Dithiole-3-thione [14] (0·4 g.) in acetic acid (10 ml.) was treated with 30% hydrogen peroxide (1 ml.), the temperature being kept below 40°. After 20 min. the solution was filtered, treated with 70% perchloric acid (0·5 ml.) and diluted with ether, to precipitate 1,2-*dithiolium perchlorate* (0·3 g.), no definite m. p., which recrystallised from acetic acid containing a little perchloric acid (Found: C, 17·7; H, 1·5; Cl, 18·1; S, 32·4. $C_3H_3ClO_4S_2$ requires C, 17·8; H, 1·5; Cl, 17·5; S, 31·6%).

(*b*) 1,3-*Dithiolium perchlorate.* 1,3-Dithiole-2-thione (0·47 g.) in acetic acid (8 ml.) was treated with 30% hydrogen peroxide (1·2 ml.) with stirring and cooling to below 30°, and after 1 hr. the solution was decanted from an oil which had been formed. Dilution with ether caused separation of a mixture of oil and water which, on treatment in methanol (5 ml.) with 70%

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[10] Schönberg and Iskander, *J.*, 1942, 90.

[11] Baumann and Fromm, *Ber.*, 1891, **24**, 1456.

[12] Runge, El-Hewehi, Renner, and Taeger, *J. prakt. Chem.*, 1960, **11**, 296.

[13] Challenger, Mason, Holdsworth, and Emmott, *J.*, 1953, 292.

[14] Mayer and Kubasch, *Angew. Chem.*, 1961, **73**, 220.

perchloric acid (3 drops) and ether (5 ml.), afforded 1,3-*dithiolium perchlorate* (0·14 g.), m. p. 264° (from acetic acid–perchloric acid) (Found: C, 18·3; H, 1·5; Cl, 17·15; S, 31·6%).

(*c*) 4-*Phenyl*-1,3-*dithiolium salts*. 4-Phenyl-1,3-dithiole-2-thione (0·21 g.) in acetone (5 ml.) and acetic acid (5 ml.) was treated with 30% hydrogen peroxide (0·34 ml.), and the solution was stirred for 10 min. and set aside for 1 hr. The solution was decanted into ether (20 ml.), and the resulting precipitate was treated with charcoal in, and recrystallised from, acetic acid containing a little sulphuric acid, to give 4-*phenyl*-1,3-*dithiolium hydrogen sulphate* (0·1 g.), m. p. 180° (became brown, solidified, and remelted at 232°) (Found: C, 39·2; H, 3·1; S, 35·15. $C_9H_8O_4S_3$ requires C, 39·1; H, 2·9; S, 34·8%). Treatment, in acetic acid, with perchloric acid yielded the *perchlorate*, m. p. 161° (Found: C, 38·8; H, 2·7; Cl, 12·55; S, 23·15. $C_9H_7ClO_4S_2$ requires C, 38·7; H, 2·5; Cl, 12·7; S, 23·0%).

Condensation of Dithiolium Salts with p-*Dimethylaminobenzaldehyde*.—2-Methyl-4-phenyl-1,3-dithiolium perchlorate (0·1 g.) and *p*-dimethylaminobenzaldehyde in acetic acid (3 ml.) were boiled for 5 min. and cooled to yield 2-p-*dimethylaminostyryl*-4-*phenyl*-1,3-*dithiolium perchlorate* (0·085 g.), deep blue needles, m. p. 203—204° (Found: C, 53·3; H, 3·9; Cl, 8·65; N, 3·2; S, 15·45. $C_{19}H_{18}ClNO_4S_2$ requires C, 53·8; H, 4·25; Cl, 8·5; N, 3·3; S, 15·1%).

3-Methyl-5-phenyl-1,2-dithiolium perchlorate (0·1 g.) similarly yielded 3-p-*dimethylaminostyryl*-5-*phenyl*-1,2-*dithiolium perchlorate* (0·1 g.), green needles, m. p. 214—215° (Found: C, 53·7; H, 4·1; Cl, 8·05; N, 3·5; S, 14·9%).

TABLE 2.

Absorption spectra of dithiolium perchlorates.

Compound	$\lambda_{max.}$ (mμ) with log ε (in parentheses)			
Ia		233 (4·01)		381 (4·36)
Ib	219 (3·98)		295 (3·84)	354 (4·33)
IIa	218 (4·16)	242 (4·20)	305 (3·80)	392 (4·20)
II; Ph_3	221 (4·40)		303 (3·98)	399 (4·18)
IIc	209 (4·05)		269 (3·57)	362 (4·19)
IIb		232 (4·06)	310 (3·89)	
IIf		232 (4·01)	306 (3·88)	
Ie		245 (3·62)	288 (3·59)	
IIe	212 (3·53)	254 (3·58)		
Ig *		263 (3·97)	363 (4·17)	644 (4·49)
IIg *		250 (4·20)	332 (3·89)	636 (4·72)

* In 10% aqueous ethanol.

Ultraviolet and Visible Absorption Spectra.—The absorption maxima of dithiolium salts, measured (unless otherwise stated) for ethanol solutions containing a little perchloric acid, with a Unicam S.P. 500 quartz spectrophotometer, are recorded in Table 2.

3,4-*Diphenylthiophen Derivative*.—Sodium phenyl(dithioacetate) (2·5 g.) in water (12·5 ml.) was added slowly to phenacyl bromide (2·2 g.) in boiling ethanol (50 ml.), and the solution was boiled for a further 10 min. Dilution with water, extraction with ether, and evaporation of the alkali-washed and dried ($CaCl_2$) extract gave a red oil. This was chromatographed in benzene on alumina; the eluted orange oil crystallised from light petroleum (b. p. 40—60°) by cooling to −70°, affording a pale yellow solid (putative 3,4-*diphenylthiophen*-2-*thiol* or a tautomer) (2·03 g.), m. p. 60—62° (Found: C, 72·2; H, 4·2; S, 23·45. $C_{16}H_{12}S_2$ requires C, 71·6; H, 4·5; S, 23·8%). The compound (0·2 g.) was treated with Raney nickel (large excess) in boiling ethanol for 1 hr., the nickel was removed, and the solution was diluted with water. After 2 days at room temperature crystals of *meso*-2,3-diphenylbutane, m. p. 125° (lit.,[15] m. p. 126—127°), had separated.

The authors thank the University of Edinburgh for the award of a Demonstratorship (to W. A. H. R.) and the Department of Scientific and Industrial Research for a maintenance grant (to D. M. M.).

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF EDINBURGH. [*Received, May 7th*, 1962.]

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[15] Ott, *Ber.*, 1928, **61**, 2138.