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THE ACID CATALYSED REACTION OF 1,4-DIKETONES WITH HYDROGEN SULPHIDE

A CONVENIENT ROUTE TO SUBSTITUTED THIOPHENS

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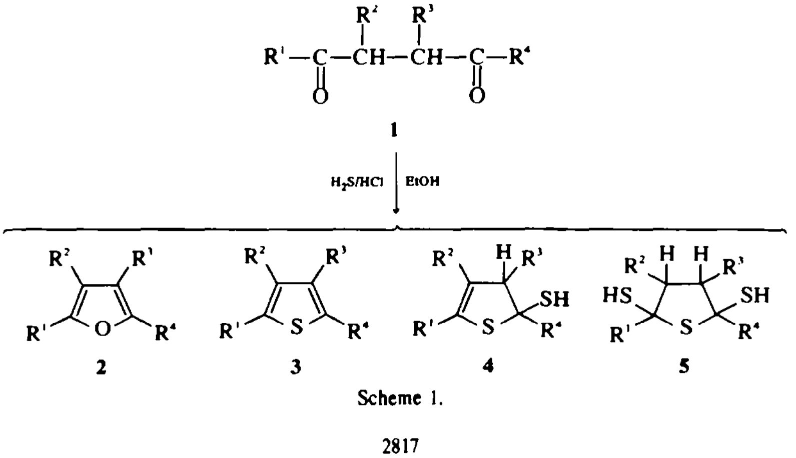
Abstract—Various 1,4-diketones and 2-ethoxycarbonyl-1,4-diketones have been reacted with H_2S in acidic ethanol to give 2,5- or higher substituted thiophens as resulting from a spontaneous ring-closure reaction of initially formed sulphur analogues of the starting diketones. In some cases the corresponding 2-mercapto-2,3-dihydrothiophens and/or 2,5-dimercaptotetrahydrothiophens were formed as by-products. 1,4-Diphenyl-1,4-diketones behaved exceptionally under similar reaction conditions yielding preferentially 2,5-diphenylfurans.

The reaction of 1,4-diketones with thionation agents such as P_2S_5[1-8] and P_2S_3,[9,10] resulting in the formation of 2,5-disubstituted thiophens, is unsatisfactory, due to unpredictable yields, and because it frequently leads to formation of non-thiophenoid and tarry products.[7] Doubtless, the requisite relatively drastic reaction conditions and the ability of the phosphorus sulphide to act as dehydrating agent as well as a sulphurizing agent are of importance for the reaction course. Thus it has been demonstrated[11] that 2-ethoxycarbonyl-1,4-diketones react with P_2S_5 in boiling xylene to give, not the expected 2,5-disubstituted 3-ethoxycarbonylthiophens, but rather the corresponding 2,5-disubstituted 3-ethoxythiocarbonylfurans—a clear indication of the occurrence of an initial P_2S_2-promoted ring-closure/dehydration process followed by a secondary thionation process at the C atom of the ester CO Group. In contrast to these results, it was observed[12] recently that 3 - ethoxycarbonyl - 2,5 - hexanedione reacts with H_2S at − 35° in acidic media to give 3 - ethoxycarbonyl - 2,5 - dimethylthiophen. Apparently, these conditions prevent initial ring-closure to furans, but still effect thionation.[13] Consequently, it was decided to study the reactivity of 1,4-diketones and, especially, 2 - ethoxycarbonyl - 1,4-diketones towards H_2S under the influence of acid catalysis. Previously, 2,5-dimethylthiophen has been synthesized from acetonylacetone in a yield of 35% by treatment with H_2S at 325° in the presence of Al_2O_3,[14] and in a yield of 33% by reaction with H_2S in acidic ethanol at − 35°;[12] 2,3 - diacetylnorbornane, 5,6 - diacetyl - 2 - norbornene, 2,3 - diacetylbicyclo[2.2.2]octane and 5,6 - diacetylbicyclo[2.2.2]oct - 2 - ene have been converted into the derived thiophens by acid catalysed reaction with H_2S,[15] and Campaigne and Foye[7] have synthesized some 2,5 - diarylthiophens through reaction of parental 1,2 - diaroylethanes with H_2S in the presence of zinc chloride or stannic chloride.

RESULTS AND DISCUSSION

The 1,4-diketones **1a–d** and the 2 - ethoxycarbonyl - 1,4 - diketones **1e–l** reacted with gaseous H_2S and HCl in ethanolic solution under conditions similar to those used previously[13,16] in the syntheses of β-thioxo esters, i.e. at a suitably low temperature (Experimental). Scheme 1 gives a survey of the general reaction and the products obtained (in no case were all four products formed simultaneously), and relevant experimental results are summarized in Table 1. In no case could unreacted starting material be recovered from or detected in the product.

In the preliminary investigations of this reaction it was found[12] that acetonylacetone (**1a**) reacted with H_2S/HCl at − 35° to give a mixture of three products, 2,5 - dimethylthiophen (**3a**), 2,5 - dimethyl - 2 - mercapto - 2,3 - dihydrothiophen (**4a**), and 2,5 - dimethyl - 2,5 - dimercaptotetrahydrothiophen (**5a**), in yields of 33%, 3%, and 15%, respectively. At least **5a** requires the intermediacy of an open-chain *gem*-dithiol, probably **12a**. The dihydrothiophen **4a** may be generated either from inter-



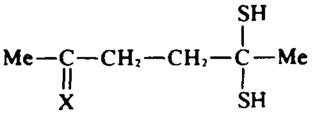
Scheme 1.

Table 1. Survey of experimental results

	Substituents[a]				Reaction temperature t°C	Yields of products[a]			
	R^1	R^2	R^3	R^4		**2**	**3**	**4**	**5**
a	Me	H	H	Me	-35^b	-	33%	3%	15%
					≤ -50	-	49%	0.9%	13%
b	t-Bu	H	H	Me	≤ -50	-	85%	-	-
c	Ph	H	H	Me	≤ -50	-	82%	-	-
d	Ph	H	H	Ph	$-10 \leq t \leq 10^c$	53%	29%	-	-
					$-50 \leq t \leq 0^{c,d}$	33%	53%	-	-
e	Me	CO_2Et	H	Me	-35^b	-	57%	17%	-
					-40	-	53%	20%	-
f	Me	CO_2Et	Me	Me	-50	-	52%	-	32%
g	Me	CO_2Et	H	Ph	-40	-	48%	19%	-
h	Me	CO_2Et	Me	Ph	-40	-	73%	-	-
i	Ph	CO_2Et	H	Me	-40	-	46%	$5\%^e$	-
j	Ph	CO_2Et	Me	Me	-40	-	48%	12%	-
k	Ph	CO_2Et	H	Ph	$-10 \leq t \leq 10^c$	80%	-	-	-
l	Ph	CO_2Et	Me	Ph	$-10 \leq t \leq 10^c$	64%	-	-	-

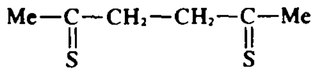
[a] see scheme 1. [b] data from preliminary paper.[12] [c] the temperature raised to the maximum value during the supply of HCl gas (Experimental). [d] the solvent was a mixture of EtOH and $CHCl_3$ (2:1). [e] this product was not obtained pure (Experimental).

mediately formed **8a** by intramolecular ring-closure and subsequent dehydration, or from **9a** via enethiolization and subsequent cyclization.



$$Me-\underset{\underset{X}{\|}}{C}-CH_2-CH_2-\overset{SH}{\underset{SH}{\overset{|}{\underset{|}{C}}}}-Me$$

8a: X = O
12a: X = S



$$Me-\underset{\underset{S}{\|}}{C}-CH_2-CH_2-\underset{\underset{S}{\|}}{C}-Me$$

9a

Recent studies[13,17,18] have shown that the formation of *gem*-dithiols in the acid catalysed reactions of ketones with H_2S can be avoided at sufficiently low temperatures, by which the corresponding thioketones are formed instead. When acetonylacetone was again reacted with H_2S/HCl, but now at −50°, the yield of the thiophen **3a** was increased but **5a** was still a product. The 1,4-diketones **1b** and **1c**, however, gave under the same reaction conditions merely the respective thiophens in excellent yields. Because aryl ketones are known not to form *gem*-dithiols in reactions with H_2S/HCl,[13,19,20] 1,4-diphenyl-1,4-butanedione (**1d**) was allowed to undergo the reaction at a somewhat higher temperature, both in ethanolic solution (some starting material precipitated on cooling the solution to − 10°), and in a mixture of ethanol and chloroform. In both cases a mixture of 2,5-diphenylfuran (**2d**) and 2,5-diphenylthiophen (**3d**) was obtained, whereas no starting material could be detected in the product. This result, which was confirmed, suggests the occurrence of a considerably slower thionation reaction of the aroyl group relative to that of an aliphatic acyl group (in accordance with expectations, see Ref. 13)—with the consequence that dehydration and ring-closure to the furan becomes a competitive process. In a similar experiment Campaigne and Foye[7] also observed only partial formation of **3d**, but, surprisingly, these authors report that their product in addition to **3b** contained unreacted 1,4-diphenyl-1,4-butanedione (**1d**) and no 2,5-diphenylfuran (**2d**)—in spite of the fact that their experiment was performed at a slightly higher temperature and in the presence of the dehydration agent $ZnCl_2$. In this connection it should be pointed out that the 2-ethoxycarbonyl-1,4-diphenyl-1,4-diketones **1k** and **1l** upon treatment with H_2S/HCl were converted completely and exclusively into the 2,5-diphenylfurans **2k** and **2l**, respectively.

The reactions of the 2-ethoxycarbonyl-1,4-diketones **1e**–**1j** with H_2S/HCl afforded in all cases a good yield of the corresponding di- or trisubstituted 3-ethoxycarbonylthiophens (Table 1). These products were easily isolated from the crude product by application of preparative layer chromatography (PLC), by which corresponding 4-ethoxycarbonyl-2-mercapto-2,3-dihydrothiophens (**4**, $R^2 = CO_2Et$), and, in a single case, a corresponding 2,5-dimercaptotetrahydrothiophen (**5f**) were also extracted and isolated. The 3-ethoxycarbonylthiophens **3e**–**3j** are stable, distillable compounds. The 2-

mercapto - 2,3 - dihydrothiophen **4e** and the 2,5 - dimercaptotetrahydrothiophen **5f** were also found stable enough to be distilled, but attempts to distil the 2 - mercapto - 2,3 - dihydrothiophens **4g**, **4i** and **4j** led inevitably to partial decomposition to the corresponding thiophens with simultaneous evolution of H_2S. Scheme 2 gives a survey of all processes that formally may occur in the reaction, indicating also the possible reaction pathways, the probable intermediates, and the imaginable products. An understanding of the actual reaction courses and observed product distributions may be achieved by means of this scheme (introducing $R^2 = CO_2Et$) and the following summary of relevant, well-established experimental facts:

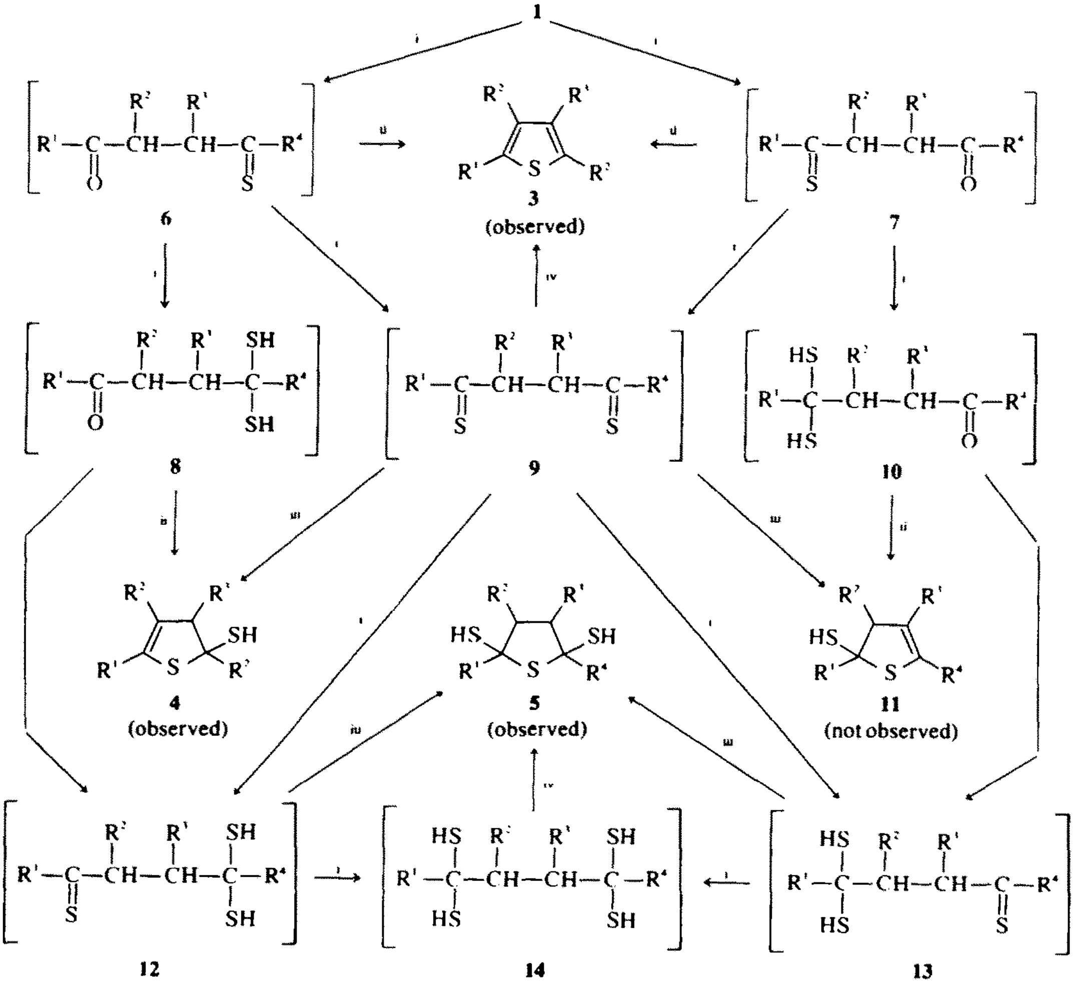
(1) Simple methyl alkyl ketones, i.e. in the actual case such ketones in which the CO group is not situated in β-position to an ethoxycarbonyl group, generally react with H_2S/HCl in ethanol at $-40°$ to $-50°$ to give *gem*-dithiols, via the corresponding, initially formed thioketones.[17,21] The conservation of the thioketones as such requires a still lower reaction temperature.[18]

(2) Methyl alkyl ketones possessing the CO group in β-position to an ethoxycarbonyl group react with H_2S/HCl under the same conditions to give the enethiol tautomers of the corresponding thioketones.[13,17] The corresponding *gem*-dithiols are the prevailing products at 0°.[17,22]

(3) Aryl alkyl ketones do not react with H_2S/HCl under the actual conditions (i.e. at $-40°$), if the CO group is situated in β-position to an ethoxycarbonyl group.[13,23] If the ethoxycarbonyl group is not present, thionation may possibly take place, but then probably very sluggishly.

(4) Aryl alkyl ketones do not form *gem*-dithiols in reactions with H_2S/HCl.[13,19,20,24]

Doubtless, the most likely routes to the 3-ethoxycarbonyl-thiophens **3** are those proceeding via the monothionated intermediates **6** (cases **e**, **f**, **i** and **j**) and **7** (cases **g** and **h**). According to the above statements, intermediate *gem*-dithiols of structure **8** are possible in cases **e**, **f**, **i** and **j**—corresponding ring-closure products **4** were actually produced in cases **e**, **i** and **j**. The formation of a dithiodiketone **9** is possible in the cases **e**, **f**, **g** and **h**—and the derived ring-closure products **4** were isolated in cases **e** and **g**. The non-appearance of the theoretically possible products **4f** and **4h** is assumed to depend on the special structural properties ($R^3 = Me$) and the conse-



(i) H_2S/HCl
(ii) ring-closure by dehydration
(iii) intramolecular cyclo-addition
(iv) intramolecular cyclization with H_2S-elimination

Scheme 2.

quent alterations in the kinetics of the competitive processes. Thus the irreversible cyclization/dehydration process **7h**→**3h** completely predominates the thionation process **7h**→**9h**, whereas the ring-closure processes **8f**→**4f** and/or **9f**→**4f** are ousted by the thionation reaction(s) leading to **12f**, the probable precursor of the observed product **5f**. It is noteworthy that even traces of **4f** could not be found. On the other hand, **5e** was also undetectable as a product, although formation of the intermediate **12e** is theoretically possible. According to the above statements, the *gem*-dithiol **10** is in no case a likely intermediate; this was verified by the experimental fact that a mercaptodihydrothiophen of structure **11** in no case appeared as a product.

The structures of the products were established by means of their NMR and IR spectra, and by elemental analysis. The NMR data† are listed in Tables 2–4, whereas all other characteristics are found in the Experimental.

It is likely that each of the products **4a**, **4e**, **4g** and **4i** in fact has been produced and isolated as a mixture of two geometrical isomers, indistinguishable by NMR. However, the NMR spectrum of **4j** shows that also in this case only one pair of NMR spectroscopically indistinguishable isomers has been produced and isolated, although in fact four isomeric forms are theoretically possible. It is considered likely that sterical requirements play a part in the cyclization reaction **8j**→**4j**, and hence that the isolated product is composed of a racemic mixture of the two geometrical isomers, in which the Me groups in positions 2 and 3 are located *trans* to each other. With four centres of chirality, **5f** may theoretically be produced in 16 stereoisomeric forms, which two by two will be indistinguishable by NMR (enantiomers). Nevertheless, the NMR spectrum of **5f** (Table 4) clearly shows that only one pair of enantiomers has been formed. There are several reasons to assume that the isolated pair of enantiomers is that represented by the structure shown in Table 4, together with its reflected image. Firstly, the observed coupling between the ring protons in positions 3 and 4 is of a magnitude (J = 12.2 – 12.4 Hz) that clearly indicates a

Table 2. ^{1}H NMR chemical shifts (δ-values, ppm) and coupling constants (Hz) of furans and thiophens[a]

Comp.	solv.	R^1		$R^{2\,b}$	R^3		R^4	
		Me	Ph	H	H	Me	Me	Ph
3a	CCl_4	2.34 m^c	-	6.41 m^c	6.41 m^c	-	2.34 m^c	-
3b	CCl_4	1.32 s	-	6.35 m^d	6.35 m^d	-	2.35 m^c	-
2c	CCl_4	-	7.0-7.7 m	6.39 d (3.4)	5.93 dq (3.4/1.2)	-	2.33 d (1.2)	-
3c	CCl_4	-	7.1-7.6 m	7.01 d (3.6)	6.61 dq (3.6/1.0)	-	2.47 d (1.0)	-
2d	$CDCl_3$	-	7.1-7.8 m	6.63 s	6.63 s	-	-	7.1-7.8 m
3d	$CDCl_3$	-	7.1-7.7 m	7.22 s	7.22 s	-	-	7.1-7.7 m
3e	CS_2	2.58 qd (0.5/0.25)	-	-	6.86 qq (1.1/0.25)	-	2.33 dq (1.1/0.5)	-
2f	CCl_4	2.47 m^c	-	-	-	2.15 m^c	2.02 q (0.75)	-
2f	C_6D_6	2.45 q (0.5)	-	-	-	1.94 m^c	2.10 q (0.75)	-
3f	CS_2	2.53 q (0.5)	-	-	-	2.23 m^c	2.18 m^c	-

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†The NMR data of **5a** have already been published and discussed (see Ref. 12).

Table 2 (*Contd*)

Comp.	solv.	R^1		R^2[b]	R^3		R^4	
		Me	Ph	H	H	Me	Me	Ph
3f	C_6D_6	2.52 q (0.5)	-	-	-	2.03 m[c]	2.23 q (0.6)	-
2g	CCl_4	2.62 s	-	-	6.87 s	-	-	7.2-7.8 m
3g	CCl_4	2.68 s	-	-	7.53 s	-	-	7.1-7.6 m
3h	CCl_4	2.64 s	-	-	-	2.39 s	-	7.33 m
3i	CCl_4	-	7.1-7.5 m	-	7.04 q (1.15)	-	2.37 d (1.15)	-
3j	CCl_4	-	7.36 m	-	-	2.28 q (0.6)	2.21 q (0.6)	-
2k	$CDCl_3$	-	7.1-8.1 m	-	6.98 s	-	-	7.1-7.7 m
2l	CCl_4	-	7.1-7.9 m	-	-	2.40 s	-	7.1-7.7 m

[a] The following abbreviations are used: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Coupling constants are given in brackets. [b] The trivial data of the ester group protons are omitted. [c] The multiplicity could not be further specified due to limitations in resolution capacity. [d] Coalescing signals of complex multiplicity.

trans-location of the protons in question. Secondly, the observed coupling between the Me group protons and the mercaptoproton in 2-position suggests that the mercapto group is not freely rotating, evidently due to the existence of an intramolecular H-bonding to the ester CO group[13,16] (a similar coupling is not observed for the mercapto group in 5-position). A model study immediately shows that such intramolecular H-bonding is possible only if the mercapto group and the ester group are located *cis* to each other. Finally, it is considered likely that steric requirements tell in the cyclization **12f**→**5f**, thus leading to a product with the Me groups in positions 4 and 5 located *trans* to each other. In combination, the above considerations lead to a structure for **5f**, in which the more space-filling substituent in any position is always located *trans* to the adjacent more space-filling groups.

The present investigation has demonstrated that 1,4-diketones as well as 2 - ethoxycarbonyl - 1,4 - diketones (with only a few exceptions) can be neatly converted into corresponding thiophens upon treatment with H_2S/HCl in ethanol at a suitably low temperature. Due to a broader scope in general synthetic applicability, ease in performance, and acceptable yields, this reaction forms the basis of a synthetic method, which appears to be definitely superior to the similar classical one involving a phosphorus sulphide as thionation and dehydration agent.

EXPERIMENTAL

^{1}H NMR *spectra* were recorded as 10–20% solns on a Jeol C-60 HL spectrometer. TMS was used as internal reference standard. The chemical shifts are expressed as δ-values in ppm downfield from TMS, and are correct within ±0.02 ppm. The coupling constants were measured on expanded signals, and are expressed numerically in Hz with an accuracy within ±0.1 Hz.

IR *spectra* were recorded as 2–5% solns in CCl_4 on a Perkin-Elmer 457 grating spectrophotometer.

PLC was carried out on silica gel $PF_{254+366}$ (Merck) support (450 × 250 × 3 mm). B.ps and m.ps are uncorrected. Unless stated to the contrary, yields refer to the isolated quantities of the pure products.

Starting materials. Compound **1a** was commercially available. Compounds **1b**[3] and **1d**[7] were stock chemicals and **1c** was synthesized as described.[25]† The distillation of the crude product gave the desired 1,4-diketone in the yield of 31%, b.p.$_{0.1}$: 97–101°, n_D^{25}:

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†In Helberger's original experiment[24] only one product was obtained and referred to as **1c**. However, the physical data reported for this product (b.p.$_{12}$: 158°, m.p.: 28–29°) strongly suggest that it should rather be described as **2c**. Apparently, Helberger's less gentle distillation conditions have led to dehydration and ring-closure of the primarily formed **1c**.

Table 3. ^{1}H NMR chemical shifts and coupling constants of 2-mercapto-2,3-dihydrothiophens[a]

		R^1		$R^{2\,b}$	R^3/H^3		R^4		
Comp.	solv.	Me	Ph	H	Me	H	Me	Ph	SH
4a	CS_2	1.90 td (2.1/1.6)	-	5.09 tq (2.6/1.6)	-	2.90 dq (2.6/2.1)	1.83 d (0.9)	-	2.70 q (0.9)
4e	CS_2	2.24 t (1.8)	-	-	-	3.24 qd^c (1.8)	1.84 d (0.85)	-	2.74 q (0.85)
4g	CCl_4	2.38 t (1.8)	-	-	-	3.73 q (1.8)	-	7.2-7.7 m	3.36 s
4i	CCl_4	-	7.21 s	-	-	3.47 s	1.92 m^d	-	2.21 m^d
4j	CCl_4	-	7.25 s	-	1.40 d (6.5)	3.23 q (6.5)	1.94 d (0.8)	-	2.28 q (0.8)

[a] See footnote a, table 2. [b] The trivial data of the ester group protons are omitted (R^2 = CO_2Et). [c] The doublet reflects magnetic non-equivalence of the ring methylene protons (separation ~6 Hz).

[d] The multiplicity of the narrow signal could not be further specified due to limitations in resolution capacity.

1,5328 (Found: C, 74.75; H, 6.90. $C_{11}H_{12}O_2$ requires: C, 74.97; H, 6.86%). A considerable forerun was further purified by PLC (R_f = 0.65 – 0.90, 1 elution with a 1:9 mixture of ether and light petroleum) to give a 5% overall yield of **2c**, b.p.$_{0.1}$: 55°, m.p.: 37–38° (lit. m.p.: 41–42°,[26] 39–40°[27]) (Found: C, 83.25; H, 6.42. $C_{11}H_{10}O$ requires: C, 83.51; H, 6.37%).

Compounds **1e–1l** were synthesized by reaction of ethyl acetoactate or ethyl benzoylacetate with EtONa and the appropriate α-halogenoketone in EtOH. The products are thermally unstable, for which reason a modified version of the known preparative methods[11,28–31] was employed (see below). **1k** and **1l** were obtained pure by recrystallization. **1e** and **1i** (not in accordance with lit.[11,29]) could be obtained pure by simple distillation of the crude products (in high vacuum), but in all other cases attempted distillation inevitably led to decomposition. The compounds **1f**, **1g**, **1h** and **1j** were, however, easily obtained pure by PLC, by means of which also minor quantities of furanoic decomposition products were isolated in two cases. The purity of the products was in all cases carefully checked by NMR, TLC, and for compounds not described hitherto, also by elemental analysis.

General procedure for the preparation of 2 - ethoxycarbonyl - 1,4 - diketones. Preparation of 3 - ethoxycarbonyl - 4 - methyl - 2,5 - hexanedione (**1f**)

Ethyl acetoacetate (42.9 g; 0.33 moles) was added dropwise during 30 min to a soln of EtONa (22.4 g; 0.33 moles) in 200 ml of 99% EtOH under mechanical stirring and gentle reflux. Stirring was continued for 1 hr, during which the temp. in the reaction flask was allowed to reach room temp. Then 3 - bromo - 2 - butanone (49.8 g; 0.33 moles) was added dropwise under stirring during 1 hr. Stirring was continued overnight (~15 hr) at room temp. The heterogenous mixture was then extracted with a mixture of 500 ml ether and 200 ml water. The layers were separated, the aqueous layer was extracted with further 200 ml ether, and the combined etheral layers were washed with water, and dried (Na_2SO_4). After filtration, the solvent was evaporated to leave 46.2 g of a light brown oil, of which 20.0 g were subjected to PLC (10 plates, two elutions with a 1:4 mixture of ether and light petroleum). The material absorbed within the R'_f-region 0.10–0.41 was isolated to give 11.3 g of pure **1f** as a colourless oil, overall yield: 39%, b.p.$_{13}$: 113–118° (dec); NMR (CCl_4): δ 0.8–1.5 (6H, m), δ 2.1–2.3 (6H, m), δ 3.0–3.6 (1H, m), δ 3.78 (1H, d, J = 10), δ 3.9–4.4 (2H, m). IR, ν[C=O]: 1715, 1734 cm^{-1}. (Found: C, 60.34; H, 8.28. $C_{10}H_{16}O_4$ requires: C, 59.98; H, 8.05%). The material absorbed within the R'_f-region 0.73–0.91 was also isolated to give 3.8 g of pure *3 - ethoxycarbonyl - 2,4,5 - trimethylfuran* (**2f**) as a colourless oil, overall yield: 14%, b.p.$_{15}$: 107–108°, n_D^{25}: 1.4736. IR, ν[C=O]: 1711 cm^{-1}. (Found: C, 65.90; H, 7.71. $C_{10}H_{14}O_3$ requires: C, 65.91; H, 7.74%).

3-*Ethoxycarbonyl*-2,5-*hexanedione* (**1e**) was obtained by reaction of chloroacetone with ethyl acetoacetate as described above. Distillation of the crude product gave the pure compound in the yield of 34%. Colourless oil, b.p.$_{0.18}$: 63–73°, n_D^{25}: 1.4391. NMR (CCl_4): δ 1.26 (3H, t, J = 7), δ 2.12 (3H, s), δ 2.25 (3H, s), δ 2.81 and 2.94 (2H, AB-part of ABX-system, J_{AB} = 18, J_{AX} = J_{BX} = 7), δ 3.87 (1H, t (X-part of ABX-system), J = 7), δ 4.12 (2H, q, J = 7). IR, ν[C=O]: 1720, 1743 cm^{-1}. (Found: C, 58.37; H, 7.56. $C_9H_{14}O_4$ requires: C, 58.05; H, 7.58%).

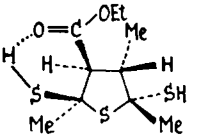
3 - *Ethoxycarbonyl* - 1 - *phenyl* - 1,4 - *pentanedione* (**1g**) was obtained by reaction of phenacylbromide with ethyl acetoacetate as described. Purified by PLC (conditions as above, R'_f = 0.22–0.36), yield: 47%; colourless, undistillable oil.[11,28,29] NMR (CCl_4): δ 1.23 (3H, t, J = 7), δ 2.32 (3H, s), δ 3.3–3.6 (2H, m), δ 3.95 (1H, t, J = 7), δ 4.12 (2H, q, J = 7), δ 7.1–8.0 (5H, m). IR, ν[C=O]: 1688, 1720, 1744 cm^{-1}. 3-*Ethoxycarbonyl* - 2 - *methyl* - 5 - *phenylfuran* (**2g**) was obtained as a by-product (R'_f = 0.73–0.89) in the yield of 21%. B.p.$_{0.35}$: 137–138°; IR, ν[C=O]: 1717 cm^{-1}. (lit.[11] b.p.$_{0.2}$: 120°).

3 - *Ethoxycarbonyl* - 2 - *methyl* - 1 - *phenyl* - 1,4 - *pentanedione* (**1h**) was synthesized according to the general procedure by

Table 4. ^{1}H NMR chemical shifts and coupling constants of 3 - ethoxycarbonyl - 2,5 - dimercapto - 2,4,5 - trimethyltetrahydrothiophen (5f)[a,b]

Solv.	$Me^{(2)}$	$SH^{(2)}$	$CO_2Et^{(3)}$	$H^{(3)}$	$H^{(4)}$	$Me^{(4)}$	$SH^{(5)}$	$Me^{(5)}$
CCl_4	1.98 d (0.7)	2.48 q (0.7)	4.22 q(~7) 1.32 t(~7)	3.27 d^c (12.2)	2.82 dq^c (12.2/6.5)	1.13 d^c (6.5)	2.28 s	1.81 s
C_6D_6	1.97 d (0.7)	2.50 q (0.7)	4.03 q^d(~7) 0.98 t(~7)	3.30 d^c (12.4)	2.83 dq^c (12.4/6.5)	0.99 d^c (6.5)	2.03 s	1.50 s
$\Delta\delta^e$	0.01	-0.02	0.19 0.34	-0.03	-0.01	0.14	0.25	0.31

[a] Racemic mixture of two NMR-spectroscopically indistinguishable enantiomers. The likely structure for one of these is



[b] See footnote a, table 2. [c] The protons $H^{(3)}$, $H^{(4)}$, and $Me^{(4)}$ appear as an ABM_3-system with J_{AB} = 12.2-12.4 Hz, J_{BM} = 6.5 Hz, and J_{AM} = 0 Hz.

[d] On the five-fold expanded scale, this signal appears as two overlapping quartets, separated by 1.4 Hz, and with different line separations (7.5 Hz in the low-field quartet, 7.2 Hz in the high-field quartet).

[e] Solvent-induced shift displacements.

reaction of α-bromopropiophenone with ethyl acetoacetate and was obtained pure in the yield of 81% by PLC (one elution with a 1:9 mixture of acetone and light petroleum, followed by a second elution with a 1:4 mixture of acetone and light petroleum, R'_f = 0.50–0.73). Colourless, undistillable oil; NMR (CCl_4): δ 1.95–2.4 (6H, m), δ 2.23 and 2.31 (3H, 2s), δ 3.9–4.2 (2H, m), δ 4.18 (2H, q, J = 7), δ 7.2–8.1 (5H, m) (Found: C, 68.84; H, 7.27. $C_{15}H_{18}O_4$ requires: C, 68.68; H, 6.92%).

2 - *Ethoxycarbonyl* - 1 - *phenyl* - 1,4 - *pentanedione* (**1i**) was synthesized by reaction of chloroacetone with ethyl benzoylacetate. Distillation of the crude product gave unexpectedly[11,29] the pure compound in the yield of 28%, b.p.$_{0.4}$: 141–150°; NMR (CCl_4): δ 1.12 (3H, t, J = 7), δ 2.13 (3H, s), δ 3.05 (2H, d, J = 7), δ 4.07 (2H, q, J = 7), δ 4.78 (1H, t, J = 7), δ 7.2–8.1 (5H, m). IR, ν[C=O]: 1688, 1721, 1741 cm^{-1}.

2 - *Ethoxycarbonyl* - 3 - *methyl* - 1 - *phenyl* - 1,4 - *pentanedione* (**1j**) was obtained according to the general procedure by reaction of ethyl benzoylacetate with 3 - bromo - 2 - butanone. Purified by PLC (two elutions with a 1:4 mixture of ether and light petroleum, R'_f = 0.18–0.41), yield: 33%; NMR (CCl_4): δ 0.85–1.3 (6H, m), δ 2.21 (3H, s), δ 3.15–3.8 (1H, m), δ 4.02 (2H, q, J = 7), δ 4.62 (1H, dd = X-part of ABX-system, $|J_{AX} + J_{BX}|$ = 22), δ 7.2–8.1 (5H, m). IR, ν[C=O]: 1687, 1718, 1740 cm^{-1}. (Found: C, 69.09; H, 7.31. $C_{15}H_{18}O_4$ requires: C, 68.68; H, 6.92%).

2 - *Ethoxycarbonyl* - 1,4 - *diphenyl* - 1,4 - *butanedione* (**1k**) was synthesized by reaction of ethyl benzoylacetate with phenacylbromide according to the general procedure. Purified by recrystallization (mixture of benzene and petroleum), yield: 31% as white crystals, m.p. 64° (lit.[11] m.p.: 65°). NMR (CCl_4): δ 1.14 (3H, t, J = 7), δ 3.53 (2H, d, J = 7), δ 4.12 (2H, q, J = 7), δ 5.01 (1H, t, J = 7), δ 7.3–8.2 (10H, m). IR, ν[C=O]: 1688, 1741 cm^{-1}.

2 - *Ethoxycarbonyl* - 3 - *methyl* - 1,4 - *diphenyl* - 1,4 - *butanedione* (**1l**) was prepared by reaction of ethyl benzoylacetate with α-bromopropiophenone. It was purified by recrystallization (cyclohexane), yield: 33%; white crystals, m.p.: 103–104°; NMR (CCl_4): δ 1.13 (3H, t, J = 7), δ 1.19 (3H, d, J = 7), δ 4.09 (2H, q, J = 7), δ 4.37 (1H, d_{AB}q, J = 10, J = 7), δ 4.77 (1H, d_{AB}, J = 10). δ 7.3–8.1 (10H, m). IR, ν[C=O]: 1688, 1740 cm^{-1}. (Found: C, 73.65; H, 6.65. $C_{20}H_{20}O_4$ requires: C, 74.05; H, 6.22%).

Reactions of 1,4 - *diketones and* 2 - *ethoxycarbonyl* - 1,4 - *diketones with* H_2S/HCl

General procedure (deviations from this procedure as well as other relevant details are described in the individual cases below): The starting material (0.02–0.1 moles) was dissolved in 200–250 ml 99% EtOH. The soln was cooled to − 60°, and a stream of H_2S gas was passed through it for 1–2 hr (until saturation), whilst the temp. was kept constant. Keeping the temp. below a certain maximum value (Table 1), HCl gas was supplied during 1–1.5 hr, after which H_2S was again supplied for 2–4 hr. The soln was then poured into a mixture of 500 ml icewater, 200 ml ether, and 200 ml light petroleum or pentane, under stirring. The layers were separated, the aqueous layer was extracted with another portion of ether and light petroleum (100 ml of each), the combined organic layers were washed with water (twice), and dried. After filtration, the solvents were removed by evaporation. The remaining crude product or product mixture was worked-up as described individually below.

2,5 - *Dimethylthiophen* (**3a**), 2,5 - dimethyl - 2 - mercapto - 2,3 -

dihydrothiophen (**4a**), and 2,5 - *dimethyl* - 2,5 - *dimercaptotetrahydrothiophen* (**5a**). Acetonylacetone (11.4 g; 0.1 mole) was dissolved in 200 ml 99% EtOH and treated with H_2S/HCl. The crude product (11.5 g) was worked-up as described[12] to give 4.9 g (49%) of **3a**, 128 mg (0.9%) of **4a**, and 2.18 g (13%) of **5a** (for physical data, see Ref. 12).

2 - *Methyl* - 5 - *t* - *butylthiophen* (**3b**). 2,2 - Dimethyl - 3,6 - heptanedione (3.43 g; 22 mmoles) dissolved in 100 ml of 99% EtOH was treated with H_2S/HCl. The crude product was distilled to give 2.88 g (85%) of pure product, b.p.$_{15}$: 66°, n_D^{25}: 1.4981 (lit. b.p.$_{19}$: 74–75°,[3] b.p.: 183°,[32] b.p.: 185.5–186.5°,[33] n_D^{20}: 1.4972,[33] n_D^{23}: 1.5031[32]). (Found: C, 69.80; H, 8.94; S, 20.47. $C_9H_{14}S$ requires: C, 70.10; H, 9.15; S, 20.75%).

2 - *Methyl* - 5 - *phenylthiophen* (**3c**). 1 - Phenyl - 1,4 - pentanedione (7.0 g; 40 mmoles) was dissolved in 150 ml of 99% EtOH and treated with H_2S/HCl. The crude product appeared as an oil which solidified rapidly. Recrystalization (EtOH) gave 5.7 g (82%) of the pure product, m.p.: 48° (lit. m.p.: 49–51°,[4] 49°,[34] 47.5–48.5°,[35] 51°[36]). (Found: C, 75.70; H, 5.90; S, 18.35. $C_{11}H_{10}S$ requires: C, 75.84; H, 5.79; S, 18.37%).

2,5 - *Diphenylfuran* (**2d**) and 2,5 - *diphenylthiophen* (**3d**). 1,4 - Diphenyl - 1,4 - butanedione (4.76 g; 20 mmoles) was dissolved in 250 ml of 99% EtOH. H_2S gas was passed through the soln for 1 hr at −10°, followed by dry HCl gas for 1.5 hr, during which the temp. raised to 10°, and some precipitated starting material was redissolved. After a further supply of H_2S gas for 4 hr at 10°, the soln was worked-up as usual. The crude product appeared as a buff solid, which was found by NMR to be composed of 65% of **2d** and 35% of **3d** (yields: 53% and 29%, resp.). Several attempts to separate the two products by PLC failed. However, repeated fractional recrystallization (EtOH) allowed separation and isolation of small quantities (200–300 mg) of the pure compounds. **2d** was obtained as small buff crystals, m.p.: 90–91° (lit. m.p.: 86–88°,[7] 88–89°,[37,38] 89.5–90°,[39] 91°,[30,40] 90–92°[41]). **3d** was obtained as light yellow crystals, m.p.: 153–154° (lit. m.p.: 148–149°,[42] 149–150°,[7] 152–153°,[5] 153°,[42] 153–154°,[10] 155–156°,[6] 156°[43]).

In another experiment 1,4 - diphenyl - 1,4 - butanedione (2.10 g; 8.8 mmoles) was dissolved in a mixture of 150 ml of EtOH and 75 ml of $CHCl_3$. The soln was cooled to −50°, and H_2S gas was passed through it during 1.5 hr, whilst the temp. was kept constant. Then dry HCl gas was passed through the soln for 1 hr, during which the temp. raised to 0°. After standing at 0° for 1 hr, the solution was worked-up as usual to give 1.76 g of a mixture of **2d** (39%, determined by NMR) and **3d** (61%). The yields of the unseparated products were calculated as 33% and 53%, respectively.

3 - *Ethoxycarbonyl* - 2,5 - *dimethylthiophen* (**3e**) and 4 - *ethoxycarbonyl* - 2 - *mercapto* - 2,5 - *dimethyl* - 2,3 - *dihydrothiophen* (**4e**). 3 - Ethoxycarbonyl - 2,5 - hexanedione (13.0 g; 70 mmoles) was dissolved in 200 ml of 99% EtOH and treated with H_2S/HCl. The crude product (16.7 g) was subjected to PLC (7 plates, 3 elutions with a 1 : 19 mixture of ether and light petroleum) to give 6.87 g (53%) of **3e** (R''_F: 0.52–0.72, b.p.$_{12}$: 114–116° (lit.[12] b.p.$_{12}$: 115°)) and 3.11 g (20%) of **4e** (R''_F: 0.32–0.48, b.p.$_{0.2}$: 88–90° (lit.[12] b.p.$_{0.17}$: 82°)). Other relevant physical data and refs are found in the preceding communication.[12]

3 - *Ethoxycarbonyl* - 2,4,5 - *trimethylthiophen* (**3f**) *and* 3 - *ethoxycarbonyl* - 2,5 - *dimercapto* - 2,4,5 - *trimethyltetrahydrothiophen* (**5f**). 3 - Ethoxycarbonyl - 4 - methyl - 2,5 - hexanedione (11.0 g; 50 mmoles) was dissolved in 200 ml of 99% EtOH and reacted with H_2S/HCl at −50°. The crude product (13.5 g) was subjected to PLC (5 plates, 2 elutions with a 7% soln of ether in light petroleum). The material absorbed within the R'_F-region 0.55–0.73 was isolated and distilled to give 5.1 g (52%) of pure **3f**, b.p.$_{14}$: 131–133°, n_D^{25}: 1.5173. IR, ν[C=O]: 1710 cm^{-1}. (Found: C, 60.80; H, 7.14; S, 15.98. $C_{10}H_{14}O_2S$ requires: C, 60.59; H, 7.12; S, 16.15%). Similarly, the material absorbed within the R'_F-region 0.36–0.54 was isolated and distilled to give 3.7 g (32%) of pure **5f**, b.p.$_{0.09}$: 93–94° (the distillate solidified). IR, ν[S–H]: 2540 cm^{-1}, ν[C=O]: 1735 cm^{-1}. (Found: C, 45.30; H, 6.45; S, 35.70. $C_{10}H_{18}O_2S_3$ requires: C, 45.11; H, 6.81; S, 36.06%).

3 - *Ethoxycarbonyl* - 2 - *methyl* - 5 - *phenylthiophen* (**3g**) *and* 4 - *ethoxycarbonyl* - 2 - *mercapto* - 5 - *methyl* - 2 - *phenyl* - 2,3 - *dihydrothiophen* (**4g**). 3 - Ethoxycarbonyl - 1 - phenyl - 1,4 - pentanedione (9.0 g; 34 mmoles) was dissolved in 200 ml of 99% EtOH and treated with H_2S/HCl. The crude product (10.8 g) was subjected to PLC (5 plates, 3 elutions with a 5% soln of acetone in light petroleum). The material absorbed within the R''_f-region 0.59–0.75 was isolated and distilled to give 4.05 g (48%) of pure **3g**, b.p.$_{0.08}$: 123° (distillate solidified), m.p.: 45° (EtOH). IR, ν[C=O]: 1715 cm^{-1}. (Found: C, 68.45; H, 5.71; S, 12.91. $C_{14}H_{14}O_2S$ requires: C, 68.28; H, 5.73; S, 13.00%). The material absorbed in the R''_f-region 0.45–0.58 was also isolated to give 1.85 g (19%) of **4g** as a colourless, undistillable oil (attempted distillation led to partial decomposition to **3g**). IR, ν[S–H]: 2550 cm^{-1}, ν[C=O]: 1705 cm^{-1}, ν[C=C]: 1605 cm^{-1}. Elemental analysis was performed on the undistilled compound. (Found: C, 60.48; H, 5.92; S, 22.06. $C_{14}H_{16}O_2S_2$ requires: C, 59.99; H, 5,75; S, 22.89%).

3 - *Ethoxycarbonyl* - 2,4 - *dimethyl* - 5 - *phenylthiophen* (**3h**). 3 - Ethoxycarbonyl - 2 - methyl - 1 - phenyl - 1,4 - pentanedione (10.0 g; 38 mmoles) was dissolved in 200 ml of 99% EtOH and treated with H_2S/HCl. The crude product (9.1 g) was subjected to PLC (5 plates, 2 elutions with a 5% soln of acetone in light petroleum). The material absorbed within the R'_f-region 0.48–0.75 was collected and distilled to give 7.18 g (73%) of pure **3h**. Colourless oil, b.p.$_{0.09}$: 128°, n_D^{25}: 1.5847. IR, ν[C=O]: 1710 cm^{-1}. (Found: C, 69.20; H, 6.25; S, 12.23. $C_{15}H_{16}O_2S$ requires: C, 69.21; H, 6.20; S, 12.25%).

3 - *Ethoxycarbonyl* - 5 - *methyl* - 2 - *phenylthiophen* (**3i**) *and* 4 - *ethoxycarbonyl* - 2 - *mercapto* - 2 - *methyl* - 5 - *phenyl* - 2,3 - *dihydrothiophen* (**4i**). 2 - Ethoxycarbonyl - 1 - phenyl - 1,4 - pentanedione (12.4 g; 50 mmoles) was dissolved in 200 ml of 99% EtOH and reacted with H_2S/HCl. The crude product (11.8 g) was subjected to PLC (6 plates, 2 elutions with a 1 : 9 mixture of ether and light pertroleum). The material absorbed within the R'_f-region 0.57–0.72 was isolated and distilled to give 5.66 g (46%) of pure **3i** as a colourless oil, b.p.$_{0.3}$: 104°, n_D^{25}: 1.5874. IR, ν[C=O]: 1710, 1725 cm^{-1} (Found: C, 68.35; H, 5.93; S, 12.88. $C_{14}H_{14}O_2S$ requires: C, 68.29; H, 5.73; S, 13.00%). The material absorbed within the R'_f-region 0.37–0.52 was also isolated to give 0.80 g of a colourless oil that appeared to be a mixture of mainly ethyl benzoylacetate (10–15%) and **4i** (75–80%). The structure **4i** was assigned (tentatively) to the latter component on the basis of the NMR spectrum (Table 3), and the fact that attempted distillation of the mixture led to decomposition of the compound in question under simultaneous formation of **3i**.

3 - *Ethoxycarbonyl* - 4,5 - *dimethyl* - 2 - *phenylthiophen* (**3j**) *and* 4 - *ethoxycarbonyl* - 2 - *mercapto* - 2,3 - *dimethyl* - 5 - *phenyl* - 2,3 - *dihydrothiophen* (**4j**). 2 - Ethoxycarbonyl - 3 - methyl - 1 - phenyl - 1,4 - pentanedione (10.0 g; 38 mmoles) was dissolved in 200 ml of 99% EtOH and treated with H_2S/HCl. The crude product (10.2 g) was subjected to PLC (5 plates, 3 elutions with a 5% soln of ether in light petroleum). The material absorbed within the R''_f-region 0.46–0.66 was isolated and distilled to give 4.8 g (48%) of pure **3j** as a colourless oil, b.p.$_{0.09}$: 117°, n_D^{25}: 1.5798. IR, ν[C=O]: 1715 cm^{-1}. (Found: C, 69.45; H, 6.35; S, 11.63. $C_{15}H_{16}O_2S$ requires: C, 69.21; H, 6.20; S, 12.30%). The material absorbed within the R''_f-region 0.34–0.44 was also isolated to give 1.4 g (12%) of **4j** as a colourless, undistillable oil. IR, ν[S–H]: 2550 cm^{-1}, ν[C=O]: 1695 cm^{-1}. (Found: C, 61.57; H, 6.44; S, 20.66. $C_{15}H_{18}O_2S_2$ requires: C, 61.21; H, 6.17; S, 21.75%).

3 - *Ethoxycarbonyl* - 2,5 - *diphenylfuran* (**2k**). 2 - Ethoxycarbonyl - 1,4 - diphenyl - 1,4 - butanedione (9.3 g; 30 mmoles) was dissolved in 200 ml of 99% EtOH and reacted with H_2S/HCl at 10°. The crude product (8.16 g) was recrystallized (EtOH) to give 7.40 g (80%) of pure **2k**; white crystals, white crystals, m.p.: 78° (lit. m.p.: 82°,[5,30] 74°[11]). IR, ν[C=O]: 1725 cm^{-1}. (Found: C, 78.30; H, 5.60. $C_{19}H_{16}O_3$ requires: C, 78.06; H, 5.52%).

3 - *Ethoxycarbonyl* - 4 - *methyl* - 2,5 - *diphenylfuran* (**2l**). 2 - Ethoxycarbonyl - 3 - methyl - 1,4 - diphenyl - 1,4 - butanedione (9.72 g; 30 mmoles) was dissolved in 250 ml of 99% EtOH and treated with H_2S/HCl at 10°. The crude product (7.8 g) appeared as a pale green oil that solidified on standing. Recrystallization (EtOH) gave 5.9 g (64%) of pure **2l** as white crystals, m.p.: 38–39°. IR, ν[C=O]: 1720 cm^{-1}. (Found: C, 78.35; H, 5.84. $C_{20}H_{18}O_3$ requires: C, 78.41; H, 5.92%).

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