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SYNTHESIS, REARRANGEMENTS, AND FRAGMENTATION OF KETENE MERCAPTALS DERIVED FROM KETONES OR β-DIKETONES AND CARBON DISULPHIDE

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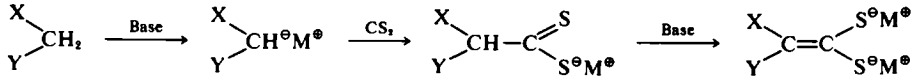
Abstract—By use of the ion pair extraction technique, tetrabutylammonium salts of acetylacetone, benzoylacetone, and dibenzoylmethane were reacted with carbon disulphide to give salts of dithioacids. Alkylation gave dithioesters and ketene mercaptals. A simple procedure for the preparation of 2-diacylmethylene-1,3-dithietanes (XYC=C(S)(S)CH$_2$) was found. Cyclisation reactions of some acetylacetone derivatives gave a 1,3-dithiolane, a mercaptothiophene, and a [2.3-b] thienothiophene. Allylic ketene mercaptals derived from acetone, cyclohexanone, acetylacetone, benzoylacetone, and dibenzoylmethane rearranged to α-allyl-dithioesters. Inversion of the migrating allyl group was observed when the ketene mercaptal had a vinylic hydrogen; otherwise retention was found. 3-[(Crotylthio-, methylthio-)methylene] acetylacetone underwent decomposition at 170° to methyl, 1-methyl-allyl sulphide and the "desaurin": 2,4-bis-(diacetyl-methylene)-1, 3-dithietane. By-products in syntheses of the dithioesters and ketene mercaptals included trithiocarbonates, alkylated β-diketones, and compounds formed by reactions of the solvent (CH_2Cl_2) with β-diketones or their carbon disulphide adducts (1,3-di-thietanes).

INTRODUCTION

In previous work,[1,2] we have been concerned with the synthesis and rearrangement of dithioacids and ketene mercaptals obtained by earlier known procedures as well as with the recently presented ion pair extraction method.[3] The latter method is the only one known for preparation of monosalts of the type **3**, as other procedures give the dithiolates **4**. The structure of some relatively stable salts **3** has been elucidated by use of ESCA (and NMR, IR, UV) spectroscopy,[2,4]

Alkylation of **3** gave a mixture of mono- and dialkylated product in a highly variable ratio depending on the substituents X and Y. Alkylation of **4** with two equivalents of an alkyl halide gave the ketene mercaptals, while one equivalent afforded the monoalkylated products.[2] It was also shown that allylic ketene mercaptals rearranged to α-allyl dithioesters at a rate greatly dependent on the substituents X and Y. Crotyl derivatives rearranged slower and with retention of the migrating group to give α-crotyl dithioesters. A four-step mechanism was proposed. In this paper we extend previous work on these subjects to other compounds, namely ketene mercaptals derived from acetone (**1a**) and cyclohexanone (**1b**), using the method of Thuiller and Vialle.[5] Ketene mercaptals derived from acetylacetone (**1c**), benzoylacetone (**1d**), and dibenzoylmethane (**1e**) were easily prepared using ion pair extraction or the method of Sandström and Wennerbeck.[6]



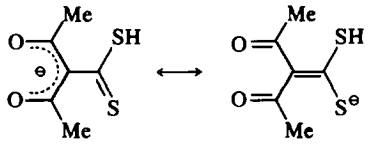
1 2 3 4 (1)

a: X = Ac, Y = H; **b**: X = $-(CH_2)_4CO=$ Y; **c**: X = Y = Ac; **d**: X = Ac, Y = Bz; **e**: X = Y = Bz.

SYNTHESIS

Formation of thiolates. The tetrabutylammonium salts (TBA salts) of **2c, d** and **e** were made from the corresponding active methylene compounds **1c, d** and **e** by extraction with 2 equivalents of $OH^{\ominus}$ and 1 equivalent of $TBAHSO_4$ into CH_2Cl_2. Subsequent reaction with CS_2 yielded the dithiocarboxylates **3c, d**, and **e**. Various modifications of the synthetic procedure were performed; **2c** was isolated as a solid

and reacted with CS_2 in ether, $CHCl_3$, or benzene to give **3c**, which could be isolated as a solid. The structure of **3c** was elucidated by means of ESCA, NMR, IR, and UV spectroscopy in connection with other similar salts and shown to have the structure

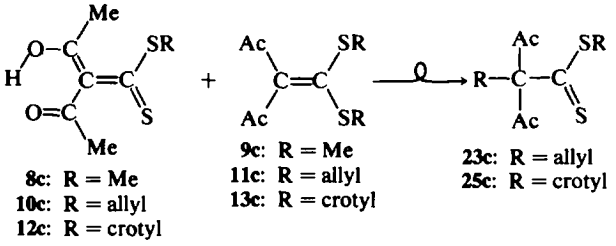


(counter ion = $TBA^{\oplus}$)

3c

While **3c** could be isolated, the corresponding salts derived from benzoylacetone or dibenzoylmethane and CS_2: **3d**, and **3e** could only be made *in situ*.

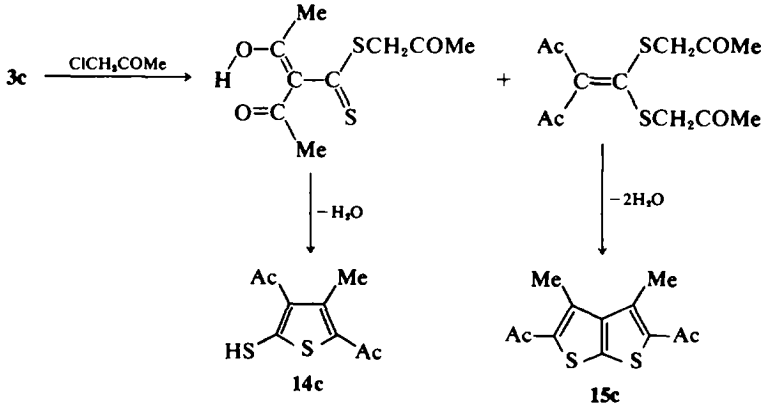
Alkylations. Alkylations of **3c** (Scheme 1, Table 1) were performed in ether, in which the salt is insoluble, $CHCl_3$, or benzene, in which the salt dissolves (method d). Mixtures of di- and monoalkylated products were formed. The monoalkylated products were separated from the dialkylated products by extraction with 2 M NaOH. Alkylation with chloroacetone yielded the thiophene, **14c**, and the thienothiophene, **15c**. However, basic extraction of the product obtained from propargyl bromide and **3c**, gave ring closure to the 1,3-dithiolane, **16c** which was converted to **17c** by acid. Alkylations of **3d** and **3e** were carried out with CH_2Cl_2 or CS_2 as solvents (methods b, c). By alkylations of **3d** and **3e**, in which 2 equivalents of base



8c: R = Me
10c: R = allyl
12c: R = crotyl

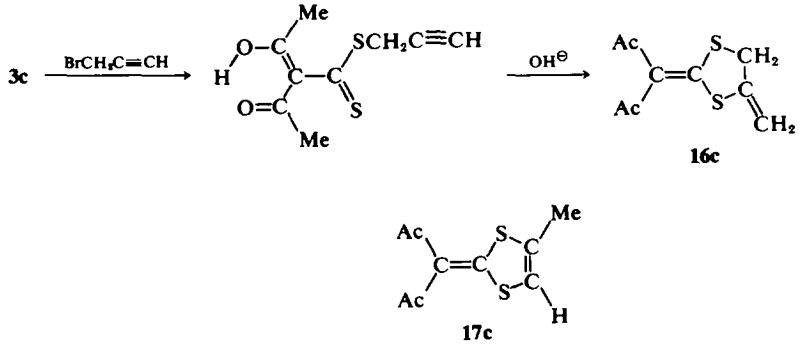
9c: R = Me
11c: R = allyl
13c: R = crotyl

23c: R = allyl
25c: R = crotyl



14c

15c



16c

17c

SCHEME 1

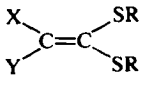
Table 1. Product distribution by alkylation of **3c** (method d) with RX

RX	Solvent	Mono-alkylated products	Yield %	Di-alkylated products	Yield* %
CH_3I	$CHCl_3$	**8c**	29	**9c**	19
CH_2=$CHCH_2Br$	ether	**10c**	48	**11** + **23**	22
CH_2=$CHCH_2I$	ether	**10c**	50	**11** + **23**	21
CH_3CH=$CHCH_2Br$	ether	**12c**	30	**13** + **25**	24
$ClCH_2COCH_3$	ether	**14c**	45	**15c**	25
$ClCH_2COCH_3$	benzene	**14c**	24	**15c**	35
HC≡CCH_2Br	ether	**16c**	38		

*The theoretical yield of dialkylated products is 50%.

were used, inseparable mixtures were obtained. However, ketene mercaptals or their rearrangement products (Table 2) derived from benzoylacetone or dibenzoylmethane, could be prepared, using excess base and $TBAHSO_4$.

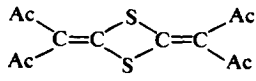
5d,e: R = H; R′ = Me
6d,e: R = R′ = Me
7e: R = H, R′ = crotyl
(Experimental)



9d,e: R = Me
11d,e: R = allyl
13d,e: R = crotyl

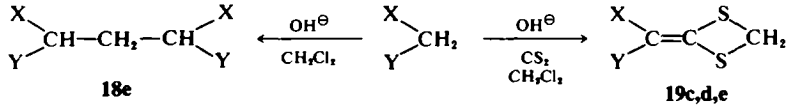
A by-product, **5e**, was formed in these reactions by alkylation of **2e**. Therefore comparison was made between the alkylation of **2** without addition of CS_2 (method a) and with addition of CS_2 (method b) (Table in Experimental). When alkylations of **2** or **3** were performed in CH_2Cl_2, the alkyl halide was introduced within 5–10 min. If **2** and **3** were allowed to stand for a longer period in CH_2Cl_2, compounds **18** and **19** were formed (2). These by-products were eliminated when CS_2 was used as solvent. However, the reaction between **3** and CH_2Cl_2 provided a simple method for the synthesis of 2-diacylmethylen-1,3-dithietanes, **19**.

Alkylation of the mono-salts **3c**, **3d**, **3e** or the di-salts **4a**, **4d**, **4e** with allyl halide produced the di-allyl ketene mercaptals **11a**, **11c**, **11d**, **11e** and/or the α-allyl dithioesters **23a**, **23c**, **23d** (Table 2). Likewise, alkylation with crotyl bromide gave the di-crotyl ketene mercaptals **13a**, **13b**, **13c**, **13d**, and **13e** in mixture with the α-(1-Me-allyl) dithioester **24a**, or the α-crotyl dithioesters **25b** and **25c**, respectively. Pure dithioesters were obtained by heating the crude products obtained by allylation or crotylation. However, dithioesters were not formed by allylation of **3e** or **4e** and crotylation of **3d**, **3e**, **4d**, or **4e**. An exception was provided by the methyl crotyl ketene mercaptal **26c**, which could only be obtained



28c

in a mixture containing 10% of **27c**, in spite of the near resemblance with the ketene mercaptals **13a–13e**. In analogy with earlier findings, **26c** decomposed at 170° to desaurin **28c** and methyl, 1-methylallyl sulphide, but MeSSMe was not found and only traces of crotyl methyl sulphide were detected. It is believed that the dithioesters are



18e **19c,d,e** (2)

Trace amounts of dialkyltrithiocarbonates **20**, **21** and **22** were detected in the reactions with **3d** and **3e**. These compounds were synthesized independently by alkylation of trithiocarbonate formed by the reaction in (3).[7]

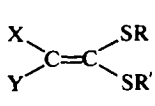
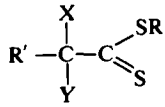
$$3CS_2 + 6OH^- \longrightarrow 2CS_3^{2-} + CO_3^{2-} + 3H_2O$$
$$CS_3^{2-} + 2RX \longrightarrow (RS)_2C{=}S \qquad (3)$$

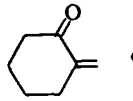
20: R = Me
21: R = Allyl
22: R = Crotyl

formed by thio-Claisen rearrangement, and not by direct alkylation on the α-carbon of the salts.[2]

Spectroscopy. The assignment of structures of compounds **8c**, **10c** and **12c** was made on the basis of NMR and IR data (Tables 3 and 5). By comparison between these data and those expected for the structures in Fig 1, it is seen that **D** could be ruled out, because no signal due to a methine proton on C-2 was observed in NMR (the chemical shift would be about 5 ppm). Structure **C** would reveal a signal at 2·2 ppm when R = Me or 3·3–5 ppm when R = allyl or crotyl (compare Table 4), while the

Table 2. Allylic ketene mercaptals and their S→C rearrangement products

Compound[a]	X	Y	R	R'	Compound	R	R'
11a[5]	H	Ac	allyl	allyl	**23a**	allyl	allyl
11c	Ac	Ac	allyl	allyl	**23c**[c]	allyl	allyl
11d	Bz	Ac	allyl	allyl	**23d**[d]	allyl	allyl
11e	Bz	Bz	allyl	allyl			
13a	H	Ac	crotyl	crotyl	**24a**	crotyl	1-Me-allyl
13b			crotyl	crotyl	**25b**	crotyl	crotyl
13c	Ac	Ac	crotyl	crotyl	**25c**	crotyl	crotyl
13d	Bz	Ac	crotyl	crotyl			
13e	Bz	Bz	crotyl	crotyl			
26c[b]	Ac	Ac	Me	crotyl	**27c**[b]	Me	1-Me-allyl

[a] These intermediates were not isolated in a pure state, except for those which were stable below 150°C.

[b] **26c** and **27c** were obtained in a mixture consisting of 90% **26c** and 10% **27c**. Decomposition at 170°C yielded **28**.

[c] Rate constant: $k_{297} = 10^{-4}$ (sec^{-1}). Conversion of 45% **11c** + 55% **23c** to 100% **23c**.

[d] Rate constant: $k_{297} = 10^{-6}$ (sec^{-1}). Conversion of 55% **11d** + 45% **23d** to 100% **23d**. (NMR measurements).

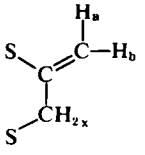
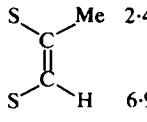
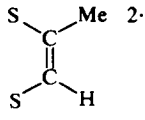
mercapto proton probably would give a signal at about 9–11 ppm (compare structure **E**). This makes the choice fall on structure **A** and/or **B**. The presence of two signals due to the acetyl groups is in favour of structure **B**. Structure **A** is expected to display one signal, because of rapid tautomerisation (compare the tautomerisation of for example ethyl 2-acetyl acetoacetate[19]). However, the observed IR band at 1800–1500 cm^{-1} indicates a strongly H-bonded carbonyl, as in structure **A**. In conclusion, **8c**, **10c**, and **12c** possess structures **A** and/or **B**.

Most of the dithioesters obtained by rearrangement of ketene mercaptals contained one or two asymmetric centers, namely C-2 and C-3 counted from the dithioester group in the Newmann projections in Fig 2, Table 4; **24a** consisted of two diastereomers, which could not be separated, but the NMR spectrum showed the presence of both isom-

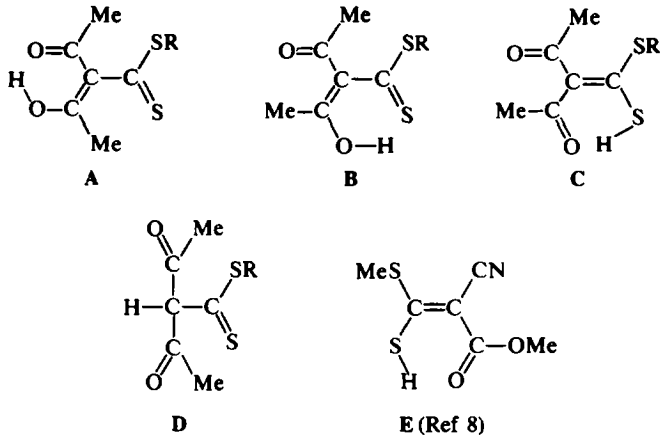
Table 3. NMR chemical shifts (δ values) and coupling constants (J c/s) of dithioesters: MeC(OH)=C(Ac)CS_2R, ketene mercaptals: XYC=C(SR)$_2$, dialkyltrithiocarbonates, and thiophenes

Compound	OH | C=CMe or Ac	$-SCH_2-$[a]	—SMe	Other signals	Solvent
8c	2·10 (s)[b]		2·70 (s)	OH: 16·50 (s)	CCl_4
9c				Me: 2·39 (s), 2·41 (s)	$CDCl_3$
9d	2·20 (s)		2·2–4 (br.)	Bz: 7·2–8·2 (m)	
9e			2·15 (s)	Bz: 7·2–8·2 (m)	$CDCl_3$
10c	2·10 (s)	3·95 (br.d)		OH: 16·55(s)	CCl_4
11c	2·32 (s)	3·49 (br.d)			CCl_4

Table 3—*Continued*

Compound	OH C=CMe or Ac	—SCH_2—[a]	—SMe	Other signals	Solven
11d	2·20 (s)	3·56 (br.d) 3·30 (br.d)		Bz: 7·2–8·0 (m)	CCl_4
11e		3·36 (br.d)		Bz: 7·2–8·2 (m)	$CDCl_3$
12c	2·09 (s)	3·85 (br.d)		OH: 16·45 (s)	CCl_4
13c	2·32 (s)	3·50 (br.d)			CCl_4
13d	2·18 (s)	3·25 br.d) 3·52 (br.d)		Bz: 7·2–8·2 (m)	CCl_4
13e		3·32 (br.d)		Bz: 7·2–8·2 (m)	$CDCl_3$
14c				Me: 2·47 (s), 2·53 (s), 2·65 (s) SH: 4·96 (br.)	CCl_4
15c				Me: 2·53 (s), 2·82 (s)	
16c	2·42 (s) 2·48 (s)	4·02 (t)		 ν_a = 5·47 ν_b = 5·34 ν_x = 4·02	$CDCl_3$, ABX_2 spin–spin splitting: J_{ax} = 1·87, J_{bx} = 1·73, J_{ab} = 1·30
16c	2·65 (s) 2·72 (s)	4·16 (t)			CF_3CO_2H
17c	2·61 (d)			 2·43 (d) 6·95 (q)	$CDCl_3$ $J_{(MeC=CH)}$ = 1·20
17c	2·72 (s)			 2·82 (d)	CF_3CO_2H
19c	2·46 (s)	4·15 (t)			$CDCl_3$
19d	1·95 (s)	4·15 (s)		Bz: 7·0–8·2 (m)	$CDCl_3$
19e		4·17 (s)		Bz: 7·0–8·2 (m)	$CDCl_3$
20			2·70 (s)		CCl_4
21		3·98 (d)			CCl_4
22		3·98 (m)			CCl_4
26c	2·31 (d) 2·38 (s)	3·42 (br.d)	2·31 (s)		CCl_4

[a] Compounds 10–13, 21, 22, and 26c: $J_{(-SCH_2CH=)}$ = 6 c/s.
[b] Two signals separated by 2 c/s.

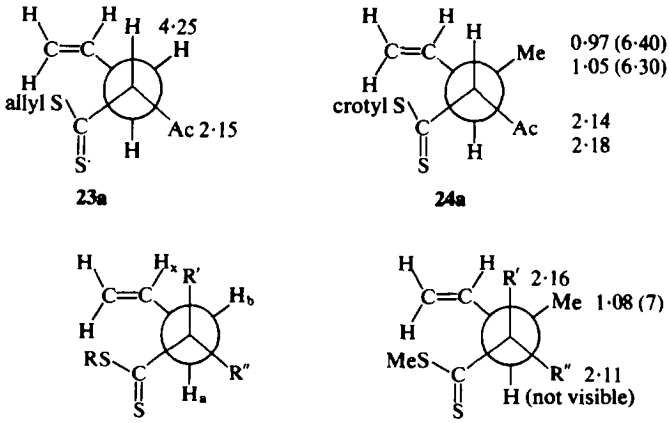


8c: R = Me; **10c**: R = allyl; **12c**: R = crotyl

Fig 1.

ers. Two signals due to acetyl protons and two doublets with different coupling constants, due to the Me protons of the 1-Me-allyl group, were observed. The methine protons on C-2 and C-3 caused AB splittings with $J_{ab} = 10$ c/s. The NMR spectrum of **23d** showed ABX splittings due to the hydrogens on C-3 and C-4. This spectrum was resolved from the AB part and only one of the two possible solutions, assuming J_{ax} and J_{bx} of the same sign, were acceptable. The NMR spectrum of **27c** was resolved from that of the mixture containing 90% **26c** and 10% **27c**, but the signal due to the C-3 proton

Fig 2 and Table 4. NMR chemical shift (δ values) and coupling constants (J c/s) of dithioesters obtained by rearrangement of ketene mercaptals. Solvent: CCl_4



23c: R = allyl, R′ = R″ = Ac
23d: R = allyl, R′ = Ac, R″ = Bz
25c: R = crotyl, R′ = R″ = Ac

Fig 2.

Table 4.

Compd.	δH_a	δH_b	J_{ab}	J_{ax}	J_{bx}	δ—SCH_2—	J	δAc	δBz
23c	3·12	3·12		6	6	3·92	(6) br.d.	2·15	
25c	3·04	3·04		6	6	3·82	(6) br.d.	2·15	
23d	3·58	3·11	14·0	5·9	7·8	3·90	(6) br.d.	2·26	7·2–8·0

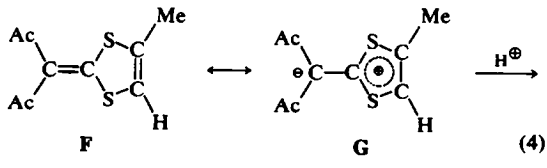
Table 5. IR and UV spectra of dithioesters: MeC(OH)=C(Ac)CS_2R, and dithioesters obtained from rearrangement of ketene mercaptals: X(Y)C(R)CS_2R

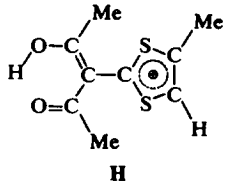
Compound	Conditions	IR ν_{max}(cm^{-1}) C=O	C=C	Other	UV(EtOH) λ_{max}(log ϵ) nm
8c	b	1600 (br.s)*		1410 (br.s)	220 (3·54), 266 (3·68), br.
	c			1060 (s)	315 (4·04)
10c	b	1600 (br.s)*		1410 (br.s)	265 (3·70), br.
	c			1015 (s)	315 (4·17)
12c	b	1600 (br.s)*		1410 (br.s)	210 (4·09), 265 (3·89), br.
	c			1055 (s)	315 (4·16)
23a	c	1733 (s)	1648 (m)		210 (3·87), 314 (3·98)
23c	c	1720 (s)	1648 (m)		321 (3·95)
		1730 (s)			
23d	c	1730 (s)	1609 (m)		208 (4·39), 246 (4·13),
		1695 (s)	1592 (m)		326 (3·93)
24a	c	1732 (s)	1648 (m)		212 (3·86), 316 (4·03)
25b	c	1720 (s)			210 (3·84), 318 (3·98)
25c	c	1735 (s)			210 (4·03), 321 (3·90)

a: KBr, b: $CHCl_3$, c: film.
*1800–1500 cm^{-1}.

was too weak to be identified. The asymmetric C-3 of compound **27c** caused the two acetyl groups to be diastereotopic, with chemical shifts as shown. The IR spectra of the rearranged products showed bands due to non conjugated acetyl groups, and the UV spectra showed absorption at 314–21 nm due to the thiocarbonyl chromophore (Table 5).

The UV spectra of **28c** and **16c** (Table 6) revealed greater absorption at longer wavelength than ketene mercaptals as for example **9c**. This might be explained by conjugation through the sulphur 3p orbital.[9] Compound **17c** also exhibited anomalous spectroscopic properties compared to simple ketene mercaptals. The NMR chemical shift of the





vinyl proton was found in the aromatic region, and was shifted further 1 ppm to lower field, when the solvent was changed from $CHCl_3$ to CF_3CO_2H (Table 3). The UV spectrum showed absorption at 385 nm, indicating a more conjugated system than **9c**, which displayed absorption at 317 nm. These properties are in agreement with an aromatic structure or a significant contribution by the mesomeric form G in (4) to the resonance picture of **17c**. The protonated form of **17c** could be visualized as structure H.

DISCUSSION

Formation of thiolates and dithiolates. The reactivity of anions derived from active methylene compounds towards CS_2 is believed to increase with increasing basicity of the anion (within series of similar anions). Furthermore, the reactivity of the anion is expected to be enhanced with decreasing solvation of the anion, and increasing solvation of the cation in the presence of for example DMF, HMPA and Crown ethers. Crown ethers, when dissolved in protic or aprotic solvents do encapsulate cations thereby increasing the basicity and nucleophilicity of anions. An alternative method to improve the reactivity of anions is to use large cations like quaternary ammonium ions and aprotic solvents like $CHCl_3$ or CH_2Cl_2. It turned out that CS_2 failed to react with the weakly basic anion of Dimedone ($pK_a = 5·2$)[10] via the ion pair extraction

Table 6. IR and UV spectra of ketene mercaptals: XYC=C(SR)$_2$

Compound	Conditions	IR ν_{max}(cm^{-1}) C=O	C=C	Other	UV(EtOH) λ_{max}(log ϵ)
9c		1690	1480		223 (3·76), 317 (3·91)
9d		1655	1478		253 (4·06), 318 (3·94)
9e	a	1670 (s) 1650 (s)	1605 (m) 1585 (m)		211 (4·20), 258 (4·30), −350 (sh)
11e	b	1665 (s)	1608 (m) 1590 (m)		212 (4·32), 258 (4·40)
13d	c	1665 (br.s)	1603 (m)		212 (4·23), 255 (4·05), 320–5 (3·79)
13e	b	1665 (s)	1600 (m)		212 (4·13), 260 (4·13)
14c	a	1650 (s) 1660 (s)	1500 (s)	2460 (m) (SH)	210 (4·13), 234 (4·11), 260 (4·07), 392 (3·88)
15c	b	1660 (s) 1670 (s)	1420 (s) 1480 (s)		289 (4·53)
16c	a	1670 (m)	1625 (s) 1450 (m)		337 (4·09)
17c	b	1620 (m)	1570 (s)	1370 (s) 1335 (s)	231 (3·98), 281 (3·84), 385 (4·28)
19c	a	1632 (s)	1588 (s)		224 (3·94), 258 (4·00), 330 (4·16)
19d		1640 (s)	1600 (s)	1580 (s)	206 (4·18), 260 (4·08), 335 (4·16)
19e	a	1625 (s)	1602 (s) 1592 (s) 1570 (s)		342
26c	c	1700 (s) 1670 (s)			212 (3·74), 320 (3·92)
28c	a	1672 (s)	1635 (m)		246 (3·93), solvent $CHCl_3$ 380 (4·45)

a: KBr, b: $CHCl_3$, c: film.

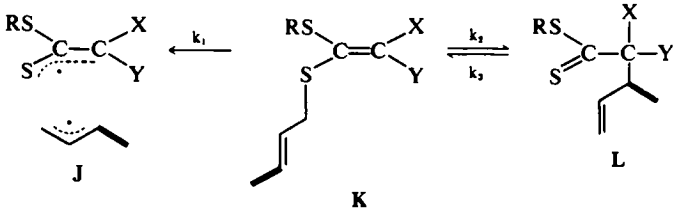
method. The anion of dibenzoylmethane (pK_a = 9·0),[11] which is also a relatively weak base, was partly converted with CS_2 by this method. In fact a mixture of **2e** and **3e** was formed, as could be derived from the products obtained by subsequent alkylation. The results support that the lower pK_a limit of diketones for successful reaction with CS_2 will be 6–8. The quaternary ammonium ions can be applied for the preparation of mono-anions as well as for di-anions. Favourable conditions for extracting the dianions into the CH_2Cl_2 layer requires a high lipofility of the quaternary ammonium ions, or of the anion itself. These conditions are fulfilled if the quaternary ammonium ions or the anion have a relatively high number of C atoms. However, there are few previous examples of di-anion formation using TBA counter ions, as opposed to the tetrahexylammonium ion.[12]

By-products. The use of CH_2Cl_2 or $CHCl_3$ as solvents in ion pair extraction implies advantages, because they solvate ammonium ions, and are easily evaporated from the reaction mixture. However, disadvantages might appear due to reactions of these solvents with other species, present in the reaction mixture. $CHCl_3$ reacts with base to give dichlorocarben, **3a**, while CH_2Cl_2 can act as an alky-

lation reagent in the presence of nucleophiles, as observed in the present work. The dialkyl trithiocarbonates, which were formed in small amounts in preparations with **3d** and **3e**, are believed to be formed by the reaction between hydroxide and CS_2, and subsequent alkylation (Eq 3). The trithiocarbonate was formed to a greater extent in the preparation of the dithiolates **4a**, **4b**, **4d**, and **4e**, and is probably due to the presence of stronger bases in these preparations.

The thermal instability of allylic ketene mercaptals. Two reaction pathways of the thermally instable allylic ketene mercaptals have been observed. The thio-Claisen rearrangement, which leads to α-allylic dithioesters, and fragmentations which lead to desaurins and allylic sulphides.

Mutual comparison of the diallyl ketene mercaptal rearrangements shows that the rate of rearrangement is decreased in the order given in Table 7. It is also shown in this Table that the order of decreasing rates is identical to the sum of increasing σ_p values of X and Y, except for compounds containing a benzoyl group. This means that the rates are retarded, when a substituent X or Y is interchanged with another X or Y substituent, which has a larger σ_p value ($\rho < 0$, in Hammett's Eq). Whether the rates are linearly dependent on the Hammett values or not has not been investigated. The reason why allylic ketene mercaptals bearing two cyano groups (X=Y=CN),[2] or compounds **13d**, **11e**, or **13e**, did not rearrange, might be that the activation energy was higher than that of



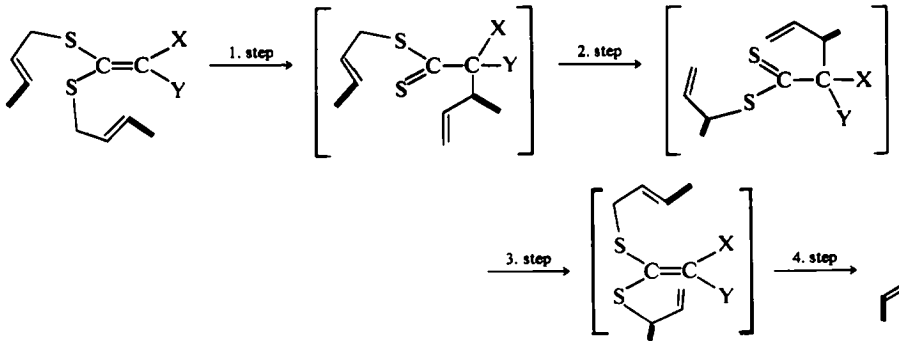
(5)

Fragmentation reactions were observed for methyl, crotyl ketene mercaptals which only rearranged to some extent to α-(1-methyl allyl)dithioesters, L in (5), by a reversible reaction. When this mixture was heated sufficiently, the equilibrium was shifted to the left, by the irreversible cleavage reaction (L → K → J). Diallyl or dicrotyl ketene mercaptals, which could rearrange, did not undergo cleavage because the intermediate L in (5) could rearrange further to the stable α-crotyldithioester (6).

decomposition, i.e. $k_1 > k_2$ in (5). Another, or a contributing reason, might be that the equilibrium constant of rearrangement was too small, that is, $k_2 < k_3$ in (5).

EXPERIMENTAL

Apparatus. NMR spectra were recorded at 60 Mc/s on a Varian A-60 spectrometer. The temps of the 15–20% solns (w/w) were 33 ± 1°. TMS was used as internal reference standard and the chemical shifts are expressed in δ-values downfield from TMS and are believed to be correct within



(6)

Table 7. Decreasing rate (from left to right) of thio-Claisen rearrangement of allylic ketene mercaptals XYC=C(SR)₂, depending on the substituents X and Y.*

X	CO_2Et[2]	COMe[13]	COMe	CO_2Et[2]	COPh	COPh	CN[2]
Y	CO_2Et	CO_2Et	COMe	CN	COMe	COPh	CN
$\Sigma\sigma_p$	0·90	0·95	1·00	1·11	0·96	0·92	1·32

*Comparison with Hammett σ_p values, from G. B. Barlin and D. D. Perrin, Quart. Rev. **20**, 75 (1966).

±0·02 ppm. The coupling constants, expressed numerically in c/s, were measured with an accuracy of ±0·1 c/s on the 50 c/s scale. The IR spectra were recorded as 5% solns on a Beckman IR 18 and the UV spectra on a Bausch & Lomb Spectronic 505 spectrophotometer with EtOH as solvent. B.ps are uncorrected. Analyses were made by Novo microanalytic Laboratory, Copenhagen. PLC was carried out on silica gel $PF_{254+366}$ (Merck) support (200 × 400 × 3 mm) and eluted with light petroleum-diethyl ether. Yields are calculated as if all the crude products were worked up, i.e. the actual yields are multiplied by the whole amount of the crude material and divided by the amount which was worked up.

General procedures in alkylation of ketones and β-diketones and their CS_2 adducts

Alkylation of **2d, e** (TBA *salts*)

(a) An amount of the β-diketone (0·01 mol) dissolved in 10 ml CH_2Cl_2 was mixed with a soln prepared from $TBAHSO_4$ (0·01 mol), NaOH (0·02–3 mol) and 10 ml water. Then an alkyl halide (0·02 mol) was added and the mixture stirred for 30 min. The CH_2Cl_2 phase was separated from the neutral water phase, and the CH_2Cl_2 dried and evaporated. The residue was treated with both ether and benzene, which after filtration and evaporation gave the crude product. Further work up with PLC followed by distillation gave the pure products.

Alkylation of **3c, d, e** (TBA *salts*)

(b) An amount of the β-diketone (0·01 mol) and excess CS_2 (1·5–5 ml), dissolved in 10 ml CH_2Cl_2 was mixed with a soln prepared from $TBAHSO_4$ (0·01 mol), NaOH (0·02–5 mol) and 10 ml water. After 5 min an alkyl halide was added, and the mixture stirred for 30 min. Work up as described under (a).

(c) An amount of the β-diketone (0·05 mol) dissolved in 50 ml CS_2 was added to a mixture of $TBAHSO_4$ (0·1 mol), NaOH (0·2 mol) in 100 mol) in 100 ml water. After 10 min, an alkyl halide (0·15 mol) was added. After 1 hr the layers were separated, the CS_2 phase dried and evaporated. The residue was either recrystallized or purified with PLC.

(d) A quantity of **2c** (34 g; 0·1 mol) was stirred with excess CS_2 (15 ml) in 100 ml ether, $CHCl_3$ or benzene. After 1 hr, excess alkyl halide (0·2 mol) was added and the mixture stirred for 30 min—3 hr depending on the reactivity of the alkyl halide. The mixture was filtered and the soln treated with excess cold 2 M NaOH. the remaining organic soln (A) was washed with water, dried and the solvent evaporated. The basic aqueous soln was acidified with 4 M HCl and extracted with ether and benzene. The ether/benzene soln (B) was dried and the solvent evaporated. The products were either distilled or recrystallized.

(e) An amount of the β-diketone (0·1 mol), CS_2 (11·4 g; 0·15 mol), and 100 ml CH_2Cl_2 were dropped into a stirred mixture of $TBAHSO_4$ (68 g; 0·2 mol) in 200 ml 2 M NaOH (0·4 mol). After 18 hr the CH_2Cl_2 phase was separated, washed with water, dried, and the solvent evaporated. The remaining solid was recrystallized in MeOH or EtOH.

Alkylation of **4a, b, d, e** (*potassium salts*)

(f) An amount of the ketone (0·1 mol) was dissolved in t-BuOH and t-BuOK (0·2 mol) was added. Then CS_2 (0·1 mol) was added and the mixture stirred for 3 hr. The temp was maintained at about 5°. Then an alkyl halide (0·2 mol) was added. After stirring for 18 hr, the mixture was washed with water, dried, and the solvent evaporated. The crude product was analysed with NMR and TLC. Further work up with thin layer or column chromatography and distillation gave the pure products.

(g) A quantity of the β-diketone (0·2 mol) in 25 ml dry benzene was added dropwise to a suspension of 50% NaH (0·4 mol) in 25 ml dry benzene. Then CS_2 (0·2 mol) was added together with 90 ml dry HMPA. The red mixture was stirred for 3 hr and then the alkyl halide (0·4 mol) was added. The temp was kept at about 25°. After stirring for 18 hr the mixture was worked up as described under (e).

Acetone derivatives

3-Dithiocarballyloxy-5-hexen-2-on, **23a**, was prepared by method (f) from acetone (5·8 g; 0·1 mol), t-BuOK (22·4 g; 0·2 mol), and allyl bromide (24·2 g; 0·2 mol). Distillation of the crude material gave 10·8 g, of which 3·1 g were separated on a silicagel column. The support was

Table 8. Methylation of the TBA-salts of benzoylacetone (**2d**) and dibenzoylmethane (**2e**) and their CS_2 adducts (**3d, e**), by methods a and b. Relative % yields were estimated from NMR of crude products

Salt	mmol of diketone	mmol of NaOH	Products, rel. % yields			
			1d,e	**5d,e**	**6d,e**	**9d,e**
2d	10·0	20·0	11	78	11	
2d	10·0	21·2	6	88	6	
2d	8·65	31·2			100	
2e	9·70	21·4	13	74	13	
2e	10·0	20·4	30	70		
3d	10·0	19·7	unseparable mixtures			
3e	9·74	20·0		25		75

In all cases were used 10·0 mmol $TBAHSO_4$. The alkylation reagent was methyl iodide.

5d;[14] NMR(CCl_4): 1·38 (3H, d, 7); 2·05 (3H, s); 4·42 (1H, q, 7); 7·2–8·2 (5H, m). 1·47 (6H, s); 2·05 (3H, s); 7·2–8·2 (5H, m). **5e**:[15] NMR($CDCl_3$): 1·56 (3H, d, 7); 5·29 (1H, q, 7); 7·2–8·2 (10H, m). **6e**:[16] NMR($CDCl_3$): 1·65 (6H, s); 7·2–8·2 (10H, m). **9d,e** (Table 3).

light petroleum/diethylether in a 3:1 (w/w) mixture. Eluates yielded **21** (0·32 g) and **23a** (2·1 g; 37%), b.p. 76–7°/0·05 mmHg; $n_D^{25} = 1·5650$. (Found: C, 55·72; H, 6·51. $C_{10}H_{14}OS_2$ requires: C, 56·07; H, 6·59%).

3-Dithiocarbocrotyloxy-4-methyl-5-hexen-2-on, **24a**, was prepared by method (f) from acetone (5·8 g; 0·1 mol), t-BuOk (22·4 g; 0·2 mol), and crotyl bromide (27·0 g; 0·2 mol). Distillation gave 13·0 g of which 7·1 g were worked up on a silicagel column. The support was light petroleum/diethylether in a mixture of 3:1 (w/w). Eluates yielded **22** (2 g) and **24a** (5 g; 38%), b.p. 98–9°/0·05 mmHg; $n_D^{25} = 1·5540$. (Found: C, 58·96; H, 7·34; S, 26·02. $C_{12}H_{18}OS_2$ requires: C, 59·49; H, 7·49; S, 26·42%).

Cyclohexanone derivatives

2-Crotyl-2-dithiocarbocrotyloxy-cyclohexanon, **25b**, was prepared by method (f) from cyclohexanon (9·8 g; 0·1 mol), t-BuOK (22·4 g; 0·2 mol), and crotyl bromide (27·0 g; 0·2 mol). Distillation yielded pure **25b** (10·1 g; 36%), b.p. 146–8°/0·1 mmHg; $n_D^{25} = 1·5716$. (Found: C, 63·18; H, 7·85; S, 22·5. $C_{15}H_{22}OS_2$ requires: C, 63·81; H, 7·85; S, 22·7%).

Acetylacetone derivatives

Tetrabutylammonium acetylacetonate, **2c**, was prepared according to Brändström *et al.*[3a]: acetylacetone (50 g; 0·5 mol) in 200 ml CH_2Cl_2 were treated with a mixture of $TBAHSO_4$ (170 g; 0·5 mol), NaOH (40 g; 1 mol) and 500 ml water in a separatory funnel. The CH_2Cl_2 layer was separated, dried, and the solvent evaporated. The remaining solid was washed with cold acetone (~ −70°), yield 108 g (64%) of m.p. 150°, (lit m.p. 155°).

Tetrabutylammonium dithiocarboxy acetylacetone, **3c**, was prepared from **2c** (34 g; 0·1 mol) and CS_2 15 g (excess), which were stirred in 100 ml ether for 1 hr. Evaporation of the solvent and excess CS_2 gave 41 g (100%), m.p. 52–6°. (Found: C, 62·06; H, 10·82; S, 13·3; N, 3·30. $C_{22}H_{43}NO_2S_2$ requires: C, 63·28; H, 10·38; S, 15·3; N, 3·35%). Attempts to recrystallize **3c** in i-PrOH failed as **2c** was reproduced (m.p. 140–50°. Found: C, 72·78; H, 12·53; N, 4·08. $C_{21}H_{43}NO_2$ requires: C, 73·84; H, 12·69; N, 4·10%).

Dithiocarbomethoxy acetylacetone, **8c**, was prepared by method (d) with MeI as alkylation reagent, yield 5·5 g (26%) of **8c** from soln B, b.p. 60–2°/0·05 mmHg; $n_D^{25} = 1·6120$. (Found: C, 44·25; H, 5·27; S, 33·4. $C_7H_{10}O_2S_2$ requires: C, 44·21; H, 5·30; S, 33·6%). From soln A, **9c** was isolated (3·9 g; 19%).

Bis-(methylthio)-methylene acetylacetone, **9c**,[6] was also prepared by method (c) in 42% yield.

Dithiocarballyloxy acetylacetone, **10c**, *bis-(allylthio)-methylene acetylacetone*, **11c**, *and α-allyl dithiocarballyloxy acetylacetone*, **23c**, were prepared by method (d) with allyl bromide (iodide, see Table) as alkylation reagent, yield: 4·75 g (22%) of **10c** from soln B, b.p. 80–4°/0·05 mmHg; $n_D^{25} = 1·6024$. (Found: C, 50·15; H, 5·64; S, 29·3. $C_9H_{12}O_2S_2$ requires: C, 50·00; H, 5·60; S, 29·3%). From soln A, **11c** + **23c** were isolated (10·2 g; 48%). After a few hr soln A contained pure **23c**, b.p. 113–4°/0·1 mmHg; $n_D^{25} = 1·5673$. (Found: C, 55·59; H, 6·28. $C_{12}H_{16}O_2S_2$ requires: C, 56·24; H, 6·29%). In another experiment **23c** was prepared as **26c** from **10c** (5·68 g; 0·026 mol), NaH (1·25 g; 0·026 mol), and allyl bromide (4·00 g; 0·033 mol), yield: 4·77 g (72%) of **23c**.

Dithiocrotyloxy acetylacetone, **12c**, *bis-(crotylthio)-methylene acetylacetone*, **13c**, and *α-crotyl dithiocarbocrotyloxy acetylacetone*, **25c**, were prepared by method (d) with crotyl bromide as alkylation reagent, yield: 6·9 g (30%) of **12c** from soln B, b.p. 89–91°/0·05 mmHg; $n_D^{25} = 1·5925$. (Found: C, 52·53; H, 6·04; S, 28·07. $C_{10}H_{14}O_2S_2$ requires: C, 52·17; H, 6·13; S, 27·8%). From soln A, **13c** + **25c** were isolated (6·9 g; 24%), b.p. 124°/0·05 mmHg; $n_D^{25} = 1·5633$. (Found: C, 58·51; H, 6·93; S, 22·77. $C_{14}H_{20}O_2S_2$ requires: C, 59·14: H, 7·09; S, 22·5%).

3,5-Diacetyl-2-mercapto-4-methyl thiophene, **14c**, and *2,5-diacetyl-3,4-dimethyl-[2.3-b]thienothiophene*, **15c**, were prepared by method (d) from **2c** (10·00 g; 0·0293 mol), 5 ml CS_2, and 25 ml ether. After 1 hr chloroacetone (2·8 g; 0·03 mol) were added at such a rate that the mixture was boiling. Work-up after stirring for 4 hr gave **14c** (2·81 g; 45%) from soln B, m.p. 101–4° (EtOH). (Found: C, 50·38; H, 4·57; S, 30·2. $C_9H_{10}O_2S_2$ requires: C, 50·47; H, 4·71; S, 29·9%). From soln A, **15c** was isolated (1·84 g; 25%), m.p. 157–8° (EtOH). (Found: C, 56·87; H, 4·89; S, 25·6. $C_{12}H_{12}O_2S_2$ requires: C, 57·14; H, 4·80; S, 25·2%).

2-Diacetylmethylene-5-methylene-1,3-dithiolane, **16c**, *and 2-diacetylmethylene-5-methyl-1,3-dithiolene*, **17c**, were prepared by method (d) from **2c** (10·00 g; 0·0293 mol) in 25 ml ether, 5 ml (excess) CS_2, and propargyl bromide (4 g; 0·42 mol) and worked-up after 1 hr. The combined fractions of soln A and B were recrystallized from ether yielding **16c** (2·39 g; 38%), m.p. 70–2°. (Found: C, 50·19; H, 4·69; S, 30·0. $C_9H_{10}O_2S_2$ requires: C, 50·47; H, 4·71; S, 29·9%). When **16c** was dissolved in trifluoracetic acid immediate conversion occurred to **17c**, m.p. 106–7°. (Found: C, 50·23; H, 4·64; S, 29·9. $C_9H_{10}O_2S_2$ requires: C, 50·47; H, 4·71; S, 29·9%).

2-Diacetylmethylene-1,3-dithietane, **19c**, was prepared by method (e) in 19% yield, m.p. 118–9° (sublimated at $100°/10^{-4}$ mmHg). (Found: C, 44·75; H, 4·34; S, 33·8. $C_7H_8O_2S_2$ requires: C, 44·69; H, 4·29; S, 34·0%).

Crotylthio-methylthio-methylene acetylacetone, **26c**. A quantity of **12c** (3·18 g; 0·0138 mol) in 10 ml benzene was added dropwise to a suspension of NaH (0·662 g; 0·0138 mol, 50%) in 10 ml benzene. When the H_2 evolution had ceased, MeI (2·35 g; 0·0167 mol) was added and the mixture stirred for 18 hr. Work-up for method (f) gave a mixture consisting of 90% **26c** + 10% of **27c**, (2·51 g; 75%) b.p. 132–6°/0·05 mmHg; $n_D^{25} = 1·5747$. (Found: C, 53·76; H, 6·69; S, 25·60. $C_{11}H_{16}O_2S_2$ requires: C, 54·09; H, 6·60; S, 26·21%).

Bis(diacetylmethylene)-1,3-dithietane, **28c**. A quantity of 90% **26c** + 10% of **27c** (1·02 g) was heated in a vigreux distillation apparatus to 170° at 0·05 mmHg. The receiver was cooled in solid CO_2/acetone. The distillate amounted to 0·431 g of methyl 1-methyl-allyl sulphide and traces of methyl crotyl sulphide (identified by NMR and MS/GLC).[2] The remnant was filtered and washed with CCl_4. The solid **28c** amounted to 0·111 g (9%), while the liquid contained 0·395 g of starting material, m.p. 230° (dec) (sublimation at $150°/10^{-4}$ mmHg). (Found: C, 50·67; H, 4·20; S, 22·5. $C_{12}H_{12}O_4S_2$ requires: C, 50·71; H, 4·26; S, 22·5%).

Benzoylacetone derivatives

Bis-(methylthio)-methylene benzoylacetone,[6] **9d**, was prepared by method (c) in 52% yield.

Bis-(crotylthio)-methylene benzoylacetone, **13d**, was prepared by method (g) from benzoylacetone (8·1 g; 0·05 mol), NaH (5·3 g; 0·1 mol, 50%), CS_2 (5·7 g; 0·075 mol), and crotyl bromide (13·5 g; 0·1 mol), yield of crude material: 11·7 g. An amount of 4·92 g was separated

with PLC, with light petroleum/diethyl ether in a mixture of 3:1 (w/w), yield: 0·365 g of **22**, and 1·465 g (20%) of **13d**, b.p. 110°/10^{-4} mmHg; n_D^{25} = 1·6059. (Found: C, 65·71; H, 6·42; S, 18·2. $C_{19}H_{22}O_2S_2$ requires: C, 65·88; H, 6·40; S, 18·5%).

2-Acetylbenzoylmethylene-1,3-dithietane, **19d**, was prepared by method (e) in 40% yield, m.p. 98–9° (EtOH). (Found: C, 57·59, H, 3·94; S, 25·19. $C_{12}H_{10}O_2S_2$ requires: C, 57·60; H, 4·03; S, 25·58%).

α-Allyl dithiocarballyloxy benzoylacetone, **23d**, was prepared by method (g) from benzoylacetone (8·1 g; 0·05 mol), NaH (5·3 g; 0·1 mol), CS_2 (5·7 g; 0·075 mol), and allyl bromide (24·2 g; 0·2 mol). The crude product amounted to 15·7 g of which 8·01 g were worked up on a silicagel column with light petroleum/diethyl ether support in a mixture of 3:1 (w/w), yield: 0·29 g of **21**, and 4·76 g (29%) of **23d**, b.p. 65°/10^{-4} mmHg; n_D^{25} = 1·6132. (Found: C, 64·01; H, 5·58; S, 20·1. $C_{17}H_{18}O_2S_2$ requires: C, 64·14; H, 5·70; S, 20·1%). In another experiment **23d** was synthesized by method (c). Crude product amounted to 16·5 g of which 2·1 g were worked up with PLC, yield: 1·28 g (63%) of **23d**, together with 0·3 g of **1d**, and 0·18 g of **21**.

Dibenzoylmethane derivatives

Bis-(methylthio)-methylene dibenzoylmethane, **9e**, was prepared by method (c) in 75% yield, m.p. 66–7°. (Found: C, 65·60; H, 4·70; S, 19·3. $C_{18}H_{16}O_2S_2$ requires: C, 65·85; H, 4·91; S, 19·5%).

Bis-(allylthio)-methylene dibenzoylmethane, **11e**, was prepared by method (b) from dibenzoylmethane (2·24 g; 0·01 mol), CS_2 (1·5 ml), $TBAHSO_4$ (3·39 g; 0·01 mol), NaOH (1·2 g; 0·02 mol) and allyl bromide (2·5 g; 0·021 mol). The crude product amounted to 5·2 g, which was worked up with PLC. The support was light petroleum/diethyl ether in a mixture of 5:2 (w/w), yield: 0·078 g of **21** and 2·06 g (54%) of **11e**, b.p. 100–20°/10^{-4} mmHg. (Found: C, 69·23; H, 5·28. $C_{22}H_{20}O_2S_2$ requires: C, 69·45; H, 5·27%).

Bis-(crotylthio)-methylene dibenzoylmethane, **13e**, was prepared by method (g) from dibenzoylmethane (22·4 g; 0·1 mol), CS_2 (11·4 g; 0·15 mol), NaH (9·6 g; 0·2 mol), and crotyl bromide (27 g; 0·2 mol). The crude material amounted to 37·4 g of which 4·1 g were separated with PLC (support: light petroleum/diethyl ether in a 10:1 (w/w) mixture), yield: 0·243 g of **22** and 3·04 g of **7e** + **13e**. Distillation of this fraction gave **7e** (0·55 g; 20%), m.p. 85–7°; NMR ($CDCl_3$): 1·6 (3H, br.d., 6); 2·8 (2H, m); 5·30 (1H, t, 6·5); 5·4–7 (2H, m); 7·2–8·2 (10H, m); IR (KBr) ν_{max} (cm^{-1}): 1700 (s), 1680 (s), 1610 (m), 1590 (m). UV (EtOH) λ_{max} (log ε): 212 nm (4·38), 252 nm (4·59). (Found: C, 81·88; H, 6·49. $C_{19}H_{18}O_2$ requires: C, 81·98; H, 6·52%). The remnant consisted of **13e**, yield 2·40 g (55%).

1,1,3,3-Tetrabenzoylpropane,[17] **18e**, was isolated in a preliminary experiment in the synthesis of **9e** by method (b). Work-up on TLC yielded 10% of **18e**, m.p. 174°; NMR ($CDCl_3$): 2·80 (2H, t, 7); 5·75 (2H, t, 7); 7·2–8·2 (10H, m); IR (KBr) ν_{max} (cm^{-1}): 1700 (s), 1680 (s), 1610 (s), 1590 (s). UV (EtOH) λ_{max} (log ε): 212 nm (4·38), 252 nm (4·59).

2-Dibenzoylmethylene-1,3-dithietane, **19e**, was prepared by method (e) in 16% yield, m.p. 148–50° (MeOH). (Found: C, 64·19; H, 3·96; S, 20·6. $C_{17}H_{12}O_2S_2$ requires: C, 65·38; H, 3·87; S, 20·5%).

Dimethyltrithiocarbonate,[7] **20**. An amount of CS_2 (23 g; 0·3 mol) in 50 ml DMSO was dropped into KOH (40 g; 0·6 mol) in 50 ml water. The mixture was stirred for 1 hr, heated to 100°, and immediately afterwards cooled to about 40°. MeI (0·4 mol) was added dropwise to the soln which was stirred for 4 hr. Extraction with light petroleum, drying and evaporation of the solvent gave the crude product, which was then distilled, yield 22 g (80%).

Diallyltrithiocarbonate,[18] **21**, was prepared as above with allyl bromide in 58% yield.

Dicrotyltrithiocarbonate, **22**, was prepared as above with crotylbromide in 30% yield, n_D^{25} = 1·6200. (Found: C, 49·58; H, 6·44. $C_9H_{14}S_3$ requires: C, 49·54; H, 6·47%).

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