# Synthesis of 3-hydroxythiophenes and thiophen-3(2*H*)-ones by pyrolysis of alkylsulfanylmethylene Meldrum's acid derivatives[1]

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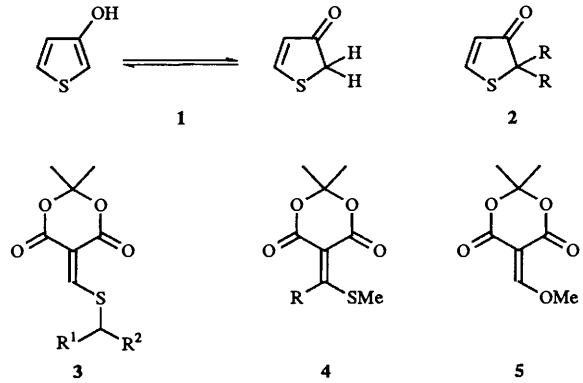
3-Hydroxythiophene [thiophen-3(2*H*)-one] **1** and a range of its 2-substituted, 2,2-disubstituted and 5-substituted derivatives have been made by flash vacuum pyrolysis (FVP) of an appropriate alkylsulfanylmethylene derivative of Meldrum's acid **3** or **4**. These compounds are readily obtained, either by reaction of methoxymethylene Meldrum's acid with alkylthiols in refluxing acetonitrile, or *via* the bis(methylsulfanyl) compound **18** by known procedures. The pyrolysis proceeds by a hydrogen-transfer–cyclisation mechanism in which there is extensive loss of configuration of a chiral centre at the reaction site. The NMR and mass spectra of the Meldrum's acid precursors and the mass spectra of the 3-hydroxythiophenes [thiophen-3(2*H*)-ones] are briefly discussed.

Because of their sensitive nature, simple 3-hydroxythiophenes [thiophen-3(2*H*)-ones] **1** lacking electron-withdrawing (stabilising) substituents have been prepared only with difficulty by low yielding and/or multi-step procedures.[2] As we have shown for the corresponding 3-hydroxypyrroles [1*H*-pyrrol-3(2*H*)-ones],[3] such problems are often readily circumvented by application of gas-phase pyrolysis (FVP) methodology, and multi-gram scale procedures have been developed which have allowed the fundamental chemistry of these pyrroles to be studied.[4] Here we give a full account of an extension to this work which has led to useful syntheses of unsubstituted, 2-substituted- or 5-substituted-3-hydroxythiophenes **1**, and to 2,2-disubstituted thiophen-3(2*H*)-ones **2**. Preliminary reports of the methods have appeared,[1,5] together with some applications.[6] Chuche, Pommelet and co-workers[7,8] have also synthesised some examples by a similar route, and the intermediates generated in the pyrolyses have been studied spectroscopically.[9,10]

In order to apply the Meldrum's acid pyrolysis method to the synthesis of thiophenones, we required a good route to the alkylsulfanylmethylene derivatives **3** and **4**. Substitution of the methoxy group of methoxymethylene Meldrum's acid **5** by mercaptans has been reported in a patent,[11] but the yields were low and the work-up involved purification by HPLC. However, when acetonitrile is used as the solvent for the reaction, the alkylsulfanylmethylene derivatives **7**–**17** were obtained directly in high (70–95%) yield as crystalline solids after removal of solvent. These reactions of **5** with thiols generally required heating under reflux for a few hours, in contrast to the corresponding displacement by amines, which is complete in a few minutes at room temperature in acetonitrile as solvent.[3] However, the conditions are sufficiently general to be applicable even to weakly nucleophilic thiols such as thiophenols.[12]

Because of the problems in handling methanethiol, the methylsulfanyl compound **6** was not prepared in this way. Condensation of Meldrum's acid with a very large excess of the commercially available tris(methylsulfanyl)methane gave the required product, but in unacceptably low yield with respect to the orthothioester. However, this reaction proceeds smoothly when acetic anhydride at 55 °C is used as solvent and under the influence of a trace of aluminium trichloride as catalyst [80% with respect to Meldrum's acid; 27% with respect to tris(methylsulfanyl)methane] (*cf.* ref. 13).

The key precursor for the 5-substituted- 3-hydroxythiophenes is the bis(methylsulfanyl)methylene derivative of Meldrum's acid **18** first prepared by Huang and Chen.[14] These workers also showed that one methylsulfanyl group of **18** can be displaced selectively by THF solutions of Grignard reagents,[15] and this procedure was used, with minor modifications, to obtain the substrates **19**–**22**. Unfortunately, the yields in these reactions proved to be variable, and on some occasions the crude products had to be purified by dry-flash chromatography. However, the reaction of **18** with 2-thienylmagnesium bromide was particularly efficient and gave the Meldrum's acid derivative **22** reproducibly in 80% yield.

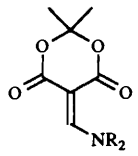


**1** **2** **3** **4** **5**

**6** $R^1 = R^2 = H$
**7** $R^1 = Me$, $R^2 = H$
**8** $R^1 = R^2 = Me$
**9** $R^1—R^2 = (CH_2)_5$
**10** $R^1 = Ph$, $R^2 = H$
**11** $R^1 = Ph$, $R^2 = Me$ (racemic)
**12** $R^1 = Ph$, $R^2 = Me$ (*R*-isomer)
**13** $R^1$ =  , $R^2 = H$
**14** $R^1 = CO_2Et$, $R^2 = H$
**15** $R^1 = CH_2OH$, $R^2 = H$
**16** $R^1 = CH_2CO_2H$, $R^2 = H$
**17** $R^1 = CH{=}CH_2$, $R^2 = H$

**18** R = MeS
**19** R = Ph
**20** R = *p*-Bu$^t$-$C_6H_4$
**21** R = Me
**22** R = 

The spectra of the alkylsulfanylmethylene derivatives **6**–**17** may be usefully compared with those of the corresponding aminomethylene compounds **23**.[3] Representative X-ray crystal structures have already been published.[16] In the $^1H$ NMR spectra, the methine proton appears as a singlet at $\delta_H$ 8.9–9.1 for the sulfur examples, which is significantly deshielded by comparison with the amino compounds ($\delta_H$ 8.0–8.6). The $^{13}C$



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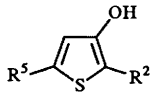
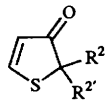
NMR spectra of the sulfur compounds exhibit two carbonyl resonances at $\delta_C$ 159–161, showing that there is a higher barrier to rotation around the methylene double bond at room temperature than is shown by the corresponding aminomethylene derivatives.[17] Poorer electron donation from the sulfur *vis-a-vis* nitrogen atom is also reflected in the chemical shifts of C-5 ($\delta_C$ 107–110 and 82–87, respectively) and of the methylene carbon atoms ($\delta_C$ 169–173 and 155–160, respectively), although the chemical shifts of the C-4 and C-6 (carbonyl) resonances are almost the same in both series (centred at *ca.* $\delta_C$ 160). The additional group at the methylene position in compounds **18–22** causes deshielding at the site of substitution (to $\delta_C$ 175–192) which is often substantial by comparison with the other *S*-alkyl compounds. The C-5 resonance of the bis(methylsulfanyl) compound **18** ($\delta_C$ *ca.* 103) is slightly shifted to low frequency but the corresponding signal of the *C*-substituted compounds **19–22** is little affected.

The mass spectra of Meldrum's acid derivatives are generally characterised by sequential loss of acetone, carbon dioxide and carbon monoxide from the molecular ion,[18] but these alkylsulfanyl derivatives can follow a range of different fragmentation patterns. Thus, consistent initial loss of acetone may be followed by cleavage of carbon dioxide (**6**, **8**, **15**), or an alkyl fragment (**6**, **10**, **11**), or carbon monoxide (**13**, **14**) or water (**9**, **10**), and indeed more than one fragmentation pattern is evident for several examples. Loss of water has also been reported for some aminomethylene examples,[19] though the mechanism remains unclear. In addition **18–22** show an intense signal at $(M - Me_2CO - CO_2 - MeS)^+$ which is the base peak of the spectrum in most cases.

Flash vacuum pyrolysis of most of the Meldrum's acid precursors **6–14** at 600–625 °C gave good to excellent yields of 3-hydroxythiophenes [thiophen-3(2*H*)-ones] **24–27** and **33–35** respectively. (Compounds capable of tautomerism are shown



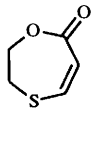


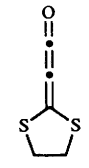
**24** $R^2 = R^5 = H$
**25** $R^2 = Me$, $R^5 = H$
**26** $R^2 = Ph$, $R^5 = H$
**27** $R^2 = CO_2Et$, $R^5 = H$
**28** $R^2 = H$, $R^5 = MeS$
**29** $R^2 = H$, $R^5 = Ph$
**30** $R^2 = H$, $R^5 = p\text{-}Bu^tC_6H_4$
**31** $R^2 = H$, $R^5 = Me$
**32** $R^2 = H$, $R^5 =$ 

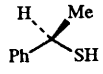
**33** $R^2 = R^{2'} = Me$
**34** $R^2—R^{2'} = (CH_2)_5$
**35** $R^2 = Me$, $R^{2'} = Ph$

here in the hydroxy form for consistency, though in the Experimental section the spectra of the major tautomer is reported. Further details of the effect of structure on the tautomeric forms and NMR spectra of these compounds will be published in due course.) The isolation of the unstable parent compound **24** in 80% yield by this route is particularly significant, since solution methods are known to proceed in very low yield.[20,21] Pyrolysis of Meldrum's acid derivatives obtained from other primary alkanethiols gave 2-substituted products and, as found in the pyrrolone series, yields were especially high for benzyl derivatives giving 2-aryl-3-hydroxythiophenes. In contrast, the furfuryl example **13** failed to give significant quantities of cyclisation products, probably because of the instability of this precursor at the temperatures required for its volatilisation. However, 2-functionalised derivatives in general may be available by this route, and the yield of the 2-ethoxycarbonyl compound **27** (56% overall) compares favourably with the best synthesis of such derivatives reported to date.[22] 2,2-Disubstituted thiophen-3(2*H*)-ones **33–35** were obtained by pyrolysis of Meldrum's acid derivatives derived from secondary alkanethiols, but yields from the non-benzylic precursors were usually consistently lower than for the other examples. Nevertheless, the pyrolysis method is at least as good as an alternative route to the 2,2-dimethyl compound **33**, which culminates in an inefficient (38%) oxidation step.[23]

Thiophenone formation may not take place if other reactive functional groups are present. Thus precursors **15–17** failed to yield significant quantities of five-membered rings, and further investigation will be needed to characterise the products and elucidate the mechanisms. However, the thiepinone structure **36** was tentatively assigned to the major product from







**36** **37** **38**

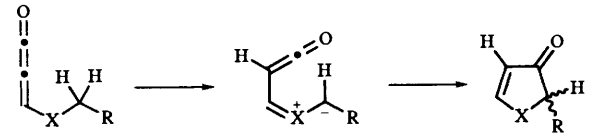
the pyrolysis of the hydroxyethyl derivative **15** on the basis of its $^1H$ NMR spectrum (see Experimental section) and by analogy with the work of Pommelet and Chuche on the corresponding hydroxyalkylamino derivatives.[24] The carboxylic acid **16** appeared to give a small amount of one major component which surprisingly showed a number of signals in the range $\delta_H$ 5.8–7.5 in its $^1H$ NMR spectrum, but was not identified; the pyrolysis of the allyl compound **17** was much more complex and gave a number of unidentified products.

5-Methylsulfanyl- 5-aryl-, 5-alkyl- or 5-heteroaryl- 3-hydroxy-thiophenes **28–32** were all obtained in excellent yields (75–86%) by pyrolysis of the Meldrum's acid precursors **18–22**. The methylsulfanyl- derivative **28** is particularly easy to prepare because of the availability of the precursor **18** and, in practice, the utility of the route for the *C*-substituted products is governed by the efficiency of the previous organometallic step. For example, the 5-phenyl compound **29** can be obtained in 48% overall yield from the bis(methylsulfanyl) compound **18**, whereas the overall yield of the 5-thienylhydroxythiophene **32** from the same precursor is over 60%.

The mass spectra of 3-hydroxythiophenes have been previously discussed, but only highly functionalised derivatives were considered and it was the substituents which controlled the major breakdown pathways.[25] The initial cleavages from the molecular ions of the simple alkyl and aryl substituted 3-hydroxythiophenes and thiophen-3(2*H*)-ones reported here generally either involve loss of CO (or HCO) [*e.g.* **24**, *m/z* 72(71%) and 71(68%)] or loss of the entire C(3)–C(4)–C(5) fragment to give the $R^2C = S^+$ unit (or the equivalent thioaldehyde or thioketone radical cation) [*e.g.* **24**, *m/z* 45(82%) and 46(88%)]. 5-Substituted examples show substantial peaks at M-74 corresponding to the C(4)–C(5) segment, due to cleavage of the C(2)–C(3)–C(4) fragment [*e.g.* **28**, *m/z* 72(44%); **29**, *m/z* 102(29%)].

The early stages of the mechanism of the pyrolytic formation of thiophenones from alkylsulfanylmethylene Meldrum's acid

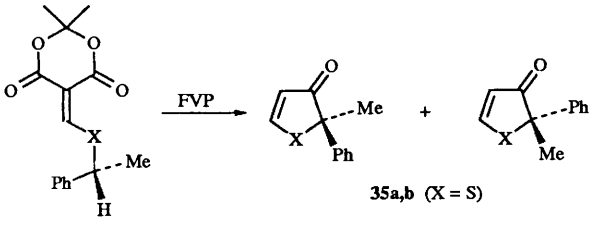
derivatives presumably involves a methyleneketene intermediate.[26] Although one such intermediate **37** has been characterised by photoelectron spectroscopy,[10] in general cyclisation to the five-membered ring is too rapid for the intermediates to be detected in this way.[9] The later stages of the mechanism are thought to involve a symmetry-allowed 1,4-hydrogen shift to generate a dipolar species **39** (with potentially planar geometry), followed by an electrocyclisation process (Scheme 1). In the pyrrolone series, we probed this aspect of



**39**

**Scheme 1**

the mechanism by incorporation of homochiral groups at the site of hydrogen atom transfer, and found that for the 1-phenylethyl case (Scheme 2, X = NPr$^i$) *ca.* 50% loss of



**35a,b** (X = S)

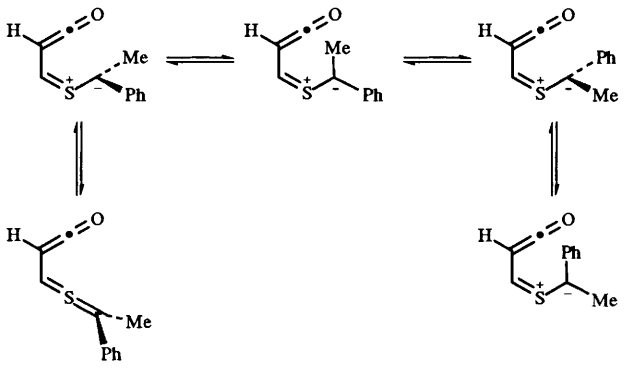
X = NPr$^i$ or S

**Scheme 2**

configuration took place (enantiomeric ratio 3:1), though this loss of configuration was greater if the reaction site was part of a ring.[27] The partial racemisation was thought to be due to the dipole being generated initially with spiral geometry and hence direct cyclisation (leading to retention of configuration) competes with bond rotation (leading to the planar dipole and loss of configuration).

It was therefore of interest to carry out a direct comparison with the chiral alkylsulfanyl derivative **12**, which was obtained from the known[28] optically pure thiol **38**. Pyrolysis of the racemate **11** and subsequent analysis by $^1$H NMR spectroscopy (see Experimental section) established that the 4-H signals of the enantiomeric thiophenones **35a** and **35b** could be separated using a chiral shift reagent. Similar treatment of the crude pyrolysate from the pure *R*-enantiomer **12** clearly showed that much more loss of configuration had taken place (enantiomeric ratio 1.23:1) than was the case for the corresponding aminomethylene derivative (Scheme 2, X = S). This result is unexpected, since the possibility of expansion of the valence shell of the sulfur atom (Scheme 3) should lead to increased preservation of the initial chirality, yet precisely the opposite result was obtained in practice. However, the effect may be rationalised by the large size of the sulfur atom, which forces the termini of the dipolar species further apart than in the case of its nitrogen analogue. This could lead to an extended lifetime of the dipolar intermediate, allowing sufficient time for C–S bond rotation and ultimately racemisation.

In conclusion, we have developed a simple, efficient and general route to 3-hydroxythiophene systems, in two steps from either Meldrum's acid itself, or methoxymethylene Meldrum's acid **5** or the bis(methylsulfanyl) compound **18**. We believe this to be the method of choice for many examples, particularly those which are reactive or sensitive to oxygen, because of the mildness of the conditions and the



**Scheme 3**

simplicity of the work-up associated with gas-phase synthetic methods.

## Experimental

$^1$H and $^{13}$C NMR spectra were recorded at 200 and 50 MHz respectively for solutions in [$^2$H]chloroform. Coupling constants are quoted in Hz.

In order to prevent the release of noxious odours of thiols, the following precautions were taken: (1) The vent from the rotary evaporator was passed through a trap cooled to −76 °C; (2) after use all glassware was immersed in a solution of commercial sodium hypochlorite in water (*ca.* 1:1) for a period of at least 48 h before being washed in the usual manner; (3) all aqueous soluble waste was quenched in sodium hypochlorite solution (as above) for 48 h before being rinsed away with large quantities of water; (4) all organic waste was stored over sodium hypochlorite solution in a waste solvent container in a fume cupboard; (5) experiments which involved heating solutions of thiols or the evolution of thiols were vented through a hypochlorite scrubber.

### Thiols

All of the thiols used were commercially available with the exception of 1-phenylethanethiol **38**, which was prepared by the literature method Harpp and Smith[28] *via* the decomposition of its xanthate ester. The procedure also allowed the preparation of one enantiomer of this chiral thiol by resolution of the diastereoisomeric xanthate esters. Hence repeated recrystallisation of the mixture of diastereoisomers gave the pure *R*-(+)-xanthate ester mp 72–74 °C, $[\alpha]_D^{20}$ +147.8 (*c* 2.38, $C_6H_6$) [lit.,[28] mp 71–73 °C, $[\alpha]_D^{20}$ +149 (*c* 2.4, $C_6H_6$)]. Decomposition of the pure *R*-(+)-xanthate ester gave *R*-(+)-1-phenylethanethiol **38**, bp 105–107 °C (24 Torr) $[\alpha]_D^{19}$ +86.2 (*c* 6.12, absolute EtOH) [lit.,[28] bp 86–87 °C (17 Torr), $[\alpha]_D^{25}$ +91.7 (*c* 6.17, absolute EtOH)].

### 5-(Methylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 6

2,2-Dimethyl-1,3-dioxane-4,6-dione (1.44 g, 10 mmol) was dissolved in dry acetic anhydride (10 ml). Tris(methylsulfanyl)-methane (4.5 g, 30 mmol) was then added followed by a catalytic amount of aluminium trichloride. The reaction mixture was heated at 55–60 °C for 3 h after which it was allowed to cool before the aluminium trichloride residues were filtered off. Evaporation of the filtrate under reduced pressure gave the crude product which after being triturated with ethanol, filtered and dried afforded the title dione **6** (80%) mp 116–117.5 °C (from ethanol) (Found: C, 47.3; H, 5.0. $C_8H_{10}O_4S$ requires C, 47.5; H, 4.95%); $\delta_H$ 8.93 (1 H, s), 2.61 (3 H, s) and 1.65 (6 H, s); $\delta_C$ 172.83, 160.88 (q), 160.34 (q), 108.33 (q), 104.86 (q), 27.29 and 20.77; *m/z* 202 ($M^+$, 47%),

187(10), 145(68), 144(77), 101(16), 100(53), 72(100) and 71(23).

**5-(Alkylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-diones 3**

A solution of the appropriate thiol (10 mmol) in acetonitrile (5 $cm^3$) was added to a stirred solution of freshly prepared 2,2-dimethyl-5-(methoxymethylene)-1,3-dioxane-4,6-dione **5** in acetonitrile (10 $cm^3$) at room temperature. The reaction mixture was heated under reflux for 3 h and then evaporated under reduced pressure to afford the product.

The following 5-(alkylsulfanylmethylene) derivatives were prepared in this way. The thiol used is indicated in brackets in each case.

**5-(Ethylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 7** (ethanethiol) (90%), mp 51–53 °C (from cyclohexane) (lit.,[11] 52–54 °C); $\delta_H$ 8.99 (1 H, s), 3.00 (2 H, q, $^3J$ 7.5), 1.68 (6 H, s) and 1.41 (3 H, t, $^3J$ 7.5); $\delta_C$ 170.94, 160.88 (q), 160.50 (q), 108.30 (q), 104.83 (q), 31.78, 27.30 and 14.98.

**5-(Isopropylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 8** (propane-2-thiol) (90%), mp 85–87 °C (from ethanol) (Found: C, 52.6; H, 6.35. $C_{10}H_{14}O_4S$ requires C, 52.2; H, 6.1%); $\delta_H$ 8.98 (1 H, s), 3.32 (1 H, sept., $^3J$ 6.9), 1.61 (6 H, s) and 1.36 (6 H, d, $^3J$ 6.9); $\delta_C$ 168.75, 160.45 (q), 160.18 (q), 107.71 (q), 104.37 (q), 41.33, 26.99 and 22.90; *m/z* 230 ($M^+$, 21%), 173(41), 172(91), 131(25), 130(57), 129(66), 128(33), 113(20), 102(51), 87(17), 86(100) and 74(47).

**5-(Cyclohexylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 9** (cyclohexanethiol) (75%), mp 101–103 °C (from ethanol) (Found: C, 57.7; H, 6.75. $C_{13}H_{18}O_4S$ requires C, 57.8; H, 6.7%); $\delta_H$ 9.00 (1 H, s), 3.07–2.01 (1 H, m), 1.98–1.23 (10 H, m) and 1.62 (6 H, s); $\delta_C$ 169.44, 160.87 (q), 160.68 (q), 107.83 (q), 104.74 (q), 50.01, 33.17, 27.29, 25.37 and 24.81; *m/z* 270 ($M^+$, 16%), 212(24), 170(38), 157(24), 130(100), 129(30), 102(30) and 87(31).

**5-(Benzylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 10** (phenylmethanethiol) (90%), mp 148.5–150.5 °C (from ethanol) (Found: C, 60.4; H, 5.1. $C_{14}H_{14}O_4S$ requires C, 60.4; H, 5.05%); $\delta_H$ 8.99 (1 H, s), 7.32–7.30 (5 H, m), 4.19 (2 H, s) and 1.67 (6 H, s); $\delta_C$ 169.90, 160.91 (q), 160.29 (q), 134.96 (q), 129.11, 128.86, 128.17, 108.60 (q), 104.97 (q), 41.59 and 27.36; *m/z* 278 ($M^+$, 1%), 220(73), 202(20), 129(43) and 91(100).

**5-[*R*-1-Phenylethylsulfanylmethylene]-2,2-dimethyl-1,3-dioxane-4,6-dione 12** [*R*-(+)-1-phenylethanethiol] (75%), mp 68–70 °C (from ethanol) and **5-[(±)-1-phenylethylsulfanylmethylene]-2,2-dimethyl-1,3-dioxane-4,6-dione 11** [(±)-1-phenylethanethiol] (75%) mp 80–82 °C (from ethanol) (Found: C, 61.6; H, 5.6. $C_{15}H_{16}O_4S$ requires C, 61.6; H, 5.5%); $\delta_H$ 8.90 (1 H, s), 7.33–7.29 (5 H, m), 4.40 (1 H, q, $^3J$ 7.2), 1.70 (3 H, d, $^3J$ 7.2), 1.66 (3 H, s) and 1.63 (3 H, s); $\delta_C$ 168.77, 160.83 (q), 160.22 (q), 140.54 (q), 129.07, 128.23, 127.23, 108.26 (q), 104.81 (q), 49.89, 27.35 and 22.12; *m/z* 292 ($M^+$, < 1%), 234(10), 129(14), 106(20), 105(100), 104(15), 103(20), 79(24), 77(31), 57(14), 53(12) and 43(62).

**5-(Furfurylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 13** (2-furylmethanethiol) (70%), mp 90–92 °C (from ethanol) (Found: C, 53.7; H, 4.45. $C_{12}H_{12}O_5S$ requires C, 53.7; H, 4.5%); $\delta_H$ 9.04 (1 H, s), 7.37 (1 H, dd, $^3J$ 1.0 and 1.6), 6.31 (2 H, m), 4.17 (2 H, s) and 1.66 (6 H, s); $\delta_C$ 169.30, 160.89 (q), 160.09 (q), 148.18 (q), 143.43, 110.74, 109.47, 108.92 (q), 104.97 (q), 33.52 and 27.37; *m/z* 210 [$(M - 58)^+$, 65%], 129(41), 81(100), 53(28), 43(24) and 32(25). ($M^+$ not detected).

**5-(Ethoxycarbonylmethylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 14** (ethyl 2-sulfanylacetate) (75%), mp 104.5–105.5 °C (from ethanol) (Found: C, 48.0; H, 5.15. $C_{11}H_{15}O_6S$ requires C, 48.2; H, 5.1%; $\delta_H$ 8.99 (1 H, s), 4.17 (2 H, q, $^3J$ 7.1), 3.68 (2 H, s), 1.66 (6 H, s) and 1.23 (3 H, t, $^3J$ 7.1); $\delta_C$ 169.20, 167.56 (q), 160.90 (q), 159.90 (q), 109.59 (q), 105.18 (q), 62.27, 38.10, 27.36 and 13.83; *m/z* 274 ($M^+$, 3%), 217(32), 216(48), 187(18), 144(21), 129(69), 126(90), 100(15), 88(100), 61(33), 60(38), 53(50) and 43(64).

**5-(2-Hydroxyethylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 15** (2-sulfanylethanol) (80%) mp 78–80 °C (from toluene) (Found: C, 46.7; H, 5.05. $C_9H_{12}O_5S$ requires C, 46.6; H, 5.15%); $\delta_H$ 9.08 (1 H, s), 3.90 (2 H, t, $^3J$ 5.7), 3.30 (1 H, br s), 3.16 (2 H, t, $^3J$ 5.7) and 1.65 (6 H, s); $\delta_C$ 172.61, 160.86 (q), 160.41 (q), 107.89 (q), 104.79 (q), 60.84, 39.95 and 26.98; *m/z* 232 ($M^+$, 8%), 174(9), 156(12), 129(20), 126(26), 115(14), 87(15) and 86(100).

**5-(2-Carboxyethylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 16** (3-sulfanylpropanoic acid) (95%) mp 153–155 °C (from ethanol) (Found: C, 46.3; H, 4.45. $C_{10}H_{12}O_6S$ requires C, 46.2; H, 4.6%); $\delta_H$([$^2H_6$]DMSO) 9.26 (1 H, s), 3.32 (2 H, t, $^3J$ 6.7), 2.74 (2 H, t, $^3J$ 6.7) and 1.66 (6 H, s); $\delta_C$ ([$^2H_6$]DMSO) 172.97 (q), 172.41, 160.63 (q), 159.75 (q), 107.77 (q), 104.54 (q), 34.28, 32.41 and 26.77; *m/z* 260 ($M^+$, 20%), 203(31), 202(24), 184(76), 140(20), 129(48), 112(26), 102(41), 86(95) and 55(100).

**5-(Allylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 17** (prop-2-enethiol) (90%), mp 100–102 °C (from ethanol) (Found: C, 52.7; H, 5.4. $C_{10}H_{12}O_4S$ requires C, 52.6; H, 5.25%); $\delta_H$ 8.90 (1 H, s), 5.78 (1 H, m), 5.34–5.21 (2 H, m), 3.55 (2 H, m) and 1.63 (6 H, s); $\delta_C$ 169.64, 160.89 (q), 160.20 (q), 131.56, 120.62, 108.91 (q), 104.88 (q), 39.45 and 27.32; *m/z* 228 ($M^+$, 15%), 187(45), 171(26), 170(30), 152(15), 129(100) and 97(42).

**5-[1,1-Bis(methylsulfanyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione 18**

The literature method[14] for the preparation of the title compound gave in our hands low yields of very poor quality material. A slight modification in the method provided a procedure which consistently gave acceptable yields of good quality product.

To a well stirred solution of 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid) (7.0 g, 50 mmol) in DMSO (25 $cm^3$) was added triethylamine (14 $cm^3$, 100 mmol) and carbon disulfide (3 $cm^3$, 50 mmol) in quick succession. The mixture was then stirred vigorously for 1 h at room temperature before being cooled in an ice-bath. Iodomethane (6.5 $cm^3$, 100 mmol) was added slowly to the reaction mixture with cooling (ice-bath). When the addition was complete the reaction mixture was allowed to warm to room temperature and was stirred for a further 4 h before being diluted with ice–water (40 $cm^3$). Scratching of the mixture precipitated the product which was filtered off and washed with light petroleum (bp 60–80 °C)–tetrahydrofuran (2:1). The material obtained at this point was normally pure enough for subsequent reactions (50%), mp 116–118 °C (lit.,[14] 119–121 °C); $\delta_H$ 2.61 (6 H, s) and 1.70 (6 H, s); $\delta_C$ 192.40 (q), 159.74 (q), 103.03 (q), 102.84 (q), 26.63 and 21.28; *m/z* 248 ($M^+$, 7%), 191(6), 172(12), 146(21), 125(27), 118(24), 100(22), 99(96) and 43(100).

**5-(1-Substituted 1-methylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-diones 4** (*cf.* ref. 15)

Grignard reagents were prepared in the usual manner in freshly distilled dry tetrahydrofuran with the exception of methylmagnesium chloride which was commercially available.

To a well stirred solution of 5-[1,1-bis(methylsulfanyl)-methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (2.48 g, 10 mmol) in dry tetrahydrofuran (25 $cm^3$) was added a solution of the Grignard reagent (30 mmol) in tetrahydrofuran (25 $cm^3$) dropwise over a period of 10 min to the mixture which was then stirred for a further 1 h under nitrogen. Hydrochloric acid (5% soln; 30 $cm^3$) was added to the reaction mixture to hydrolyse the addition product after which the organic layer was separated

and the aqueous layer was extracted with methylene dichloride (3 × 25 $cm^3$). The combined organic layer and extracts were then washed with water (3 × 30 $cm^3$), dried ($MgSO_4$), and evaporated under reduced pressure to give the crude product which could then be recrystallised.

The following 5-(1-substituted 1-methylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione derivatives were prepared. The Grignard reagent used is indicated in brackets in each example.

**5-(1-Methylsulfanyl-1-phenylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 19** (phenylmagnesium bromide) (60%) mp 162 °C (from ethanol) (lit.,[15] 164 °C); $\delta_H$ 7.47–7.43 (3 H, m), 7.07–7.03 (2 H, m), 1.87 (3 H, s) and 1.75 (6 H, s); $\delta_C$ 185.09 (q), 161.64 (q), 158.82 (q), 136.28 (q), 129.06, 128.87, 125.59, 109.56 (q), 103.55 (q), 27.08 and 17.16; *m/z* 278 ($M^+$, 0.5%), 220(27), 176(20), 175(49), 147(19), 129(100), 125(37) and 69(34).

**5-(1-*p*-*tert*-Butylphenyl-1-methylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 20** (*p*-*tert*-butylphenylmagnesium bromide) (46%) mp 145 °C (from ethanol) (Found: C, 64.4; H, 6.7. $C_{18}H_{22}O_4S$ requires C, 64.7; H, 6.6%); $\delta_H$ 7.49–7.44 (2 H, d m), 7.00–6.95 (2 H, d m), 1.88 (3 H, s), 1.74 (6 H, s) and 1.32 (9 H, s); $\delta_C$ 185.58 (q), 161.64 (q), 159.01 (q), 152.38 (q), 133.37 (q), 125.72, 125.48, 109.55 (q), 103.46 (q), 34.63 (q), 31.06, 27.04 and 17.18; *m/z* 334 ($M^+$, 40%), 277(15), 276(36), 232(24), 220(28), 219(94), 217(100), 189(32), 185(85), 176(56), 170(51), 169(20), 155(54), 142(17) and 115(22).

**5-(1-Methyl-1-methylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 21** (methylmagnesium chloride) (83%) mp 116–118 °C (from ethanol) (lit.,[15] mp 118–119 °C); $\delta_H$ 2.71 (3 H, s), 2.37 (3 H, s) and 1.54 (6 H, s); $\delta_C$ 187.85 (q), 161.65 (q), 160.25 (q), 107.79 (q), 103.03 (q), 26.67, 22.04 and 16.49; *m/z* 216 ($M^+$, 33%), 159(31), 158(47), 143(20), 140(16), 114(38), 111(15), 86(68), 85(14), 71(16) and 67(100).

**5-(1-Methylsulfanyl-2-thienylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 22** (2-thienylmagnesium bromide) (80%) mp 225–227 °C (decomp.) (Found: C, 50.4; H, 4.0. $C_{12}H_{12}O_4S$ requires C, 50.7; H, 4.25%); $\delta_H$([$^2H_6$]DMSO) 7.86–7.84 (1 H, m), 7.21–7.14 (2 H, m), 2.11 (3 H, s) and 1.73 (6 H, s); $\delta_C$([$^2H_6$]DMSO) (two quaternaries missing) 175.32 (q), 135.13 (q), 134.67 (q), 129.90, 128.63, 127.87, 103.67 (q) 26.48 and 16.86; *m/z* 284 ($M^+$, 11%), 227(18), 226(66), 181(16), 180(13), 179(100), 154(15), 153(17), 139(12), 135(89), 108(17) and 95(12).

### 3-Hydroxythiophenes [thiophen-3(2*H*)-ones]

Large-scale pyrolyses (up to 5 g) of the Meldrum's acid derivatives **3**, **4** and **18** were carried out, using our standard FVP methods.[3] Involatile solids were scraped from the trap, whereas volatile solids and liquids were washed from the trap with solvent. After the solvent had been removed under reduced pressure the crude pyrolysate was purified either by recrystallisation or bulb-to-bulb distillation. Spectra of the major tautomer are generally quoted.

The following thiophen-3(2*H*)-ones (3-hydroxythiophenes) were prepared by pyrolysis, the precursor methylene Meldrum's acid derivative and pyrolysis conditions (furnace temperature, inlet temperature, average pressure and pyrolysis time) are given for each example in brackets. The scale of the pyrolysis reactions range from *ca.* 100 mg to *ca.* 5 g.

**Thiophen-3(2*H*)-one 24** [5-(methylsulfanyl-), 600 °C, 120 °C, $10^{-3}$ Torr, 2 h] (80%), bp 68–70 °C (0.2 Torr) [lit.,[21] 38–39 °C (0.01 Torr)] (Found: C, 47.9; H, 4.1. $C_4H_4OS$ requires C, 48.0; H, 4.0%); $\delta_H$(two tautomers present in chloroform—keto tautomer quoted) 8.36 (1 H, d, $^3J$ 5.7), 6.22 (1 H, d, $^3J$ 5.7) and 3.58 (2 H, s); $\delta_C$ 203.42 (q), 164.91, 123.43 and 38.55; *m/z* 100 ($M^+$, 100%), 72(71), 71(68), 55(53), 46(88), 45(82) and 39(43).

**2-Methylthiophen-3(2*H*)-one 25** [5-(ethylsulfanyl-), 600 °C, 140 °C, $10^{-3}$ Torr, 2 h] (50%) bp 76–78 °C (0.2 Torr) [lit.,[29] bp 92–98 °C (12 Torr)]; $\delta_H$(two tautomers present in chloroform—keto tautomer quoted) 8.34 (1 H, d, $^3J$ 5.8), 6.14 (1 H, d, $^3J$ 5.8), 3.61 (1 H, q, $^3J$ 7.5) and 1.51 (3 H, d, $^3J$ 7.5); $\delta_C$ 207.23 (q), 164.46, 121.87, 48.29 and 16.67.

**2,2-Dimethylthiophen-3(2*H*)-one 33** [5-(isopropylsulfanyl-), 625 °C, 100 °C, 5 × $10^{-3}$ Torr, 2.5 h] (44%), bp 67–69 °C (0.5 Torr) [lit.,[30] bp 78–80 °C (12 Torr)]; $\delta_H$ 8.24 (1 H, d, $^3J$ 6.0), 5.98 (1 H, d, $^3J$ 6.0) and 1.33 (6 H, s); $\delta_C$ 207.68 (q), 161.37, 120.27, 56.59 (q) and 25.54; *m/z* 128 ($M^+$, 15%), 114(69), 113(100), 101(39), 100(23), 99(37), 85(40), 59(51) and 45(35).

**Spiro[cyclohexane-1,2′-2′,3′-dihydrothiophen]-3′-one 34.** [5-(cyclohexylsulfanyl-), 600 °C, 120 °C, $10^{-3}$ Torr, 1.5 h] (58%) mp 59–61 °C (from cyclohexane) (Found: C, 64.1; H, 7.25. $C_9H_{12}OS$ requires C, 64.3; H, 7.15%); $\delta_H$ 8.27 (1 H, d t, $^3J$ 5.9, $^5J$ 0.7), 6.03 (1 H, d, $^3J$ 5.9) and 1.85–1.20 (10 H, m); $\delta_C$ 207.36 (q), 161.92, 121.56, 65.54 (q), 34.77, 24.48 and 24.43; *m/z* 168 ($M^+$, 69%), 126(76), 114(31), 113(100), 81(49) and 58(48).

**2-Phenylthiophen-3(2*H*)-one 26** [5-(benzylsulfanyl-), 625 °C, 170 °C, $10^{-3}$ Torr, 2 h] (92%), bp 115–118 °C (0.2 Torr) (Found: C, 68.3; H, 4.75. $C_{10}H_8OS$ requires C, 68.2; H, 4.55%); $\delta_H$-(hydroxy tautomer) 7.67–7.20 (5 H, m), 7.08 (1 H, d, $^3J$ 5.4), 6.73 (1 H, d, $^3J$ 5.4) and 6.00 (1 H, br s); $\delta_C$ 148.73 (q), 132.80 (q), 128.90, 127.14, 126.71, 122.32, 120.55 and 117.82 (q); *m/z* 176 ($M^+$, 100%), 147(31), 122(24), 121(61), 115(10), 89(14), 78(19) and 77(33).

**2-Methyl-2-phenylthiophen-3(2*H*)-one 35** [5-(1-phenylethylsulfanyl-), 625 °C, 120 °C, 5 × $10^{-3}$ Torr, 2 h] (74%), bp 152–154 °C (0.2 Torr) (Found: C, 69.4; H, 5.3. $C_{11}H_{10}OS$ requires C, 69.5; H, 5.25%); $\delta_H$ 8.48 (1 H, d, $^3J$ 6.0), 7.38–7.28 (5 H, m), 6.16 (1 H, d, $^3J$ 6.0) and 1.90 (3 H, s); $\delta_C$ 206.30 (q), 162.52, 139.09 (q), 128.60, 127.77, 126.46, 119.56, 62.26 (q) and 24.59; *m/z* 190 ($M^+$, 100%), 175(15), 162(10), 161(40), 147(16), 136(48), 131(12), 121(72), 103(27), 78(12), 77(27), 58(12) and 51(19).

**Ethyl 3-hydroxythiophene-2-carboxylate 27** [5-(ethoxycarbonylmethylsulfanyl-), 600 °C, 140 °C, $10^{-3}$ Torr, 2 h] (76%), bp 73–75 °C (0.1 Torr) [lit.,[31] 63–65 °C (0.4 Torr)] (Found: $M^+$, 172.0194. $C_7H_8NO_3S$ requires *M*, 172.0190); $\delta_H$(hydroxy tautomer) 7.31 (1 H, d, $^3J$ 5.4), 6.69 (1 H, d, $^3J$ 5.4), 4.32 (2 H, q, $^3J$ 7.1) and 1.33 (3 H, t, $^3J$ 7.1); $\delta_C$ 166.13 (q), 164.35 (q), 131.07, 118.95, 103.82 (q), 60.82 and 14.10; *m/z* 172 ($M^+$, 8%), 149(9), 126(26), 69(13), 45(15), 44(32) and 40(100).

**5-(Methylsulfanyl)thiophen-3(2*H*)-one 28** {5-[bis(methylsulfanyl)-], 600 °C, 110 °C, $10^{-3}$ Torr, 2 h} (78%), mp 80–81 °C (from cyclohexane) (Found: C, 41.2; H, 4.15. $C_5H_6OS_2$ requires C, 41.1; H, 4.1%); $\delta_H$ 5.88 (1 H, s), 3.61 (2 H, s) and 2.45 (3 H, s); $\delta_C$ 197.92 (q), 182.49 (q), 115.73, 40.58 and 15.93; *m/z* 146 ($M^+$, 100%), 131(14), 100(18), 99(14), 85(66), 72(44), 71(16), 57(13) and 45(27).

**5-Phenylthiophen-3(2*H*)-one 29** [5-(1-methylsulfanyl-1-phenyl-), 600 °C, 150 °C, $10^{-3}$ Torr, 1 h] (80%), mp 78 °C [from light petroleum (bp 40–60 °C)] (lit.,[32] 78 °C); $\delta_H$ 7.71–7.41 (5 H, m), 6.56 (1 H, s) and 3.81 (2 H, s); $\delta_C$ 202.37 (q), 178.68 (q), 132.54 (q), 132.08, 128.88, 126.47, 118.31 and 40.58; *m/z* 176 ($M^+$, 100%), 175(33), 147(28) and 102(29).

**5-*p*-*tert*-Butylphenylthiophen-3(2*H*)-one 30** [5-(1-*p*-*tert*-butylphenyl-1-methylsulfanyl-), 625 °C, 140 °C, $10^{-3}$ Torr, 2 h] (86%), mp 109–111 °C (from cyclohexane) (Found: C, 73.5; H, 7.05. $C_{14}H_{16}OS$ requires C, 73.4; H, 6.9%); $\delta_H$ 7.61 (2 H, d m, $^3J$ 8.5), 7.46 (2 H, d m, $^3J$ 8.5), 6.53 (1 H, s), 3.77 (2 H, s) and 1.33 (9 H, s); $\delta_C$ 202.08 (q), 178.24 (q), 155.89 (q), 129.84 (q), 126.31, 125.82, 117.69, 40.40, 34.92 (q) and 30.91; *m/z* 232 ($M^+$, 58%), 218(15), 217(100), 189(10), 175(21) and 115(16).

**5-Methylthiophen-3(2*H*)-one 31** [5-(1-methyl-1-methylsulfanyl-) 625 °C, 110 °C, $10^{-3}$ Torr, 2 h] (75%), bp 57–59 °C (0.2 Torr) [lit.,[33] 53 °C (0.1 Torr)]; $\delta_H$ 5.98 (1 H, s), 3.63 (2 H, s) and 2.32 (3 H, s); $\delta_C$ 202.48 (q), 180.09 (q), 121.72, 42.37 and 19.52; *m/z* 114 ($M^+$, 100%), 113(15), 86(29), 85(24), 71(27), 67(24), 46(25) and 45(41).

**5-(2-Thienyl)thiophen-3(2*H*)-one 32** [5-(1-methylsulfanyl-2-thienyl-), 625 °C, 140 °C, $10^{-3}$ Torr, 2.5 h] (76%), mp 113–115 °C (from ethanol) (Found: C, 52.8; H, 3.25. $C_8H_6OS_2$ requires C, 52.7; H, 3.3%); $\delta_H$ 7.58–7.52 (2 H, m), 7.12 (1 H, dd, $^3J$ 5.0, 3.8), 6.39 (1 H, s) and 3.80 (2 H, s); $\delta_C$ 201.45 (q), 170.31 (q), 135.95 (q), 131.02, 129.17, 128.36, 116.93 and 40.48; *m/z* 182 ($M^+$, 100%), 153(22), 108(56), 69(12) and 45(15).

Repeated attempts at pyrolysis of the 5-(furfurylsulfanyl-) derivative resulted only in decomposition of the starting material.

**Pyrolysis of 5-(2-hydroxyethylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 15.** Pyrolysis of the Meldrum's acid derivative **15** (0.115 g, 0.5 mmol) at 600 °C and $10^{-3}$ Torr (inlet temperature 160 °C) over 3 h gave a liquid mixture which was separated by dry flash chromatography on silica. The major component was tentatively identified as 2,3-dihydro-7*H*-1,4-oxathiepin-7-one **31** on the basis of its $^1$H NMR spectrum $\delta_H$ 6.63 (1 H, d, $^3J$ 8.6), 5.31 (1 H, d, $^3J$ 8.6), 4.73 (2 H, m) and 3.24 (2 H, m).

**Pyrolysis of 5-(2-carboxyethylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 16.** The Meldrum's acid derivative **16** (0.10 g, 0.38 mmol) was distilled at 150–160 °C and $10^{-3}$ Torr through the furnace held at 600 °C over a period of 2.5 h. The $^1$H NMR spectrum of the crude pyrolysate was weak, and showed complex signals in the range $\delta_H$ 5.8–7.5 and 2.6–3.3. This material was not investigated further.

**Pyrolysis of 5-(allylsulfanylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 17.** Pyrolysis of **17** (0.21 g, 0.53 mmol) at 600 °C ($10^{-3}$ Torr, inlet temperature 120 °C, pyrolysis time 1 h) gave a complex mixture which contained at least 6 volatile components, as shown by glc on SE30.

### Chiral shift reagent studies

A chiral lanthanide shift reagent was used to determine the enantiomeric excess in the 2-methyl-2-phenylthiophen-3(2*H*)-one by $^1$H NMR spectroscopy. The tris[3-heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) derivative was found to be suitable for the analysis because of the shift of signals to higher frequency positions (*cf.* ref. 27).

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