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REACTIONS OF β-KETOESTERS AND NITRILES WITH CARBON DISULPHIDE

TAUTOMERISM OF DITHIOESTERS AND THIO-CLAISEN REARRANGEMENT OF KETENE MERCAPTALS

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Abstract—By use of the ion pair extraction technique tetrabutylammonium salts of ethyl and methyl acetoacetate, ethyl benzoylacetate, and cyanoacetone were reacted with CS_2 to give salts of dithioacids. Alkylation gave dithio-esters and ketene mercaptals. Rearrangements of allyl and crotyl ketene mercaptals of ethyl and methyl acetoacetate and ethyl benzoylacetate were studied. In the rearrangement of the dicrotyl ketene mercaptal of methyl acetoacetate an intermediate was detected supporting a four-step thio-Claisen rearrangement mechanism for dicrotyl ketene mercaptals, giving α-crotyl dithioesters with retention of the crotyl group.

The reaction between CS_2 and active methylene compounds, and subsequent alkylation leading to ketene mercaptals, has been the subject of many investigations. However, previous to our recent investigations[1,4-6] only few dithioesters[7-10] and no salts of dihioacids (monosalts) have been prepared.

In this paper we present two different ways of preparing α-dithiocarboxy derivates of ethyl acetoacetate, ethyl benzoylacetate, and cyanoacetone. Especially, the difference between preparation of methyl dithioesters by monoalkylation of a disalt and by alkylation of a monosalt was of interest.

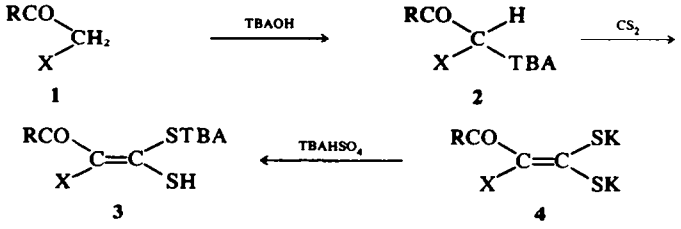
Ethylene 1,1-dithiolates are normally stable and easy to prepare. On the other hand, monosalts of ketene mercaptals are usually not stable with the exception of tetrabutylammonium salts (TBA-salts) obtained by ion pair extraction.[11] In addition, we have investigated methyl dithioesters by spectroscopic methods (IR, NMR, and in one case with ESCA[5]) in order to get information about the distribution of the possible tautomeric forms. Finally, the rearrangement of the allyl and crotyl ketene mercaptals has been investigated.

RESULTS AND DISCUSSION

Syntheses of TBA-salts of dithioacids and methyl dithioesters

The TBA salts of dithioacids **3a–c** were prepared by ion pair extraction from the corresponding active methylene compounds **1a–c**. The salts **3a** and **3c** were also synthesized by another method whereby a dipotassium ketene mercaptal **4a** or **4c** was reacted with one equivalent of $TBAHSO_4$ in a 1:1 H_2O–$CHCl_3$ mixture. This method gave a better yield of **3c**, but a poorer yield of **3a**. Compound **3b** was not prepared by ion pair extraction of **4b** because this disalt was prepared in a benzene–DMF mixture[12] which was not suitable for ion pair extraction. DMF enhances the reaction between the active methylene compound and CS_2 due to solvation of the cations. Once formed, the disalt is believed to be stable except when an acid (i.e. H_2O) is present. The acid makes the reaction reversible, giving back the methylene compound and CS_2. Therefore, the reaction has to be performed in dry solvents and ion pair extraction is inhibited.

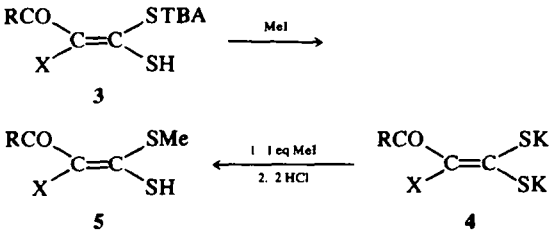
Great differences were found for the three TBA salts. Compound **3a** was a red, heavy oil containing



a: R = CH_3, X = CO_2Et;
b: R = Ph, X = CO_2Et;
c: R = CH_3, X = CN

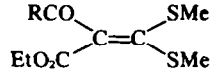
the TBA salt of ethyl acetoacetate **2a** which was impossible to separate from the mixture. The best result obtained was a mixture containing 80% of **3a** and 20% of **2a**, estimated by elemental analysis. Compound **3b** which was also an oil, contained **2b** as an impurity (68% of **3b** and 32% of **2b**). Compound **3c** was yellow, crystalline, and a stable compound which could be isolated pure.

The methyl dithioesters **5a–c** were prepared in two different ways. In one method the starting materials were the dipotassium ketene mercaptals **4a–c**



a: R = CH_3, X = CO_2Et;
b: R = Ph, X = CO_2Et;
c: R = CH_3, X = CN

which were alkylated with one equivalent of MeI at 0° in a H_2O–EtOH solvent mixture and subsequently acidified with dilute HCl. However, the method of choice was alkylation of the TBA salts **3a–c** with MeI in $CHCl_3$ at 0° (Table 1). In the preparation of **5a** and **5b** by-products like ethyl acetoacetate **1a**, ethyl benzoylacetate **1b**, respectively, and the dimethyl ketene mercaptals **6a** and **6b** were isolated. In preparing **5c** none of these

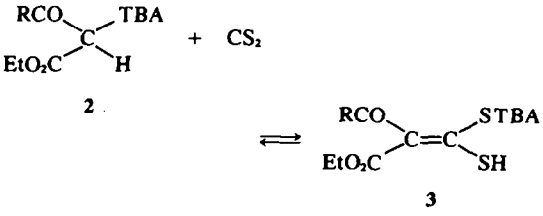


6a: R = Me
6b: R = Ph

by-products were isolated, but instead polymerization products were found.

In alkylation of **3a** and **3b**, the best yields were obtained when the TBA salts **3a** and **3b** were prepared with great excess of CS_2 (5:1), used *in situ*, and at a temperature of about 0° during the alkylation. When an equivalent amount or a smaller excess (2:1) of CS_2 was used, ethyl 2-methylacetoacetate or ethyl 2-methyl-benzoylacetate, respectively, was isolated as by-products. The same by-products were found when the isolated TBA salts **3a** and **3b** were alkylated under the same conditions.

These results can best be accounted for by an equilibrium reaction,



This can also account for the facts that **3a** and **3b** cannot be isolated in a pure state because by isolating the TBA salts, the excess of CS_2 was removed and the equilibrium shifted to the left. Therefore, **3a** and **3b** contained **2a** or **2b**, respectively.

From Table 2 is seen that the ratio of the dialkylated product **6** and the recovered starting material **1** was constantly 1:1 when *in situ* alkylation of **3** was performed.

Table 1. Yields and product distribution in preparation of methyl dithioesters (**5**) from the disalts (**4**) or the TBA salts (**3**) at 0°

	Alkylation of a disalt			Alkylation of a TBA salt		
Comp.	**5**	**6**	**1**	**5**	**6**	**1**
a	35	30[a]	3	66[b]	17	17
b	10	37[a]	28	50[b]	25	25
c	65	—	—[c]	98[d]	—	—

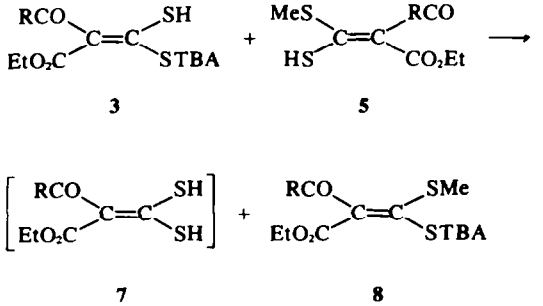
[a] Theoretical yield was 50%. [b] Yield proportional to active methylene compound. [c] No active methylene compound, but polymerization products. [d] Yield proportional to TBA salt **3c**.

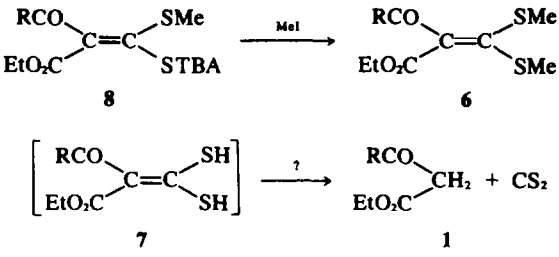
Table 2. Yields* (%) and product distribution in alkylations of TBA salts *in situ* ($CHCl_3$) at various temperatures

TBA salt	Temp. (°C)	**5**	**6**	**1** (recovered)
3a	−10	56	15	15
3a	0	66	17	17
3a	10	61	19	18
3b	−10	48	24	24
3b	0	50	25	25
3b	10	45	27	28

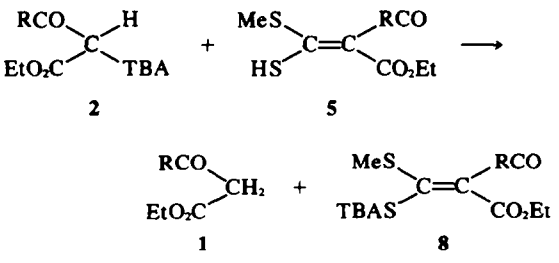
*Yields relative to the starting active methylene compound.

These observation can possibly be explained by the disproportionation proposed earlier.[4]



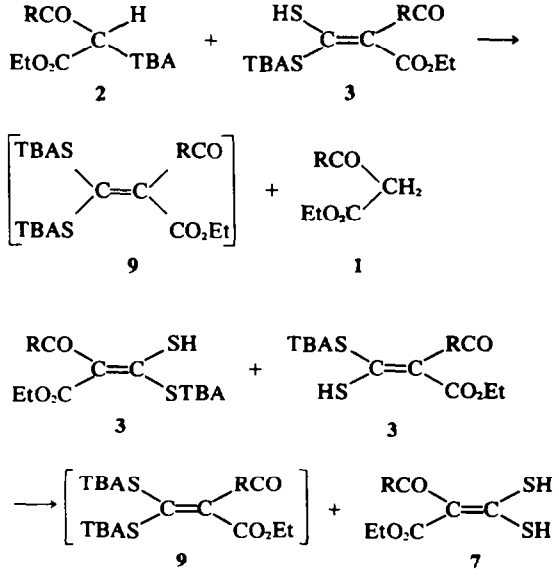


Thereby, **3a** or **3b** acts as a base towards **5a** or **5b** giving dithioacid **7** and a new TBA salt **8**. A further alkylation of **8** would give the dimethyl mercapto compound **6**. The presence of **1** was due to a decomposition of **7** to **1** and CS_2. Compound **7** has never been detected in the alkylation mixture.

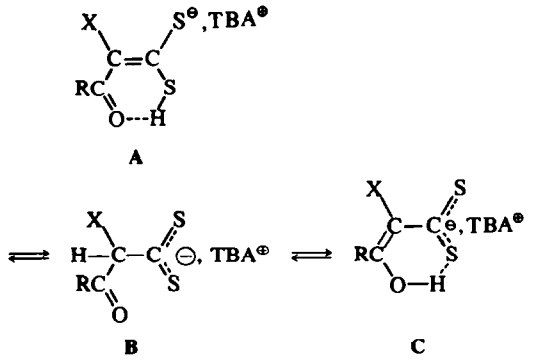


Another possible explanation is a disproportionation where **2** acts as a base towards **5** giving **1** and **8**. Further alkylation would give **6**. Also here the proportion between **1** and **6** would be 1:1.

A third type of disproportionation where **2** or **3** would act as a base towards **3** giving a TBA disalt **9**, can be excluded because **9** cannot exist in $CHCl_3$,[13] except in special cases.[14]



Structure and tautomerism. Structures of the TBA salts **3** and the monomethyl compounds **5** have all been depicted in a similar way rather than necessarily in the most likely tautomeric form.



In fact, the TBA salt **3c** is known to have the structure **C**, as shown earlier by IR, NMR, and ESCA spectroscopy.[5] On the other hand, the structures of **3a** and **3b** are not known. IR and NMR spectroscopy gave insufficient data to make any conclusions and the salts were unsuitable for ESCA investigations. Of the possible structures for the TBA salts, structure **C** is assumed to be most favourable because charge is delocalized over both sulphur atoms at the same time as its contains a hydrogen bond. To ensure a strong H-bonding and a favourable resonance, the OH group, the carbon–carbon double bond, and the dithiolate group all have to be in the same plane.

From models it can be seen that, when **3a** had the structure **C**, there would be some interaction between the CH_3 group at the α-carbon atom and the ester group (Fig 1) When **3b** had the structure **C**, the interaction between the phenyl group and the ester group was so strong that the phenyl group had to be twisted out of the plane and therefore out of conjugation with the rest of the unsaturated bonds. From this it can be concluded that the TBA salts **3a** and **3b** both have lower stability than **1c**. This can possibly be the explanation for the unfavourable position of the equilibrium between **2** and **3**.

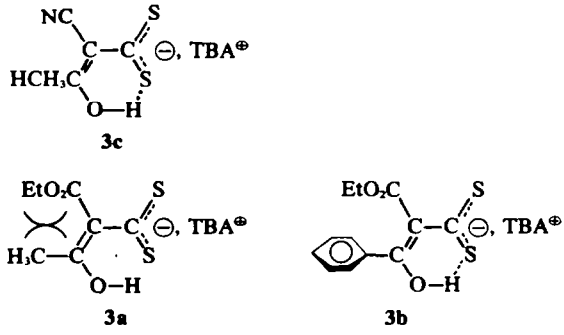
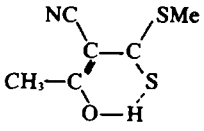


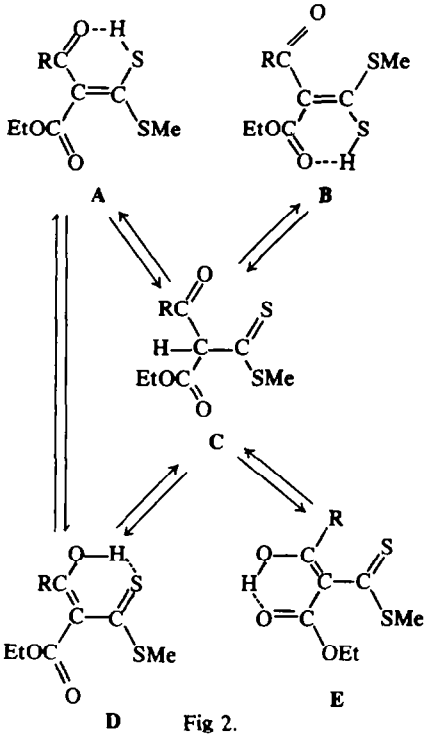
Fig 1.

Also for the monoalkylated products **5a–c** several structures could be suggested, but in case of **5c** evidences (IR, NMR, and ESCA[5]) were given for the structure shown below.



5c

Compounds **5a** and **5b** both exist as an equilibrium between different tautomeric structures. The most important of the possible structures are shown in Fig 2.

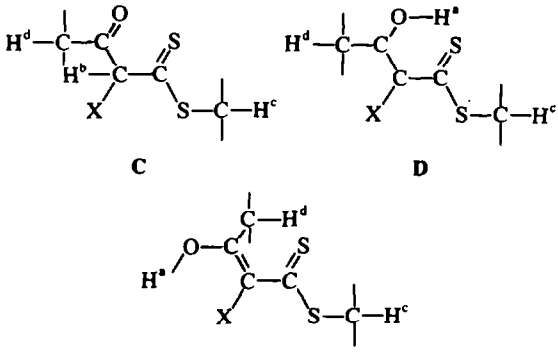


A **B** **C** **D** **E**

Fig 2.

The NMR spectrum of **5a** (Table 3) revealed two signals at low field indicating the presence of H-bonding protons. Four of the structures in Fig 2 contained H-bonding protons, but of these **B** can be excluded according to Shvo and Belsky,[15] who in the α-(methyl dithiocarboxy) cyanoacetate derivative have found the signal from the H-bonding proton at a much higher field (δ 9·20). Furthermore, no absorption corresponding to an SH group was found in the IR spectrum of **5a**. This also makes the existence of structure **A** questionable because it also contains an SH group. In monothio β-dicarbonyl compounds, in which both an enolization of a thiocarbonyl group and a carbonyl group are possible, it has been stated that enolization mostly occurs at the carbonyl group.[16]

Table 3. NMR data (δ-values, ppm) of methyl dithioesters (Solvent: $CDCl_3$)



C **D**

E

Compound	Tautomer	δ_a	δ_b	δ_c	δ_d
	C	—	5·25	2·62	2·34
5a	**D**	15·44	—	2·69(br)	2·17
	E	12·67	—	2·69(br)	2·04
	C	—	6·19	2·52	—
5b	**D**	15·79	—	2·67(br)	—
	E	13·26	—	2·67(br)	—
5c	**D**	16·08	—	2·67	2·46

(br) = broad unresolved line

The only acceptable structures are then **D** and **E**. The signal at δ 15·44 was ascribed to structure **D** by comparison with the findings for **5c**, while the signal at δ 12·67 was ascribed to structure **E**. The signal at δ 5·25 disappeared upon treatment with D_2O but much more slowly than the low field signals. Therefore, the δ 5·25 signal was believed to arise from the methine proton in structure **C**. This is also in agreement with results found by others.[4,15,17] Thus it can be concluded that **5a** consists of a mixture of three tautomers **C**, **D**, and **E**. This was confirmed by IR ($CHCl_3$) 1740 cm^{-1}, m-w (saturated ester carbonyl), 1725 cm^{-1}, m, br, (α,β-unsaturated ester carbonyl and saturated carbonyl), 1640 cm^{-1}, s (α,β-unsaturated carbonyl), 1610 cm^{-1}, s (β-ketoester, enolic). The distribution calculated from integral proportions in NMR are given in Table 4.

The two signals at low field in the NMR spectrum of **5b** (Table 3) were ascribed to the structure **D** (δ 15·36) and **E** (δ 12·69) for the same reason as for **5a**

Table 4. Distribution (%) of the tautomers of **5a–c** (Calculated from NMR integrals)

Compound	Solvent	Tautomer C	D	E
5a	$CDCl_3$	6	21	73
5a	C_6D_6	14	17	69
5a	$(CD_3)_2CO$	17	31	52
5b	$CDCl_3$	74	10	16
5c	$CDCl_3$	—	100	—

and by comparison with ethyl benzoylacetate (δ 12·25) and methyl benzoyl dithioacetate (δ 14·80).[1] Likewise, the signal at δ 6·19 was ascribed to the β-hydrogen in the structure C. From this and the integral proportions in NMR the distributions given in Table 4 were calculated.

Great differences were found in the occurrence of the tautomers in the three compounds (Table 4). These differences are probably caused by different steric interaction in the three compounds. In structures D and E (Fig 2), the carbonyl group, the thiocarbonyl group, the carbon–carbon double bond, and the OH group must be in the same plane to ensure a strong hydrogen bond and a good overlap between the π-orbitals of the sp^2 hybridized atoms. From models it can be seen that as a result of this requirement the ester group or the dithioester group is situated very close to the substituent on the α-carbon atom. In structure C the α-carbon atom is sp^3 hybridized, which from models can be seen to result in much more space between the groups bound to this atom, but both the hydrogen bond and the conjugation are lost in this structure. From this it can be expected that **5a**, which only has a CH_3 group on the α-carbon atom, should predominantly exist in the structures C and D. Structure C is expected to be much more favourable in the case of **5b** because of the steric interactions of the bulky phenyl substituent in D and E. From models it is seen that compound **5c**, which has a cyano group instead of the ester group, is expected to have a structure similar to structure D (E is impossible) because of the small cyano group. These predictions correspond very well with experiments. From models it was not possible to see whether the great occurrence of structure E, especially with compound **5a**, was caused by less steric interaction in this structure than in D.

Syntheses of allyl and crotyl compounds and their rearrangement

The methyl dithioesters **5** can be further alkylated with allyl or crotyl bromide to give the unsymmetrical ketene mercaptals **10** or **12**, respectively, or the α-substituted dithioesters **11** or **13**, respectively. The same products can be obtained from the disalts **4** by alkylation with one equivalent of MeI followed by an alkylation *in situ* with allyl or crotyl bromide.

When **5a** was alkylated with allyl bromide, only **11** was isolated while **10** was not found. When **5a** was alkylated with crotyl bromide, the main product was **12** and only small amounts of **13** were present in the crude product. The content of **13** were increased during the work-up. During a week at room temperature the mixture reached an equilibrium (57% of **12** and 43% of **13**). After heating (1 h, 100°) the mixture rearranged to **13** which on standing returned to the equilibrium mixture. By column chromatography the mixture could be separated into two fractions containing mainly **12** and **13**, respectively. By standing, both fractions again reached the equilibrium. The reason why the crotylated compound produces both **12** and **13**, while the allylated one only gave **11**, is probably steric hindrance caused by the 1-methyl-allyl group which makes **13** less favourable than **11**.

The unsymmetrical ketene mercaptals **10** and **12** can exist in two isomeric forms **10E** and **12E** and **10Z** and **12Z**. Both seem to be present in **12** because in the NMR spectrum (Table 5) there are two signals from the S—CH_2 group and also two from the S—CH_3 group.

Compound **13** contains two chiral centres at C-2 and at C-3 which might give rise to the presence of two diastereomers. Both diastereomers are present in **13** as can be deduced from NMR (Table 5).

The symmetrical allyl and crotyl ketene mercaptals were prepared by ion pair alkylation. The reaction is believed to be a two-step alkylation because only one equivalent of $TBAHSO_4$ is required, but these have to be used three equivalents of

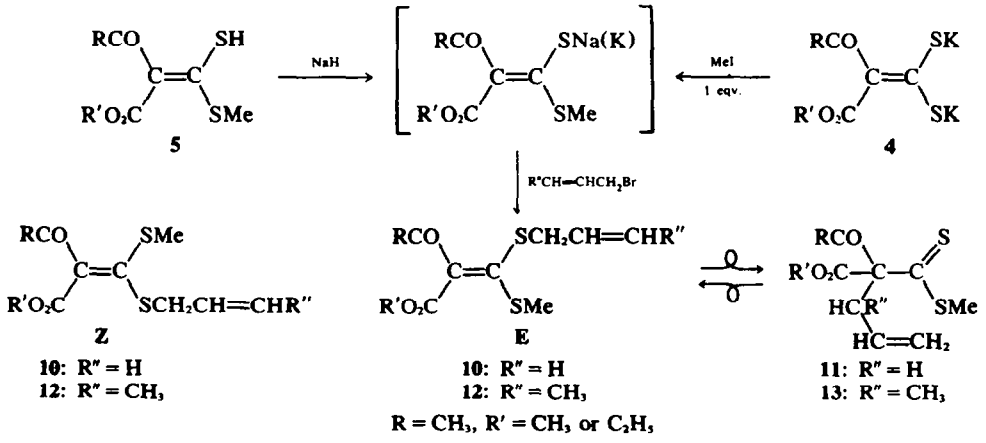
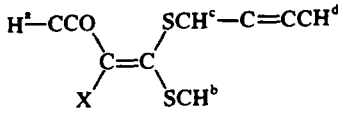


Fig 3.

Table 5. NMR data (δ-values, ppm) of S-methyl-S-allyl or S-crotyl ketene mercaptals and diallyl or dicrotyl ketene mercaptals ($CDCl_3$)



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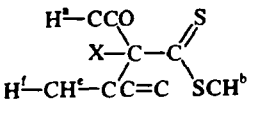
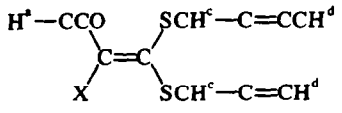
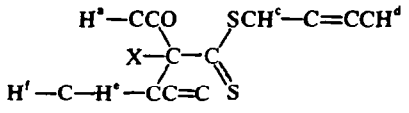


11, 13



17b, 19



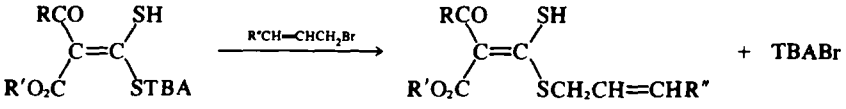
17ra, 17rb

Compound	δ_a	δ_b	δ_c	δ_d	δ_e	δ_f
11	2·30(s)	2·68(s)	—	—	2·70–3·50(m)	—
12	2·34(s)	2·46,2·49(s)	3·50,3·60(d, br)	1·71(d, br)	—	—
13	2·19,2·21(s)	2·65,2·70(s)	—	—	3·47(q)	1·12(d)
17ra	2·29(s)	—	3·91(d)	—	2·67–3·67(m)	—
17b	—	—	3·42,3·69(d)	—	—	—
17rb	—	—	3·85(d)	—	3·04–3·32(m)	—
19	—	—	3·36,3·64(d)	1·32,3·64(d)	—	—

(s): singlet; (d, br) = doublet, broad: (d) = doublet; (m) = multiplet

1. step. H_2O phase: $TBAHSO_4 + 2NaOH \rightarrow TBAOH + Na_2SO_4 + H_2O$

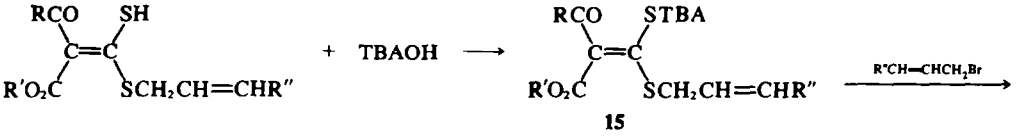
$CHCl_3$ phase: $RCOCH_2CO_2R' + TBAOH \rightarrow RCOCH(TBA)CO_2R' \xrightarrow{CS_2}$



14

2. step. H_2O phase: $TBABr + NaOH \rightarrow TBAOH + NaBr$

$CHCl_3$ phase:



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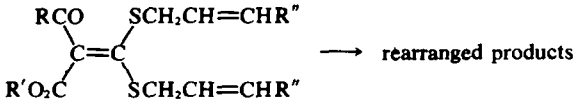


16

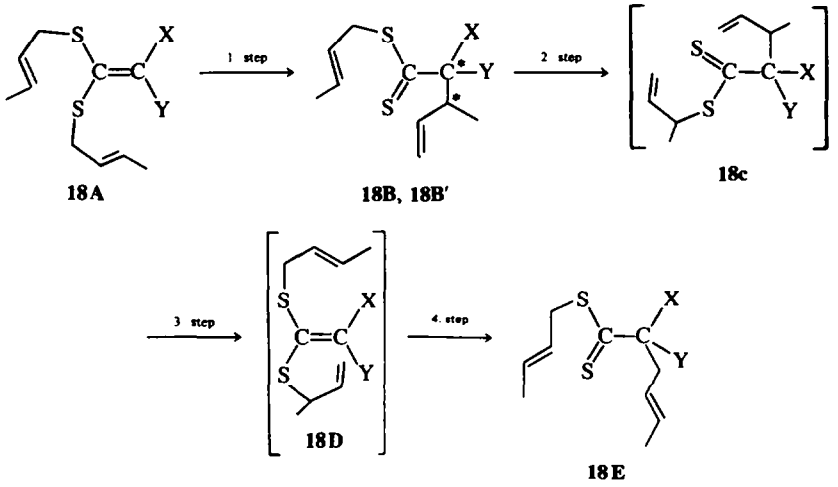
R = CH_3, Ph; R' = CH_3, C_2H_5; R" = H, CH_3

Fig 4.

NaOH. In addition, a TBA disalt cannot exist in $CHCl_3$ under the reaction conditions,[13] except in a few cases.[14]

The first step is the formation of **14** which then reacts with a molecule of TBAOH to give **15** which by subsequent alkylation produces **16**.

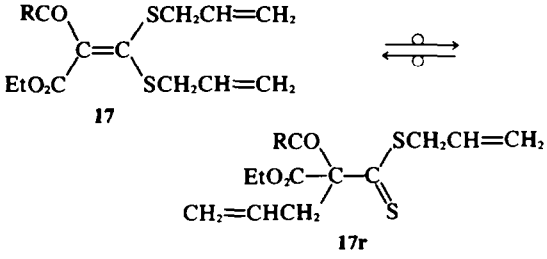
As with the unsymmetrical compounds above, the diallylated compound **17a** existed only as the rearranged form **17ra**, while **17b** in the crude product existed mainly on the form **17b** and only small amounts of **17rb** were present. By column chromatography it was possible to isolated **17b** as a



X = $COCH_3$, Y = CO_2Me, * = chiral center

Fig 5.

pure product which, however, quite easily rearranged to **17rb**.



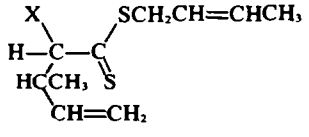
17

17r

a: R = CH_3; **b**: R = Ph

The preparation of the dicrotyl ketene mercaptal **18** resulted in a mixture of **18** and rearranged products. A four-step mechanism for the rearrangement of dicrotyl ketene mercaptals has been proposed earlier.[4,5]

A careful distillation of the mixture gave only one product which by NMR and analysis was shown to be the α-crotyl dithioester **18E** (Fig 5). This is the rearranged product normally observed,[4,5] unless in cases where the ketene mercaptal contains a β-hydrogen, then the rearranged product is a α-(1-methylallyl)dithioester.[1,6]

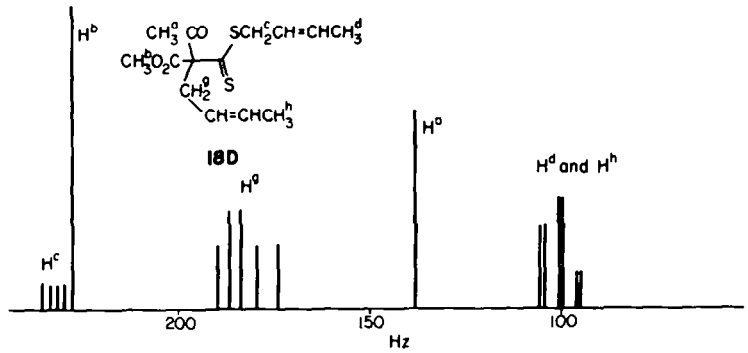


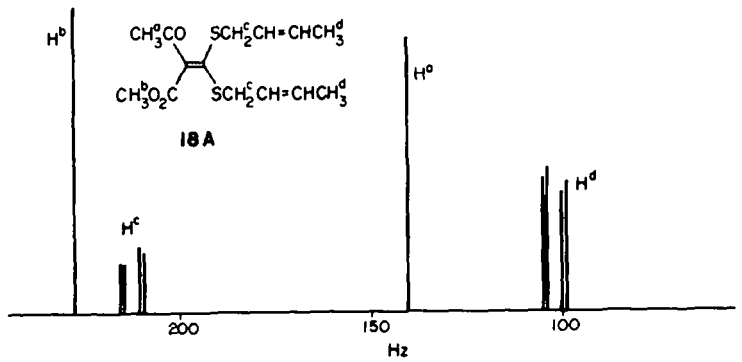
The crude product could be separated in two fractions by column chromatography. One (fraction I) consisting of 97% of **18A** and 3% of **18B'**, the other (fraction II) consisting of 12% of **18A**, 26% of **18B**, 62% of **18B'**, and traces of **18E**. Compounds **18A**, **B**, **B'**, **E** and their NMR spectra are shown in Fig 6. The structures **18B** and **18B'** are diastereomers.

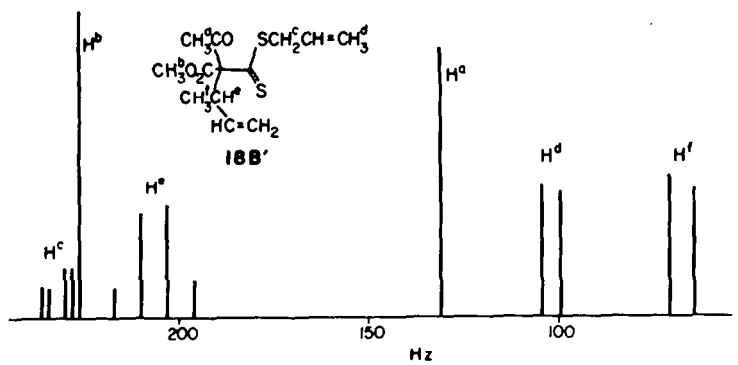
Both fractions rearranged at room temperature. The change in composition of fraction II during the first 30 h is shown in Fig 7.

From this is seen that the concentration of **18A** increased and the concentration of **18B'** decreased, while the concentration of **18B** was nearly constant. The rearrangement of fraction II was followed during additional 257 h at 25° ± 1°. During this time only small changes did occur. Compound **18E**, which was only seen as traces at the beginning, increased very slowly and the composition after the 287 h was 63% of **18A**, 16% of **18B**, 14% of **18B'**, and 7% of **18E** measured by NMR. Fraction II was now heated to 50° and again followed by NMR. The change in composition during the first 200 h at 50° ± 1° are shown in Fig 8. At this point the measurement of the composition begins to be uncertain because of the big signals from **18E**. After 700 h at 50° the composition was about 8% of **18A**, 90% of **18E**, and 2% of **18B** + **18B'**.

For fraction I it was found that the concentration of **18B** and **18B'** increased slowly during the rearrangement at 25°. Compound **18B'** increased at the beginning with the greatest rate. After 11 h the composition was 8% of **18B'**, 4% of **18B**, and 88% of **18A**. After 95 h the composition was 8% of **18B'**, 8% of **18B**, and 84% of **18A**. After 287 h was found 15% of **18B**, 12% of **18B'**, 70% af **18A**, and about 2% of **18E**. At this point the fraction was heated to 50° and followed by NMR at this temperature. It was found to behave in nearly the same way as fraction II above. After 700 h at 50° the composition of fraction I was equal to the findings for fraction II after the same reaction time.


18D
Hz
200
150
100


18A
Hz
200
150
100


18B'
Hz
200
150
100

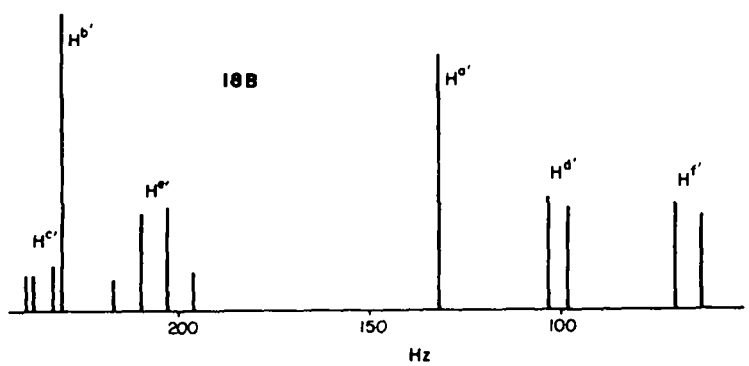

18B
Hz
200
150
100

Fig 6.

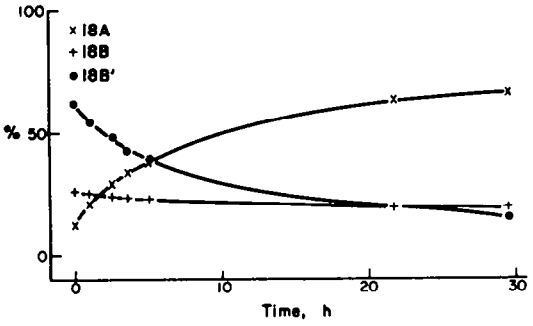


Fig 7.

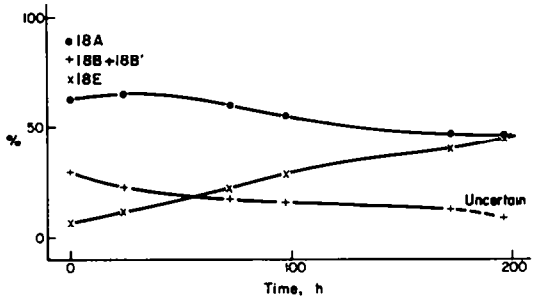


Fig 8.

From these observations it was concluded that **18E** was formed by a rearrangement of **18A** and that **18B** and **18B'** were intermediates because the only product from the rearrangement was **18E**. Compounds **18B** and **18B'** were believed to be two diastereomers as already mentioned above. The different behaviour of **18B** and **18B'** during the rearrangement was explained by different activation energies for the two diastereomers. The energy diagram for the rearrangement **18A** → **18E** is not known, but from the above results a possible energy diagram can be constructed.

In the first step of the formation of **18E** (Fig 5), the formation of **18B'** have the highest reaction rate which can be explained by a lower activation energy for **18A** → **18B'** than for **18A** → **18B**. At equilibrium the mixture contains more of **18B** than of **18B'**, from which it is concluded that **18B'** has a higher energy than **18B**. The next three steps are not known, but at least one of these has an activation energy higher than the first step as the formation of **18E** is very slow. The activation energy for the second step, **18B** or **18B'** → **18C**, is believed to be relative low because it is a rearrangement from one sulphur to another in the dithioester group.[4] But the product **18C** surely has a higher energy than **18B** or **18B'** because of the conversion of a crotyl group to an 1-methyl-allyl group. The third step, **18C** → **18D**, in the formation of **18E** is very like the reversal of the first step, **18B** → **18A**, and is believed to have nearly the same or possibly a little higher activation energy than **18B** → **18A**. The energy of **18D** surely is slightly higher than **18A** because of the 1-methyl-allyl group in **18D**. The fourth and last step is a rearrangement involving an allyl group and is believed to have relatively low activation energy because of the results found for the allyl compounds **10** and **17a**. The energy of **18E** is lower than **18A** because **18E** is the stable product from the rearrangement. The energy diagram is depicted in Fig 9.

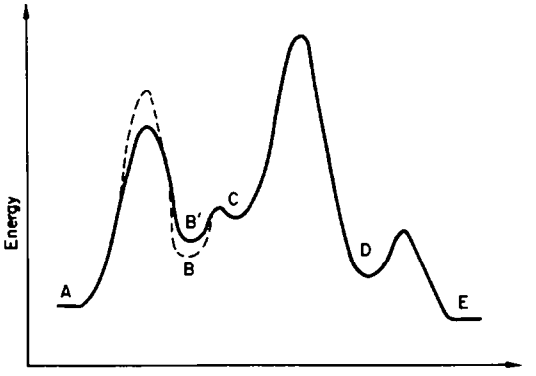
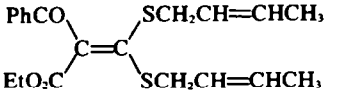


Fig 9.

The energy diagram in Fig 9 corresponds well with the fact that **18C** and **18D** were not observed in the rearrangement because both are seen to be of low stability and should therefore only be present in low concentration.

The dicrotyl ketene mercaptal of ethyl benzoyl-acetate **19** was found to be stable on the ketene mercaptal form.



19

EXPERIMENTAL

NMR spectra were recorded on a Varian A-60 spectrometer. The temp of the 15–20% solns (w/w) was 33° ± 1°. TMS was used as internal reference standard and unless stated to the contrary, the chemical shifts are expressed in δ-values downfield from TMS and are believed to be correct within ±0·02 ppm.

IR spectra were recorded as 5% solns, in $CHCl_3$ or as film on a Beckman IR-A18 spectrophotometer. Analysis were made by Løvens Kemiske Fabrik and Novo Industri A/S, Copenhagen. PLC was carried out on silica gel $PF_{254+366}$ (Merck) support (200 × 400 × 3 m). Column chrotomatography was carried out on silica gel 60 from Merck (100 g silica gel/1 g substance in a column, r = 20 mm). B.ps are uncorrected.

Preparation of dipotassium or disodium ethylene 1,1-dithiolates. In accordance with the method of Jensen and Henriksen,[16] the dipotassium salts **2a** and **2c** (Fig 1) were

prepared from ethyl (or methyl) acetoacetate or cyanoacetone, respectively, with KOH as base and dioxan as solvent.

The disodium salt **2b** was prepared by the method of Sandström and Wennerbeck[11] from 19·2 g (0·1 mole) ethyl benzoylacetate and 7·6 g (0·1 mole) CS_2 with (0·2 mole) NaH as base and 150 ml (1:1) benzene–DMF mixture as solvent and used *in situ* in the alkylation below.

Preparation of TBA salts of dithioacids. **3a** (*method a*): To a vigorously stirred ice-cooled solution of 34 g (0·1 mole) $TBAHSO_4$ and 8 g (0·2 mole) NaOH in 75 ml of H_2O was added a solution of 13 g (0·1 mole) ethyl acetoacetate and 38 g (0·5 mole) CS_2 in 75 ml $CHCl_3$. The reaction mixture rapidly became dark-red. After stirring for 5 min, the layers were separated. The $CHCl_3$ phase containing **3a** was used in the alkylation below without further treatment.

3a (*method b*): To a vigorously stirred solution of the dipotassium compound (**2a**) (0·1 mole) in 150 ml H_2O was added 34 g (0·1 mole) $TBAHSO_4$ in 150 ml $CHCl_3$. After 5 min, the layers were separated. Work-up was as in method a.

In attempts to isolate the TBA salts **3a** and **3b** the $CHCl_3$ phase was dried and evaporated. The residue was treated twice with 150 ml of ether, which was decanted off, and the residue was evaporated.

3b: 19·2 g (0·1 mole) of ethyl benzoylacetate were treated with 34 g (0·1 mole) $TBAHSO_4$, 8 g (0·2 mole) NaOH and 38 g (0·5 mole) CS_2 in the same way as described for **3a** (method a) above. Also this TBA salt was used without isolation in the alkylation below.

3c: See Ref 5.

Mono-alkylation of disalts. **5a**: To a stirred ice-cooled solution of 28·2 g (0·1 mole) of the dipotassium salt **4a** in 50 ml H_2O was added dropwise 14·2 g (0·1 mole) MeI in 5 ml EtOH. The stirring was continued with cooling for 2 h. The solution was extracted 4 times with 25 ml $CHCl_3$. The $CHCl_3$ phase was dried ($CaSO_4$) and evaporated to a red oil (9·0 g). 1 g of this oil was separated by PLC (20% diethyl ether/80% light petroleum (b.p. 50°). Two fractions: 1. (R_f = 0·25) ethyl acetoacetate **1a**. 2. (R_f = 0·17) dimethyl ketene mercaptal **6a**. Yields (calculated for the whole fraction): **6a** 7 g (30%), **1a** 0·4 g (3%). The ice-cold H_2O phase was acidic with ice-cold 2 M HCl and extracted with $CHCl_3$. The $CHCl_3$ phase was dried and evaporated to a dark-red oil (7·7 g). This was almost pure **5a**. For analytical purposes 2 g were separated with PLC (20% diethyl ether/80% light petroleum (b.p 50°)) giving 1·95 g of **5a**. Yield (calculated for the whole fraction): 7·5 g (34%). (Found: C, 43·52; H, 5·50; S, 29·05. $C_8H_{12}O_3S_2$ requires: C, 43·60; H, 5·46; S, 29·10%).

5b: To the stirred ice-cooled benzene–DMF solution of the disalt **4b** (from the preparation above) were added dropwise 15·4 g (0·11 mole) of MeI. The stirring was continued for 1 h. The solution was extracted with 100 ml ice-cold 1 M NaOH in two portions. The benzene phase was dried ($CaSO_4$) and evaporated to a light-red oil. 1 g of this oil was separated by PLC (20% diethyl ether/80% light petroleum (b.p. 50°)). Yield (calculated for the whole fraction): 28% of **1b** and 37% of **6b**, proportional to starting material **1b**. The ice-cold H_2O phase was acidified with ice-cold 1 M HCl and extracted with 100 ml $CHCl_3$ in two portions. The $CHCl_3$ phase was dried ($CaSO_4$) and evaporated to a dark-red oil (2·8 g) which contains **5b** and **1b**. Separation by PLC (20% diethyl ether/80% light petroleum (b.p. 50°)) gave 2·7 g of a mixture of **5b** and **1b** which contained about 2% of **1b**. **5b** could not be separated from **1b** and was not obtained analytically pure (perhaps **5b** is not stable on the silica gel).

5c: To a stirred ice-cooled solution of 2·35 g (0·01 mole) of the dipotassium salt **4c** in 10 ml H_2O was added dropwise 1·42 g (0·01 mole) MeI in 1 ml EtOH. The stirring was continued with cooling for 2 h. The solution was extracted three times with 5 ml $CHCl_3$. The $CHCl_3$ phase was dried ($CaSO_4$) and evaporated to a yellow crystalline compound which was recrystallized from diethyl ether yielding 1·25 g (65%) of **5c**, m.p. 90·5–92°. (Found: C, 41·60; H, 4·08; N, 7·97; S, 36·99%. $C_8H_9NOS_2$ requires: C, 41·60; H, 4·05; N, 8·10; S, 37·00%).

Alkylation of TBA salts. **5a**: To the stirred ice-cooled $CHCl_3$ solution of the TBA salt **3a** from the above preparation of **3a** was added dropwise during 15 min a solution of 28 g (0·2 mole) MeI in 25 ml $CHCl_3$. The stirring was continued with cooling for 15 min. The solvent was evaporated and the residue treated with diethyl ether. The precipitate was filtered off and the ether phase was extracted with 110 ml ice-cold 1 M NaOH in two portions. The ether phase was dried ($MgSO_4$) and evaporated to a red oil. 2 g of this oil was separated on a column, eluted with a mixture of 20% diethyl ether and 80% light petroleum (b.p. 50°). Two fractions were isolated: 1. (R_f = 0·25) etheyl acetoacetate **1a**. 2. (R_f = 0·17) dimethyl ketene mercaptal **6a**. Yield (calculated for the whole fraction): **1a**, 2·2 g (17%); **6a**, 4·0 g (17%). The ice-cooled H_2O phase was acidified with ice-cold 1 M HCl and extracted 4 times with 50 ml ether. The combined ether fractions were dried and evaporated to a red oil **5a**. Yield: 13·5 g (66%).

5b: The $CHCl_3$ solution of the TBA salt **3b** (from the preparation above) was treated with 28 g (0·2 mole) MeI in the same way as described under **5a** above. Yields: **1b**, 4·8 g (25%), **6b**, 13·6 g (48%), and **5b**, 14·6 g as a mixture of **5b** (98%) and **1b** (2%). Further attempts of purification of **5b** were not successful.

5c: See Ref 5.

Preparation of allyl and crotyl compounds. **11** (*method a*): 9 g (0·041 mole) of **5a** in 25 ml dry benzene were added dropwise to a stirred solution of 0·045 mole NaH in 25 ml dry benzene under N_2 atmosphere. The temp was kept below 30°. The mixture was stirred for additional 1 h and 5·6 (0·045 mole) of allyl bromide in 10 ml dry benzene were added dropwise to the stirred mixture. The mixture was stirred at room temp overnight. 2 ml EtOH was added. The mixture was washed three times wtih 100 ml of H_2O. The benzene phase was dried ($CaSO_4$), the solvent evaporated, and the residual oil distilled to give **11** as a dark-red oil, $b.p._{0.1}$: 126–127·5°, yield: 7·5 g (70%). (Found: C, 50·78; H, 6·22; S, 24·44. $C_{11}H_{16}O_3S_2$ requires C, 50·75; H, 6·15; S, 24·64%). IR (ν_{max}^{film}) cm^{-1}: 1730(s), 1640(w). UV (λ_{max}^{EtOH}) 317 nm.

11 (*method b*): To a stirred ice-cooled solution of 32·7 g (0·122 mole) of the dipotassium ketene mercaptal **2a** in 75 ml H_2O was added dropwise 19·1 g (0·135 mole) MeI in 75 ml EtOH. The stirring was continued with cooling for additional 1½ h. The mixture was extracted with 150 ml $CHCl_3$ in three portions. To the stirred ice-cooled aqueous phase was added dropwise 16·5 g (0·122 mole) crotyl bromide in 7·5 ml EtOH. The mixture was stirred ½ h with cooling, then 1 h at room temp. The mixture was extracted with 150 ml ether in three portions. The ether phase was dried ($MgSO_4$) and evaporated. The residual oil was worked-up as in method a, yielding 9·85 g (32%) of **11**.

12: 9 g (0·045 mole) of **5a** were treated with 0·045 mole of NaH and alkylated with 6·1 g (0·045 mole) of crotyl

bromide as for compound **11** above. Yield: 8·5 g (76%), b.p.$_{0.1}$: 133–136°. (Found: C, 52·51; H, 6·60; S, 23·24. $C_{12}H_{18}O_3S_2$ requires: C, 52·55; H, 6·57; S, 23·35%).

17a: To a vigorously stirred ice-cooled solution of 12·4 g NaOH (0·31 mole) and 34 g (0·1 mole) TBAHSO$_4$ in 100 ml H_2O was added a mixture of 13 g (0·1 mole) methyl acetoacetate and 38 g (0·5 mole) CS_2 in 100 ml $CHCl_3$. The mixture was stirred for additional 5 min. The ice-bath was removed and 25·2 g (0·2 mole) of allyl bromide were added dropwise and the mixture was stirred for additional 3 h. The layers were separated. The $CHCl_3$ phase was evaporated and the residue was treated with ether. The TBABr was filtered off and washed with ether. The combined ether fractions were dried ($CaSO_4$) and the solvent evaporated. The residual oil was distilled to give **17ar** as an orange-red oil, b.p.$_{0.1}$: 128–129°, yield: 24·6 g (86%). (Found: C, 54·50; H, 6·14; S, 22·19. $C_{13}H_{18}O_3S_2$ requires: C, 54·52; H, 6·19; S, 22·39%). IR (ν_{max}^{film}) cm^{-1}: 1730(s) (broad 1715–1745), 1635(m). UV (λ_{max}^{EtOH}) 323 nm.

17b: 1·92 g (0·01 mole) of **1b** was reacted with 3·4 g (0·01 mole) TBAHSO$_4$, 1·2 g (0·03 mole) NaOH, 3·8 g (0·05 mole) CS_2, and 2·66 g (0·022 mole) allyl bromide in the same way as described for **17a** above. The crude product was separated on a column (10% acetone/90% light petroleum (b.p. 80°)) yielding 3·0 g (86%) of **17b**. (Found: C, 62·16; H, 5·71; S, 18·21. $C_{18}H_{20}O_3S_2$ requires: C, 62·05; H, 5·75; S, 18·40%). **17b** easily rearranged to **17rb**.

18: 11·6 g (0·1 mole) of methyl acetoacetate were treated with 34 g (0·1 mole) TBAHSO$_4$, 12·4 g (0·31 mole) NaOH, and 38 g (0·5 mole) CS_2 and then alkylated with 27 g (0·2 mole) crotyl bromide in the same way as for **17a** above, giving **18** as a red oil. Half of this oil was distilled giving 6·6 g (88% calculated for the whole fraction) of **18E**, b.p.$_{0.05}$: 142–146° (decomposition easily occurs). (Found: C, 56·03; H, 6·65; S, 21·24. $C_{14}H_{20}O_3S_2$ requires: C, 56·00; H, 6·67; S, 21·33%). 5 g of the crude product were separated on a column (r = 40 mm) packed with 300 g silica gel and eluated with a mixture of 10% acetone and 90% light petroleum (b.p. 80°) to remove by-products. 1 g of the product from this column was again separated on a column (r = 20 mm, 10% acetone/90% light petroleum) giving two fractions both with analysis equal to what was found for **18E**. (Rearrangement investigations were performed in a thermostat on these two fractions as described in the text.)

19: 1·92 g (0·01 mole) ethyl benzoylacetate were treated with 3·4 g (0·01 mole) TBAHSO$_4$, 1·24 g (0·031 mole) NaOH, and 3·8 g (0·05 mole) CS_2 and then alkylated with 2·97 g (0·022 mole) crotyl bromide in the same way as for **15a** above giving a red oil. 2 g of this oil were separated on a column (10% acetone/90% light petroleum, b.p. 60–80°). Yield of **19** (calculated for the whole fraction): 3·45 g (91%). (Found: C, 63·85; H, 6·36; S, 16·93. $C_{20}H_{24}O_3S_2$ requires: C, 63·82; H, 6·38; S, 17·02%). IR (ν_{max}^{film}) cm^{-1}: 1715(s), 1675(s), 1605(m), 1590(m). UV (λ_{max}^{EtOH}): 251 nm.

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