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SYNTHESIS AND THERMAL REARRANGEMENT OF *m*-DITHIINS

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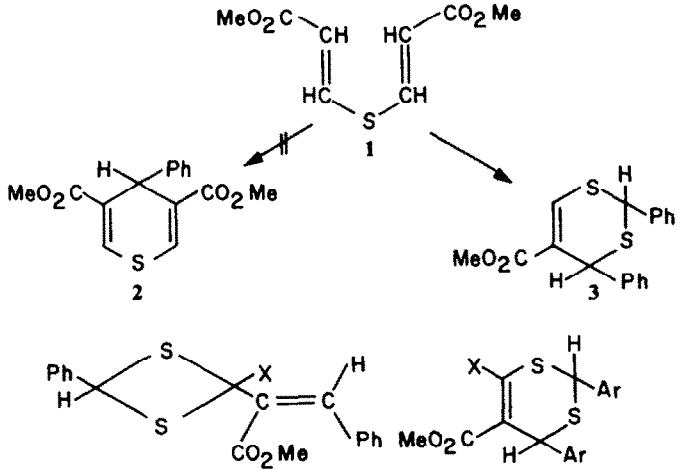
Abstract—Synthesis of *m*-dithiins from acetylenic esters, aromatic aldehydes and hydrogen sulphide is described. The thermal rearrangement of dimethyl 2,4-diphenyl-*m*-dithiin-5,6-dicarboxylate **5** to the isomeric dihydro-*o*-dithiin **11** is reported. Structural evidence is presented and mass spectral fragmentations are discussed.

IN AN ATTEMPTED synthesis of the thiopyran **2**, dimethyl *trans-trans*-3,3'-thiodiacrylate (**1**) was reacted with benzaldehyde in the presence of BF_3. This afforded a solid, $C_{18}H_{16}O_2S_2$, in 35% yield after isolation by chromatography. The NMR spectrum showed four singlets at τ 6·28 (3H), 5·17 (1H), 4·64 (1H), 1·79 (1H) and a peak in the aromatic region (10H). These data exclude **2** but are consistent with the *m*-dithiin structure **3** or the dithietane structure **4a**.



From the structure of the product it was clear that the immediate precursor was not the diester **1** but one of its decomposition products, *e.g.* methyl propiolate or methyl 3-mercaptoacrylate. The reaction was accordingly carried out with methyl propiolate, benzaldehyde and hydrogen sulphide in the presence of BF_3, when the same product **3** was obtained in 61% yield. When 2,4,6-triphenyl-1,3,5-trithiane was used instead of benzaldehyde and hydrogen sulphide the yield was 70%.

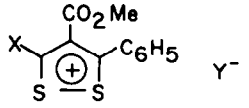
Other aromatic aldehydes could be used instead of benzaldehyde, and dimethyl

acetylenedicarboxylate instead of methyl propiolate. In this way the analogues **5**, **6** and **7** were prepared. However, no *m*-dithiins were isolated when aliphatic aldehydes (formaldehyde, acetaldehyde) or other acetylenes (phenyl-or diphenyl-acetylene, methyl phenylpropiolate, or acetylene) were used.

The NMR spectrum of the product from benzaldehyde and dimethyl acetylenedicarboxylate lacked the signal in the olefinic region thus ruling out structure **4b**. The alternative structure (**4a**; CO_2Me instead of H) may be ruled out on mechanistic grounds and hence a *m*-dithiin structure is indicated.

Desulphurisation of **3** gave methyl 2-benzylpropionate which, while confirming the correctness of the proposed structure, does not distinguish between **3** and **4a**.

Lüttringhaus *et al.*[1] have described the oxidative rearrangement of *m*-dithiins to 1,2-dithiolium salts. Treatment of **3** with sulphuryl chloride followed by perchloric acid according to the above workers[1] afforded the dithiolium salt **8a** in 18% yield, together with benzaldehyde, identified as the 2,4-dinitrophenylhydrazone.



8 **a** X=H, Y = ClO_4
b X=H, Y = Br
c X = CO_2Me, Y = ClO_4
d X = CO_2Me, Y = Br

The salt **8a** was characterized by elemental analysis and by its spectral characteristics which are in excellent agreement with literature values.[2] The action of Br_2 on **3** afforded the corresponding bromide **8b** in 6% yield. Similarly, **5** afforded **8c** in 25% yield on treatment with sulphuryl chloride and perchloric acid, and the hygroscopic bromide **8d** in 64% yield on treatment with bromine.

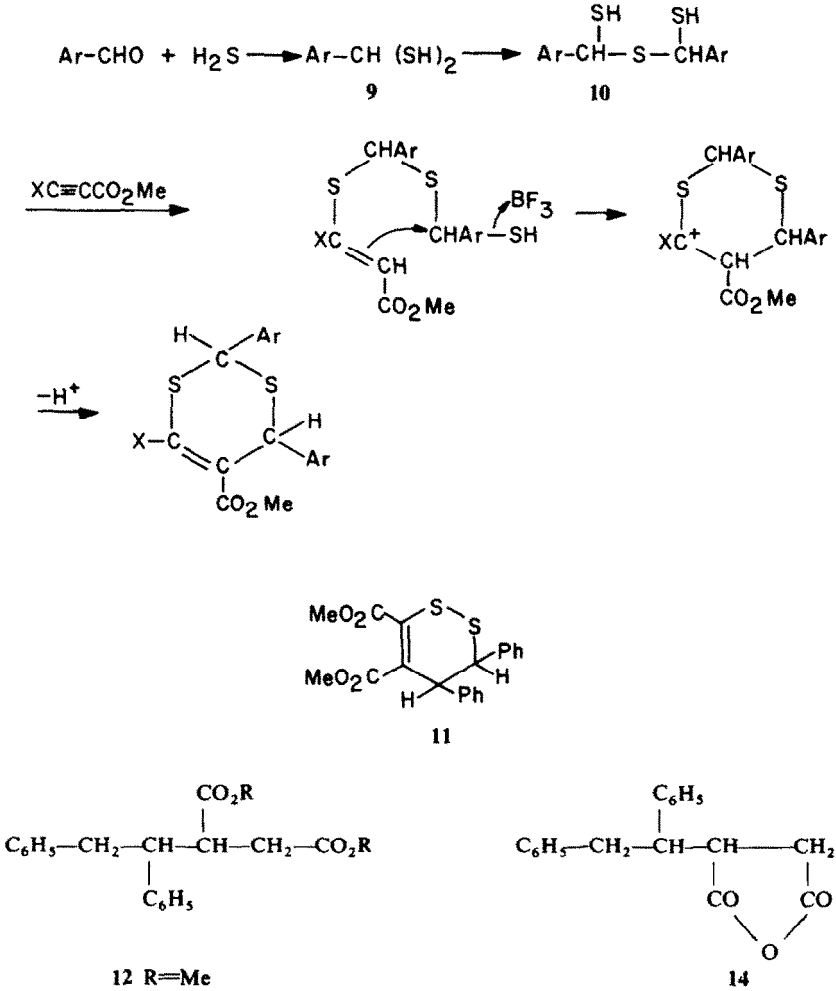
The low yield of **8b** is probably due to the competitive addition of bromine to the less hindered double bond of **3**. The salts (**8**) are the first representatives of 1,2-dithiolium salts with ester substituents.

The above reactions conclusively establish the *m*-dithiin structure for the products from the acetylenic esters. Very few *m*-dithiins have been described[1, 3–6] and no derivatives of *m*-dithiincarboxylic acids have been previously reported.

Mechanistically formation of the *m*-dithiins may be visualised as proceeding *via* the *gem.*-dithiol **9** which undergoes self-condensation to form **10** (for an example of an analogue of **10** see ref. 7). Nucleophilic addition to the acetylenic ester is followed by cyclisation as shown.

When the *m*-dithiin **5** was briefly heated at 185° a new isomeric product was obtained in quantitative yield. The NMR spectrum of this compound showed an AB quartet centered at τ 5·57 (J_{AB} 6·5 Hz) as well as signals for the ester protons (τ 6·52 and 6·16) and aromatic protons (τ 2·74 and 2·82). These data are consistent with the dihydro-*o*-dithiin structure **11**. The UV and IR characteristics are also in accord with this formulation. The product had λ_{max} 332, 272, 219 nm (ε 1,900, 4,900 and 15,100) which resembles the UV spectrum of the *m*-dithiin **5** (λ_{max} 287, 221 nm, ε 9,900, 15,100). The additional band at 332 nm is assigned to the cyclic disulphide grouping.[8]

Desulphurisation of the dihydro-*o*-dithiin **11** led to the oily diester **12** the structure of which was established by elemental analysis, NMR spectrum and conversion into



11

12 R=Me
13 R=H

14

the corresponding known acid[9] (**13**) and anhydride[10] (**14**). The presence of the disulphide grouping in **11** was confirmed by specific colour tests.[11,12]

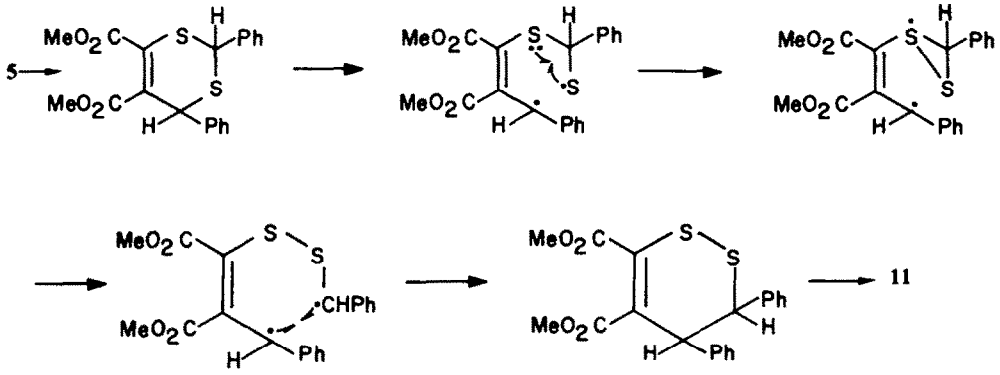
Little work has been done on *o*-dithiins and their dihydro derivatives.[3,13–15] The unstable 3,6-dihydro-*o*-dithiin has been described[16] and a compound alleged to be 3,5,6-triphenyl-5,6-dihydro-*o*-dithiin was reported[17] without any structural evidence.

The mechanism of this unusual rearrangement might involve fission of a C—S bond with formation of an allylic diradical followed by redistribution of bonds as shown. The existence of sulfur radicals R_3S has recently been established.[18]

An alternative mechanism involving a reverse Diels-Alder reaction was considered to be unlikely.

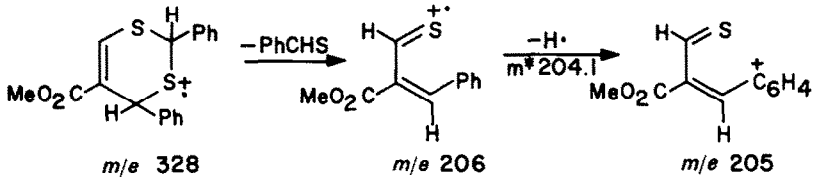
Mass spectra

The mass spectra of the *m*-dithiins **3**,**5**,**6**,**7** show that they fragment without skeletal

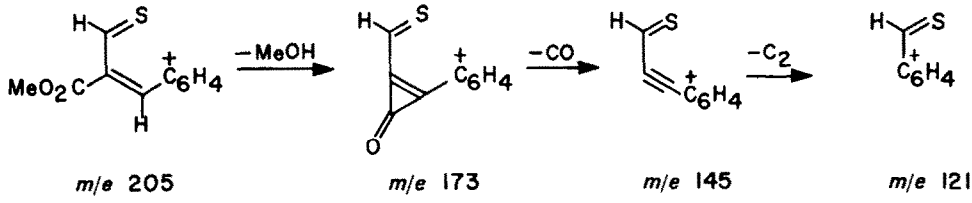


rearrangement and undergo a general mode of fragmentation with the following common features.

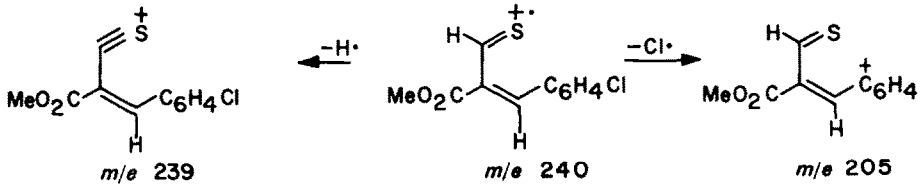
(a) In all cases the molecular ion loses ArCHS by a reverse Diels–Alder process followed by loss of H· from the resulting odd-electron ion. This is shown for **3** in which this fragmentation is confirmed by a metastable peak.



This accounts for the intense peaks at *m/e* 263 for **5**, *m/e* 219 for **6** and *m/e* 239 for **7**. Further fragmentation involves loss of MeOH, CO and C_2 as follows.



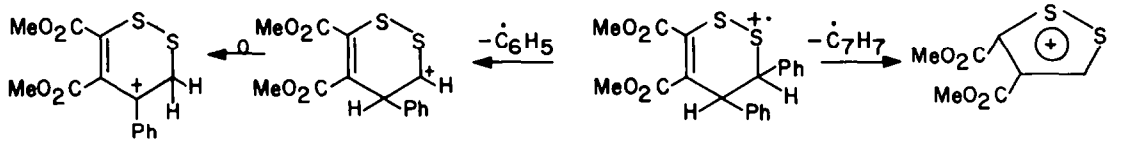
(b) The odd-electron peaks (M – ArCHS) of **6** and **7** fragment in two possible modes, either by loss of a hydrogen radical or by loss of the substituent on the benzene ring, *i.e.* ·CH_3 for **6** and ·Cl for **7**, which accounts for the base peak at *m/e* 205 for both these compounds. The isotopic ratio of this peak for **7** confirms the absence of chlorine.



(c) To account for peaks at *m/e* 147 in **3**, *m/e* 205 in **5**. *m/e* 161 in **6** and *m/e* 181 in **7** it is postulated that the molecular ion loses the radical ArC(=O)=S followed by loss of MeOH. CO and H. even though the relative abundance of the intermediate ions is small.

The mass spectrum of the dihydro-*o*-dithiin **11** resembles that of the isomeric **5**. Disulphides are known[19] to lose S·, HS· and H_2S but this does not appear to take place with **11**. The fragment corresponding to (M-33) which is formed from **11**, but also from the *m*-dithiins **3**,**5**,**6** and **7**, is probably due to loss of MeOH followed by loss of H· rather than loss of ·SH. The base peak for **11** at *m/e* 263 is again due to loss of PhCHS followed by loss of H· as confirmed by a metastable peak at *m/e* 262·1. The relatively abundant ion at *m/e* 205 together with its characteristic fragment ions at *m/e* 173. 145 and 121 is present in **11** as well as in **3** and **5**.

The disulphide **11**, on the other hand, has relatively abundant ions at *m/e* 309 and 295 which are formulated as $(M-C_6H_5)$ and $(M-C_7H_7)$. respectively.



The former is an example of α-cleavage which has also been observed for 2-phenyl-1.3-dithiane.[20] The initially formed ion A can rearrange to the stabilized ion B by a 1.2-hydrogen shift. Loss of a C_7H_7 fragment leads to the aromatic dithiolium ion. Surprisingly, the *m*-dithiins **3**.**5**.**6** and **7** do not fragment in this way although relatively unimportant peaks corresponding to $C_6H_5^+$ at *m/e* 77 and to $C_7H_7^+$ at *m/e* 91 are given by all the compounds.

EXPERIMENTAL

Unless otherwise stated, m.ps were determined on a Thomas Hoover capillary apparatus. UV spectra were measured in MeOH on a Cary 14 instrument and IR spectra were recorded on a Perkin-Elmer model 137 spectrometer in nujol. The NMR spectra were recorded on a Varian A-60 in $CDCl_3$. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-7 spectrometer and used for molecular weight determinations.

GLC was carried out on an Aerograph Autoprep model A-70. Precoated silica gel TLC plates (Brinkmann) were used. C_6H_6 as the eluent.

*Methyl 2,4-diphenyl-*m*-dithiin-5-carboxylate* (**3**). (a) *From dimethyl 3,3'-thiodiacrylate* (**1**). Dimethyl 3,3'-thiodiacrylate was prepared by the method of Lown *et al.*[21] using benzene as solvent. which afforded the *trans-trans* isomer as main product, pure after two crystallisations from MeOH. This ester (6g), benzaldehyde (3·3 ml; 3·5 g) containing $BF_3.Et_2O$ (15 ml) in benzene (150 ml) was refluxed overnight, cooled, washed with distilled water (3 × 100 ml) and dried. On removal of the solvent a dark brown oil (8·54 g) was obtained. The product was chromatographed on alumina (activity I; 250 g) in benzene giving a white solid (1·38 g; 35%). m.p. 132–133°. R_f 0·37. Crystallisation from *n*-hexane gave pure *methyl 2,4-diphenyl-*m*-dithiin-5-carboxylate* (**3**), m.p. 134–135°. (Found: C, 66·38; H, 4·86; S, 19·50; M^+ 328. $C_{18}H_{16}O_2S_2$ requires C, 65·85: H. 4·91: S, 19·53%; MW 328); λ_{max} 282 nm (ε 14,500); ν_{max} 1695 (CO_2Me), 1235 (C—O) cm^{-1}: τ 1·78 (s, 6—H), 2·68 (s, C_6H_5), 4·64. 5·17 (s, CHPh), 6·29 (s, CO_2CH_3).

(b) *From methyl propiolate.* (i) Methyl propiolate (3·3 ml) in benzene (25 ml) was treated with benzaldehyde (4 ml) and $BF_3.Et_2O$ (6 ml) in benzene (25 ml). H_2S was passed into the solution for five min. The mixture was stirred and refluxed until all the solid had dissolved (30 min.). cooled. washed with water (3 × 50 ml) and dried. Removal of solvent yielded a brown oil (8·1 g) which crystallised on treatment with MeOH (10 ml), (2·9 g; 61%) m.p. 126–128°, m.m.p. with the product obtained under (a), 132–133°.

(ii) 2,4,6-Triphenyl-1,3,5-trithiane[22] (3·66 g) in benzene (40 ml) was treated with a mixture of methyl propiolate (1·3 ml) and $BF_3.Et_2O$ (4 ml) in benzene (10 ml) dropwise with stirring and the solution refluxed for 2·25 hr. The dark mixture was cooled and the unreacted trithiane filtered. The filtrate was worked up as under (i) to yield crude product. 3·43 g (70%).

The following analogues were prepared according to procedure (i).

Dimethyl 2,4-*diphenyl*-m-*dithiin*-5,6-*dicarboxylate* (**5**). Benzaldehyde (2 ml), dimethyl acetylenedicarboxylate (2·84 g), $BF_3.Et_2O$ (3 ml) in benzene (30 ml) were treated with H_2S for 5 min. and the solution was refluxed for 15 min. *Dimethyl* 2,4-*diphenyl*-m-*dithiin*-5,6-*dicarboxylate* (3·85 g; ~ 100%) crystallised from MeOH and had m.p. 156–157°, R_f 0·22. (Found: C, 61·89; H, 4·69; S, 16·58; M^+ 386. $C_{20}H_{18}O_4S_2$ requires C, 62·16: H, 4·69; S, 16·59%; MW 386); λ_{max} 221, 287 nm (ε 15,100, 9,900); ν_{max} 1745, 1725 (CO_2Me), 1235, 1225 (C—O) cm^{-1}; τ 2·68 (s, C_6H_5), 4·53, 5·14 (s, CHPh), 6·12, 6·34 (s, CO_2CH_3).

Methyl 2,4-*di*-p-*tolyl*-m-*dithiin*-5-*carboxylate* (**6**). *p*-Tolualdehyde (2·4 ml), methyl propiolate (1·68 ml) and $BF_3.Et_2O$ (3 ml) in benzene (50 ml) were treated with H_2S and the solution refluxed for 30 min. *Methyl* 2,4-*di*-p-*tolyl*-m-*dithiin*-5-*carboxylate* (3·55 g; ≃ 100%) was crystallised from cyclohexane and had m.p. 176–177°, R_f 0·43. (Found: C, 67·33; H, 5·51; S, 17·56; M^+ 356. $C_{20}H_{20}O_2S_2$ requires C, 67·42; H, 5·56; S, 18·00%; MW 356); λ_{max} 224, 282 nm (ε 19,900, 14,200); ν_{max} 1695 (CO_2Me), 1235 (C—O) cm^{-1}; τ 1·85 (s, 6—H), 2·87 (s, Ar), 4·67, 5·17 (s, CHAr), 6·31 (s, CO_2CH_3) 7·67 7·71 (s, $ArCH_3$).

Methyl 2,4-*di*-p-*chlorophenyl*-m-*dithiin*-5-*carboxylate* (**7**). *p*-Chlorobenzaldehyde (2·82 g), methyl propiolate (1·5 ml), $BF_3.Et_2O$ (5 ml) in benzene (50 ml) were treated with H_2S for 5 min and the solution refluxed for 30 min. *Methyl* 2,4-*di*-p-*chlorophenyl*-m-*dithiin*-5-*carboxylate* (3·95 g; ≃ 100%) was crystallised from MeOH, m.p. 135–136°, R_f 0·45. (Found: C, 54·55; H, 3·83; Cl, 17·65; S, 15·78; M^+ 396. $C_{18}H_{14}Cl_2O_2S_2$ requires C, 54·43: H, 3·55; Cl, 17·84; S. 16·14%; M.W. 396); λ_{max} 228. 283 nm (ε 26, 200, 14.900); ν_{max} 1695 (CO_2Me), 1225 (C—O) cm^{-1}; τ 1·84 (s, 6—H), 2·72 (s, Ar), 4·67, 5·25 (s, CHAr), 6·28 (s. CO_2CH_3).

Desulphurisation of methyl 2,4-*diphenyl*-m-*dithiin*-5-*carboxylate* **3**. Raney Ni (~ 10 g) was washed several times with water and MeOH, suspended in MeOH (50 ml) and treated with the *m*-dithiin (3) in MeOH (50 ml). The mixture was refluxed for 2 hr., cooled, catalyst filtered off and washed with MeOH (25 ml). The combined filtrates were evaporated. The pleasant smelling oily residue (1·1 g) was purified by GLC on a 15% apiezon column. Under the conditions used (column temperature. 100–110°; detector temperature. 170–180°; injector temperature. 140–150°; gas flow. 20 p.s.i.), the retention time was 6·5 min. The NMR of the purified sample showed signals for aromatic protons at 2·7 τ (5H), ester protons at 6·39 τ (3H), a multiplet at 7·25 τ (3H) and doublet at 8·86 τ (3H) for the C-Me protons; ν_{max}(liquid film) 2840 (C—H), 1605 (C=C), and 1740 (CO_2CH_3) cm^{-1}.

Methyl 2-benzylpropionate was prepared from commercially available α-methylcinnamic acid by hydrogenation in MeOH, using PtO_2 as catalyst, followed by esterification with CH_2N_2. The IR and NMR spectra of this product were identical with those of the above desulphurisation product.

4-*Methoxycarbonyl*-3-*phenyl*-1,2-*dithiolium perchlorate* (**8a**). The method of Lüttringhaus[1] was followed using methyl 2,4-diphenyl-*m*-dithiin-5-carboxylate (**3**; 4 g). SO_2Cl_2 (4 ml) and 40% $HClO_4$ (4 ml). A pale yellow solid (0·69 g; 18%) was obtained, crystallised from AcOH containing 1% $HClO_4$, m.p. 196–197° (d.). (Found: C, 40·07; H, 2·67; Cl, 10·53; S, 18·57. $C_{11}H_9ClO_6S_2$ requires C, 39·22; H, 2·69; Cl, 10·53; S, 19·01%); λ_{max}(AcOH containing 1% $HClO_4$) 248. 353 nm (ε 6.100. 9.300); τ-0·78 (s, nuclear proton), 2·58 (s, C_6H_5), 6·43 (s, CO_2CH_3) (CD_3CN, TMS external).

The filtrate from the above reaction was treated with 2,4-dinitrophenylhydrazine and afforded benzaldehyde 2,4-dinitrophenylhydrazone.

4-*Methoxycarbonyl*-3-*phenyl*-1,2-*dithiolium perchlorate* (**8a**). The method of Lüttringhaus[1] was followed using methyl 2,4-diphenyl-*m*-dithiin-5-carboxylate (**3**; 0·51 g) and Br_2 (0·31 ml) in AcOH (15 ml). This gave a pale yellow solid (30 mg; 6%). m.p. 185° (d); λ_{max} 248. 353 nm.

4,5-*Dimethoxycarbonyl*-3-*phenyl*-1,2-*dithiolium perchlorate* (**8c**). Dimethyl 2,4-diphenyl-*m*-dithiin-5,6-dicarboxylate (**5**; 4 g). SO_2Cl_2 (2 ml) and 40% $HClO_4$ (2 ml) were used as above. The precipitated yellow solid (1 g; 25%) was filtered and crystallised from AcOH containing 1% $HClO_4$. m.p. 162–163°. (Found: C, 39·27; H. 2·71; Cl, 9·02; S, 16·02. $C_{13}H_{11}O_8ClS_2$ requires C, 39·54; H, 2·81; Cl. 8·98; S, 16·25%). λ_{max} (AcOH containing 1% $HClO_4$) 248. 380 nm (ε 11.000. 10.800); τ 2·58 (s, C_6H_5) 6·25. 6·40 (s, CO_2CH_3) (CD_3CN. TMS external). The filtrate was concentrated and steam distilled into a solution of 2,4-dinitrophenylhydrazine. The resulting solid (0·95 g) had m.p. 234–235°, undepressed on admixture of benzaldehyde 2,4-dinitrophenylhydrazone.

4,5-*Dimethoxycarbonyl*-3-*phenyl*-1,2-*dithiolium bromide* (**8d**). Dimethyl 2,4-diphenyl-*m*-dithiin-5,6-dicarboxylate (**3**; 10 g) and Br_2 (2·83 ml) in AcOH (15 ml) were reacted as above. The yield was 7·5 g (64%).

The bromide (**8d**) which had λ_{max} 380 and 248 nm (AcOH containing 1% $HClO_4$). was highly hygroscopic and could not be converted into the perchlorate or iodide.

Pyrolysis of dimethyl 2,4-*diphenyl*-m-*dithiin*-5,6-*dicarboxylate* (**5**). (a) The ester (**5**; 0·6 g) was placed in a tube fitted with a gas inlet. N_2 was passed over the sample while the tube was heated in an oil bath at 185–190° and samples withdrawn at intervals. It was shown by NMR that the reaction was complete after 15 min.

(b) The ester (**5**; 2 g) was pyrolysed for 15 min. as above. The product was chromatographed on silica gel (50 g) using benzene as eluent. The oily product was dissolved in MeOH (50 ml) and the solvent allowed to evaporate slowly when crystals separated. Crystallisation from MeOH gave *dimethyl* 3,4-*dihydro*-3,4-*diphenyl*-o-*dithiin*-5,6-*dicarboxylate* (**11**), m.p. 77–78°;* R_f 0·23. (Found: C, 61·98; H, 4·73; S, 16·41; M^+ 386. $C_{20}H_{18}O_4S_2$ requires C, 62·16; H, 4·69; S, 16·59%; MW 386); ν_{max} 1745, 1725 (CO_2Me), 1605 (C=C) cm^{-1}.

Desulphurisation of dimethyl 3,4-*dihydro*-3,4-*diphenyl*-o-*dithiin*-5,6-*dicarboxylate* (**11**). Raney Ni (≃ 2 g) was washed several times with water and MeOH. A slurry of the catalyst in MeOH (30 ml) was added to the ester (**11**; 1 g) in MeOH (20 ml) and the mixture refluxed for 1 hr. The reaction was followed by TLC and was complete after 50 min. The catalyst was filtered and the filtrate evaporated, affording a pleasant smelling liquid (0·82 g). Distillation gave α-(1,2-diphenylethyl) succinate (**12**), b.p. 165–170°/100 μ (Found: C, 73·45; H, 6·77; M^+ 326. Calc for $C_{20}H_{20}O_4$: C, 73·59; H, 6·79%; MW 326).

The above ester (**12**; 200 mg) was refluxed with 10% NaOH (10 ml) for 4 hr. Unreacted ester was removed by extraction with ether. The aqueous layer was made acidic with dilute HCl and extracted with ether. The ether layer was washed with water and dried. On removal of the ether, α-(1,2-diphenylethyl) succinic acid (**13**; 151 mg), m.p. 75–90°, crystallised. After two crystallisations from benzene it had m.p. 167–168° (lit.,[9] m.p. 167–168°). The NMR showed acidic protons at −0·58 τ (s, 2H), aromatic protons at 2·77 and 2·83 τ (total 10H) and multiplets at 6·82 τ and 7·47 τ (total 6H).

The above acid (33 mg) was refluxed with AcCl (30 ml) for 2 hr., with exclusion of moisture. The mixture was evaporated and the residue treated with anhydrous ether (2 ml). The anhydride separated on cooling and crystallised from petroleum ether (b.p. 30–60°). m.p. 99–100°. (lit., [10] m.p. 102–103°).

Tests for disulphide grouping. Tests described by Schöberl *et al.*,[11] and Cheronis and Entrikin[12] were performed.

The disulfide **11** in MeOH on treatment with 15% $NaHSO_3$ solution and Folin's reagent gave a blue colour. It also gave a transient violet colour when treated with *M*-KCN solution and saturated sodium nitroprusside solution. The disulphide (**11**; ≃ 30 mg.) was added to a saturated solution of hydroxylamine hydrochloride in MeOH (1 ml) and a few mg of Zn dust added. The mixture was shaken for one min and filtered. The filtrate was treated with a saturated solution of $Pb(OAc)_2$ in MeOH (≃1 ml) when a yellow precipitate formed.

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* *Added in proof*: A second crystalline modification of **11**, m.p. 113°, has been isolated.

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