Tetrahedron Vol. 28, pp. 5923 to 5947. Pergamon Press 1972 Printed in Great Britain

THE INFLUENCE OF SUBSTITUENTS ON PREPARATION AND TAUTOMERISM OF OPEN-CHAIN β-THIOKETOESTERS

STRUCTURE DETERMINATION BY NMR AND IR SPECTROSCOPY

F. DUUS*

Department of Chemistry, Aarhus University, 8000 Aarhus C, Denmark

(*Received in the UK* 25 *July* 1972; *Accepted for publication* 14 *August* 1972)

Abstract– With special regard to the synthesis of β-thioketoesters, the acid catalysed reactions of 36 differently substituted β-keto esters with H_2S have been studied under various conditions in order to determine the influence of the substituents on reaction course. *gem*-Dithiols may also be obtained in good yields by this reaction. Treatment of Tl(I)-salts of β-thioketo esters with alkyl halides results exclusively in S-alkylation. A slow *cis-trans* isomerization of S-alkylated α,β-unsaturated β-mercapto esters through rotation about the C=C double bond is demonstrated. Ethyl thioacetothionoacetate has been prepared by self-condensation of ethyl thionoacetate.

The tautomerism of the β-thioketo esters has been studied by NMR and IR spectroscopy. In the α-H esters, the intramolecularly H-bonded *cis*-enethiol tautomer is predominant. This tautomer is also important in the α-substituted esters but due to steric crowding, H-bonding occurs to the alkoxy O-atom as well as to the carbonyl O-atom; further, the *trans*-enethiol form appears in percentages comparable with those of the *cis*-enethiol form. Ethyl α-isopropyl thioacetoacetate exists almost exclusively in the thione form.

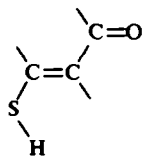
^{1}H NMR chemical shifts and couplings of informative value for structure determination are reported and discussed. The application of the chemical shift of potentially chelated enethiolic protons as an indicator of intramolecular H-bonding is confirmed, although a general application of it (and also of corresponding proton chemical shifts in related systems) as a measure on H-bonding strength is questioned. An intramolecular H-bonding involving chlorine as acceptor atom is presented. New long-range "through bondings" couplings as well as a "through space" coupling involving enethiolic protons are also presented.

INTRODUCTION

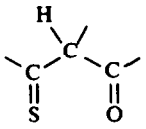
IN A preliminary paper[1] a short description of the tautomerism of some different types of β-thioketo esters was given on the basis of results from NMR and IR spectroscopic investigations. In accordance with these results, the common designation "enethiols" was preferred for the above mentioned and related thiocarbonyl compounds, as the intramolecularly H-bonded *cis*-enethiol tautomer in fact is predominating among both the β-thioketo esters,[1] the β-thioketo thiolesters,[2] and the α-thioacyl lactones.[3] However, the existence of a stable *trans*-enethiol tautomer has also been proved.[3] The tautomer, in which the mercapto group and the CO-containing group are located *cis* to each other with respect to the enethiolic double bond,

* Present address: I.P.S.O.I., Faculté des Sciences, St. Jerome, 13-Marseille (13e), France. Address after October 1st.: Department of Chemistry, Odense University, Niels Bohrs Allé, 5000 Odense, Denmark.

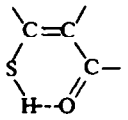
is designated as the *cis*-enethiol form, regardless of the nature of any other substituents on the ethylenic C atoms:



A *trans*-enethiol



B



C *cis*-enethiol

It may often be desirable to compare the same tautomeric forms of different CO-conjugated enethiols. For this reason the above mentioned nomenclature is preferable as compared to the generally more well-defined E,Z-nomenclature,[4] as the use of the latter may give rise to confusion (*e.g.*, the Z-form of ethyl β-mercaptocrotonate equals the *cis*-form, whereas the Z-form of ethyl α-chloro-β-mercaptocrotonate is equal to the *trans*-form).

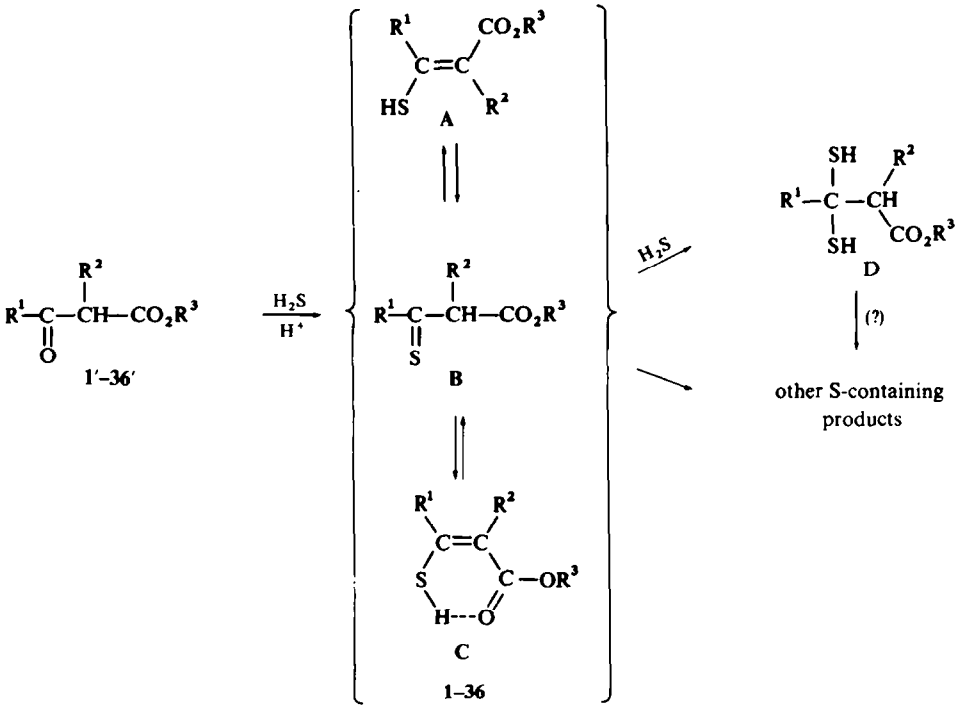
The basic structures **A–C** allow of free variation of one substituent on each of the three C atoms. The influence of these substituents on preparation and structure of the enethiols is the particular subject of the present paper. In order to exclude the consideration of an enol tautomer, the substituents on the CO-carbon atom have been limited to the type —OR, where R is an alkyl group.

RESULTS AND DISCUSSION

Synthetic aspects

The applicability of the enethiols as precursors for several types of S-heterocyclic compounds is easily imagined and has in fact been demonstrated in a few cases.[5–8] However, a more extensive application is conditioned by a convenient synthetic accessibility of the enethiols. With reference to this consideration, a more detailed investigation of the acid catalysed reaction between open-chain β-keto esters and H_2S has been carried out. Often a favourable reaction progress of this, in principle simple reaction, is determined by specific reaction conditions.[1–3,9,10] An uncontrolled reaction may give rise to the formation of other products (*gem*-dithiols,[1,2,9] *sym*-trithianes,[1] cyclic condensation or rearrangement products[1,3,11]) which often complicates the isolation of the enethiol, if at all the latter is present in the reaction mixture (Scheme 1). However, by a suitable choice of reaction medium and reaction temperature, it was found possible to obtain a great number of the desired enethiols in high yields through short-time syntheses.

The β-mercaptocrotonates **1–14** are easily prepared in excellent yields by passing H_2S and dry HCl gas at −60° for 2–3 hr through solutions of the appropriate acetoacetates in MeCN. This method is also usuable for the preparation of β-mercaptothiolocrotonates.[2] The importance of the low reaction temperature is demonstrated by the fact that the same reaction carried out at −40° give rise to a mixture which, besides the desired enethiol, contains about 10% of the corresponding *gem*-dithiol.



SCHEME 1

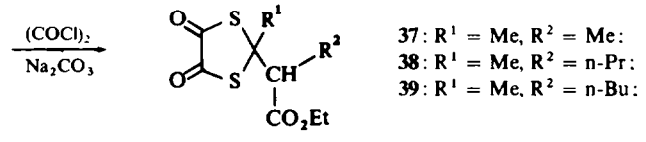
1–14 (R^1 = Me, R^2 = H) R^3	15–21 (R^2 = H, R^3 = Et) R^1	22–26 (R^3 = Et) R^1	R^2
1 Me	**15** Et	**22** Me	Me
2 Et	**16** n-Pr	**23** Me	Et
3 n-Pr	**17** iso-Pr	**24** Me	n-Pr
4 iso-Pr	**18** t-Bu	**25** Me	iso-Pr
5 n-Bu	**19** CH_2—CO_2Et	**26** Me	n-Bu
6 iso-Bu	**20** Ph	**27** Me	$n\text{-}C_8H_{17}$
7 sec Bu	**21** $p\text{-}NO_2$—C_6H_4	**28** Me	$CH_2CH_2CO_2Et$
8 $iso\text{-}C_5H_{11}$		**29** Me	CO_2Et
9 —CH(*iso*-Bu)(Me)		**30** Me	Cl
10 —CH(CH_2-sec.-Bu)(Et)		**31** Ph	Me
		32 Me	allyl
		33 Me	CH_2CO_2Et
		34 Me	CN
		35 Me	COMe
		36 Me	COPh

11 cyclohexyl
12 allyl
13 benzyl
14 1-phenylethyl

The enethiols **15–19** are also obtainable in high yields by use of the above mentioned method. However, with increasing bulkyness of R^1, a complete conversion is conditioned by a simultaneous prolongation of the reaction time (**18**), and a somewhat increased reaction temperature (**17–19**). The known enethiols **20** and **21** are best prepared in ethanolic solutions at 0° during 6–8 hr.[12–14]

The ambiguity of the reaction between β-keto esters and H_2S finds expression especially, when the first mentioned compounds possess an α-substituent. The following description is a result of more than 50 experiments, in which the miscellaneous β-keto esters **22′–36′** were treated with H_2S/HCl under widely varied conditions, and all experiments were during the reaction progress as well as at different steps in the working-up procedure supervised by NMR spectroscopy.

Treatment of the keto esters **22′–24′** and **26′–28′** during few hours with H_2S/HCl in MeCN results even at −60° in a nearly quantitative yield of the corresponding *gem*-dithiols (**D**). However, attempts to obtain the latter compounds analytically pure were rather unsuccessful. Even gentle distillation caused detectable evolution of H_2S due to a partial decomposition of the *gem*-dithiols to the corresponding enethiols. The purity of the distilled *gem*-dithiols was estimated to 90% on the basis of their NMR spectra and elementary analyses. On the other hand, the α-substituated *gem*-dithiols are easily characterized as the stable 1,3-dithiolane-4,5-diones, obtainable by treatment of the dithiols with oxalyl chloride:[9]



When the reaction of one of the keto esters in question (**22′–24′** and **26′–28′**) with H_2S/HCl is carried out at about −40° in ethanolic solution, a mixture containing the derived enethiol as the main component is obtained. Fractional distillation of this crude mixture through an efficient column gives an enethiol of 90–95% purity. Subsequent purification *via* the lead salt of the enethiol leads to the analytically pure product. The preceding distillation seems important, as treatment of the crude mixture directly with $Pb(OAc)_2$ as a rule leads to the formation of a paste or a dingy suspension, dependent on the relative amounts of unreacted ester, *gem*-dithiol, and other decomposition products in the mixture.

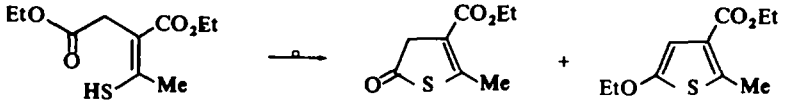
The treatment of ethyl α-isopropyl acetoacetate (**25′**) with H_2S/HCl for some hours at −40° in ethanol results in a mixture of an intensive wine-red colour. This indication on an appreciable content of the thione tautomer **25B** is verified by the NMR analysis of the crude mixture: besides negligible amounts of the *gem*-dithiol **25D**, contents of about 70% of **25B** and 25% of unreacted keto ester could be determined. A considerable extended reaction time had no influence on the product distribution. This is in accordance with the general concept of a thermodynamically controlled reaction, being especially reflected in the present case due to the apparently lacking ability of the thione **25B** to undergo further stabilization by enethiolization. In contact with moisture, the pure thione, obtainable from the crude mixture by fractional distillation through an efficient column, also shows increased tendency to

hydrolysis as compared to the other investigated enethiols. On standing for months, the colour fades due to the formation of a polymer (trimer?),[1] which, however, on attempted distillation again is pyrolysed to the thione **25B** (Experimental).

The syntheses of the enethiols **29–31** by reaction of the corresponding keto esters with H_2S/HCl are not troubled by the formation of *gem*-dithiols. Thus, **29** and **30** are obtained pure in high yields. On the other hand, the sterically crowded ethyl α-methylbenzoylacetate (**31'**) is rather inert towards the H_2S attack, and even a mediocre yield of the enethiol **31** is obtained only under forced reaction conditions.

The preparation of the enethiols **32** and **33** is complicated by the accompanying spontaneous intramolecular cyclization reactions:

32A

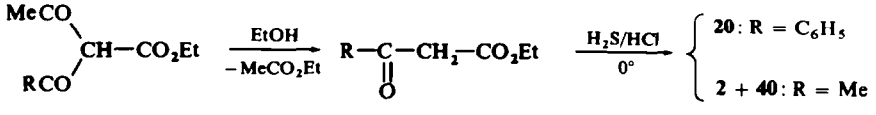


33A

NMR spectroscopic investigations show that only the *trans*-enethiols undergo the cyclization. The former reaction is sufficiently slow to allow for isolation of **32**, but **33** cannot be isolated, although its existence is clearly verified by the NMR spectrum of the mixture. However, these and related cyclization reactions will be described in detail in a forthcoming paper.[15]

Ethyl α-cyanoacetoacetate is completely inert towards the H_2S/HCl treatment, a fact presumably being related to its very high degree of enolization[16] in connexion with a slow tautomerization process. Fortunately, the desired enethiol **34** is easily accessible in another way.[17]

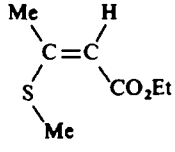
The β-tricarbonyls **35'** and **36'**, also being almost completely enolized,[18,19] are quite unreactive towards H_2S/HCl in MeCN. In ethanolic solution still no reaction occurs at −40°, but at 0° **35'** reacts to give a mixture of ethyl thioacetoacetate (**2**) and the corresponding *gem*-dithiol, ethyl 3,3-dimercaptobutyrate (**40**), whereas **36'** is converted solely to the enethiol **20**. These reaction products are explicable by the assumption of initial solvolysis reactions, after which the produced β-keto esters react with H_2S in the normal way:



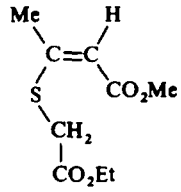
This assumption is supported by the fact that ethyl diacetylacetate (**35'**) in the absence of H_2S, but otherwise under the same reaction conditions as described above, is decomposed to ethyl acetoacetate (**2'**).[20]

As demonstrated above, MeCN may, when used as reaction medium instead of EtOH, decisively affect the reaction course. This is bound up with its greater dissolution capacity (especially at temperatures about or below $-40°$) towards the reacting gases, being directly reflected by the considerably greater increase in the total volume of the mixture during the gas supply. Therefore, the observed alterations should be considered simply as the consequencies of the alterations in reaction rate and existent thermodynamic equilibria being induced by the increased H_2S-concentration.

In contrast to the corresponding β-keto esters,[21] no C-alkylation occurs on treatment of the thallium(I) salts of α-unsubstituted β-thioketo esters with alkyl halides. As expected, the reaction results exclusively in S-alkylation. Normally a mixture of *cis* and *trans* isomers is obtained. Apparently no relationship exists between the *cis–trans* ratio of the alkylated enethiol and that of the enethiol itself, the isomerization thus being merely a consequence of slow rotation about the C=C double bond,[22] and the equilibrium *cis–trans* ratio being sterically determined. For example, on standing at room temperature for a sufficient period of time, the pure *cis*-isomers **41C** and **42C** are converted to isomer mixtures containing 18% and 72%, respectively, of the *trans*-isomer.



41C



42C

Tautomerism and structure elucidation

In earlier studies of thione–enethiol equilibrium systems, Sen[23] and Mitra[24] introduced the iodine titration method, the usefulness of which is based on the assumption of a well-defined, rapid oxidation of the enethiol tautomer to a disulphide. However, this method often leads to erroneous results,[25] and further, it excludes distinction between *cis–trans* isomeric enethiol forms. Therefore, spectroscopic methods of estimation seem preferable, particularly because the possibility of chemical perturbation of the equilibrium position thus is eliminated. Quantitative measuring of equilibrium concentrations of the three possible tautomeric forms **A–C** (Scheme 1) for a given compound is easily carried out with a good accuracy NMR spectroscopically. The lower limit for quantitative determination of concentration (as percentages) was found to be $\sim 2\%$, being determined by the (optimated) signal to noise ratio of the apparatus. However, percentages equal to or less than 2 are still within the measuring uncertainty, therefore the tautomers concerned are neglected in Tables (1, 2, and 4), although they, in fact, in some cases by NMR and as a rule by IR spectroscopy, are unambiguously detectable.

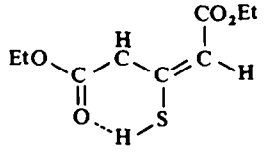
In agreement with temporarily published results,[1–3] all investigated compounds show a more or less pronounced domineering of the *cis*-enethiol form **C**. The less efficient overlap between the sulphur 3p orbital and the carbon 2p orbital in the thione group relative to the corresponding 2p–2p overlap in the ketone group leads

naturally to a more pronounced tendency of enethiolization for thiones as compared to the tendency of enolization for ketones, being well demonstrated in a recent investigation of simple aliphatic thiones.[26] The predominance of the **C**-form relative to the **A**-form is doubtless connected with the additional possibility of stabilization of the former by the formation of an intramolecular H-bonding. Thus, in the IR spectra, the ester CO stretching vibration bands of **C**-forms generally appear at wavenumbers 20–30 cm^{-1} lower than those of corresponding **A**-forms, the latter appearing in the normal region for conjugated ester CO bands (Table 3). In the NMR spectra, *cis*-enethiolic protons, as a consequence of the H-bonding, are markedly deshielded as compared to *trans*-enethiolic protons. Unless special substituent effects operate, also the chemical shifts of the α-protons of R^1 are characteristic for each of the three forms **A–C**: for R^1 = Me, δ_{R^1} (**C**) = 2·07–2·20 ppm, δ_{R^1} (**A**) = 2·38–2·47 ppm*, and, influenced by magnetic anisotropy and electric field screening in the thione group, δ_{R^1} (**B**) = 2·67–2·73 ppm. However, signals arising from the thione tautomer (**B**) are not common in the NMR spectra, although the existence of a small amount of this tautomer in most cases is manifested in the IR spectra by the appearance of a weak band in the normal region of isolated ester carbonyl group stretchings (~1740 cm^{-1}). Apart from **25**, in which the **B**-form is predominant, the otherwise too low thione concentration makes the assignment of a thiocarbonyl stretching vibration in the very band-rich region 1050–1300 cm^{-1} rather questionable. On the other hand, the IR spectrum of **25** in contrast to the IR spectra of all other investigated compounds shows a strong absorption band at 1150 cm^{-1} which is assigned to the thiocarbonyl stretching vibration. The wavenumber value is somewhat lower than those recently reported[27] for simple aliphatic thiones. However, the affiliation of this band to the thione function seems incontestable, as the intensity of it is decreased in time in agreement with the slowly proceeding polymerization of the thione.

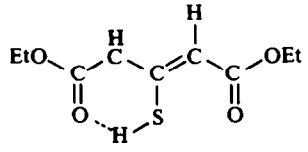
NMR data of the α-unsubstituted β-thioketoesters **1–21** are listed in Table 1 which also contains the calculated percentages of the two enethiol forms, **A** and **C**. Representative NMR spectra for this class of compounds can be found in the preliminary reports.[1,2] Quite generally, the *cis*-enethiol form (**C**) is predominating. The *trans*-enethiol form (**A**) appears as small percentages, whereas the thione form (**B**) in most cases is negligible. Increased bulkyness of the ester alkyl group R^3 (**1–14**) generally leads to a somewhat increased equilibrium concentration of the *trans*-enethiol form (**A**), an effect which is also found in the case of the corresponding thioloesters.[2] With increasing bulkiness of R^1 (**15–18, 20, 21**), the percentages of the *trans*-enethiol form (**A**), evidently due to the simultaneously increased steric crowding in the latter as confirmed by model studies, clearly decrease. Still, the NMR spectrum of **19** (Table 1) shows a comparatively high equilibrium concentration of the *trans*-enethiol form. After all, this is quite understandable, as the tautomer in question also possess the possibility of stabilization through H-bonding formation (**19A**‡). A comparison of IR spectra of enethiols containing similar percentages of the *trans*-enethiol form reveals that this tautomer alone cannot account for the relative intense carbonyl band at 1720 cm^{-1} (ν[C=O], konj.) present in the IR spectrum of **19** (Table 3). It is therefore concluded that also the *cis*-enethiol rotamer **19C**‡ exists.

* In preliminary papers,[1,2] signals in this region were erroneously assigned to thioacetyl protons.

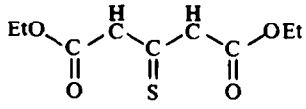
although this form obviously cannot be separately observed in the NMR spectrum due to a too fast rotation (NMR time scale) about the C—S single bond. Further, in the NMR spectrum of **19**, the four magnetically equivalent methylene protons of the thione tautomer (**19B**) appear at 3·87 ppm as a singlet with an intensity sufficient for the reliable determination of the three thione percentages.



19A‡



19C‡



19B

In the NMR spectrum of the parent β-keto ester **19′**, the corresponding methylene proton signal appears at 3·44 ppm.[20] Hence, the replacement of the ketonic O atom by a S atom gives rise to a downfield displacement of the methylene proton signal of 0·43 ppm which agrees well with the 0·45 ppm as predicted according to an empirically found rule.[26] The same rule was corroborated also in the case of the observed thioacetyl proton signals.

The introduction of an α-alkyl substituent in β-ketoesters and β-diketones generally affects a displacement in the tautomeric equilibrium in favour of the keto tautomer.[16,28,29] This is most probably due to the increased steric crowding between R^1, R^2, and CO_2R^3 in the "planar" *cis*-enol tautomer, combined with the

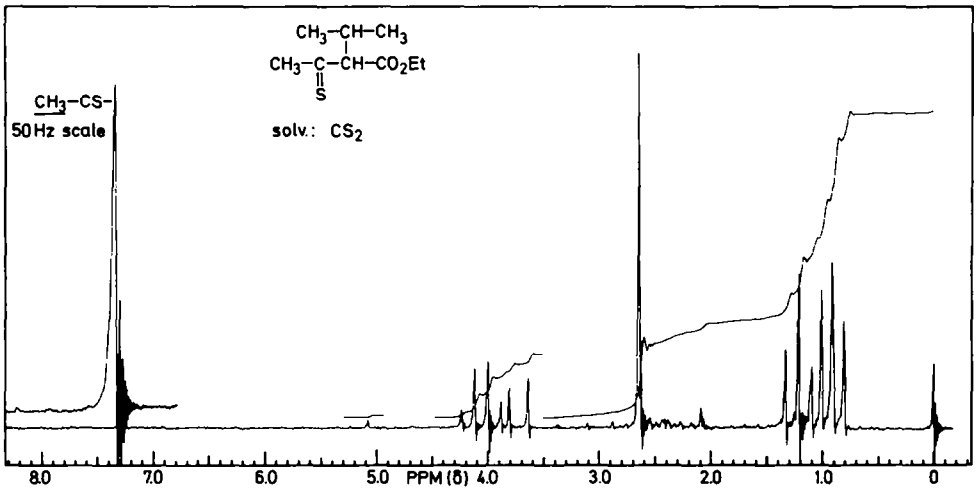


FIG 1. NMR spectrum of ethyl 2-isopropyl-thioacetoacetate (**25**) demonstrating predominance of the thione tautomer. (Solvent: CS_2).

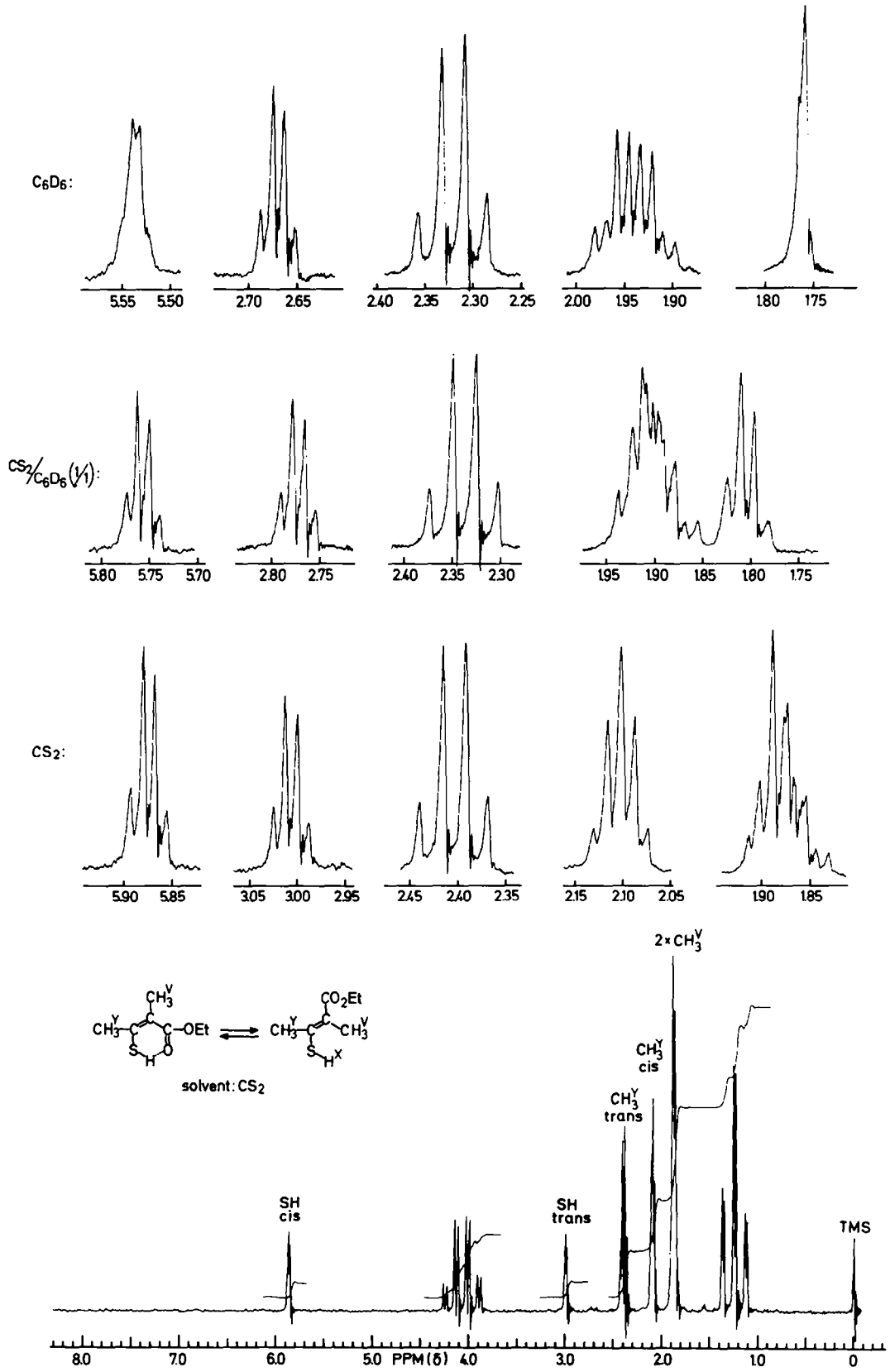
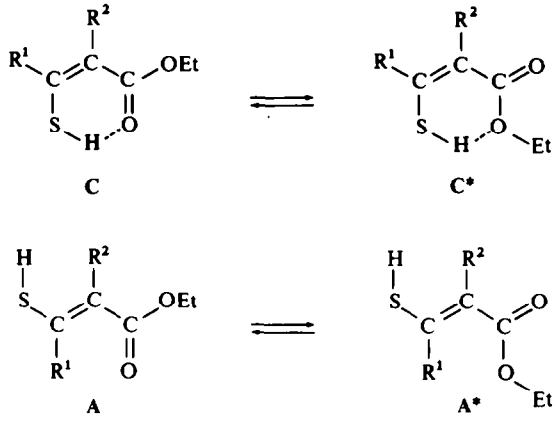


FIG 2. NMR spectrum of ethyl 2-methyl-thioacetoacetate (**22**) showing comparable percentages of the *cis*- and *trans*-enethiol tautomers (solvent: CS_2). The extraction of the coupling constants J_{XY}, J_{YV}, and J_{XV} (Table 2) for both of the tautomers by use of C D

electron-donating effect of the α-alkyl group, which gives rise to an increased electron density in the vicinity of the α-proton in the keto tautomer, thus impeding proton release, and consequently also enolization.[16, 28, 29] Therefore, the investigation of the α-alkylated β-thioketo esters appeared of particular interest with regard to the possible observation of a considerable equilibrium concentration of the thione tautomer. The results are listed in Tables 2 (NMR data, equilibrium percentages) and 3 (IR data). According to expectation the NMR spectrum of **25** (Fig. 1) shows predominance (96%) of the thione tautomer **25B**, but no enhanced thione percentages are found in the cases of **22–24**, **26–28**, **31**, and **32**. Instead considerably increased percentages of the *trans*-enethiol tautomer are observed, as exemplified by the NMR spectrum of **22** (Fig 2). This reflects *a priori* the general instability of the thiocarbonyl function as compared to the CO function.

However, in order to obtain a better understanding of the observed diminution in the *cis–trans* ratio, a more closely model study of all possible CO-conjugated enethiol structures was performed on the assumption that, besides H-bondings, only steric factors are of importance for the estimation of their relative stability (Scheme 2).



SCHEME 2

It was found that the steric crowding is considerably more pronounced in the "normal" intramolecularly H-bonded *cis*-enethiol structure **C**, than it is in the structures **A**, **A***, and **C***. Whereas the structures **A** and **A*** certainly are spectroscopically indistinguishable, a sufficiently slow rotation of the ester group (as probably affected by the H-bondings) should give rise to spectroscopic distinction between **C** and **C***. The NMR spectra of all enethiols in question show the presence of only one *cis*-enethiol form (Table 2), but, characteristically, in all cases the *cis*-enethiolic proton signal appears at a much higher field (1·2–1·5 ppm) as compared to the same signal in the α-unsubstituted analogues (*cis*(**C**)-enethiol form). Evidently, H-bondings are less effective in the α-alkylated compounds, as also indicated by the reduced coupling between the β-Me protons (R^1), and the *cis*-enethiolic proton (J_{XY}, see below). However, inspection of the IR spectra (Table 3) clearly reveals the importance of structure **C***: For all α-alkylated enethiols, the absorption band originating from

the vibration of the chelating, conjugated ester-CO function is of exceptionally weak intensity, while the band originating from the non-chelating, conjugated ester-CO vibration is of extremely strong intensity. It is concluded that for the α-alkylated *cis*-enethiols, in contrast to the α-unsubstituted analogues, an equilibrium exists between the predominant **C***-structure and the **C**-structure. In the latter, the stabilizing effect of the intramolecular H-bonding is neutralized by the enhanced steric crowding. The **C**–**C*** conversion is slow enough to allow for IR spectroscopic distinction between the rotamers, but too fast for distinction by NMR spectroscopy. Hence, an average signal at higher field is observed for the *cis*-enethiolic proton. The individual *cis–trans* ratios are merely determined by the actual steric crowding in the structures **A**, **A***, **C**, and **C***. For example, the steric interaction between R^1 and the CO_2Et group is greater in **31A** than in **22A** which, in connection with the greater bulkyness of the CO_2Et group relative to the Me group, give rise to relatively high percentages of the *cis*-form **31C** (84%) as compared to those of **22C** (52%).*

On the basis of the above mentioned results, it becomes clear that electron-withdrawing α-substituents, which in the cases of β-keto esters and β-diketones cause enhanced degree of enolization,[16, 29, 30] hardly can affect greater displacements in the tautomeric equilibrium of the β-thioketo esters. Thus, **29**, **30**, and **34** are practically completely enethiolized. In the cases of **29** and **34** only the *cis*-enethiol tautomer exists. Apparently, the **C***-rotamer is completely unimportant in the former, and of diminished importance in the latter compound (Table 3). In the case of the α-chloro substituted compound **30**, model studies suggest a likely contribution of the **C**-structure (Scheme 2) to the thereby more stabilized *cis*-enethiol tautomer, as also conformed by the IR spectrum (Table 3). It is therefore interesting to observe that the equilibrium percentages of the *cis*- and *trans*-enethiol forms in fact are comparable. Moreover, the *cis–trans* isomerization process is found to proceed anomalously slowly. These facts indicates the existence of a stabilizing intramolecular H-bonding also in the *trans*-form, in which the chlorine atom acts as acceptor. The existence of the H-bonding is further verified by the NMR spectrum of **30** (Fig 3): the *trans*-enethiolic proton signal appears at a remarkably low field, exhibiting a well-defined quartet structure in consequence of an exceptional coupling (see below) between the mercapto-proton and the methyl protons (R^1).

Although an unusual low field appearance of the NMR signal of a potentially chelated proton is generally accepted as an indication on the existence of an intramolecular H-bonding,[16, 31, 32] any general conclusion concerning the strength of the H-bonding as being directly reflected by the chelated proton chemical shift[1, 16, 31, 32] should be avoided. Evidently, any type of rotamism (for example **C** ⇄ **C***) may influence the latter, and the effect of possible intermolecular proton exchange processes[32] should as well not be neglected. Apart from special cases,[34] H-bondings involving oxygen as acceptor atom are generally stronger than those involving an accepting S atom.[35] Thus, compared with **2**, ethyl thioacetothionacetate (**43**) exhibits greater equilibrium percentages of the *trans*-enethiol form (10% in **43** as compared to 4% in **2** (Tables 4 and 1, respectively)) which indicates the relatively less effective H-bonding in **43C**. Nevertheless, the *cis*-enethiolic proton signal appears at a considerably lower field in the case of **43C** (Table 4) as in the case of **2C** (Table 2), but

* For simplicity, no distinction is made here between the rotamers **C** and **C***.

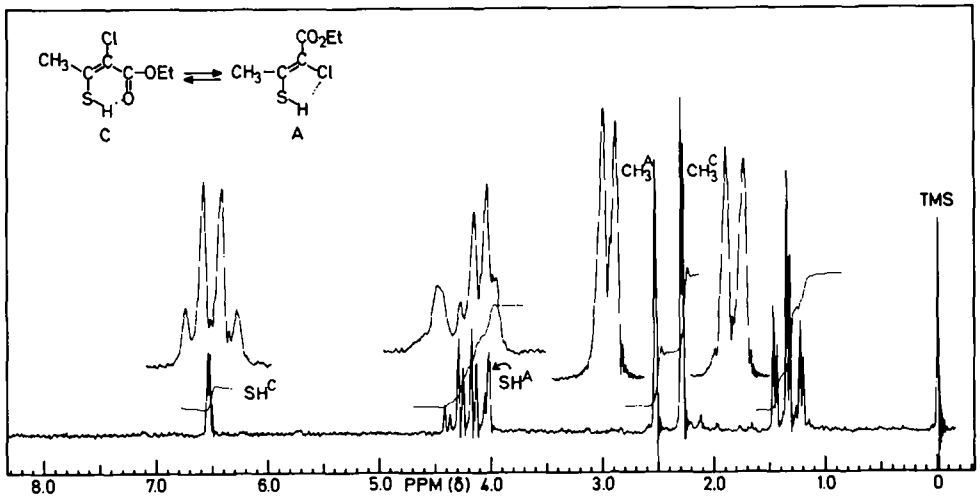
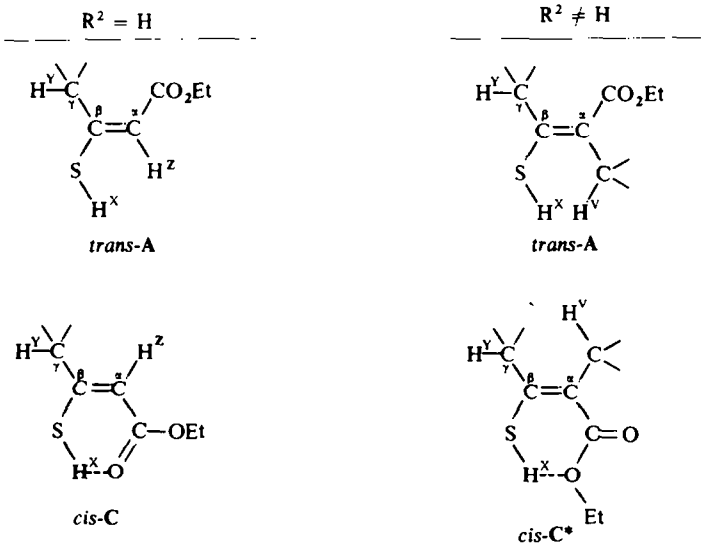


FIG 3. NMR spectrum of ethyl 2-chloro-thioacetoacetate (**30**) showing predominance of the *cis*- and *trans*-enethiol tautomers in comparable percentages (solvent: CCl_4).

this phenomenon is probably connected with the higher paramagnetic screening effect of the C=S group relative to the C=O group.[36]

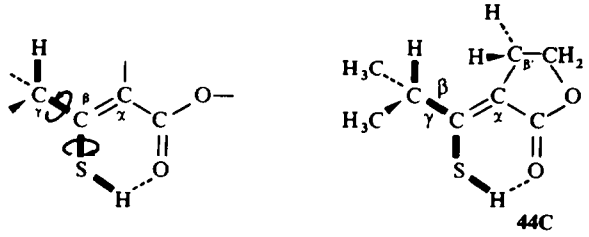
Long-range ^1H NMR couplings in the enethiols

For all investigated β-thioketo esters existing partly or completely in the *cis*-enethiol form, the latter is characterized by a long-range coupling ($^4J_{XY}$) between the *cis*-enethiolic proton and the γ-protons (Scheme 3). This appears quite interesting as



SCHEME 3

a similar coupling, with the exception of certain medium-sized 2-ethoxycarbonyl cyclanones,[37] is absent in corresponding enol forms of β-keto esters.[16] Moreover, the same coupling is never observed for the *trans*-enethiol forms which neither are capable of forming an intramolecular H-bonding. Thus, a relationship between the existence of the latter and the presence of the coupling in question seems obvious. Due to the H-bonding, the free rotation about the C—S single bond becomes restricted, as the *cis*-enethiolic proton preferentially occupies the "chelated" position. However, this is favourable for coupling to the γ-protons, as hereby the important "straightest zig-zag" path for "through bondings" coupling is obtained.[38] This conception is further supported by the fact that the α-chlorosubstituted ester **30** both in the *cis*- and the *trans*-enethiol form exhibits this coupling, in the latter case due to H-bonding between the thiolic proton and the α-Cl atom. If one or two of the γ-protons are substituted by an alkyl group, $^4J_{XY}$ decreases. However, this may be expected. Due to the free roration about the C^β—C^γ single bond, the γ-proton(s) will occupy for simple statistical reasons the position most favourable for maximum coupling (as depicted below) to a lesse extent in the latter cases. It should be noted that for the α-thioacyl lactones,[3] $^4J_{XY}$ increases, when γ-alkyl substitution occurs. However, in this case, as also confirmed by model studies, the rotation about the C^β—C^γ bond is greatly sterically affected by the β′-ring protons, thus giving rise to the preferred conformation exemplified below by the *cis*-enethiol form of 2-thio-isobutyryl-γ-butyrolactone[3] (**44C**):



44C

Moreover, the "effective" coupling constant ($^4J_{XY}$) is always greater in the α-unsubstituted *cis*-compounds (existing in the rotameric **C**-form) than in the α-substituted analogues. In the latter case, where the **C***-rotameric structure is important, the H-bonding apparently is less efficient, and the rotation about the C—S single bond therefore becomes less restricted. Finally, the coupling in question is slightly smaller in the thionester **43C** than in the corresponding ester **2C** (0·8 Hz, and 1·2 Hz, resp.), a fact, which confirms the conception of the reduced H-bonding capacity of the thiocarbonyl S-atom as compared to the carbonyl O-atom. Thus, for the enethiols, intermolecular proton exchange processes evidently are too slow to have any appreciable influence on $^4J_{XY}$. This need not necessarily be so in the corresponding enols, and a considerably faster exchange process of the enolic proton may very well account for the apparent non-existence of the coupling in question in the latter compounds.

The allylic coupling ($^4J_{YZ}$) present in the α-unsubstituted compounds is unexceptional, and seems to be of the same magnitude in both the *cis*- and the *trans*-enethiol forms (**43**, Table 4). In the α-alkylated compounds, the homoallylic coupling constant $^5J_{YV}$ is somewhat more variable, but generally, within the same pair of

isomers, the *trans*-coupling is always the greater. This is in accordance with the findings from the study on the related thioacyl lactones.[3]

In the α-unsubstituted compounds (R^2 = H), a small coupling between the *cis*-enethiolic proton and the vinylic proton ($^4J_{XZ}$) is measurable in a few cases. In the α-alkyl substituted compounds **22–24** and **26–28**, an interesting coupling ($^5J_{XV}$) occurs between the thiolic proton and the α-protons of the α-substituent (Scheme 3), but only in the *trans*-enethiol forms. Evidently, this coupling must be regarded as a "through space" coupling, as no evidence at all is found for the existence of a similar coupling in the *cis*-enethiol forms.

TABLE 1. ^{1}H NMR CHEMICAL SHIFTS (δ-VALUES, ppm) AND COUPLING CONSTANTS (Hz) OF β-THIOKETO-ESTERS **1**–**21**.[a] PERCENTAGES OF ENETHIOL TAUTOMERS[b] IN EQUILIBRIUM AT 38°

The following abbreviations are used: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br. (broad). For further explanation of used symbols, see Schemes 1 and 3. Unless stated to the contrary, the solvent used is CCl_4

	trans-**A**		*cis*-**C**						
	δ_{R^1}	%	δ_{R^1}	δ_{SH}[c]	δ_{HZ}	J_{XY}	J_{YZ}	J_{XZ}	%
1	2·46	5	2·13 t	7·26 q	5·78 q	1·1	1·1	–	95
2	2·46	4	2·13 t	7·30 q	5·76 q	1·2	1·2	—	96
3	2·43	5	2·13 t	7·32 q	5·75 q	1·1	1·1	–	95
4	2·44	5	2·11 t	7·31 q	5·71 q	1·15	1·15	—	95
5	2·47	6	2·13 t	7·34 q	5·79 q	1·1	1·1	—	94
6	2·44	7	2·13 t	7·30 q	5·76 q	1·15	1·15	–	93
7	2·44	6	2·13 t	7·33 q	5·75 q	1·15	1·15	–	94
8	2·43	7	2·12 t	7·33 q	5·73 q	1·1	1·2	–	93
9	2·44	7	2·12 t	7·33 q	5·71 q	1·15	1·15	—	93
10	2·45	10	2·12 t	7·32 q	5·73 q	1·1	1·1	—	90
11	2·43	9	2·11 t	7·32 q	5·72 q	1·1	1·15	—	91
12	2·45	5	2·14 t	7·23 q	5·78 q	1·1	1·1	—	95
13	2·42	8	2·07 t	7·21 q	5·78 q	1·1	1·1	—	92
14	2·40	9	2·07 t	7·21 q	5·78 q	1·1	1·1	—	91
14[d]	2·38	7	2·14 dd	5·68 m	5·88 dq	0·5	1·15	0·3	93
15	–	⩽2	2·36 br. q[e] 1·20 t[e]	7·37 t	5·75 t	0·9	0·95	–	⩾98

	trans-A		*cis*-C						
	δ_{R^1}	%	δ_{R^1}	δ_{SH}[c]	δ_{HZ}	J_{XY}	J_{YZ}	J_{XZ}	%
16		≤2	2·32 br. t[e] 1·63 br. m[e] 0·95 t[e]	7·43 t	5·74 t	1·0	0·85	—	≥98
17	—	≤2	2·57 br. m[e] 1·22 d[e]	7·64 d	5·78 d	0·65	0·65		≥98
18	—	~0	1·24 s	8·19 s	5·82 s	—	—	—	~100
19[f]	3·70	8	3·23 br. t	7·23 dt	5·88 dt	1·05	0·9	0·3	89
20[g]		≤2	7·2–7·7 m	7·94 s	6·10 s	—	—	—	≥98
21		≤2	7·6–8·3 m[h]	8·08 d	6·13 d	—		0·3	≥98

[a] The trivial NMR data of estergroup protons are omitted (see Ref 1).

[b] Thione percentages have been neglected. Although the presence of small amounts of the thione tautomer in most cases is indicated by the pale colour of the compounds and by IR (Table 3), NMR signals corresponding to this tautomer are (with the exception of **19**, see text) either not observable or detectable only to an extent allowing for estimation of the thione percentages as less than 2 (small peaks at ~2·67 ppm corresponding to the thioacetyl protons were observed for **3**, **9**, **13** and **14**).

[c] In rather concentrated solutions, δ_{SH} is normally sensitive to small changes in concentration. The tabulated values are obtained by extrapolation to zero concentration.[1]

[d] Solvent: CD_3CN (compare Ref 2).

[e] J = 7–7·5 Hz.

[f] Solvent: CS_2·δ_HZ(A): 5·91 ppm (t, J = 0·65 Hz). Percentages of thione tautomer: 3 (for a further discussion of the spectrum, see text).

[g] Compare Ref 12.

[h] Well-defined AA'BB' pattern.

TABLE 2. ^{1}H NMR CHEMICAL SHIFTS (δ-VALUES, ppm) AND COUPLING CONSTANTS (Hz) OF α-SUBSTITUTED β-THIOKETOESTERS.[a] RELATIVE PERCENTAGES OF ENETHIOL TAUTOMERS[b] AT EQUILIBRIUM AT 38°

the following abbreviations are used: s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), m (multiplet), and br. (broad). For further explanation of the used symbols, see Schemes 1 and 3. Unless stated to the contrary, the solvent used is CCl_4

	δ_{R^1}	δ_{SH}[c]	δ_{R^2}	J_{XY}	J_{XV}	J_{YV}	%
22A	2·44 q	2·87 q	1·91 dq	—	0·7	1·45	48
22C	2·13 p	6·08 q	1·91 q	0·8	—	0·9	52
23A	2·41 t	2·76 t	2·40 br. q[d] 1·03 t[d]	—	0·65	0·75	47

	δ_{R^1}	δ_{SH}[c]	δ_{R^2}	J_{XY}	J_{XV}	J_{YV}	%
23C	2·17 p (dt)	5·88 q	2·40 br. q[d] 1·01 t[d]	0·75	—	0·35	53
24A	2·40 t	2·74 t	2–2·5 1–1·7 m 0·93 t[d]	—	0·6	0·75	49
24C	2·17 p (dt)	5·76 q	2–2·5 1–1·7 m 0·91 t[d]	0·7	—	0·35	51
25C[e]	2·09[f]	5·08[g] m	?	—	—	—	~4
26A	2·39 t[h]	2·73 t	2·1–2·6 1·1–1·6 m 0·93 t[h]	—	0·6	?	48
26C	2·18 p[h]	5·78 q	2·1–2·6 1·1–1·6 m 0·93 t[h]	0·7	—	?	52
27A	2·40 m[h]	2·73 t[h]	2·1–2·5 0·7–1·5 m	—	?	?	37
27C	2·15 m[h]	5·78 q[h]	2·1–2·5 0·7–1·5 m	0·7	—	?	63
28A[i]	2·39 t[h]	3·03 t	2·0–2·9 br. m	—	0·5	~0·7	37
28C[i]	2·16 p[h]	5·88 q	2·0–2·9 br. m	0·75	—	~0·3	63
29[j]	2·20 d	6·85 q	—	1·0	—	—	~100
30A	2·54 d	4·02 q	—	0·65	—	—	51[k]
30C	2·30 d	6·77 q	—	0·95	—	—	49[k]
31A	7·0–7·5 m	2·99[j] q	2·07 d	—	0·65	—	16
31C	7·0–7·5 m	5·10 s	1·74 s	—	—	—	84
32A	2·44 t	2·92 t	3·12 dm 4·7–5·2 5·4–6·1 m	—	0·6	0·7	32[m]

	δ_{R^1}	δ_{SH}[c]	δ_{R^2}	J_{XY}	J_{XV}	J_{YV}	%
32C	2·15 p (dt)	6·16 q	3·12 dm 4·7–5·2 5·4–6·1 m	0·8	—	0·35	68[n]
34C	2·54 d[o]	7·89 q[o]	–	0·9	—	—	~100

[a] The trivial NMR data for the estergroup protons[1] are not tabulated. The chemical shifts are different for the isomeric enethiols, the *cis*-protons always being more deshielded than the *trans*-protons ($\Delta\delta_{CH_3} \simeq 4$ ppm, $\Delta\delta_{CH_2} \simeq 3$ ppm).

[b] With the exception of **25**, where the thione form is predominant, the tabulated enethiol percentages have been calculated neglecting the existence of the thione tautomer. The latter, whose presence is indicated by the colour of the compounds and in some cases by IR (Table 3), has been detected by NMR only in few cases (thioacetyl protons: 2·73 ppm (**22**), 2·68 ppm (**23**, **24**, **27**)), and the percentages could be estimated as equal to or less than 2.

[c] Chemical shifts at infinite dilution. On dilution, SH-signals are displaced against limit positions (δ_{SH}(**A**): upfield, δ_{SH}(**C**): downfield[1, 3]) as a consequence of diminished intermolecular interactions (intermolecular H-bondings).

[d] $J \simeq 7$ Hz

[e] NMR data for **25B**: δ_{CH_3CS} (2·68, s); δ_{CHCS} (3·76, d, J = 10·1); δ^2_{CH} (2·1–2·8, m); $\delta^2_{CH_3}$ (0·88, d, J = 6·1, and 0·98, d, J = 6·1, magnetic nonequivalence): estergroup δ_{CH_2} (4·11, q, J = 7·0), and δ_{CH_3} (1·24, t, J = 7·0). **25A** is not detectable.

[f] The intensity of the signal increases in time in consequence of the slow formation of the trimer (see Experimental).

[g] Extrapolation to zero concentration is not possible due to the low percentages.

[h] Distorted signals.

[i] Solvent: CS_2.

[j] A≡C

[k] Slow equilibrium process.

[l] Value at normal concentration.

[m] Remarkable shielding of estergroup protons: δ_{CH_3} = 0·75 ppm, δ_{CH_2} = 3·75 ppm (**31C**: δ_{CH_3} = 1·33 ppm, δ_{CH_2} = 4·24 ppm).

[n] Percentages are measured shortly after preparation (*i.e* presumably not at equilibrium) due to the spontaneous, slowly proceeding cyclization of the *trans*-enethiol.

[o] Coupling is observed only in diluted solution, otherwise the Me-signal appears as a singlet, and the SH-signal as a broad singlet (compare Ref 16), presumably in consequence of intermolecular interactions between mercaptoprotons and CN-groups (J_{XY}'s are generally diminished in CD_3CN solution, see Ref. 2 and **14**, Table 1).

TABLE 3. IR ABSORPTION BANDS OF β-THIOKETO ESTERS

Frequencies are in cm^{-1}. Intensities are indicated as follows: s (strong), m (medium), w (weak), vw (very weak), br. (broad), sh (shoulder): solvent: CCl_4

	ν[S–H]	ν[C=O][a]	ν[C=O][b]	ν[C=O][c]	ν[C=C]
1	2455 m, br.	1745 w, sh	1715 w, sh	1690 s	1605 s
2	2455 m, br.	1745 w, sh	1715 w, sh	1690 s	1605 s

TABLE 3– *continued*

	ν[S– H]	ν[C=O][a]	ν[C=O][b]	ν[C=O][c]	ν[C=C]
3	2450 m, br.	1740 w, sh	1710 w, sh	1685 s	1600 s
4	2450 m, br.	1740 w, sh	1710 w, sh	1685 s	1605 s
5	2445 m, br.	1740 wmsh	1710 w, sh	1685 s	1605 s
6	2450 m, br.	1740 w, sh	1710 w, sh	1685 s	1600 s
7	2440 m, br.	1735 w, sh	1705 w, sh	1685 s	1605 s
8	2445 m, br.	1740 w, sh	1710 w, sh	1685 s	1605 s
9	2440 m, br.	1735 vw, sh	1705 w, sh	1685 s	1600 s
10	2440 m, br.	1735 w, sh	1705 w, sh	1680 s	1600 s
11	2445 m, br.	1735 w, sh	1710 w, sh	1680 s	1600 s
12	2450 m, br.	1745 w, sh	1715 w, sh	1690 s	1605 s
13	2455 m, br.	1745 w, sh	1715 w, sh	1690 s	1600 s
14	2450 m, br.	1740 w, sh	1705 w, sh	1685 s	1600 s
15	2440 m, br.	1740 w, sh	1705 w, sh	1685 s	1600 s
16	2440 m, br.	1740 vw, sh	1705 w, sh	1680 s	1595 s
17	2445 m, br.	1745 vw, sh	1710 vw, sh	1680 s	1595 s
18	2420 m, br.	1745 vw	—	1685 1675 s	1585 s
19	2455 m, br.	1750 vs	1720 m	1690 s	1605 s
20	2435 m, br.	1750 w, sh	1705 vw, sh	1675 s	1590 1575 s
21	2430 m, br.	—	1710 vw, sh	1685 s	1610 w, sh 1590 s
22	~2460 w, v br.	—	1710 s	1680 w, sh	1610 m, br.
23	~2470 w, v br.	—	1705 s	1675 w, sh	1600 m, br.
24	~2460 w, v br.	-	1710 s	1675 vw, sh	1600 m, br.
25[d]	~2470 vw, v br.	1740 vs	—		~1600 vw, br.
26	~2470 w, v br.	—	1710 s	1680 w, sh	~1580 m, br.

	ν[S—H]	ν[C=O][a]	ν[C=O][b]	ν[C=O][c]	ν[C=C]
27	~2470 w, v br.	1735 vw, sh	1705 s	1675 w, sh	~1580 m, br.
28	~2470 vw, v br.	1740 vs	1710 s, br.	1680 w, sh	~1580 m, br.
29	2455 m, br.	1740 vs	1720? vw, sh	1695 s	1590 s
30	2470 w, br.	–	1715 s	1680 m	1580 s, br.
31	~2470 vw, v br.	1745 vw, sh	1705 s	1680 w, sh	1590 m, br.
32	~2460 w, v br.	1745 vw, sh	1705 s	1675 w, sh	1640[e] w ~1600 m, br.
34[f]	2420 m, br.	–	1720 m	1690 s	1545 s

[a] Non-chelating, non-conjugated estercarbonyl stretchings (thione form, or other estergroups in the molecule).
[b] Non-chelating, conjugated estercarbonyl stretchings (*trans*-enethiol form).
[c] Chelating, conjugated estercarbonyl stretchings (*cis*-enethiol form).
[d] ν[C=S]: 1150 cm^{-1} (s).
[e] α-allyl group.
[f] ν[C≡N]: 2220 cm^{-1} (s, sharp).

TABLE 4. ^1H NMR DATA OF S-ALKYLATED ENETHIOLS AND OF ETHYL THIOACETOTHIONOACETATE

For explanation of abbreviations and symbols, see Tables 1 and 2. The solvent is CCl_4

	δ_{CH_3Y}	δ_{HZ}	δ_{SHX}	δ_{SCH_2}	δ_{SCH_3}	δ_{CH_2}[a]	δ_{CH_3}[a]	J_{XY}	J_{YZ}
41A	2·35 d	5·34 q	—	—	2·27 s	4·07 q[b]	1·24 t[b]	–	1·10
41C	2·18 d	5·69 q	—	—	2·30 s	4·07 q[b]	1·24 t[b]	–	1·15
42A	2·36 d	5·53 q	—	3·51 s	—	4·16 q[b]	1·28 t[b] 3·62 s	–	1·10
42C	2·24 d	5·73 q	—	3·51 s	—	4·15 q[b]	1·28 t[b] 3·62 s	–	1·20
43A[c]	2·44 d	6·30 q	?	—	—	4·46 q[b]	1·41 t[b]		1·0
43C[c]	2·22 t[d]	6·43 q	8·55 q		—	4·46 q[b]	1·41 t[b]	0·8	1·0

[a] Estergroup protons.
[b] J = 7 Hz.
[c] Percentages of tautomers in equilibrium in CCl_4 at 38°: **A**, 10%: **B**, 3% (δ_{CH_3CS} = 2·77 ppm): **C**, 87%.
[d] Hardly resolved dd.

EXPERIMENTAL

^{1}H *NMR spectra* were recorded at 60 MHz on a Varian A-60 spectrometer. Unless stated to the contrary, the temps of the 20% solns (w/w) were 38° ± 2. TMS was used as internal reference standard, and the chemical shifts are expressed in δ-values (ppm) downfield from TMS, and are correct within ±0·02 ppm. The coupling constants, measured on the 50 Hz scale, are expressed numerically in Hz with an accuracy within ±0·1 Hz.

Equilibrium concentrations were determined on solns kept in closed tubes at 38° for 6–14 days before determination. 6–10 integrations of all usable signals allowed for calculation of percentages of tautomers with an uncertainty less than 2%.

IR spectra were recorded as 5% solns in CCl_4 on a Beckman IR 18 spectrophotometer or, where a better resolution was desirable, on a Perkin–Elmer 521 spectrophotometer.

UV spectra were measured on a Bausch & Lomb Spectronic 505 spectrophotometer. The solvent was EtOH.

M.ps and b.ps are uncorrected. Unless stated otherwise the yields refer to the isolated, pure products. The purity was checked by NMR and elementary analysis.

General procedure for preparation of open-chain α-H β-*thioketo esters and* α-*alkyl* β,β-*dimercaptobutyrates*

Method A. 0·1–0·3 moles of the β-keto ester were dissolved in 250 ml MeCN. After cooling to −60°, the soln was saturated with H_2S by passing dry H_2S gas through it for 1 hr. Keeping the temp below −50°, dry HCl gas was passed through the soln for 1 hr, followed by H_2S gas for a further 1–2 hr. The mixture was poured into a light petroleum/ice–water mixture under stirring, the layers were separated, and the organic layer washed with water until neutral, and dried ($CaSO_4$). The solvent was removed and the remaining oil distilled.

Preparation of open-chain α-*alkyl* β-*thioketo esters*

Method B. 0·1 mole of the β-keto ester was dissolved in 250 ml 99% EtOH. The soln was cooled to −40° and a stream of dry H_2S gas passed through it for 1 hr, followed by dry HCl gas also for 1 hr. Keeping the temp at −40° to −35°, dry H_2S gas was passed through the soln for further 3–4 hr. The mixture was worked-up as described under method A. The crude product was purified by distillatiion through a 25 cm column or through a Fischer slit-tube column. Further purification *via* the lead salt of the enethiol (see below) could be necessary.

Purification of enethiols forming stable lead salts

Method C. An excess of a saturated soln of $Pb(OAc)_2$ in 50% aqueous EtOH was added to a 5% soln (w/w) of the enethiol in EtOH under stirring. After standing for ½–1 hr, the yellow ppt was collected, washed carefully with EtOH, and finally with ether. Then the lead salt was suspended in ether (or light petroleum), and dil H_2SO_4 was added slowly under stirring (exothermic reaction). When the yellow colour had completely disappeared, the organic layer was separated, washed with water, and dried ($CaSO_4$). The solvent was removed and the remaining oil distilled.

Purification of enethiols forming less stable lead salts

Method D. 200 ml of a saturated soln of $Pb(OAc)_2$ in 50% aqueous EtOH was added to 100 ml of a 10–20% soln (w/w) of the enethiol in EtOH under stirring. The heterogeneous mixture was transferred into a 1 l. separating funnel and 150–200 ml water added. The mixture was washed 3–4 times with 300 ml portions light petroleum. 200 ml light petroleum was added, and then 4 N H_2SO_4 was added very slowly (exothermic reaction) under frequent shaking, until the lead salt was completely decomposed. The layers were separated and the organic layer washed with water and dried ($CaSO_4$). The solvent was removed and the remaining oil distilled.

Individual characteristics of the synthesized compounds, named in accordance with the predominating tautomeric form, are given below.

Methyl 3-mercaptocrotonate (**1**). Prepared according to method A, yield: 80%: pink oil, b.p.$_{14}$: 67°, n_D^{25}: 1·5102 (lit[39] b.p.$_{12}$: 68–69°, $n_D^{29.5}$: 1·5222): λ_{max} (log ε_{max}): 270 nm (4·00), 324 nm (sh). (Found: C, 45·49: H, 6·10: S, 23·78. $C_5H_8O_2S$ requires: C, 45·45: H, 6·10: S, 24·22%).

Ethyl 3-mercaptocrotonate (**2**). Method A, yield: 84%: pink oil, b.p.$_{12}$: 77°, n_D^{25}: 1·4962 (lit b.p.$_{12}$: 72·5–74·5°,[1] b.p.$_1$: 46–47°,[9] b.p.$_{18}$: 77°,[39] b.p.$_{12}$: 75–80°,[40] b.p.$_9$: 75–80°,[41] $n_D^{29.5}$: 1·5375,[39] n_D^{18}: 1·5026[41]): λ_{max} (log ε_{max}): 270 nm (4·04), 3·22 nm (sh).

Propyl 3-mercaptocrotonate (**3**). Method A, yield 85%; pink oil, b.p.$_{11}$: 90–91°, n_D^{27}: 1·4937 (lit[1] b.p.$_{12}$: 93–94°): λ_{max} (log ε_{max}): 270 nm (3·93), 324 nm (sh).

Isopropyl 3-mercaptocrotonate (**4**). Method A, yield: 86%, pink oil, b.p.$_{10}$: 79–80°, n_D^{25}: 1·4891: λ_{max} (log ε_{max}): 270 nm (4·03), 322 nm (sh). (Found: C, 52·16; H, 7·54; S, 19·67. $C_7H_{12}O_2S$ requires: C, 52·49; H, 7·55; S, 19·98%).

Butyl 3-mercaptocrotonate (**5**). Method A, yield: 80%, pink oil, b.p.$_{12}$: 104–105°, n_D^{25}: 1·4890 (lit[1] b.p.$_{11}$: 103·5°): λ_{max} (log ε_{max}): 271 nm (3·97), 322 nm (sh).

Isobutyl 3-mercaptocrotonate (**6**). Method A, yield: 83%, pink oil, b.p.$_{12}$: 99–100°, n_D^{25}: 1·4885: λ_{max} (log ε_{max}): 271 nm (4·04), 324 nm (sh). (Found: C, 54·97; H, 8·05; S, 18·41. $C_8H_{14}O_2S$ requires: C, 55·16; H, 8·10; S, 18·37%).

sec. *Butyl 3-mercaptocrotonate* (**7**). Method A, yield: 95%, pink oil, b.p.$_{12}$: 96–97, n_D^{25}: 1·4881: λ_{max} (log ε_{max}): 270 nm (4·01), 322 nm (sh). (Found: C, 55·08; H, 8·26; S, 17·63. $C_8H_{14}O_2S$ requires: C, 55·16; H, 8·10; S, 18·37%).

Isoamyl 3-mercaptocrotonate (**8**). Method A, yield: 89%, pink oil, b.p.$_{11}$: 116–117°, n_D^{25}: 1·4880: λ_{max} (log ε_{max}): 270 nm (3·98), 320 nm (sh). (Found: C, 56·81; H, 8·62; S, 17·56. $C_9H_{16}O_2S$ requires: C, 57·43; H, 8·57; S, 17·00%).

2-(4-*Methylpentyl*) *3-mercaptocrotonate* (**9**). Method A, yield: 88%, pink oil, b.p.$_{11}$: 113–114°, n_D^{25}: 1·4824: λ_{max} (log ε_{max}): 270 nm (4·07), 320 nm (sh). (Found: C, 59·34; H, 8·88; S, 15·60. $C_{10}H_{18}O_2S$ requires: C, 59·38; H, 8·97; S, 15·82%).

3-(5-*Methylheptyl*) *3-mercaptocrotonate* (**10**). Method A, yield: 83%, pink oil, b.p.$_{12}$: 138°, n_D^{25}: 1·4848: λ_{max} (log ε_{max}): 271 nm (4·03), 322 nm (sh). (Found: C, 62·54; H, 9·61; S, 13·86. $C_{12}H_{22}O_2S$ requires: C, 62·58; H, 9·63; S, 13·89%).

Cyclohexyl 3-mercaptocrotonate (**11**). Method A, yield 77%, pink oil, b.p.$_{12}$: 140°, n_D^{25}: 1·5187: λ_{max} (log ε_{max}): 270 nm (4·02), 322 nm (sh). (Found: C, 59·60; H, 8·08; S, 15·65. $C_{10}H_{16}O_2S$ requires: C, 59·98; H, 8·05; S, 15·98%).

Allyl 3-mercaptocrotonate (**12**). method A, yield: 84%, pink oil, b.p.$_{12}$: 92–93°, n_D^{25}: 1·5141: λ_{max} (log ε_{max}): 271 nm (4·04), 322 nm (sh). (Found: C, 52·77; H, 6·37; S, 20·35. $C_7H_{10}O_2S$ requires: C, 53·16; H, 6·37; S, 20·24%).

Benzyl 3-mercaptocrotonate (**13**). Method A, yield: 80%, pink oil, b.p.$_{0·05}$: 98°, n_D^{25}: 1·5650 (lit.[42] b.p.$_{0·05}$: 98°, $n_D^{21·5}$: 1·5665): λ_{max} (log ε_{max}): 271 nm (4·02), 324 nm (sh).

1-*Phenylethyl 3-mercaptocrotonate* (**14**). Method A, yield: 70%, pink oil, b.p.$_{0·05}$: 95–96, n_D^{25}: 1·5577: λ_{max} (log ε_{max}): 271 nm (4·05), 322 nm (sh). (Found: C, 64·34; H, 6·35; S, 14·43. $C_{12}H_{14}O_2S$ requires: C, 64·85; H, 6·35; S, 14·40%).

Ethyl 3-mercaptopent-2-enoate (**15**). Method A, yield: 78%, pink oil, b.p.$_{12}$: 90–91°, n_D^{25}: 1·4975: λ_{max} (log ε_{max}): 372 nm (3·98), 324 nm (sh). (Found: C, 52·10; H, 7·56; S, 20·07. $C_7H_{12}O_2S$ requires: C, 52·49; H, 7·55; S, 19·98%).

Ethyl 3-mercaptohex-2-enoate (**16**). Method A, yield: 91%, pink oil, b.p.$_{10}$: 98–99°, n_D^{25}: 1·4928: λ_{max} (log ε_{max}): 273 nm (4·04), 325 nm (sh). (Found: C, 55·29; H, 7·98; S, 17·90. $C_8H_{14}O_2S$ requires: C, 55·16; H, 8·10; S, 18·37%).

Ethyl 3-mercapto-4-methylpent-2-enoate (**17**). Method A (reaction temp ≤ −40°), yield: 90%, pink oil, b.p.$_{10}$: 93°, n_D^{25}: 1·4906: λ_{max} (log ε_{max}): 274 nm (4·00). (Found: C, 55·28; H, 8·06; S, 17·93. $C_8H_{14}O_2S$ requires: C, 55·16; H, 8·10; S, 18·37%).

Ethyl 4,4-dimethyl-3-mercaptopent-2-enoate (**18**). Method A (reaction temp ≤ −40°), yield: 88%, pink oil, b.p.$_{10}$: 100–101°, n_D^{25}: 1·4937: λ_{max} (log ε_{max}): 278 nm (4·01). (Found: C, 57·85; H, 8·68; S, 17·09. $C_9H_{16}O_2S$ requires: C, 57·43; H, 8·57; S, 17·00%).

Ethyl 4-ethoxycarbonyl-3-mercaptocrotonate (**19**). Method A (reaction temp: −40°), yield: 65%, pink oil, b.p.$_{0·09}$: 90–91°, n_D^{25}: 1·4959 (lit b.p.$_{0·3}$: 94·5–95·5°,[1] b.p.$_{15}$: 128° (dec)[40]), λ_{max} (log ε_{max}): 273 nm (3·99), 324 nm (sh).

Ethyl 3-mercaptocinnamate (**20**). Method A (reaction temp: −30°). Purification according to method C, yield: 37%, bluish-violet oil, b.p.$_{0·25}$: 114–115°, n_D^{25}: 1·5865 (lit b.p.$_{0·2}$: 110°,[1] b.p.$_{0·1}$: 114–115°,[12] b.p.$_{0·7}$: 102°,[13] n_D^{25}: 1·5840[41]): λ_{max}: 234, 255, 292 nm. A 52% yield was obtained, when the reaction was carried out in EtOH at 0°, second H_2S supply: 7 hr (compare refs 1, 12, 13, and 41).

Ethyl 3-mercapto-(p-*nitrocinnamate*) (**21**). Known method.[14] The yield was increased to 82% by lowering the crystallization temp to −40°. White crystals with a bluish-green tinge, m.p. 79–80° (lit[14] yield: 37%, m.p. 80–81°), λ_{max}: 265 nm, 314 nm (sh).

Ethyl 2-methyl-3-mercaptocrotonate (**22**). Method B. Purification according to method C, yield: 24%,

pink oil, b.p.$_{11}$: 90–91°, n_D^{25}: 1·5075 (lit[43] b.p.$_{10}$: 95°): λ_{max} (log ε_{max}): 268 nm (4·00). (Found: C, 52·25: H, 7·58: S, 19·71. $C_7H_{12}O_2S$ requires: C, 52·49: H, 7·55: S, 19·88%).

Ethyl 2-ethyl-3-mercaptocrotonate (**23**). Method B. Purification: method D, yield: 40%, pink oil, b.p.$_{12}$: 102–103°, n_D^{25}: 1·4996 (lit[44] b.p.$_{14}$: 85°*): λ_{max} (log ε_{max}): 269 nm (3·96). (Found: C, 54·70: H, 8·01: S, 18·40. $C_8H_{14}O_2S$ requires: C, 55·16: H, 8·10: S, 18·37%).

Ethyl 2-propyl-3-mercaptocrotonate (**24**). Method B. Purification: method D, yield: 23%, pink oil, b.p.$_{12}$: 110–112°, n_D^{25}: 1·4897: λ_{max} (log ε_{max}): 269 nm (3·95). (Found: C, 57·51: H, 8·41: S, 16·54. $C_9H_{16}O_2S$ requires: C, 57·43: H, 8·57: S, 17·00%).

Ethyl 2-isopropyl-thioacetoacetate (**25**). Method B. The NMR spectrum of the crude reaction product showed contents of the desired product (71%), of parent β-keto ester (25%), and of corresponding *gem*-dithiol (4%, δ_{Me} = 1·86 ppm (compare *gem*-dithiols below)). Distillation through the 30 cm Fischer slit-tube column gave the pure product in 36% yield. Intensive wine-red coloured liquid, b.p.$_{12}$: 95–96°, n_D^{25}: 1·4693. (Found: C, 57·42: H, 8·42: S, 16·73. $C_9H_{16}O_2S$ requires: C, 57·43: H, 8·57: S, 17·00%).

In one experiment the second H_2S-supply was prolonged to 8 hr (−35°). The NMR analysis of the crude product showed no deviation from that described above with the exception of a small, extra content (~5%) of a polymer (presumably a trimer,[1] δ_{Me} = 2·12 ppm). In another experiment, the mixture obtained according to method B, was allowed to stand at −20° for 16 hr before working-up. The NMR spectrum of the crude oil was very complex, showing, besides a lot of peaks arising from unidentified products, peaks corresponding to contents of *gem*-dithiol (~30%), of polymer (~3 %), and of the thione and the β-keto ester (traces).

On standing at room temp for 4 months, the colour of the crude product, obtained according to method B, faded, and simultaneously the sample viscosity increased. The NMR spectrum of the pale yellow-red oil showed an increased content of β-keto ester (hydrolysis of the thione by moist), and, as main component, the polymer. Attempted fractionated distillation at low pressure (0·15 torr) through the slit-tube column allowed for complete separation of the keto ester, but the polymer decomposed to the thione which distilled over (analytically pure), leaving an unidentified very high-boiling residue in the distillation flask.

Apparently, it is not possible to purify the thione *via* the lead salt. The latter, which on attempted preparation was formed slowly and only incompletely, was pasty and decomposed rapidly to a dingy suspension.

Ethyl 2-butyl-3-mercaptocrotonate (**26**). Method B. Purification: method D, yield: 22%, pink oil, b.p.$_{0.13}$: 62–63°, n_D^{25}: 1·4924. λ_{max} (log ε_{max}): 269 nm (3·96). (Found: C, 59·13: H, 8·98: S, 16·08. $C_{10}H_{18}O_2S$ requires: C, 59·38: H, 8·97: S, 15·82%).

Ethyl 2-octyl-3-mercaptocrotonate (**27**). Method B. Purified by distillation, yield: 20%, pink oil, b.p.$_{0.12}$: 110°, n_D^{25}: 1·4850: λ_{max} (log ε_{max}): 271 nm (3·90). (Found: C, 64·83: H, 10·11: S, 12·29. $C_{14}H_{26}O_2S$ requires: C, 65·08: H, 10·14: S, 12·39%).

Ethyl 2-(2-ethoxycarbonylethyl)-3-mercaptocrotonate (**28**). Method B. Purification: method D, yield: 27%, pink oil, b.p.$_{0.07}$: 92 93°, n_D^{25}: 1·4954 (lit[9] b.p.$_{0.6}$: 121°, n_D^{20}: 1·4938): λ_{max} (log ε_{max}): 281 nm (3·97). (Found: C, 53·71: H, 7·41: S, 12·86. $C_{11}H_{18}O_4S$ requires: C, 53·65: H, 7·37: S, 12·99%).

Ethyl 2-ethoxycarbonyl-3-mercaptocrotonate (**29**). Method B. Second H_2S supply prolonged to 20 hr at room temp. Purified by distillations, yield: 63%, pale pink oil, b.p.$_{11}$: 138°, n_D^{25}: 1·4957 (lit b.p.$_{13}$: 138–139°,[1] b.p.$_{12}$: 124–125°,[17] b.p.$_4$: 120°[43]), λ_{max} (log ε_{max}): 277 nm (4·00), 325 nm (sh).

Ethyl 2-chloro-3-mercaptocrotonate (**30**). Method B, second H_2S supply: 18 hr, during which the temp was raised to −5°. Purified by distillation, yield: 96%, pink oil, b.p.$_{12}$: 100–101°, n_D^{25}: 1·5255 (lit[9] b.p.$_{0.4}$: 57 58°, n_D^{20}: 1·5275): λ_{max} (log ε_{max}): 277 nm (3·96). (Found: C, 40·02: H, 5·03: S, 18·01: Cl, 20·17. $C_6H_9ClO_2S$ requires: C, 39·89: H, 5·02: S, 17·75: Cl, 19·63%).

Ethyl 2-methyl-3-mercaptocinnamate (**31**). Method B, second H_2S supply: 90 hr at room temp. The crude oil was dissolved in 400 ml of MeCN and a slight excess of a saturated soln of $Pb(OAc)_2$ in 50% aqueous EtOH was added under stirring. After standing for ½–1 hr, the precipitated lead salt was filtered, washed with MeCN, with light petroleum, and dried (excicator). The bright yellow powder was suspended in light petroleum and H_2S gas was passed through the suspension for 2 hr. Precipitated PbS was filtered off, the filtrate was dried ($CaSO_4$), and after removal of solvent, the remaining oil was distilled, yield: 17%, pale blue oil, b.p.$_{0.09}$: 88–89°, n_D^{25}: 1·5665: λ_{max} (log ε_{max}): 279 nm (3·99). (Found: C, 65·19: H, 6·38: S, 14·73. $C_{12}H_{14}O_2S$ requires: C, 64·85: H, 6·35: S, 14·40%).

Ethyl 2-allyl-3-mercaptocrotonate (**32**). Method B, purification: method D, yield: 30%, pink oil, b.p.$_{0.2}$:

* Purity questionable. Starting material: b.p.$_{10}$: 76–78°.

64–65°, n_D^{25}: 1·5097 (immediately after the distillation): λ_{max} (log ε_{max}): 275 nm (3·97). (Found: C, 58·34: H, 7·63: S, 16·87. $C_9H_{14}O_2S$ requires: C, 58·05: H, 7·58: S, 17·19%).

Ethyl 2-cyano-3-mercaptocrotonate (**34**). Known method.[17] Overall yield: 42%. White crystals which are coloured red by sunlight, m.p.: 77° (lit[17] m.p.: 71°: λ_{max} (log ε_{max}): 290 nm (3·97), 3·41 nm (3·99).

Action of H_2S *on ethyl diacetylacetate* (**35'**). Four experiments in 0·1 mole scale were carried out:

(a) under conditions as described under method A. The tricarbonyl compound was regenerated almost quantitatively.

(b) as method A with the exception that the second H_2S supply was maintained for 20hr during which the temp was allowed to rise to 0° (ice -water bath). Otherwise, following the usual working-up procedure, the starting material was regenerated (78%).

(c) as method B. Second H_2S supply: 5 hr. The reaction temp was carefully kept below −50°. Regeneration of starting material (83%).

(d) as method B. The second H_2S supply was prolonged to 16 hr, and the temp was allowed to increase to 0°. In contrast to the three preceding experiments, the NMR spectrum of the crude oil clearly indicated a reaction having taken place. On distillation, 8·6 g of a fraction with $b.p._{11}$: 93–103° was collected. Its NMR spectrum showed the presence of two compounds, the enethiol **2** (17%, overall yield: 8%), and the *gem*-dithiol, ethyl 3,3-dimercaptobutyrate (**40**)[1] (83%, overall yield: 41%).

Preparation of ethyl 3-mercaptocinnamate (**20**) *by action of* H_2S *on ethyl 2-acetylbenzoylacetate* (**36'**): 10·4 g (45 mmoles) of **36'** were dissolved in 150 ml of 99% EtOH and reacted with H_2S/HCl as described under experiment (d) above. Distillation of the crude oil gave pure **20** (yield: 76%).

Ethyl 2-methyl-3,3-dimercaptobutyrate (**22D**). Method A, yield: 79% (90% purity, calc. from elementary analysis and the NMR spectrum), $b.p._{0·13}$: 52–54°, n_D^{25}: 1·4967 (lit[9] $b.p._{0·5}$: 65°, n_D^{20}: 1·5008): NMR (CS_2): 1·25 (3H, t, J = 7), 1·32 (3H, d, J = 7), 1·78 (3H, m), 2·79 (1H, q, J = 7), 2·96 (2H, m), 4·09 (2H, q, J = 7). (Found: C, 44·25: H, 7·35: S, 31·65. $C_7H_{14}O_2S_2$ requires: C, 43·29: H, 7·27: S, 32·96%).

Ethyl 2-propyl-3,3-dimercaptobutyrate (**24D**). Method A, yield: 83% (90% purity), $b.p._{0·25}$: 80°, n_D^{25}: 1·4883 (lit[9] $b.p._{0·5}$: 78°, n_D^{20}: 1·4918): NMR (CS_2): 1·25 (3H, t, J = 7), 0·8–1·5 (5H, br.m), 1·5–1·9 (2H, br.m), 1·77 (3H, m), 2·5–2·8 (1H, m), 2·89 (2H, m), 4·09 (2H, q, J = 7). (Found: C, 49·57: H, 8·21: S, 27·59. $C_9H_{18}O_2S_2$ requires: C, 48·64: H, 8·16: S, 28·80%).

Ethyl 2-butyl-3,3-dimercaptobutyrate (**26D**). Method A, yield: 88% (90% purity), $b.p._{0·35}$: 92°, n_D^{25}: 1·4875: NMR (CS_2): 0·89 (3H, br.t, $J \sim 6$), 1·25 (3H, t, J = 7), 1·0–1·5 (4H, br.m), 1·6–2·0 (2H, br.m), 1·75 (3H, m), 2·5–2·8 (1H, m), 2·88 (2H, m), 4·09 (2H, q, J = 7). (Found: C, 51·61: H, 8·58: S, 25·98. $C_{10}H_{20}O_2S_2$ requires: C, 50·83: H, 8·53: S, 27·09%).

2-Methyl-2-(1-ethoxycarbonylethyl)-1,3-dithiolan-4,5-dione (**37**). 9·7 g (50 mmoles) of **22D** were treated with 6·7 g (50 mmoles) of oxalyl chloride according to a known method,[9] yield: 1·7 g (13%), white crystals, m.p. 70–71° (lit[9] m.p. 70–71°): IR, ν[C=O]: 1740 cm^{-1}(s), 1710 cm^{-1} (vs).

2-Methyl-2-(1-ethoxycarbonylethyl)-1,3-dithiolan-4,5-dione (**37**). 9·7 g (50 mmoles) of **22D** were treated with 6·7 g of oxalyl chloride,[9] yield: 2·1 g (15%), $b.p._{0·18}$: 142–146°, m.p. 28° (EtOH): IR, ν[C=O]: 1740 cm^{-1} (s), 1710 cm^{-1} (vs). (Found: C, 47·82: H, 5·88: S, 22·69. $C_{11}H_{16}O_4S_2$ requires: C, 47·82: H, 5·84: S, 23·17%)

2-Methyl-2-(1-ethoxycarbonylpentyl)-1,3-dithiolan-4,5-dione (**39**). 11·8 b (50 mmoles) of **26D** were treated with 6·7 g of oxalyl chloride,[9] yield: 2·3 g (16%), $b.p._{0·09}$: 133–140°, m.p. 33–34 (EtOH): IR, ν[C=O]: 1740 cm^{-1} (s), 1710 cm^{-1} (vs). (Found: C, 49·35: H, 6·19: S, 22·15. $C_{12}H_{18}O_4S_2$ requires: C, 49·65: H, 6·25: S, 22·05%).

Ethyl 3-(methylmercapto)-crotonate (**41**). 24·9 g (0·1 moles) thallous ethoxide dissolved in 25 ml light petroleum were added dropwise during 15 min to an ice-cooled, stirred soln of 14·6 g (0·1 moles) of **2** in 100 ml light petroleum. Stirring was continued at 0° for 30 min. Then a soln of 14·2 g (0·1 moles) MeI in 25 ml light petroleum was added under stirring during 5 min, and the mixture was refluxed overnight. After cooling, the mixture was filtered. The solvent was removed from the filtrate and the remaining colourless oil was distilled, yield: 12·4 g (78%), $b.p._{12}$: 116–130° (mixture of *cis*- and *trans*-isomers, 83·5% and 16·5% resp., calculated from the NMR spectrum). Repeated fractional distillatiion gave the pure *cis*-isomer **41C**, $b.p._{12}$: 124–126°, n_D^{25}: 1·5255: λ_{max} (log ε_{max}): 287 nm (4·10). IR, ν[C=O]: 1710 cm^{-1} (s): ν[C=C]: 1600 cm^{-1} (s). (Found: C, 52·38: H, 7·53: S, 19·98. $C_7H_{12}O_2S$ requires: C, 52·49: H, 7·55: S, 19·98%).

A sample of pure **41C** was kept in a closed tube at 5° for 6 months. The subsequent NMR analysis showed contents of both the *cis*- and the *trans*-isomer, 82·5 ± 1% and 17·5 ± 1%, respectively.

Methyl 3-(ethoxycarbonylmethylmercapto)-crotonate (**42**). 13·2 g (0·1 moles) of **1** were treated with

equivalent amounts of TlOEt and MeI as described above. After removal of precipitated TlI from the mixture (filtration), the latter was kept at −15° for 20 hr. The precipitated white crystals were isolated by filtration and dried. The solvent was removed from the filtrate which, after distillation, gave 5·2 g of a colourless oil, b.p.$_{12}$: 162–170°. This was identified by NMR as a pure mixture of the isomers **42A** (76%) and **42C** (24%). (Found: C, 49·36: H, 6·28: S, 14·36. $C_9H_{14}O_4S$ requires: C, 49·54: H, 6·47: S, 14·67%).

The white crystals obtained by the filtration (5·1 g) were identified by NMR as pure **42C**, m.p. 34°; λ_{max} (log ε_{max}): 272 nm (4·11); IR, ν[C=O]: 1740 cm^{-1} (s), 1715 cm^{-1} (s), ν[C=O]: 1605 cm^{-1} (s). On standing at room temp, the crystals slowly liquefied. This process was followed by NMR and found to be due to progressive isomerization. Equilibrium was reached after 4-6 months (**42A**: 79 ± 1%, **42C**: 21 ± 1%).

Ethyl 3-mercaptothionocrotonate (**43**). 20·8 g (0·2 moles) ethyl thionoacetate were added dropwise at room temp to a stirred soln of EtONa in EtOH (2·3 g Na dissolved in 100 ml EtOH) during 30 min. Stirring was continued for 30 min at room temp and subsequently for 1 hr at reflux temp. After standing overnight at room temp, 400 ml H_2O was added, and the aqueous soln washed twice with ether. 100 g of crushed ice and 400 ml ether were added. Then, under stirring, 4 N HCl was added until the H_2O-layer showed acid reaction. The layers were separated, the ether layer was washed with 0·01 N HCl, and dried ($CaSO_4$). After removal of ether, the remaining dark-red oil was distilled twice to give 3·8 g (23%) of **43**: orange-red, loathfully smelling oil, b.p.$_{11}$: 111–112°, n_D^{25}: 1·6075 (lit[45] b.p.$_{0.5}$: 70-81°); λ_{max} (log ε_{max}): 273 nm (3·75), 328 nm (3·97), 411 nm (3·12): IR, ν[C=C]: 1570 cm^{-1} (s). (Found: C, 44·05: H, 6·14: S, 39·18. $C_6H_{10}OS_2$ requires: C, 44·44: H, 6·22: S, 39·47%).

Acknowledgement— I wish to express my gratitude to Dr. S.-O. Lawesson for his interest and for discussions, and to Mrs. Tove Buchholt, Miss Randi Dyrnesli, Mrs. Ingerbeth Ottzen, Mrs. Anne Gylling, Miss Rigmor Søeberg Hansen, Miss Hanne Weiling, Mr. Arne Lindahl, and Mr. Leif Mortensen for benevolent technical assistance. I am also grateful to Dr. W. O. Godtfredsen and his staff at the microanalytical laboratory, Løvens kemiske Fabrik, Billerup, who kindly carried out the elementary analyses.

REFERENCES

[1] F. Duus and S.-O. Lawesson, *Arkiv Kemi* **29**, 127 (1968)
[2] F. Duus, P. Jakobsen and S.-O. Lawesson, *Tetrahedron* **24**, 5323 (1968)
[3] F. Duus, E. B. Pedersen and S.-O. Lawesson, *Ibid.* **25**, 5703 (1969)
[4] IUPAC Tentative Rules for the Nomenclature of Organic Chemistry. Section E. Fundamental Stereochemistry. *J. Org. Chem.* **35**, 2849 (1970)
[5] N. K. Chakrabarty and S. K. Mitra, *J. Chem. Soc.* 1385 (1940)
[6] R. Mayer and P. Barthel, *Chem. Ber.* **93**, 428 (1960)
[7] F. K. Splinter and H. Arnold, *J. Prakt. Chem.* **38**, 142 (1968)
[8] B. Hedegaard, J. Z. Mortensen and S.-O. Lawesson, *Tetrahedron* **27**, 3853 (1971)
[9] S. Bleisch and R. Mayer, *Chem. Ber.* **100**, 93 (1967)
[10] R. Mayer, *Organosulfur Chemistry* (Edited by M. J. Janssen) p. 219. Wiley, New York (1967)
[11] F. Duus and S.-O. Lawesson, *Tetrahedron* **27**, 387 (1971)
[12] H. Scheibler and B. Frenz, *J. Prakt. Chem.* **2**, 127 (1955)
[13] Z. Reyes and R. M. Silverstein, *J. Am. Chem. Soc.* **80**, 6367 (1958)
[14] Z. Reyes and R. M. Silverstein, *Ibid.* **80**, 6373 (1958)
[15] F. Duus, to be published
[16] J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.* **86**, 2105 (1964)
[17] K. Hartke and L. Peshkar, *Arch. Pharmaz.* **301**, 601 (1968)
[18] P. Courtôt, J. Le Saint and N. Platzer, *Bull. Soc. Chim. Fr* 3281 (1969)
[19] D. C Nonhebel, *Tetrahedron* **26**, 4443 (1970)
[20] F. Duus, unpublished observation
[21] E. C. Taylor, G. H. Hawks and A. McKillop, *J. Am. Chem. Soc.* **90**, 2421 (1968)
[22] Y. Shvo and I. Belsky, *Tetrahedron* **25**, 4649 (1969)
[23] D. C. Sen, *J. Indian Chem. Soc.* **13**, 268 (1936)
[24] S. K. Mitra, *Ibid.* **15**, 205 (1938)
[25] R. Mayer, S. Scheithauer, S. Bleisch, D. Kunz, G. Bähr and R. Radeglia, *J. Prakt. Chem.* **311**, 472 (1969)

[26] D. Paquer and J. Vialle, *Bull. Soc. Chim. Fr* 3595 (1969)
[27] C. Andrieu and Y. Mollier, *Tetrahedron Letters* 1573 (1971)
[28] H. Wamhoff, G. Höffer, H. Lander and F. Korte, *Liebigs Ann.* **722**, 12 (1969)
[29] G. Allen and R. A. Dwek, *J. Chem. Soc.* (B) 161 (1966)
[30] Z. Yoshida, H. Ogoshi and T. Tokumitsu, *Tetrahedron* **26**, 5691 (1970)
[31] S. Forsén, F. Merényi and M. Nilsson, *Acta Chem. Scand.* **18**, 1208 (1964)
[32] J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy* Vol. 1: p. 550. Pergamon Press, Oxford (1965)
[33] Ref. 32: p. 546.
[34] E. A. Allan and L. W. Reeves, *J. Phys. Chem.* **66**, 613 (1962)
[35] G. C. Pimentel and A. L. McClellan, *The Hydrogen bond* p. 201. Freeman, London (1960)
[36] P. V. Demarco, D. Doddrell and E. Wenkert, *Chem. Comm.* 1418 (1969)
[37] S. J. Rhoads, *J. Org. Chem.* **31**, 171 (1966)
[38] R. A. Y. Jones, *Annual Review of NMR Spectroscopy* (Edited by E. F. Mooney) Vol. 1: p. 27. Academic Press, London (1968)
[39] H. Scheibler, H. T. Topouzada and H. A. Shculze, *J. Prakt. Chem.* **124**, 1 (1930)
[40] S. K. Mitra, *J. Indian Chem. Soc.* **10**, 71 (1933)
[41] S. H. H. Chaston, S. E. Livingstone, T. N. Lockeyer, V. A. Pickles and J. S. Shannon, *Austral. J. Chem.* **18**, 673 (1965)
[42] F. Duus, S.-O. Lawesson, J. H. Bowie and R. G. Cooks, *Arkiv Kemi* **29**, 191 (1968)
[43] S. K. Mitra, *J. Indian Chem. Soc.* **15**, 31 (1938)
[44] S. K. Mitra, *Ibid.* **10**, 491 (1933)
[45] J. V. Koštíř and V. Král, *Chem. Listy* **41**, 92 (1947)