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SYNTHESES AND REARRANGEMENTS OF KETENE MERCAPTALS DERIVED FROM SOME ACTIVE METHYLENE COMPOUNDS AND CARBON DISULPHIDE

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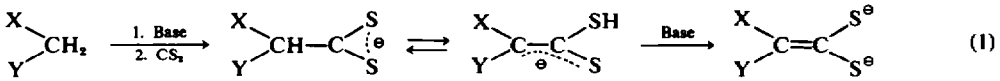
Abstract– By use of the ion pair extraction technique, tetrabutylammonium salts of diethyl malonate, methyl cyanoacetate or malodinitrile were reacted with carbon disulphide giving salts of dithioacids (or of the tautomeric gem-mercapto thiolates) and of ketene mercaptals. Ketene methyl allyl mercaptals derived from diethyl malonate or methyl cyanoacetate rearranged at room temp to dithioesters by S → C allyl migration. The corresponding methyl crotyl derivatives gave equilibrium mixtures of the ketene mercaptals and the dithioesters, each of which were shown to undergo S → C and C → S rearrangements, respectively, with inversion of the crotyl group. Contrary to this the ketene dicrotyl mercaptals rearranged during distillation (at about 150°) with retention of the crotyl group. Methyl [(methylthio, crotylthio)methylene] cyanoacetate underwent fragmentation at 170° to MeSSMe, MeScrotyl, MeS(1-methylallyl) and the "desaurin": 2,4-bis-(carbomethoxy-cyan-methylen)-1,3-dithiocyclobutan. Similarly bis(allylthio)methylene malodinitrile yielded diallyl sulphide.

INTRODUCTION

In the course of our investigation of rearrangements of some enethiol derivatives[1] we decided to extend this work to other types of α,β-unsaturated sulphur compounds. The thio-Claisen rearrangement of allyl thienyl sulphides[2] has been described earlier and rearrangement of ketene allyl mercaptals derived from β-hydroxy dithiocinnamic acid is also known.[3] In the same investigation[3] it was shown that ketene alkyl allyl mercaptals and ketene diallyl mercaptals rearranged smoothly to α-allyl dithioesters with inversion of the migrating allyl group as it is also found in other cases.[4] In this and forthcoming papers the synthesis and rearrangement of compounds obtained by the reaction of active methylene compounds with carbon disulphide in the presence of base, will be described. This reaction has been studied for a large number of active methylene compounds (**1**) and generally follows the equation below. (For an extended list of papers on this reaction, see Ref 3).



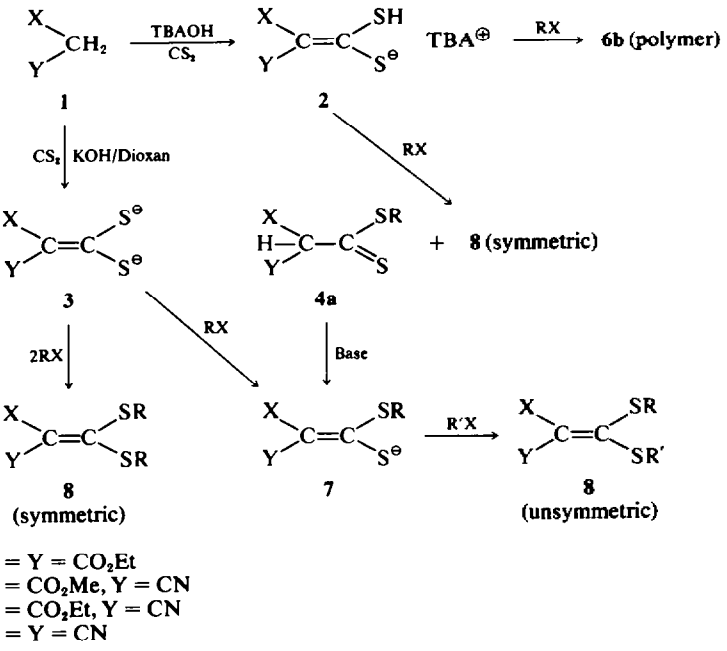
1 **2** **3** (1)

While the chemistry of compounds derived from **3** by alkylation is thoroughly investigated, the corresponding salt, **2**, and its dithioesters have only scarcely been studied.[5–9] The present paper deals with synthesis and rearrangement of ketene diallyl mercaptals and methyl allyl mercaptals, obtained from diethyl malonate (**1a**), methyl- and ethyl cyanoacetate (**1b** and **1c**) and malodinitrile (**1d**).

The synthetic intermediates were the monosalts **2**, prepared by use of the ion pair extraction technique,[10] the disalts **3** obtained by the method of Gommper and Töpfl,[5] and the salts **7** obtained by monoalkylation of **2** or **3**.

Formation and structure of thiolates

The tetrabutylammoniumsalts (TBA salts) of **2b** and **2d** were synthesized in pure crystalline state, while **2a** could only be isolated as an oil which was not purified further. On the basis of the IR spectrum of **2b** which showed bands at 2195 cm^{-1} (m), and 1670 cm^{-1} (s), assigned to the stretching of an α,β-unsaturated nitrile, and an α,β-unsaturated ester CO, respectively, **2b** was considered to possess the enethiol structure as shown in Eq 1. The IR spectrum of **2d** similarly showed the presence of an α,β-unsaturated nitrile. The choice of this structure for compounds **2b** and **2d** is also supported by ESCA-investigations (for review, see Ref 11 and Refs cited therein). The binding energy for the $S(2p_{3/2})$ electrons, the kinetic energy of the expelled $S(2p_{3/2})$ electrons and the energy of the exciting X-ray photons are related by the following equation, where ϕ_{sp} is an apparatus constant in-



a: X = Y = CO_2Et
b: X = CO_2Me, Y = CN
c: X = CO_2Et, Y = CN
d: X = Y = CN

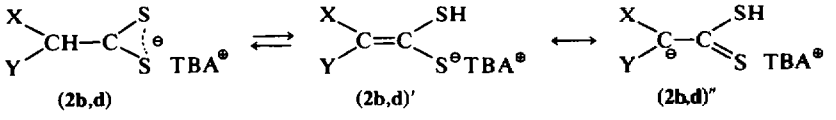
SCHEME 1

cluding among others the work-function of the spectrometer material

$$E_{x\text{-}ray} = E_{bind} + E_{kin} + \phi_{sp} \quad (2)$$

The exciting X-ray radiation was the AlK_α-line (1486·6 eV), and ϕ_{sp} was determined by special calibrations to be 9·5 eV. The investigated compounds were placed in the X-ray beam on a small platinum plate. When the layer of the sample was thin enough, it was possible to use the binding energy of the $Pt(4f_{5/2})$ electrons as a standard value, energies of the $S(2p_{3/2})$ electrons calculated from the kinetic energies using the formula in Eq 2 with $\phi_{sp} = 9{\cdot}5$ eV.

The ESCA spectra show two peaks of equal intensity for each compound separated by 1·7 eV and 1·8 eV, respectively, indicating two different S atoms in the investigated molecules. Comparing these results with the ESCA-investigation[12] of compounds containing the structure-elements of the two proposed tautomeric structures **(2b,d)** **(2b,d)'** makes the choice fall on **(2b,d)'** ↔ **(2b,d)"**.



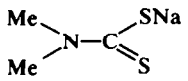
(3)

which will be of essential interest in future comparisons with this experiment. The data from the investigation are collected in Table 1, in which the kinetic energies of the $S(2p_{3/2})$ electrons are shown together with the kinetic energy of the $Pt(4f_{5/2})$ electrons. In the last column is shown the binding

The ESCA-spectrum of compounds **10**[12] and **11**[12] shows one common signal for the binding energy of the $S(2p_{3/2})$ electrons, while the ESCA-spectrum of compound **12**[12] mainly in the mesomeric form **12'**, shows two signals for the binding energy of the $S(2p_{3/2})$ electrons separated by 2·0 eV.

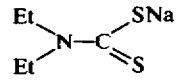
Table 1. ESCA data: Measured kinetic energies of the $S(2p_{3/2})$ and the $Pt(4f_{5/2})$ electrons. Calculated binding energies of the $S(2p_{3/2})$ electrons

	E_{kin} $S(2p_{3/2})$		E_{kin} $Pt(4f_{5/2})$		E_{bind} $S(2p_{3/2})$
2b	1313·8 eV	1315·5 eV	1402·7 eV	163·3 eV	161·6 eV
2d	1313·5 eV	1315·3 eV	1402·7 eV	163·6 eV	161·8 eV



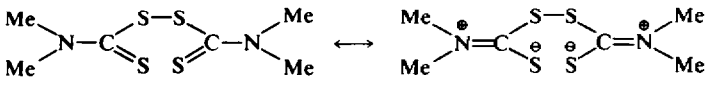
10

One S($2p_{3/2}$) ESCA-signal



11

One S($2p_{3/2}$) ESCA-signal (4)



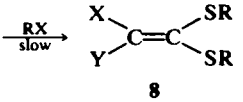
12 ⟷ 12'

Two S($2p_{3/2}$) ESCA-signals

Alkylations

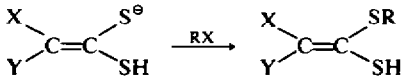
Alkylation of **2a** with ethyl- or allyl bromide gave a 1:2:1 mixture of **1a**, **4a**, and **8a** (R = Et or allyl), while methylation with MeI or Me_2SO_4 gave a 4:2:1 ratio probably because diethyl malonate was contaminating the starting material, **2a**. Relative yields were estimated by integrals of NMR signals of the methylene protons of diethyl malonate (**1a**), the alkyl protons of the dithiocarbalkoxy group (**4a**), and the alkyl protons of the bis(alkylthio)methylene group (**8a**). By alkylation of **2b** with MeI, $MeSO_3F$, Me_2SO_4, EtBr, Me_2CHI, $PhCH_2Br$ or $PhCH_2Cl$ a polymer **6b** was formed together with **8b**. The polymer was insoluble in acidic and neutral solvents but soluble in bases like $OH^{\ominus}/H_2O$, Et_3N or pyridine. Acidification of the basic solution resulted in the formation of the monomer **4b**, while alkylation gave **8b** e.g. **8b** (R = Me, R' = $PhCH_2$) by alkylation with $PhCH_2Cl$ and MeI, respectively. As to the content of Z and E isomers, it was exactly the same in the two cases, when Et_3N was used as base, which is not surprising as the barrier of rotation (ΔG^+) about the double bond has been found to be as low as 22 kcal/mol.[18] The dithiolate **3b** gave mostly the monoalkylated product **7b** when treated with one equivalent of MeI, because **3b** is a stronger nucleophile (base) than **7b**. The choice of solvent in monoalkylation of **3b** was crucial. Most organic solvents dissolved **7b** better than **3b**, and thereby caused more dialkylation than if the reaction were run in water in which **7b** solidified.

3 7

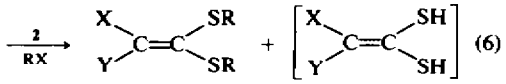


8 (5)

The reason why the monosalts **2** yielded mixtures as described above can be accounted for by equal basicities of **2** and **7**. This means that **2** is capable of abstracting a proton from **4**, which can be alkylated further to **8**. However, the experimental conditions do not allow any mechanistic proposals to be made for the subsequent reactions of the protonated form of **2** as no products from this intermediate were found.[13-15]



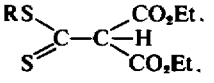
2 4



8 (6)

In other cases, treatment of salts of type **2** *i.e.* TBA salts[3] or alkali salts[5] of substituted β-hydroxydithiocinnamic acids with alkyl halide has been reported to give monoalkylated products of type **4** in high yield. This might be explained by assuming that the salts corresponding to **2** are not capable of abstracting a proton from the monoalkylated product **4**, leading to the formation of **7** which could then be alkylated.

The physical and spectroscopical data of **4a** (R = Me) were in agreement with the findings of Shvo and Belsky[9] who proposed a dithioester structure for **4a** (R = Me) (from dimethyl malonate)



4a

on the basis of ^{1}H—NMR which showed a singlet at $\delta = 5{\cdot}00$ ppm, while IR exhibited a CO band at 1730 cm^{-1} characteristic of a saturated ester. Here we provide additional proof: The 25·12 MHz proton noise-decoupled natural abundance ^{13}C NMR spectrum (single scan) of **4a** (R = Me) showed (singlet) signals at $\delta = 179$ ($\underline{C}H_3CH_2$—), 172 ($\underline{C}H_3S$), 130 ($\underline{C}H_2O$), 122 ($\underline{C}$—H), 29 (—$\underline{C}O_2Et$), −29 ($\underline{C}S_2Me$) ppm relative to CS_2 (the chemical shift scale was taken positive in the high field direction). The single frequency off resonance proton

decoupled ^{13}C spectrum[16] (irradiation at $\delta = 4{\cdot}22$ ppm in the ^1H spectrum) showed a residual doublet splitting $J^r_{CH} = 6$ c/s at $\delta = 122$ ppm, and a singlet at $\delta = 130$ ppm. Similarly irradiation at $\delta = 5{\cdot}00$ ppm in the ^1H spectrum gave a triplet $J^r_{CH} = 6$ c/s at $\delta = 130$ ppm and a singlet at $\delta = 122$ ppm. From the expression given by Ernst[17]

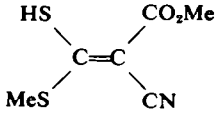
$$J^r_{CH} = \frac{2\pi\Delta\nu J_{CH}}{\gamma H_2}$$

it is seen that J_{CH} of the C—H group is of the same magnitude as J_{CH} of the CH_2O group.

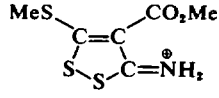
In contrast to this, compounds **4b** have the ketene mercaptal structure and have been found to be quite unstable solids.[5–9] However, in the present work we did not isolate the monomer of **4b** from alkylation of **2b**, but a polymer **6b**, which we suggest to have the structure shown in (8), as confirmed by the IR (KBr) bands at 3300 cm^{-1} (N—H), 1700 cm^{-1} (α,β-unsaturated ester CO) and 1600 cm^{-1} (C=C and/or C=N). The possibility that the compound could be the known dimer[13] **5b** was ruled out, as the dimer showed a sharp band at 2200 cm^{-1} in IR, due to the nitrile group while the polymer showed no band in this region.

Rearrangement and fragmentation

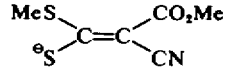
Alkylation of the dithiolates **3a, c, d** with two equivalents of allyl or crotyl bromide was expected to yield the symmetric ketene mercaptals **8a, c** and **d** (Table 2). However, treatment of **3a** with allyl bromide gave a mixture of **8a** and **9a**. On standing the spectra and TLC of the crude product mixture changed, as **8a** rearranged to **9a**. It is believed that **9a** is only formed by rearrangement from **8a**, and not by direct alkylation on the α-carbon of **3a**, because only alkylation on the S atoms of **3a**[8] have



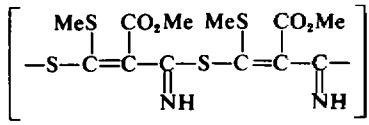
4b



5b

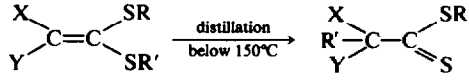


(8)



6b

Table 2.



8 **9**

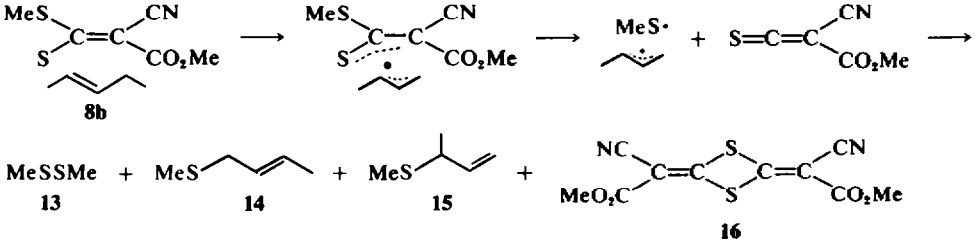
a: X = Y = CO_2Et
b: X = CO_2Me, Y = CN
c: X = CO_2Et, Y = CN
d: X = Y = CN

		8	**9**
Alkylation of **3**	a	R = R′ = allyl	R = R′ = allyl
	a	R = R′ = crotyl	R = R′ = crotyl
	c	R = R′ = allyl	R = R′ = allyl
	c	R = R′ = crotyl	R = R′ = crotyl
	d	R = R′ = allyl	decompose 170°C
	d	R = R′ = crotyl	decompose 170°C
7	a	R = Me, R′ = allyl	R = Me, R′ = allyl
		R = Me, R′ = crotyl	R = Me, R′ = 1-Me-allyl
	a	R = Me, R′ = 1-Me-allyl	R = Me, R′ = crotyl
	b	R = Me, R′ = allyl	R = Me, R′ = allyl
	b	R = Me, R′ = crotyl	R = Me, R′ = 1-Me-allyl*, decomp. 170°C

*Trace amounts of two diastereomers: IR ν^{film}_{max} (cm^{-1}) 1740. NMR (CCl_4) 1·10 ppm (d, $J = 7{\cdot}0$ c/s) and 1·30 ppm (d, $J = 6{\cdot}5$ c/s) due to the 1-Me group.

been observed with other alkylating agents. The corresponding ketene diallyl mercaptal **8c** obtained from **3c** was more stable than the diethyl malonate derivative **8a**. The crude product was nearly pure **8c**, but easily underwent rearrangement, while that derived from **3d** was stable and instead of rearrangement underwent decomposition during distillation at about 170° yielding diallyl sulphide and a non-distillable residue. The rate of rearrangement was also retarded in going from allyl to crotyl derivatives of **8a** and **c** (Experimental).

Unsymmetrical methyl allyl, methyl crotyl, and methyl 1-methylallyl ketene mercaptals were prepared by alkylation of **7a, b** (R = Me) (as potassium or ammonium salts) or in one case the dimer of **5b** in the presence of base. The rearrangement of these derivatives did not proceed quite analogously to symmetrical ones. The allyl and 1-methylallyl derivatives **8a** (R = Me, R′ = allyl, 1-methylallyl) rearranged completely to **9a** (R = Me, R′ = allyl, crotyl) while the crotyl derivatives **8a** (R = Me, R′ = crotyl) gave mixtures of rearranged [**9a** (R = Me, R′ = methylallyl)] and unrearranged material [**8a** (R = Me, R′ = crotyl)], which were separated by PLC and each shown to give an equilibrium mixture (**9a**:**8a** = 1·6) on standing at room temp. However, **8b** (R = Me, R′ = crotyl) did not rearrange to a substantial amount as only traces of **9b** (R = Me, R′ = 1-methyl allyl) was found (IR showed a weak band at 1740 cm^{-1}). At higher temp. (170°) **8b** (R = Me, R′ = crotyl) decomposed according to the scheme



The products were identified by NMR spectrometry and GLC connected to MS spectrometry. By heating **8b** (R = Me, R′ = $PhCH_2$) under the same conditions, only trace amounts of CH_3SCH_2-Ph could be detected (TLC/MS).

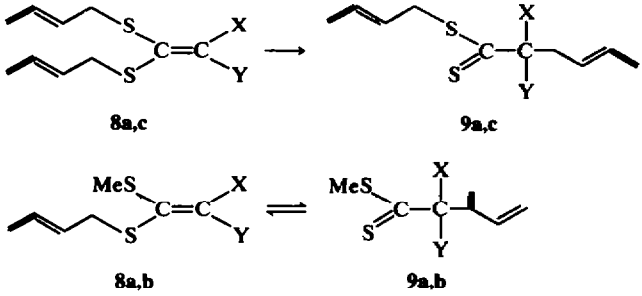
The difference in physical and spectroscopic properties of **8a** and **9a** (diallyl and dicrotyl derivatives) was pronounced. The chemical shift of the methylene protons of the allylic groups bonded to sulphur (δ = 3·48 ppm) changed so that the methylene protons of the allylic dithioester function were shifted to lower field (δ = 3·76 ppm) while those of the allylic group bonded to the α-carbon were shifted to higher field (δ = 2·92 ppm). In the case of **8c** the methylene protons of the allylic groups bonded to sulphur were non-equivalent giving signals at δ = 3·62 ppm and 3·73 ppm while the rearranged products **9c** (and **9b**) showed signals at δ = 3·01 ppm and 3·85 ppm.

The IR spectra of **8a, c** (diallyl and dicrotyl derivatives) showed an α,β-unsaturated ester CO at 1700 cm^{-1} which changed to 1740 cm^{-1} due to the saturated ester CO in **9a, c**, while the nitrile stretching frequency at 2215 cm^{-1} of **8c** weakened or disappeared in **9c**. The UV absorption band of the ketene mercaptals: 310–15 nm (**8a**) or 330–35 nm (**8c**) changed to that of a dithioester:[3] 315–20 nm (log ε = 3·96–4·07) (**9a, c**). The unsymmetric ketene mercaptals and their rearrangement products showed similar spectroscopic patterns.

DISCUSSION

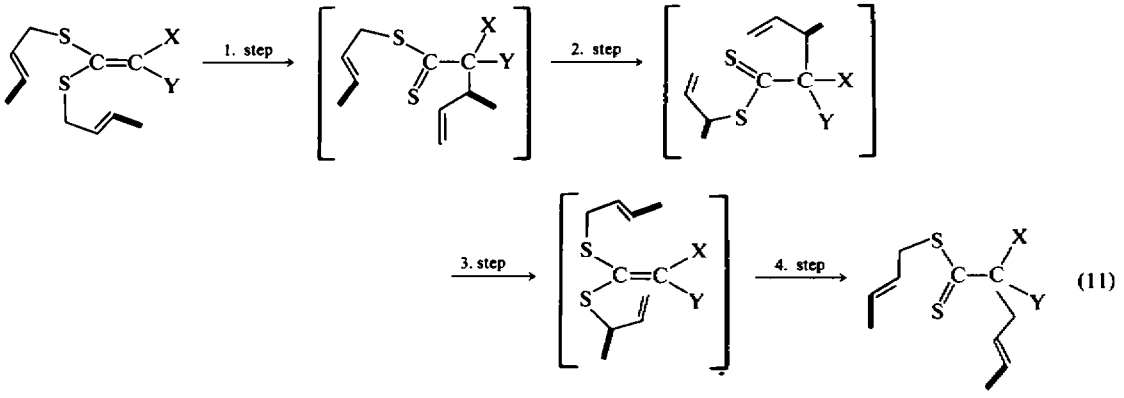
It is believed that the observed allylic migrations do not involve free radicals (or ions), because such mechanisms do not account for the fact that **8a, b** (R = Me, R′ = crotyl) are in equilibrium with **9a, b** (R = Me, R′ = 1-methylallyl), whereas **8a, c** (R = R′ = crotyl) are converted completely to **9a, c** (R = R′ = crotyl).

The difference in orientation of the allylic group by rearrangement of the symmetric ketene dicrotyl



(10)

mercaptals and the unsymmetric ketene methyl crotyl mercaptals might be a consequence of a multiple rearrangement of the symmetric ones. The following mechanism is proposed, based on the assumption that the reaction is concerted and reversible, leading to the thermodynamically most stable product. The reversibility is probably due to the steric crowding between the crotyl group and the ethoxy-carbonyl groups in the rearranged product, differing from previously reported cases of rearrangement of allyl ketene mercaptals, which had a hydrogen on the C-2 atom of the ketene double bond.[3,4]



(11)

The first step (S → C) was supported by the analogous reaction of **8a, b** (R = Me, R′ = crotyl) to **9a, b** (R = Me, R′ = 1-methyl-allyl). The second step (S → S) is a rearrangement of a crotyl dithioester to a 1-methyl-allyl dithioester. This intermediate is believed to be present in low concentration as a 1-methyl-allyl dithioester seems to have a higher energy than a corresponding crotyl dithioester, because this is the structure obtained by the isolated product **9**. Crotyl acetates and similar compounds are known to rearrange[19] (O → O) in the gas phase to 1-methyl-allyl acetate at about 300°, while allyl and crotyl thionobenzoate are converted (O → S) to allyl and 1-methyl-allyl thiolbenzoate at about 100°, respectively.[20] The third step (C → S) is believed to consist of a migration of the 1-methyl-allyl group from carbon to sulphur with inversion to a crotyl group, which also occurred in the case of **9a** (R = Me, R′ = 1-methyl-allyl) to **8a** (R = Me, R′ = crotyl). The last step (S → C) was supported by the analogous reaction of **8a** (R = Me, R′ = 1-methyl-allyl) to **9a** (R = Me, R′ = crotyl). This 4-step mechanism accounts for the fact that allyl derivatives rearranged faster than crotyl derivatives.

The reason why **8a** rearranged faster than **8b, c** and why **8d** did not rearrange is ascribed to the stabilizing effect of the cyano group on the conjugated system of the ketene mercaptals. This stabilization was also observed for **4b, c, d** which possessed the ketene mercaptal structure[5-9] contrary to the dithioester structure obtained by **4a**.[9] Also the rotational barrier about the C—C double bond of the ketene mercaptals has been shown to rise on nitrile substitution.[18]

EXPERIMENTAL

NMR spectra were recorded at 60 Mc/s on a Varian A-60 spectrometer. The temps ot 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 ±0·02 ppm. ^{13}C spectra were recorded on a Varian XL-100-15 spectrometer operating in the c.w. mode at 25·2 MHz. Internal field-frequency lock was provided by the ^{2}H resonance of acetone-d_6 as solvent. Carbon line positions were measured relative to the carbon resonance of internal CS_2. Noise-modulated and single-frequency proton decoupling experiments were performed by means of the Varian Gyrocode spin decoupler. The sample solution was contained in a 12 mm tube. 70 eV mass spectra were obtained on a Bell and Howell CEC 21-104 single focussing mass spectrometer. The ESCA-measurements were made on an ES 100 Electron Spectrometer from AEI Scientific Apparatus Ltd. The size of the spectrometer entrance slit was 100 thou., which was the middle of three possible values. This choice gave a reasonable combination of resolution and intensity. The spectra were run at an effect of 15 kV, 18 mA from the X-ray tube. The measurements were made at room temperature and at a pressure of about 10^{-7} torr. The sample was dissolved in $CHCl_3$ and a drop of this dilute soln was placed on a small Pt plate, which after evaporation of the chloroform, was placed on the source holder of the spectrometer. The layer was kept so thin that it was possible to detect the ejected electrons from the Pt plate. The IR spectra were recorded as 5% solns, film, or as KBr pellets on a Perkin-Elmer infracord 137 and the UV spectra on a Bausch & Lomb Spectronic 505 spectrophotometer with EtOH as solvent. B.ps are uncorrected. 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 mm) and eluated with light petroleum ether-diethyl ether.

Tetrabutylammonium salts, **2a, b,** *and* **d.** 0·1 mol of diethyl malonate, methyl cyanoacetate or malodinitrile

and about 50 ml (excess) CS_2 were poured into a mixture of 34 g (0·1 mol) tetrabutylammonium hydrogen sulphate, 8 g (0·2 mol) NaOH, 100 ml water and 100 ml chloroform. After a short time (10 min – 1 hr) the chloroform was separated, dried, and evaporated. The residue oil could be crystallized in the case of **2b** and **d**.

Diethyl (tetrabutylammonium dithiocarboxy) malonate, **2a**. From 16 g (0·1 mol) diethyl malonate **2a** was obtained as an oil, which was washed with ether and then used directly for further reactions.

Tetrabutylammonium methyl [bis(mercapto)methylene] cyanoacetate, **2b**. From 9·9 g (0·1 mol) methyl cyanoacetate were obtained 35·4 g (yield 85%) (M = 416) of **2b**, which could be recrystallized from MeOH or *i*-PrOH yielding 27·2 g (yield 65%) of m.p. 69°. (Found: C, 60·71; H, 9·79; N, 6·69; S, 15·19. $C_{21}H_{40}N_2O_2S_2$ requires: C, 60·55; H, 9·68; N, 6·72; S, 15·36%); NMR ($CDCl_3$): δ ppm (*J* c/s): 1–2 (28H, m); 3–3·5 (8H, m); 3·68 (3H, s); IR ν_{max}^{KBr} (cm^{-1}) 3000–2860 (s), 2195 (s), 1670 (m), 1635 (s); UV (EtOH) λ_{max} 350 nm.

Tetrabutylammonium [bis(mercapto)methylene] malodinitrile, **2d**. From 6·6 g (0·1 mol) malodinitrile were obtained 32·9 g (yield 86%) (M = 384) which could be recrystallized from MeOH or *i*-PrOH yielding 12·6 g (yield 33%); m.p. 104–105°. (Found: C, 62·66; H, 9·78; N, 10·78; S, 16·73. $C_{20}H_{37}N_3S_2$ requires: C, 62·63; H, 9·72; N, 10·96; S, 16·69%); NMR ($CDCl_3$): 1–2 (28H, m), 3–3·5 (8H, m); IR ν_{max}^{KBr} (cm^{-1}) 3060–2860 (s), 2195 and 2170 (s); UV (EtOH) λ_{max} 345 mm.

General procedure by alkylation of **2a**. The amount of **2a** was treated with excess alkyl halide (or sulphate) in chloroform and stirred for about 18 hr at room temp. The solvent was evaporated and the residue oil extracted with ether, which was then extracted with excess of 2 M NaOH. Acidification of the aqueous phase with 4 M HCl and extraction with ether yielded **4a**, which could be distilled at 60°/~ 10^{-4} mmHg.

Diethyl (dithiocarbomethoxy) malonate, **4a** (R = Me). 33·2 g (0·07 mol) **2a** and Me_2SO_4 gav e 5·8 g (33%); n_D^{25} = 1·5215. (Found: C, 43·39; H, 5·90; S, 25·22. $C_9H_{14}O_4S_2$ requires: C, 43·20; H, 5·64; S, 25·58%); NMR (CCl_4) 1·27 (6H, t, *J* = 7 c/s); 2·67 (3H, s); 4·22 (4H, q, *J* = 7 c/s); 5·00 (1H, s); IR ν_{max}^{film} (cm^{-1}) 2967 (m); 1740 (s); UV (EtOH) λ_{max} 315 nm.

Diethyl (dithiocarbethoxy) malonate, **4a** (R = Et). 17 g (0·035 mol) **2a** and EtBr gave 2·8 g (30%); n_D^{25} = 1·5250. (Found: C, 45·32; H, 6·23; S, 24·18. $C_{10}H_{16}O_4S_2$ requires: C, 45·45; H, 6·10; S, 24·22); NMR ($CDCl_3$): 1·28 (6H, t, *J* = 7 c/s); 1·35 (3H, t, *J* = 7 c/s); 3·25 (2H, q, *J* = 7 c/s); 4·22 (4H, q, *J* = 7 c/s); 4·94 (1H, s); IR ν_{max}^{film} (cm^{-1}) 2960 (m), 1740 (s). UV (EtOH) λ_{max} 318 nm.

Diethyl (dithiocarballyloxy) malonate **4a** (R = allyl). 14·4 g (0·03 mol) **2a** and allyl bromide gave 2·4 g (29%), n_D^{25} = 1·5265; (Found: C, 47·76; H, 5·91; S, 23·04. $C_{11}H_{16}O_4S_2$ requires: C, 47·82; H, 5·84; S, 23·17%); NMR (CCl_4) 1·27 (6H, t, *J* = 7 c/s); 3·90 (2H, broad d, *J* = 6 c/s); 4·20 (4H, q, *J* = 7 c/s); 4·96 (1H, s), 5·0–6·2 (3H, m); IR ν_{max}^{film} (cm^{-1}) 3050 (w), 2990 (m), 1740 (s). UV (EtOH) λ_{max} 320 nm.

In another experiment 1·00 g of the crude product (before extraction with base) was worked up with TLC giving 0·304 g (67% **4a** (R = allyl) + 33% **1a**) and 0·125 g of **8** (R = R′ = allyl).

Alkylation of **2b**

6b (R = Me *polymer*). 41·6 g (0·1 mol) of **2b** in 30 ml chloroform were treated with excess of MeI under ice cooling. (When the slightly exothermal process ceased, the mixture was allowed to stand at room temp for 18 hr). A solid was formed almost immediately, but the yield was increased by allowing the mixture to stand overnight. Filtration and washing with chloroform gave 6·1 g (32%) of a polymer **6b** (R = Me); dec. at about 160°; IR ν_{max}^{KBr} (cm^{-1}) 3300 (m), 1705 (s), 1625 (s), 1500 (m); UV (EtOH) λ_{max} 245, 328 nm; UV (EtOH + NaOH) λ_{max} 223, 288, 344 nm.

Compound **6b** (R = $PhCH_2$) 41·6 g (0·1 mol) of **2b** in 30 ml $CHCl_3$ were treated with excess of benzyl chloride under ice cooling and then allowed to stand at room temp for 4 days. Filtration and washing with chloroform gave 1·62 g (6%) of a polymer of **6b** (R = $PhCH_2$); dec. at about 160°; IR ν_{max}^{KBr} (cm^{-1}) 3220 (m), 1710 (s), 1625 (s), 1500 (m); UV (EtOH) λ_{max} 208, 332 nm; UV (EtOH + NaOH) λ_{max} 213, 290, 345 nm. The solvent was evaporated from the filtrate and the residue extracted with ether and benzene to give after evaporation of the solvent 15 g (42%) of **8b** (R = R′ = ϕCH_2) identified by its NMR spectrum[8] and m.p.[5] 99–102°.

Alkylation of **2d**

(Methylthio-, allylthio-) methylene malodinitrile, **8d** (R = Me, R′ = allyl). 6·8 g (0·018 mol) of **2d** in 20 ml DMF were treated with 3·2 g (0·023 mol) MeI at room temp and stirred for 2 hr. Then, 1·12 g (0·02 mol) of solid KOH, 5 ml water, and 2·6 g (0·022 mol) of allyl bromide, were introduced and the mixture stirred for another 2 hr. Extraction with water and ether gave 2·6 g of crude product obtained from the ether phase, after drying and evaporating of the solvent. Work up of 1·04 g on TLC gave 0·18 g **8d** (R = R′ = Me), 0·11 g **8d** (R = R′ = allyl), and 0·39 g (28%) **8d** (R = Me; R′ = allyl) n_D^{25} = 1·6200; (Found: C, 48·96; H, 4·19; N, 14·46. $C_8H_8N_2S_2$ requires: C, 48·98; H, 4·11; N, 14·28%); NMR ($CDCl_3$): 2·70 (3H, s), 3·76 (2H, broad d, *J* = 6 c/s), 5·0–6·0 (3H, m); IR $\nu_{max}^{CHCl_3}$ (cm^{-1}) 3020, 2220, 1470; UV (EtOH) λ_{max} (log ε) 333 nm (4·0).

Alkylation of **3a**

Diethyl (dithiocarballyloxy) allylmalonate **9a** (R = R′ = allyl). 75 g (0·24 mol) of **3a** were treated with 58 g (0·48 mol) of allyl bromide in 500 ml ether and stirred for about 18 hr at room temp. The mixture was then filtered, washed with water, dried, and the solvent evaporated. NMR of crude product showed a mixture. Distillation gave 60 g (80%); b.p. 132–34°/0·1 mmHg; n_D^{25} = 1·5285; (Found: C, 52·69; H, 6·32; S, 19·90. $C_{14}H_{20}O_4S$ requires: C, 53·16; H, 6·37; S, 20·23%); NMR (CCl_4) 1·25 (6H, t, *J* = 7 c/s), 3·01 (2H, broad d, *J* = 6 c/s), 3·85 (2H, broad d, *J* = 6 c/s), 4·16 (4H, q, *J* = 7 c/s), 4·8–6·2 (6H, m); IR ν_{max}^{film} (cm^{-1}) 3050 (w), 2920 (w), 1740 (s); UV (EtOH) λ_{max} (log ε) 320 nm (4·07).

Diethyl (dithiocarbcrotyloxy) crotylmalonate, **9a** (R = R′ = crotyl). 15·6 g (0·05 mol) of **3a** were treated with 13·5 g (0·1 mol) of crotyl bromide in 150 ml ether and stirred for about 18 hr at room temp. The mixture was then filtered, washed with water, dried, and the solvent evaporated. NMR of crude product showed nearly pure **8a** (R = R′ = crotyl). Distillation gave **9a** (R = R′ = crotyl), 12·8 g (75%), b.p. 143°/0·1 mmHg; n_D^{25} = 1·5293; (Found: C, 55·67; H, 7·08; S, 18·45. $C_{16}H_{24}O_4S_2$ requires: C, 55·80; H, 7·03; S, 18·59%) of **9a** (R = R′ = crotyl); NMR (CCl_4) 1·22 (6H, t, *J* = 7 c/s), 1·6–1·7 (6H, broad d, *J* ~ 6 c/s), 2·92 (2H, broad d, *J* ~ 6 c/s), 3·76 (2H, broad

d, $J \sim 6$ c/s), 4·15 (4H, q, $J = 7$ c/s), 5·2–5·9 (4H, m); IR ν_{max}^{film} (cm^{-1}) 1740. UV (EtOH) λ_{max} (log ϵ) 320 nm (3·96).

Alkylation of **3c**

Ethyl (dithiocarballyloxy) allyl cyanoacetate, **9c** (R = R′ = allyl). 26·7 g (0·1 mol) of **3c** were treated with 30 g (0·25 mol) allyl bromide in 100 ml abs EtOH and stirred for 3 hr at room temp. The solvent was evaporated and the residue extracted with CH_2Cl_2 and washed with water. The organic phase was dried and the solvent evaporated yielding nearly pure **8c** (R = R′ = allyl). Distillation gave **9c** (R = R′ = allyl), 13·2 g (49%) b.p. 130–32°/0·1 mmHg; $n_D^{25} = 1{\cdot}5440$; (Found: C, 53·25; H, 5·55; N, 5·02. $C_{12}H_{15}NO_2S_2$ requires: C, 53·53; H, 5·62; N, 5·20%). NMR (CCl_4) 1·34 (3H, t, $J = 7$ c/s), 3·10 (2H, broad d, $J = 6$ c/s), 3·96 (2H, broad d, $J = 6$ c/s), 4·28 (2H, q, $J = 7$ c/s), 5·0–6·2 (6H, m); IR ν_{max}^{film} (cm^{-1}) 3020 (m), 2990 (m), 1750 (s), UV (EtOH) λ_{max} (log ϵ) 318 nm (3·96).

Ethyl (dithiocarbocrotyloxy) crotylcyanoacetate, **9c** (R = R′ = crotyl), was prepared as above. The crude product consisted of **8c** (R = R′ = crotyl). Distillation gave **9c** (R = R′ = crotyl), 17·1 g (54%) b.p. 152–54°/0·2 mmHg, $n_D^{25} = 1{\cdot}5376$. (Found: C, 56·98; H, 6·33; N, 4·32. $C_{14}H_{19}NO_2S_2$ requires: C, 56·56; H, 6·44; N, 4·71%); NMR (CCl_4) 1·30 (3H, t, J = c/s), 1·72 (6H, broad d, $J = 6$ c/s), 2·95 (2H, broad d, $J = 6$ c/s), 3·83 (2H, broad d, $J = 6$ c/s), 4·23 (2H, q, $J = 7$ c/s), 5·3–6·0 (4H, m); IR ν_{max}^{film} (cm^{-1}) 3020 (m), 2990 (m), 1750 (s); UV (EtOH) λ_{max} (log ϵ) 318 (3·88).

Preliminary kinetic measurements on the rearrangement of **8c** (R = R′ = allyl) *and* **8c** (R = R′ = crotyl). A mixture consisting of 86% **8c** (R = R′ = allyl) and 14% **9c** (R = R′ = allyl) was heated to 48·8–49·4° in the NMR tube (solvent CCl_4) and the integrals of the signals at 3·62–3·73 ppm and 3·01–3·85 ppm were measured. A good first order correlation was obtained, with a rate constant $k = 1{\cdot}3 \cdot 10^{-4}\ sec^{-1}$ corresponding to a reaction half-life $t_{1/2} = 89$ min. Similarly $k = 3{\cdot}6 \cdot 10^{-4} sec^{-1}$ and $t_{1/2} = 31$ min was measured at 60·5–9°. However, for the conversion of 100% **8c** (R = R′ = crotyl) to **9c** (R = R′ = crotyl) the reaction order was less well defined, but rate constants were measured, assuming a first order reaction. (For an explanation of this deviation see Eq 11). The reaction was run in *o*-dichlorobenzene. At 100·0–7°: $k = 1{\cdot}2 \cdot 10^{-4} sec^{-1}$ and $t_{1/2} = 93$ min. At 109°: $k = 3{\cdot}2 \cdot 10^{-4}\ sec^{-1}$, $t_{1/2} = 36$ min. At 120°: $k = 5{\cdot}5 \cdot 10^{-4}$, $t_{1/2} = 21$ min.

Alkylation of **3d**

Bis (allylthio) methylene malodinitrile, **8d** (R = R′ = allyl), was prepared as above from 11 g (0·05 mol) **3d** and 12·1 g (0·1 mol) allyl bromide. Distillation gave 4·5 g (41%) b.p. 122–124°/0·1 mm Hg; $n_D^{25} = 1{\cdot}6052$. (Found: C, 53·75; H, 4·56; N, 12·53; $C_{10}H_{10}N_2S_2$ requires: C, 54·06; H, 4·54; N, 12·61%); NMR (CCl_4) 3·85 (4H, broad d, $J = 6$ c/s), 5·2–6·2 (6H, m); IR ν_{max}^{film} (cm^{-1}) 3020 (w), 2220 (s), 1630 (m), 1450 (s); UV (EtOH) λ_{max} 335 nm.

Bis (crotylthio) methylene malodinitrile, **8d** (R = R′ = crotyl) was prepared as above from 11 g (0·05 mol) **3d** and 13·5 g (0·1 mol) crotyl bromide. Distillation gave 7·4 g (59%) b.p. ~100°/10^{-4} mmHg; $n_D^{25} = 1{\cdot}5974$. The compound crystallized on standing m.p. 36–37°. (Found: C, 57·03; H, 5·72; N, 10·97. $C_{12}H_{14}N_2S_2$ requires: C, 57·59; H, 5·64; n, 11·19%); NMR (CCl_4) 1·72 (6H, broad d, $J = 6$ c/s), 3·80 (4H, broad d, $J = 6$ c/s), 5·1–6·0 (4H, m); IR ν_{max}^{film} (cm^{-1}) 3020 (w), 2990 (w), 2220 (s), 1630 (w), 1440 (s); UV (EtOH) λ_{max} (log ϵ 330 (4·04).

Alkylation of **4**

Diethyl (dithiocarbomethoxy) allylmalonate, **9a** (R = Me, R′ = allyl). 6·0 g (0·022 mol) **4a** (R = allyl) were stirred with 1·2 g (0·022 mol) KOH in 25 ml THF and then treated with 5 g (excess) MeI for 2 hr at room temp. The mixture was filtered and the solvent evaporated. Distillation gave 3·8 g (63%) b.p. 120–26°/0·1 mmHg; $n_D^{25} = 1{\cdot}5223$. (Found: C, 49·81; H, 6·29; $C_{12}H_{18}O_4S_2$ requires: C, 49·65; H, 6·25%); NMR (CCl_4) 1·25 (6H, t, J = = 7 c/s), 2·62 (3H, s), 3·03 (2H, broad d, $J = 6$ c/s), 4·18 (4H, q, $J = 7$ c/s), 4·8–6·0 (3H, m); IR ν_{max}^{film} 1730 (s); UV (EtOH) λ_{max} 317 (3·97).

Diethyl (methylthio-, crotylthio-) methylene malonate, **8a** (R = Me, R′ = crotyl), *and diethyl (dithiocarbomethoxy) 1-methylallylmalonate*, **9a** (R = Me, R′ = 1-methylallyl). 5·0 g (0·020 mol) **4a** (R = Me) were stirred with 1·2 g (0·022 mol) KOH in 50 ml THF and then treated with 5 g (excess) crotyl bromide for 18 hr at room temp. Work up as above gave 4·3 g (71%) b.p. 128–30°/0·05 mmHg; $n_D^{25} = 1{\cdot}5319$; NMR showed a mixture of **8a** (R = Me, R′ = crotyl) and **9a** (R = Me, R′ = 1-methylallyl), and further work up on TLC of 0·94 g of the distilled fraction gave nearly pure **9a**: 0·33 g; $n_D^{25} = 1{\cdot}5270$, NMR (C_6D_6) 1·00 (6H, t, $J = 7$ c/s), 1·34 (3H, d, $J = 7$ c/s), 2·23 (3H, s), 3·2–3·9 (1H, m), 4·04 (4H, q, $J = 7$ c/s), 4·8–5·2 (2H, m), 6·0–6·6 (1H, m); IR ν_{max}^{film} (cm^{-1}) 1730 (s); UV (EtOH) λ_{max} (log ϵ) 317 nm (3·97), **8a**: 0·36 g; $n_D^{25} = 1{\cdot}5361$. (Found: C, 51·21; H, 6·84; $C_{13}H_{12}O_4S_2$ requires: C, 51·31; H, 6·63%); NMR (C_6D_6) 1·03 (3H, t, $J = 7$ c/s), 1·10 (3H, t, $J = 7$ c/s), 1·48 (3H, broad d, $J = 5$ c/s), 2·08 (3H, s), 3·30 (2H, broad d, $J \simeq 5$ c/s), 4·05 (2H, q, $J = 7$ c/s), 4·13 (2H, q, $J =$ 7 c/s), 5·23–5·7 (2H, m); IR ν_{max}^{film} (cm^{-1}) 1705(s), 1510(m); UV (EtOH) λ_{max} 315 nm; NMR of these two fractions showed both a mixture of **9a**: **8a** = 1·6 on prolonged standing at room temp.

Diethyl (dithiocarbomethoxy) crotylmalonate, **9a** (R = Me, R′ = crotyl) was prepared from 6 g (0·024 mol) **4a** (R = Me), 1·44 g (0·026 mol) KOH in 25 ml THF, and 7 g (excess) 1-methyl-allyl chloride. The mixture was stirred overnight and then boiled for 3 hr. Work up as usual gave 5·7 g (78%) b.p. 130–32°/0·05 mmHg, $n_D^{25} = 1{\cdot}5238$. (Found: C, 51·42; H, 6·84. $C_{13}H_{20}O_4S_2$ requires: C, 51·31; H, 6·63%); NMR (CCl_4) 1·24 (6H, t, $J = 7$ c/s), 1·6 (3H, broad d, $J \simeq 5$ c/s), 2·60 (3H, s), 2·93 (2H, broad d, $J \simeq 5$ c/s), 4·13 (4H, q, $J = 7$ c/s), 5·3–5·6 (2H, m); IR ν_{max}^{film} (cm^{-1}) 3020 (w), 2960 (m), 2220 (w), 1740 (s), 1630 (m); UV (EtOH) λ_{max} 315 nm.

Alkylation of **3b**

(a) **7b** (R = Me K salt) was synthesized from 25 g (0·1 mol) **3b** dissolved in 50 ml water by adding 14 g (0·1 mol) MeI at 0–5°. After 3 hr the formed solid was filtered and washed with water and chloroform. Drying in exsiccator gave 20 g (88%). Recrystallization from MeOH gave m.p. 234°. (b) 25 g (0·1 mol) **3b** in 150 ml MeOH were treated with 14 g (0·1 mol) MeI at 15° for 6 hr. The mixture was filtered and the solvent evaporated. The residue was extracted with chloroform giving 5 g (25%) of **8b** (R = R′ = Me).[5]

Methyl [*(methylthio, crotylthio)methylene*] *cyanoacetate*, **8b** (R = Me, R′ = crotyl). Alkylation of **7b** (R = Me; K salt) was performed by the usual procedure by alkylation in MeOH with crotyl bromide giving **8b** (R = Me, R′ = crotyl) in 38% yield, and by ion pair extraction in 69% yield: 22·7 g (0·1 mol) **7b** (R = Me; K salt) were dissolved in a water/MeOH mixture and treated with a mixture of 3·4 g (0·01 mol) tetrabutylammonium-

hydrogensulphate and 5 ml (0·01 mol) 2 N NaOH. Then 100 ml chloroform and 14 g (0·14 mol) crotyl bromide were added. After 2 hr the chloroform was separated, washed with water and evaporated. The residue was poured in ether, filtered, and the solvent evaporated. Distillation gave **8b** (R = Me, R′ = crotyl) 16·6 g (69%); b.p. 60°/ ~ 10^{-4} mmHg, n_D^{25} = 1·5964. (Found: C, 49·25; H, 5·37; N, 5·59. $C_{10}H_{13}NO_2S_2$ requires: C, 49·38; H, 5·39; N, 5·76); NMR (CCl_4) 1·74 (3H, broad d, J = 6 c/s), 2·54 and 2·73 (3H, s), 3·7–3·9 (2H), 3·82 (3H, s), 5·3 (2H, m); IR ν_{max}^{film} (cm^{-1}) 2210 (m), 1700 (s), 1450 (m); UV (EtOH) λ_{max} (log ϵ) 330 nm (4·04).

Alkylation of **6b** (R = Me; polymer)

Methyl [(methylthio, benzylthio)methylene] cyanoacetate, **8b** (R = Me, R′ = $PhCH_2$). 2·28 g (0·0121 mol) **6b** (R = Me; polymer) were dissolved in Et_3N and the excess Et_3N evaporated. The residue oil was dissolved in CH_2Cl_2 and treated with 5 ml (excess) benzyl chloride and stirred for 5 hr at room temp. The solvent was evaporated and the residue extracted with ether. Evaporation of this gave 0·72 g (26%) crystals of m.p. 77–79° (lit.[18] 78–80°) of **8b** (R = Me, R′ = $PhCH_2$).

Alkylation of 1·33 g (0·005 mol) **6b** (R = $PhCH_2$) with excess MeI by the same procedure as above gave 1·0 g (72%) of **8b** (R = Me, R′ = $PhCH_2$).

Thermolysis of **8b** (R = Me, R′ = crotyl). 5·84 g (0·023 mol) **8b** was placed in a vigreux distillation apparatus and heated on an oil bath to 170° at 0·05 mmHg for about ½ hr. The receiver was cooled in solid CO_2/acetone and the distillate (1·80 g) was analysed by NMR, GLC and MS. GLC/MS showed three peaks: **13** (8%) of *m/e* 94 with retention time identical to an authentic sample of MeSSMe. **14** (45%) and **15** (47%) with nearly identical mass spectra (*m/e*): 104 (6%), 103 (8%), 102 (72%), 87 (60%), 55 (100%). The NMR (CCl_4) spectrum of the mixture was interpreted as follows and found to be consistent with lit.[21] data on MeScrotyl and MeS(1-Me allyl): 8% **13**, 1·98 (6H, s) 43% **14**, 1·73 (3H, broad d, J = 5 c/s), 1·93 (3H, s), 2·96 (2H, broad d, J = 5 c/s), 5·3–6·0 (2H, m). 49% **15**, 1·30 (3H, d, J = 7 c/s), 1·93 (3H, s), 3·14 (1H, p, J = 7 c/s), 4·7–6·0 (3H, m). The remaining solid in the distillation flask was washed with CCl_4 yielding 2·50 g (77%) m.p. ~ 230° (lit.[5] m.p. 245–250°) of 2,4-bis-(carbomethoxy-cyan-methylen)-1,3-dithia-cyclobutan; IR ν_{max}^{KBr} (cm^{-1}) 2220 (m), 1700 (s), 1610 (w), 1570 (s), 1300 (s); MS (direct inlet): 284 (10%), 283 (12%), 282 (95%), 253 (5%), 252 (5%), 251 (58%), 224 (18%), 193 (23%), 141 (25%), 110 (33%), 97 (45%), 82 (58%), 59 (97%), 44 (100%). (For MS of similar compounds see Ref 22).

Thermolysis of **8d** (R = R′ = allyl). 2·1 g (0·0096 mol) of **8d** (R = R′ = allyl) were treated as above at 180° for ½ hr. The distillate amounted to 0·36 g (30%), n_D^{25} = 1·4898 identical with an authentic sample of allylsulphide (n_D^{27} = 1·4877). From the remaining tar 0·3 g of starting material was extracted.

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