The Dithiole Series. Part V.[1] Reactions of 1,2-Dithiole-3-thiones and 1,3-Dithiolan-2-thiones with Acetylenic Esters and with Benzyne

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5-Substituted and 4,5-disubstituted 1,2-dithiole-3-thiones react with dimethyl acetylenedicarboxylate to give 1:1 adducts, containing a 2-thioacylmethylene-1,3-dithiole system, and 1:2 adducts containing a thiopyran-4-spiro-2'-(1,3-dithiole) system. 4-Phenyl-1,2-dithiole-3-thione and 1,2-benzodithiole-3-thione give 1:2 adducts only. 5-Phenyl-1,2-dithiole-3-thione, with esters of acetylenic monocarboxylic acids, gives only 1:1 adducts and the 4-phenyl isomer gives a derivative of 1,4-bis-(1,3-dithiol-2-ylidene)but-2-ene. Related products are formed when 1,2-dithiole-3-thiones react with benzyne. 1,3-Dithiolan-2-thiones react with dimethyl acetylenedicarboxylate and with benzyne to give dimethyl 2-thioxo-1,3-dithiole-4,5-dicarboxylate and 1,3-benzodithiole-2-thione, respectively; a molecule of olefin is eliminated.

THE addition reactions of 1,2-dithiole-3-thiones with acetylenic dipolarophiles were reported almost simultaneously from three different laboratories [2-4] including our own. We now give details of our work including studies on the related 1,3-dithiolan-2-thiones and on the use of benzyne as a dipolarophile.

Reactions with Acetylenic Esters.—5-Phenyl-1,2-dithiole-3-thione (1a) gave two products with dimethyl acetylenedicarboxylate (2 mol. equiv.) in benzene at room temperature, a brown 1:1 adduct and a yellow 1:2 adduct. The u.v.–visible spectrum of the 1:1 adduct was similar to that of 4-phenyl-2-thiophenacylidene-1,3-dithiole [1] (4) and suggested the structure (2a), which subsequently received support from the work of Behringer and his co-workers.[2] It seemed probable that the 1:2 adduct, which could also be obtained from the 1:1 adduct by further treatment with the acetylenic

[1] Part IV, E. I. G. Brown, D. Leaver, and D. M. McKinnon, *J. Chem. Soc.* (*C*), 1970, 1202.

[2] (*a*) H. Behringer and R. Wiedenmann, *Tetrahedron Letters*, 1965, 3705; (*b*) H. Behringer, D. Bender, J. Falkenburg, and R. Wiedenmann, *Chem. Ber.*, 1968, **101**, 1428.

[3] D. B. J. Easton and D. Leaver, *Chem. Comm.*, 1965, 585.

[4] H. Davy, M. Demuynk, D. Paquer, A. Rouessac, and J. Vialle, *Bull. Soc. chim. France*, 1966, 1150; 1968, 2057.

ester, was the spiro-compound (3a), formed by a [2 + 4]-cycloaddition reaction. This structure was confirmed by desulphurisation with Raney nickel to give dimethyl succinate and dimethyl (3-phenylpropyl)succinate. Similar 1 : 1 and 1 : 2 adducts were obtained from the dithiolethiones (1c—e).

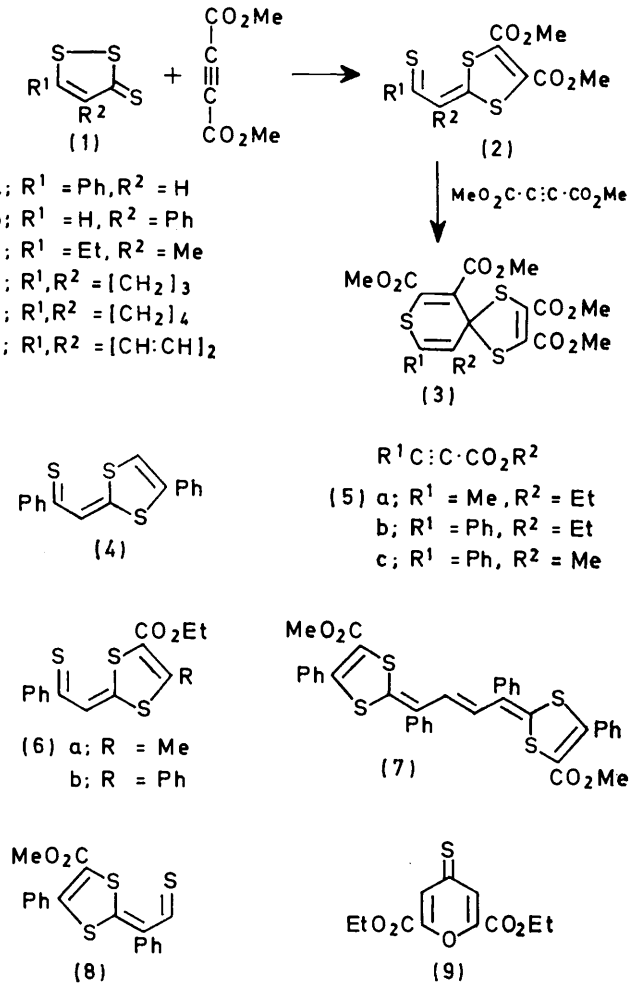
The 1,2-benzodithiole-3-thione (1f), on the other hand, gave only a 1 : 2 adduct; when the reactants were used in equimolar proportions, half of the thione was recovered. The structure (3f) for this adduct was again established by Raney-nickel desulphurisation, which gave dimethyl succinate and dimethyl benzylsuccinate. Presumably, the second molecule of acetylenic ester adds more rapidly than the first owing to the highly reactive quinonoid structure (2f) of the intermediate 1 : 1 adduct. A similar result was obtained with 4-phenyl-1,2-dithiole-3-thione (1b), though here the 1 : 2 adduct was non-crystalline and could not be obtained analytically pure. Its structure (3b) follows from the similarity of its ^{1}H n.m.r. spectrum to that of the isomeric adduct (3a). In this case, the factor that enhances the reactivity of the 1 : 1 adduct and prevents its isolation is the presence of a thioaldehyde group.

The acetylenic monocarboxylates (5a) and (5b) were much less reactive than the dicarboxylate and yielded only the 1 : 1 adducts (6a) and (6b) after being heated with 5-phenyl-1,2-dithiole-3-thione (1a) for several days in benzene under reflux. Under the same conditions, methyl phenylpropiolate (5c) reacted with the 4-phenyl compound (1b) to give a red product, the structure of which (7) is assigned on the basis of elemental analysis, molecular weight, and its reaction with Raney nickel (followed by ester hydrolysis) to give 3-phenylpropionic acid and 2,5-diphenylhexane.

The formation of compound (7), presumably from two molecules of the 1 : 1 adduct (8), is an example of the well known [5] thermal conversion of thiocarbonyl compounds into symmetrically substituted ethylenes. The only other example known to occur at a comparably low temperature is the conversion [6] of the pyran-4-thione (9), at its m.p. (51°), into the corresponding bi(pyranylidene).

In view of the ease with which 1,2-dithiole-3-thiones reacted with dimethyl acetylenedicarboxylate, we investigated the reactivity of the isomeric 1,3-dithiole-2-thiones under similar conditions, the 4-phenyl compound (10a) being chosen as the most convenient representative. As we expected, this compound was completely unreactive towards the diester in cold or boiling benzene. In boiling xylene, or at 195° in the absence of a solvent, however, it gave low yields (7—10%) of a 1 : 2 adduct of undetermined structure.

More encouraging results emerged from a study of 1,3-dithiolan-2-thiones. When the parent compound (11) was slowly heated with dimethyl acetylenedicarboxylate, no reaction was evident at first but, at 140°, ethylene was evolved and a high yield of dimethyl 2-thioxo-1,3-dithiole-4,5-dicarboxylate (10b) was formed.



The corresponding reactions of *cis*- and *trans*-4,5-diphenyl-1,3-dithiolan-2-thiones were complete within 10 min at 120°. The stilbene formed from the *cis*-thione, after 5 min at 120°, contained approximately 90% of the *cis*-isomer * and the *trans*-thione gave entirely *trans*-stilbene under the same conditions. Since the proportion of *trans*-stilbene obtained from the *cis*-thione had increased to 20% after a further 5 min at 120°, we believe that the initial reaction occurs stereospecifically and that isomerisation of *cis*-stilbene is responsible for its contamination with the *trans*-isomer.

These results suggest that the reaction, which involves the transfer of a trithiocarbonate grouping from an olefin to an acetylene, is a concerted *cis*-elimination occurring *via* a bicyclic transition state such as (12). In view of the mild reaction conditions and high conversions, the reaction might offer a useful alternative to the stereospecific synthesis of olefins of Corey and his co-workers [7]

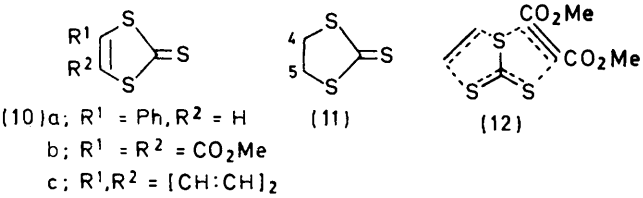
* Our previously reported [3] finding that the stilbene formed in this reaction contained only 42% of the *cis*-isomer was probably due to isomerisation during g.l.c. analysis, the column temperature being too high. We thank the referees for drawing our attention to this possibility.

[5] E. Campaigne, *Chem. Rev.*, 1946, **39**, 50; A. Schönberg and W. Asker, *ibid.*, 1945, **37**, 1.

[6] F. Arndt and P. Nachtwey, *Ber.*, 1923, **56**, 2406.

[7] E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Amer. Chem. Soc.*, 1965, **87**, 934; E. J. Corey, *Pure Appl. Chem.*, 1967, **14**, 19.

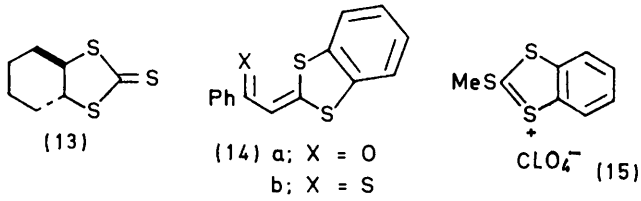
from 1,3-dithiolan- or 1,3-dioxolan-2-thiones by reaction with trivalent phosphorus compounds. Further evidence for a concerted mechanism was provided by the behaviour of the *trans*-bicyclic thione (13), most of which was recovered after being heated with dimethyl acetylenedicarboxylate for 1 h at 145—150°; the dithiolethione (10b) was not formed. As in the reactions studied by Corey and his co-workers, elimination is blocked when the concerted pathway would lead to an excessively strained structure (in this case, *trans*-cyclohexene).



(10) a; R^1 = Ph, R^2 = H
b; R^1 = R^2 = CO_2Me
c; R^1,R^2 = [CH:CH]$_2$

(11)

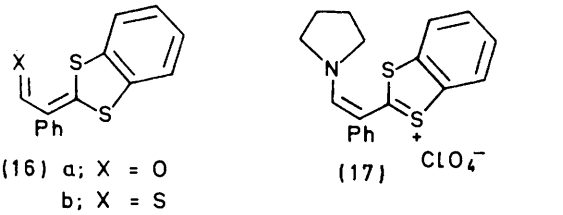
(12)



(13)

(14) a; X = O
b; X = S

(15)



(16) a; X = O
b; X = S

(17)

Reactions with Benzyne.—Benzyne reacted with 5-phenyl-1,2-dithiole-3-thione to give 2-thiophenacylidene-1,3-benzodithiole (14b), identical with a specimen synthesised from the 2-methylthiobenzodithiolylium salt (15) by reaction with sodium benzoylacetate [1] and treatment of the resulting phenacylidene compound (14a) with phosphorus pentasulphide. The best yield (55%) of this adduct was obtained when benzyne was generated [8] from 1-aminobenzotriazole and lead tetra-acetate, in benzene at room temperature. With anthranilic acid and isopentyl nitrite,[9] in benzene–tetrahydrofuran under reflux, the thione gave a moderate yield (28%) of the adduct but with preformed benzenediazonium-2-carboxylate, it gave only a trace. A low yield (7%) was obtained with diphenyliodonium-2-carboxylate [10] in boiling γ-butyrolactone.

The procedure using 1-aminobenzotriazole and lead tetra-acetate was the only one that yielded a characterisable product from 4-phenyl-1,2-dithiole-3-thione. Elemental analysis of the product, and the presence of a one-proton singlet at τ 0·7 in its ^{1}H n.m.r. spectrum, suggested that it might be the aldehyde (16a) rather than the corresponding thioaldehyde (16b) which is the expected initial product of addition of benzyne to the thione. Oxidation by lead tetra-acetate could be held responsible for the replacement of S by O in the labile thioaldehyde group. The suggested structure was confirmed by comparison with an authentic specimen of the aldehyde, synthesised by hydrolysis of the salt (17). The latter was obtained from the benzodithiolylium salt (15) by reaction with β-pyrrolidinostyrene (an extension of our previously described [1] use of enamines for the synthesis of dithiolylidene ketones).

Generation of benzyne by oxidation of 1-aminobenzotriazole was again the most successful method for reaction with 1,3-dithiolan-2-thione, the product (13%) being the known [11] benzodithiolethione (10c). The same product (9%) was obtained by using diphenyliodonium-2-carboxylate as the benzyne precursor, but the anthranilic acid–isopentyl nitrite method gave only an ill-defined, amorphous substance showing i.r. carbonyl absorption at 1695 cm^{-1}.

EXPERIMENTAL

N.m.r. data refer to solutions in deuteriochloroform, with tetramethylsilane as internal standard, and were recorded at 60 MHz with a Perkin-Elmer R10 spectrometer. Electronic spectral data refer to solutions in ethanol and were recorded with a Perkin-Elmer 137 u.v. spectrophotometer. Alumina for chromatography was Spence type H and Kieselgel G (Merck) was used for t.l.c. Light petroleum was the fraction of b.p. 60—80°. Extracts were dried over anhydrous sodium sulphate and all evaporations were carried out under reduced pressure.

Reactions of Dimethyl Acetylenedicarboxylate with 1,2-Dithiole-3-thiones.—General procedure. The ester (2 mol. equiv.) was added to a solution of the appropriate thione (1 mol. equiv.) in benzene (*ca.* 30 ml per g of thione) at room temperature. The solutions, all of which darkened rapidly, were kept overnight and worked up as described individually below. Yields quoted are based on thione.

(a) *Reaction with 5-phenyl-1,2-dithiole-3-thione.* The solution deposited a brown solid which was filtered off and recrystallised from nitromethane to give dimethyl 2-thiophenacylidene-1,3-dithiole-4,5-dicarboxylate (2a) (43%) brown plates, m.p. 149—151° (lit.,[2b] 152—153°) (Found: C, 51·1; H, 3·4; S, 26·9. Calc. for $C_{15}H_{12}O_4S_3$: C, 51·1; H, 3·4; S, 27·3%), $\lambda_{max.}$ 268, 342, and 466 nm (log ε 4·32, 4·01, and 4·17). Evaporation of the filtrate and recrystallisation of the residue from methanol yielded *tetramethyl 6-phenylthiopyran-4-spiro-2′-(1,3-dithiole)-2,3,4′,5′-tetracarboxylate* (3a) (44%), yellow needles, m.p. 116—117° (Found: C, 51·1; H, 3·2; S, 19·4. $C_{21}H_{18}O_8S_3$ requires C, 51·0; H, 3·6; S, 19·4%), τ 2·4—2·6 (5H, m, Ph), 3·26 (1H, s, 5-H), 6·06 (3H, s, OMe), 6·14 (3H, s, OMe), and 6·21 (6H, s, 2 × OMe). The same 1 : 2 adduct (93%) was obtained when the 1 : 1 adduct (0·2 g) and dimethyl acetylenedicarboxylate (0·09 g) were heated in benzene (25 ml) under reflux for 30 min.

(b) *Reaction with 4-phenyl-1,2-dithiole-3-thione.* Evaporation of the solution gave the 1 : 2 adduct (2b) as a viscous gum which failed to crystallise after chromatography on

[8] C. D. Campbell and C. W. Rees, *J. Chem. Soc.* (*C*), 1969, 742, 748.
[9] L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, 1963, **85**, 1549.
[10] F. M. Beringer and S. J. Huang, *J. Org. Chem.*, 1964, **29**, 445.
[11] W. R. H. Hurtley and S. Smiles, *J. Chem. Soc.*, 1926, 1821.

alumina, in benzene. The n.m.r. spectrum of the gum [τ 2·4—2·8 (*ca.* 8H, m, Ph and occluded benzene), 3·59 (1H, s, H-6), 6·09 (3H, s, OMe), 6·14 (3H, s, OMe), and 6·28 (6H, s, 2 × OMe)] showed the presence of occluded benzene but it was otherwise very similar to that of adduct (3a). Attempted removal of the benzene by keeping the gum in vacuum for several days led to slight decomposition.

(c) *Reaction with 5-ethyl-4-methyl-1,2-dithiole-3-thione.* Evaporation of the solution gave an oil which solidified on being triturated with light petroleum. Recrystallisation from methanol yielded *tetramethyl 6-ethyl-5-methylthiopyran-4-spiro-2'-(1,3-dithiole)-2,3,4',5'-tetracarboxylate* (3c) (96%), yellow plates, m.p. 118—119° (Found: C, 46·9; H, 4·5; S, 20·8. $C_{18}H_{20}O_8S_3$ requires C, 46·9; H, 4·4; S, 20·9%). Repetition of the reaction with equimolar quantities of reactants gave, after chromatography on alumina (i) a trace of recovered thione, (ii) *dimethyl 2-(1-methyl-2-thioxobutylidene)-1,3-dithiole-4,5-dicarboxylate* (2c) (65%), brown needles, m.p. 98—100° (from methanol) (Found: C, 45·1; H, 4·3; S, 30·2. $C_{12}H_{14}O_4S_3$ requires C, 45·3; H, 4·4; S, 30·2%), and (iii) a trace of the 1 : 2-adduct (3c).

(d) *Reaction with 4,5-trimethylene-1,2-dithiole-3-thione.* Evaporation of the solution and chromatography of the residue, on alumina, in benzene gave (i) *dimethyl 2-(2-thioxocyclopentylidene)-1,3-dithiole-4,5-dicarboxylate* (2d) (78%), brown needles, m.p. 121—122° (from methanol) (Found: C, 45·7; H, 3·4; S, 30·0. $C_{12}H_{12}O_4S_3$ requires C, 45·6; H, 3·8; S, 30·4%) and (ii) *tetramethyl 5,6-trimethylenethiopyran-4-spiro-2'-(1,3-dithiole)-2,3,4',5'-tetracarboxylate* (3d) (9·5%), yellow needles, m.p. 122—123° (from methanol) (Found: C, 47·1; H, 3·9; S, 20·8. $C_{18}H_{18}O_8S_3$ requires C, 47·2; H, 4·0; S, 21·0%).

(e) *Reaction with 4,5-tetramethylene-1,2-dithiole-3-thione.* Work-up as in (d) gave (i) *dimethyl 2-(2-thioxocyclohexylidene)-1,3-dithiole-4,5-dicarboxylate* (2e) (17%), brown needles, m.p. 152—153° (Found: C, 47·3; H, 4·0; S, 29·3. $C_{13}H_{14}O_4S_3$ requires C, 47·3; H, 4·3; S, 29·1%) and (ii) *tetramethyl 5,6-tetramethylenethiopyran-4-spiro-2'-(1,3-dithiole)-2,3,4',5'-tetracarboxylate* (3e) (56%), yellow needles, m.p. 119—120° (Found: C, 48·6; H, 3·9; S, 20·15. $C_{19}H_{20}O_8S_3$ requires C, 48·3; H, 4·3; S, 20·4%).

(f) *Reaction with 1,2-benzodithiole-3-thione.* The solution was evaporated and the residue was recrystallised from methanol to yield *tetramethyl benzo*[b]*thiopyran-4-spiro-2'-(1,3-dithiole)-2,3,4',5'*-tetracarboxylate (3f) (*ca.* 100%), yellow prisms, m.p. 117—118° (Found: C, 48·7; H, 3·2; S, 20·1. $C_{19}H_{16}O_8S_3$ requires C, 48·7; H, 3·4; S, 20·5%).

Reactions of Acetylenic Monocarboxylic Esters with 1,2-Dithiole-3-thiones (with D. M. McKinnon).—(*a*) A solution of 5-phenyl-1,2-dithiole-3-thione (1·5 g) and ethyl but-2-ynoate (0·8 g) in benzene (100 ml) was heated under reflux for 7 days. The solution was then evaporated and the residue was chromatographed on alumina. Elution with light petroleum–benzene (1 : 1) yielded a small amount of the original thione and further elution with benzene gave *ethyl 5-methyl-2-thiophenacylidene-1,3-dithiole-4-carboxylate* (6a) (1·7 g, 74%), reddish brown needles, m.p. 110—111° (from ethanol–benzene) (Found: C, 55·8; H, 4·3; S, 29·6. $C_{15}H_{14}O_2S_3$ requires C, 55·9; H, 4·4; S, 29·8%).

(*b*) A solution of 5-phenyl-1,2-dithiole-3-thione (2·1 g) and ethyl phenylpropiolate (1·8 g) in benzene (30 ml) was heated under reflux for 4 days. Evaporation of the solution and recrystallisation of the residue from benzene–ethanol gave ethyl 5-phenyl-2-thiophenacylidene-1,3-dithiole-4-carboxylate (6b) (3·4 g, 92%), brown prisms, m.p. 123—125° (lit.,[2b] 123—125°).

(*c*) 4-Phenyl-1,2-dithiole-3-thione (8·4 g) and methyl phenylpropiolate (7·3 g) were treated as in (*b*) and yielded *1,4-bis-(4-methoxycarbonyl-5-phenyl-1,3-dithiol-2-ylidene)-1,4-diphenylbut-2-ene* (7) (5·4 g, 40%), red needles, m.p. 268—274° (from pyridine) (Found: C, 67·5; H, 4·5; S, 18·5%; M^+, 676. $C_{38}H_{28}O_4S_4$ requires C, 67·5; H, 4·2; S, 18·9%; *M*, 676).

Raney-nickel Degradations.—(*a*) The yellow adduct (2 g) obtained from 5-phenyl-1,2-dithiole-3-thione and dimethyl acetylenedicarboxylate, was heated with Raney nickel (20 g) in boiling methanol (100 ml) for 5 h. The nickel was filtered off and washed with methanol and the filtrate and washings were evaporated to yield an oil. Distillation of the oil yielded (i) dimethyl succinate (0·3 g), b.p. 160—170° at 14 mmHg, i.r. spectrum identical with that of an authentic specimen, and (ii) dimethyl (3-phenylpropyl)-succinate (0·67 g), b.p. 150—165° at 0·01 mmHg, i.r. spectrum identical with that of a specimen synthesised by esterification of cinnamylidenesuccinic acid [12] and catalytic hydrogenation (PtO_2) of the ester.

(*b*) The yellow adduct (2 g) obtained from 1,2-benzodithiole-3-thione and dimethyl acetylenedicarboxylate was treated as in (*a*) and yielded (i) dimethyl succinate (0·38 g), b.p. 160—170° at 14 mmHg, and (ii) dimethyl benzylsuccinate (0·62 g), b.p. 115—125° at 0·01 mmHg, both of which gave i.r. spectra identical with those of authentic specimens.*

(*c*) The red product (0·5 g), obtained from 4-phenyl-1,2-dithiole-3-thione and methyl phenylpropiolate, was heated with Raney nickel (2 g) in ethanol (10 ml) for 16 h. The nickel was filtered off and washed with methanol and the filtrate and washings were evaporated to yield an oil (0·3 g). The oil was boiled with aqueous 10% sodium hydroxide for 4 h and the aqueous solution was separated from residual oil and was acidified. Extraction with ether yielded 3-phenylpropionic acid (0·07 g), m.p. and mixed m.p. 47—48°, i.r. spectrum identical with that of an authentic specimen. The i.r. spectrum of the residual oil, after purification by preparative t.l.c., was identical with that of a specimen of 2,5-diphenylhexane synthesised by catalytic hydrogenation (Pd–C) of 2,5-diphenylhexa-2,4-diene.[13] G.l.c. [2% poly(ethylene glycol adipate)–Celite at 135°] showed that both specimens of the hydrocarbon contained the same two, incompletely resolvable components. These were, presumably, the *meso* and racemic diastereoisomers.

Reaction of Dimethyl Acetylenedicarboxylate with 4-Phenyl-1,3-dithiole-2-thione.—The thione (1 g) and the ester (0·68 g) were mixed and heated slowly, the progress of the reaction being monitored by t.l.c. When the temperature reached 195°, all the thione had reacted. Chromatography on alumina, in benzene, then yielded an *adduct* (0·18 g, 11%), a yellow powder, m.p. 198—199° (from methanol) (Found: C, 51·2; H, 3·7. $C_{21}H_{18}O_8S_3$ requires C, 51·0; H, 3·6%), τ 2·6—2·8 (5H, m), 3·81 (1H, s), and 6·10, 6·12, 6·14, and 6·21 (12H, all s). The same adduct (7%) was obtained by heating the reactants in boiling xylene for 20 h.

Reactions of Dimethyl Acetylenedicarboxylate with 1,3-Dithiolan-2-thiones.—(a) *Reaction with 1,3-dithiolan-2-thione.* The thione (4·1 g) was heated with the ester (4·3 g) at 140° for 5 min and the liberated gas was condensed in a Carius tube cooled in liquid nitrogen and containing 2,4-dinitro-

* We are grateful to Dr. H. Heller for a specimen of dimethyl benzylsuccinate.

[12] F. Fichter and S. Hirsch, *Ber.*, 1901, **34**, 2188.
[13] J. P. Freeman, *J. Org. Chem.*, 1957, **22**, 1608.

benzenesulphenyl chloride (1·5 g) in acetic acid (36 ml). The dark brown residue in the reaction flask was treated with methanol and yielded *dimethyl 2-thioxo-1,3-dithiole-4,5-dicarboxylate* (10b) (7·4 g, 99%), as yellow needles, m.p. 86—87° (from methanol) (Found: C, 33·9; H, 2·6; S, 38·5. $C_7H_6O_4S_3$ requires C, 33·6; H, 2·4; S, 38·4%). The compound (0·2 g) was characterised by treatment with mercury(II) acetate, in acetic acid–chloroform, to give dimethyl 2-oxo-1,3-dithiole-4,5-dicarboxylate (0·12 g), m.p. 69—70° (lit.,[14] 70°).

The Carius tube was sealed and shaken for 16 h. The contents were then diluted with water and the solid that precipitated was recrystallised from ethanol to give 2-chloroethyl 2,4-dinitrophenyl sulphide (0·21 g), m.p. 93—94° (lit.,[15] 94—94·5°), identical (mixed m.p. and i.r. spectrum) with an authentic specimen.

(b) *Reaction with* cis-*4,5-diphenyl-1,3-dithiolan-2-thione*. The *cis*-thione [1] (0·72 g) was heated with the ester (0·36 g) at 120° for 5 min. Analysis of the product by g.l.c. [5% poly(neopentyl glycol succinate)–Chromosorb P at 170°] showed the presence of *cis*- and *trans*-stilbene in the approximate ratio 9 : 1. After a further 5 min at 120°, the proportion of *trans*-stilbene had increased to 20%. Chromatography of a similar mixture on alumina, in benzene, yielded the 1,3-dithiole (10b) (0·56 g, 90%), m.p. 85—86°.

(c) *Reaction with* trans-*4,5-diphenyl-1,3-dithiolan-2-thione*. The *trans*-thione [16] was treated as in (b). No *cis*-stilbene was detected by g.l.c. but *trans*-stilbene (62%) and the dithiole (10b) were isolated by chromatography on alumina.

(d) *Reaction with* trans-*4,5-tetramethylene-1,3-dithiolan-2-thione*. The thione [17] (1 g) was heated with the ester (0·75 g) from 105 to 150° during 15 min. Chromatography on alumina led to recovery of the thione (91%). After heating a similar mixture at 145—150° for 1 h, the recovery of thione was 68% and small amounts of two brown, uncharacterisable oils were also eluted from the column.

Reactions of Benzyne.—(a) *With 5-phenyl-1,2-dithiole-3-thione*. (i) A solution of lead tetra-acetate (1·11 g) and a solution of 1-aminobenzotriazole (0·34 g), both in dry benzene (30 ml), were added concurrently, during 10 min, to a stirred solution of the thione (0·53 g), in dry benzene (20 ml), under nitrogen. The solution was filtered and evaporated and the residue was chromatographed, on alumina, in light petroleum–benzene (1 : 2), to give (i) an unidentified reddish purple oil (0·14 g) and (ii) a solid (0·57 g) which, on being triturated with acetone, gave 2-thiophenacylidene-1,3-benzodithiole (14b) * (0·35 g; 55%), greenish brown plates, m.p. 187—188° (from ethanol), identical (m.p., mixed m.p., and i.r. spectrum) with a specimen synthesised as described later.

(ii) A solution of anthranilic acid (1·37 g) in tetrahydrofuran (25 ml) and a solution of isopentyl nitrite (1·17 g) in benzene (25 ml) were added concurrently, during 3 h, to a solution of the thione (1·05 g) in boiling benzene (50 ml). The solution was then boiled for a further 15 min and evaporated. Chromatography of the residue on alumina gave the thiophenacylidene compound (14b) (0·4 g, 28%).

* A violet compound, m.p. 130—131°, formed (0·5%) by reaction of the thione (1a) with benzenediazonium-2-carboxylate in dichloromethane, has been reported [20] to possess this structure. Professor Behringer has informed us, however, that the violet compound is, in fact, the isomeric 3-thiophenacylidene-1,2-benzodithiole, identical with a specimen synthesised previously.[18]

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(b) *With 4-phenyl-1,2-dithiole-3-thione*. The reaction was carried out with the same quantities, and under the same conditions, as in (a) (i). Chromatography yielded (i) recovered thione (0·13 g) and (ii) 2-(1,3-benzodithiol-2-ylidene)-2-phenylethanal (16a) (0·09 g), yellow needles, m.p. 102—103° (from ethanol), identical (m.p., mixed m.p., and i.r. spectrum) with a specimen synthesised as described later.

(c) *With 1,3-dithiolan-2-thione*. Solutions of lead tetra-acetate (1·11 g) and 1-aminobenzotriazole (0·34 g) were added to a solution of the thione (0·34 g), following the procedure described in (a) (i). Chromatography yielded (i) 1,3-benzodithiole-2-thione (10c) (0·06 g, 13%), yellow needles, m.p. 165—166° (lit.,[11] 165°), identical (mixed m.p. and i.r. spectrum) with an authentic specimen, and (ii) recovered thione (0·16 g).

2-Phenacylidene-1,3-benzodithiole (14a).—2-Methylthio-1,3-benzodithiolylium perchlorate (15) (1·5 g) was added to a suspension which had been prepared by adding benzoylacetic acid (1·65 g) to sodium ethoxide [from sodium (0·27 g) and ethanol (100 ml)]. After being heated under reflux for 30 min, the solution was concentrated, diluted with water, and extracted with ether. Evaporation of the extract and recrystallisation of the residue from ethanol yielded the *phenacylidene compound* (0·4 g), pale yellow needles, m.p. 178—179° (Found: C, 66·5; H, 3·6; S, 23·5. $C_{15}H_{10}OS_2$ requires C, 66·7; H, 3·7; S, 23·7%), $\lambda_{max.}$ 229, 237, 245, 260, and 399 nm (log ε 4·36, 4·20, 4·22, 4·12, and 4·46).

2-Thiophenacylidene-1,3-benzodithiole (14b).—The phenacylidene compound (0·1 g) was heated with phosphorus pentasulphide (0·3 g) in boiling benzene (50 ml) for 3 h. The solution was then filtered, concentrated, and applied to a column of alumina. Elution with benzene yielded the *thiophenacylidene compound* (0·1 g), greenish brown plates, m.p. 187—188° (from ethanol) (Found: C, 62·9; H, 3·6; S, 33·5. $C_{15}H_{10}S_3$ requires C, 62·9; H, 3·5; S, 33·5%), $\lambda_{max.}$ 226sh, 267, 340, and 470 nm (log ε 4·37, 4·22, 4·06, and 4·46).

2-(1,3-Benzodithiol-2-ylidene)-2-phenylethanal (16a).—β-Pyrrolidinostyrene [19] (1·5 g) in dry acetone (10 ml) was added to a solution of 2-methylthio-1,3-benzodithiolylium perchlorate (1·5 g) in dry acetone–acetonitrile (1 : 1 v/v; 40 ml). The solution was kept for 20 min at room temperature and then evaporated (at 40°) to give a yellow syrup which was presumed to consist largely of the salt (17). The crude salt was hydrolysed by boiling with aqueous 2M-hydrochloric acid (30 ml) and acetonitrile (30 ml) for 30 min. After being evaporated to half its volume, the solution was extracted several times with benzene and the extract was dried and evaporated. Chromatography of the residue on alumina, in benzene, gave the *aldehyde* (0·075 g), yellow needles, m.p. 102—103° (from ethanol) (Found: C, 66·6; H, 4·3; S, 23·8. $C_{15}H_{10}OS_2$ requires C, 66·7; H, 3·7; S, 23·7%), $\nu_{max.}$ (Nujol) 1630 cm^{-1}, τ 2·4—2·9 (9H, m, aromatic protons) and 0·7 (1H, s, CHO).

We thank the S.R.C. for maintenance grants (to D. B. J. E. and T. J. R.).

[1/1263 *Received, July 23rd*, 1971]

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