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STUDIES ON ENETHIOLS—III†

SYNTHESES AND SPECTROSCOPIC INVESTIGATIONS OF β-THIOKETOTHIOLESTERS

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Abstract—β-Thioketothiolesters have been prepared by the acid catalysed reaction between β-ketothiolesters and hydrogen sulphide. NMR, IR, and UV spectroscopic investigations show that the title compounds exist mainly as intramolecularly hydrogen-bonded α,β-unsaturated β-mercaptothiolesters both in the pure liquid state and in solution. The thermochromism exhibited by the β-thioketothiolesters has been studied by NMR and is attributed to a shift in the thioketo-enethiol equilibrium. The effect of different solvents on the chelated enethiol system is described and discussed.

INTRODUCTION

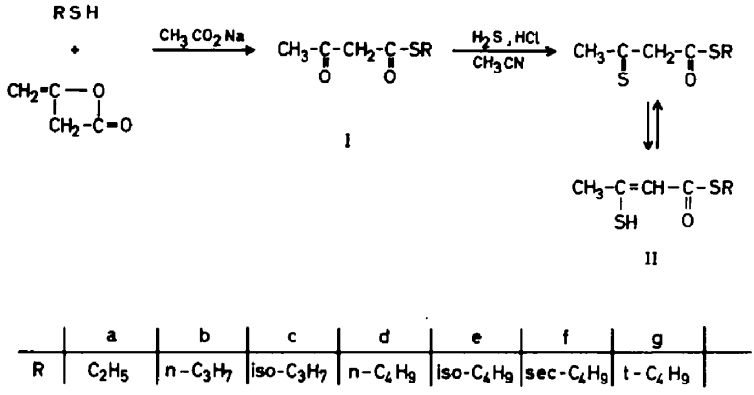
IN OUR first paper[1] NMR and IR studies of β-thioketoesters were described. Contrary to common β-ketoesters,[2] in which the keto-form is dominating, the corresponding sulphur homologues exist mainly as chelated enethiols.[1] As a continuation of our synthetic and spectroscopic studies on enethiols, we have now prepared a series of the hitherto unknown thioacetylthiolesters. The related thiobenzoylthiolesters have previously been synthesized by Yokoyama and Tanaka[3] by treatment of the appropriate thiolpropiolic esters with thiourea and *p*-toluenesulphonic acid and subsequent hydrolysis of the formed isothiuronium salts. In a recent paper,[4] the thioketo-enethiol equilibrium of these compounds[3] was studied using Mitra's method[5] (for a critical discussion of the method, see Barnikow and Strickmann[6]). It was thus shown[4] that there is a tautomeric equilibrium between the thioketo and the chelated *cis*-enethiol forms, whereas the contribution of the *trans*-enethiol form can be neglected. Thus the applicability of Meyer's rule[7] was established. The thioketo-*cis*-enethiol equilibrium was greatly dependent on the solvent used as a more polar solvent effected a greater percentage of the thioketo tautomer. This is also in agreement with the results from studies on ethyl thiobenzoylacetate.[8]

SYNTHESES

The starting materials, the β-ketothiolesters, I, have been reported in the literature only in isolated cases. Thus, ethyl acetothiolacetate[14,15] and t-butyl acetothiolacetate[14] have been prepared in moderate yields by Claisen condensation of the corresponding thiolacetates. A more convenient method of preparation involves the reaction between diketene and a mercaptan.[16–18]

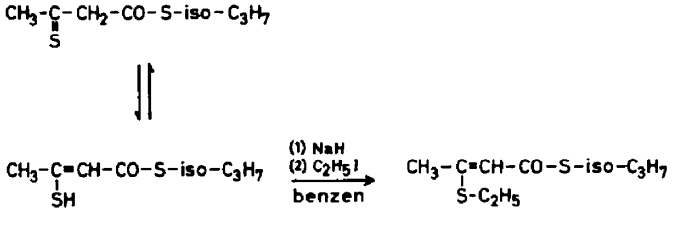
The compounds Ia-g, prepared according to this method, are rather unstable at elevated temperature as they decompose to the mercaptans and dehydroacetic acid.

† Part II: see Ref. 13.



Monothio-β-dicarbonyl compounds are mostly synthesized by reaction of the corresponding β-dicarbonyl compounds with hydrogen sulphide in the presence of either a base[9] or an acid catalyst.[1,8,10–12] Usually polar solvents such as alcohols[1,8,11,12] are used as reaction medium, and often a low reaction temperature is necessary in order to avoid formation of by-products,[11,12] e.g. *gem* dithiols and *sym* trithianes.[1] It has now been found that when the reaction is carried out for a short time at −60° with acetonitrile as solvent,[13] pure products in high yields are obtained. Therefore, the thioacetylthiolesters were synthesized under these conditions.

The procedure for the preparation of II is as follows: After passing hydrogen sulphide and dry hydrogen chloride through a solution of the corresponding acetothiolacetate, I, the cooling-bath is removed. The yellow reaction mixture is then allowed to stand for 10 to 30 minutes before it is poured into ice-water and worked up (Experimental). However, in one case (Ic) the reaction mixture was allowed to stand for 12 hr at −10°C before working up. A reddish oil was obtained, which contained about 60% of the *gem* dithiol and about 40% of n-propyl thioacetothiolacetate, IIc, (calculated from the NMR spectrum). This confirms an observation by Bleisch and Mayer[12] that the reaction temperature is of great significance for the product distribution. Treatment of this mixture with lead acetate followed by regeneration of the thiols with hydrogen sulphide[1,8] yielded a new oil, which still contained 8% of the *gem* dithiol. The presence of the *gem* dithiol in the regenerated products thus indicates that the *gem* dithiols are also capable of forming lead complexes to some extent.[12,19]

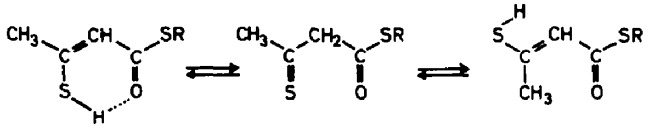


IIc IIIc

Isopropyl β-(ethylmercapto)-thiolcrotonate (IIIc) was synthesized by alkylating the sodium salt of IIc with ethyl iodide in an inert solvent.

SPECTROSCOPIC STUDIES

The thioacetothiolesters can exist in three different forms, namely the chelated *cis*-enethiol form (A), the thioketo form (B), and the *trans*-enethiol form (C). The IR



A B C

spectra of the thioacetothiolesters are very much alike. They all show a strong band at 1622–1630 cm^{-1} (ν[C═O, conjugated, chelated]) with a weak shoulder at about 1670 cm^{-1} (presumably ν[C═O], thioketo form) and in some cases also about 1640 cm^{-1} (presumably ν[C═O, conjugated], *trans*-enethiol form). A strong band at 1562–1569 cm^{-1} is assigned to the C═C stretching vibration. In the SH stretching

TABLE 1: IR ABSORPTION BANDS OF β-THIOKETOTHIOLESTERS

	ν[S—H] *cis*-enethiol	ν[C═O] thio-keto	ν[C═O] *trans*-enethiol	ν[C═O] *cis*-enethiol	ν[C═C] *cis*-enethiol	δ[═CH—] *cis*-enethiol
IIa	2420 m	1670 sh, w	1645 sh, w	1629 s	1564 s	830 s
IIb	2418 w	1675 sh, w		1628 s	1564 s	826 s
IIc	2420 m	1662 sh, w	1644 sh, w	1628 s	1565 s	831 s
IId	2424 w	1670 sh, vw		1630 s	1566 s	830 s
IIe	2420 m	1670 sh, vw		1630 s	1568 s	830 s
IIf	2420 w	1673 sh, w		1630 s	1566 s	830 s
IIg	2418 m	1666 sh, w	1640 sh, w	1623 s	1562 s	830 s
IIIc				1659 s	1565 s	836 s

Frequencies are in cm^{-1}. Intensities are indicated as follows: s = strong; m = medium; w = weak; vw = very weak; sh = shoulder.

vibration region two bands are found at 2420 cm^{-1} and at 2460 cm^{-1}. Comparison with IR spectra of related compounds[1,3] lead to assignment of the former to the chelated SH stretching vibration, whereas the other is regarded as a combination band (ν[C=O, conj., chel.] + δ[=CH—]). The IR data are listed in Table 1, and a typical IR spectrum is shown in Fig. 1. Characteristic bands from the IR spectrum of IIIc are also listed in Table 1.

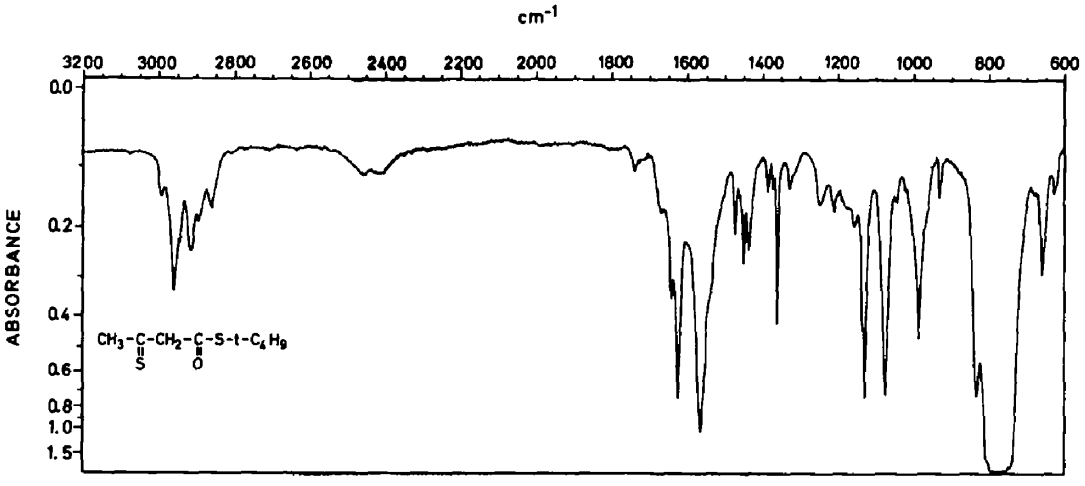


FIG. 1 IR spectrum of *t*-butyl thioacetothiolacetate (IIg)

The UV spectra of IIa–g in cyclohexane (Table 2) show intense bands at 302 mμ due to a $\pi \rightarrow \pi^*$ transition in the carbonyl-conjugated ethylenic system with a bathochromic shift contribution from the S-atoms. IIIc also shows absorption at 302 mμ, but the intensity is about 1·5 times greater than in II. This difference in intensity cannot be attributed to tautomerism alone, and presumably the hydrogen bondings in II must also play a rôle.

TABLE 2. UV ABSORPTION SPECTRA OF β-THIOKETO-THIOLESTERS

	λ_{max}, mμ	ε_{max}		λ_{max}, mμ	ε_{max}
IIa	301	12,700	IIe	302	14,500
IIb	302	13,200	IIf	302	12,700
IIc	302	13,500	IIg	303	13,700
IId	302	14,000	IIIc	302	21,600

The IR and UV spectra can thus indicate that the chelated *cis*-enethiol form does in fact predominate, but quantitative data are lacking. This information is, however, yielded from a study of the NMR spectra. From a typical NMR spectrum (Fig. 2) is seen that form A predominates and the appearance of the thiolic proton at a relatively

low field is a strong indication of a chelated system. Long range couplings between the allylic protons and the vinyl proton and between the allylic protons and the thiolic proton are demonstrated and the thioacetyl group protons (form B) can also be observed. Chemical shifts and coupling constants from the NMR spectra of the thio-

TABLE 3. CHEMICAL SHIFTS (δ-VALUES, ppm) AND COUPLING CONSTANTS (c/s) FROM NMR SPECTRA OF β-THIOKETOTHIOLESTERS

	Chelated *cis*-enethiol form					Thioketo form	
	SH^X	$=CH-^Y$	$CH_3{}^Z$	J_{XZ}	J_{YZ}	CH_3	$-CH_2-$
IIa	7·17 7·37[a]	6·11	2·12	1·1	1·1	2·47	—
IIb	7·20 7·36[a]	6·12	2·14	1·1	1·1	2·47	3·38
IIc	7·20 7·37[a]	6·08	2·11	1·0	1·1	2·47	—
IId	7·17 7·37[a]	6·05	2·10	1·0	1·1	2·45	3·32
IIe	7·20 7·33[a]	6·13	2·12	1·1	1·1	2·47	3·38
IIf	7·13 7·38[a]	6·00	2·08	1·0	1·1	2·47	3·32
IIg	7·20 7·34[a]	6·01	2·08	1·1	1·1	2·43	—

Estergroup protons: $-COS-C^{\alpha}-C^{\beta}-C^{\gamma}-C^{\delta}$

	H^{α}	H^{β}	H^{γ}	H^{δ}	$J_{\alpha\beta}$	$J_{\beta\gamma}$	$J_{\gamma\delta}$
IIa	2·92	1·29	—	—	7·0	—	—
IIb	2·92	1·65	1·00	—	7·0	7·0	—
IIc	3·72	1·51	—	—	7·0	—	—
IId	2·90	~1·50	~1·50	0·94	7·0	—	7·0
IIe	2·84	~1·83	0·96	—	6·7	—	6·7
IIf	3·53	1·30[b] ~1·50[c]	0·96	—	6·7 7·0	6·7	—
IIg	—	1·50	—	—	—	—	—

[a] At infinite dilution.[1]
[b] Methylgroup protons.
[c] Methylene group protons.

TABLE 4. CALCULATED PERCENTAGES[a] OF THE CHELATED *cis*-ENETHIOL FORM IN β-THIOKETO-THIOLESTERS AND OF THE CHELATED *cis*-ENOL FORM IN THE CORRESPONDING β-KETOTHIOLESTERS[1] (SOLVENT: CCl_4)

	a	b	c	d	e	f	g
I	28	34	33	36	36	38	32
II	94	93	93	93	92	93	91

[a] Accuracy: ±2%.
[b] Calculated from NMR integrals.

acetothiolesters in CCl_4-solution are listed in Table 3, and the percentages of the different tautomeric forms in Table 4.

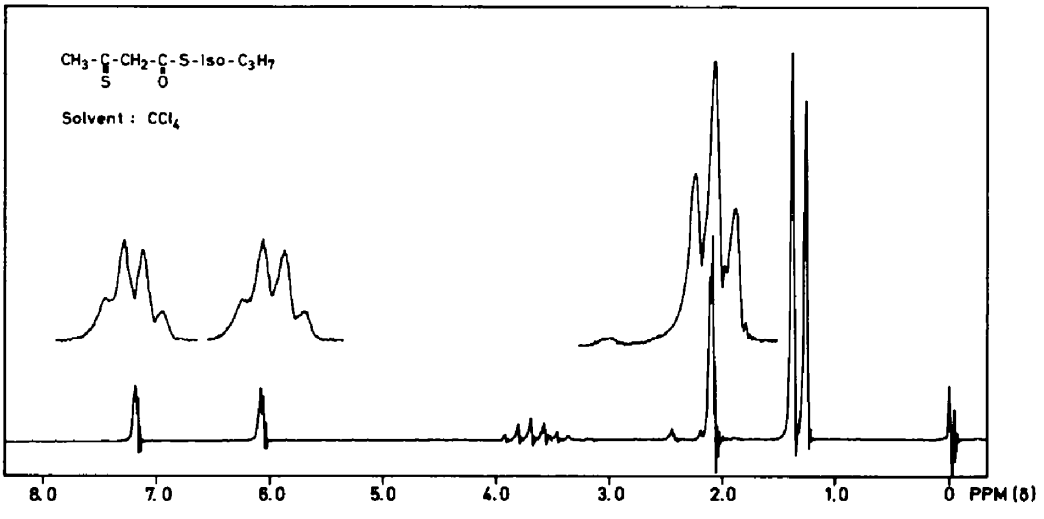


FIG. 2 NMR spectrum of *iso*-propyl thioacetothiolacetate in CCl_4.

Freshly distilled thioacetothiolesters are wine-red, oily liquids. On standing the colour fades, but on warming it reappears. Thermochromism of thiocarbonyl compounds have earlier been reported[6, 10, 21–23] but more detailed investigations have not been carried out. In an attempt to study this phenomenon, NMR spectra of the pure liquids at various temperatures were recorded and the intensities of the signals compared. Whereas the intensities of the signals corresponding to the A-form protons decreased at elevated temperatures, the intensity of the thioacetyl group protons in B clearly increased (Fig. 3). Thus, the exhibited thermochromism seems to be due to a shift in the thioketo-enethiol equilibrium, the red thioketo-form being more favoured at elevated temperatures.

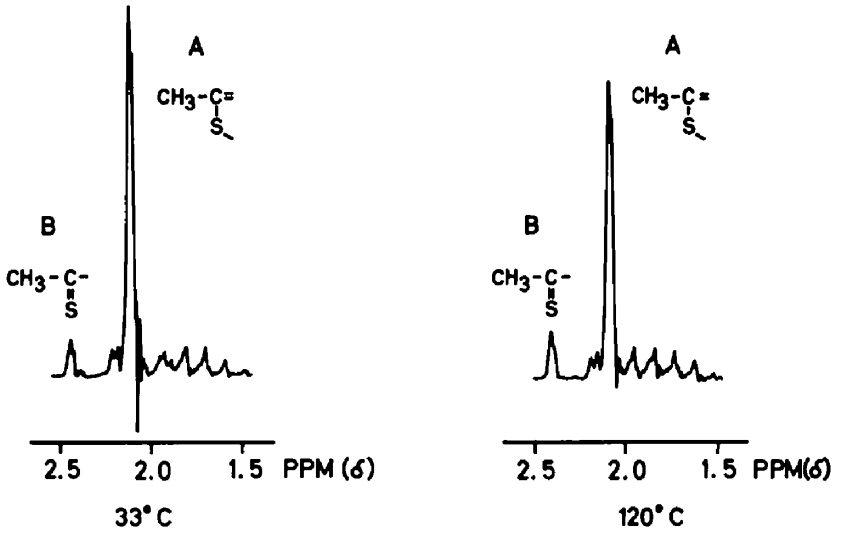


FIG. 3 Signals from allylic protons (form A) and thio-acetyl protons (B) at 33° and at 120° demonstrating the thermochromism as a tautomeric effect.

The effect of different solvents (CS_2, C_6D_6, and CD_3CN) on the intensity of the signals and on the chemical shifts was also studied. It was found that the thioketo-enethiol equilibrium is not affected. The NMR spectrum of IIc in C_6D_6 shows the following signals (δ-values): 6·74 ppm (SH), 5·99 ppm (=CH—), 3·74 ppm (ester-group —CH), 2·26 ppm (Me, form B), 1·63 ppm (Me, form A), and 1·20 ppm (ester-group —Me). Comparison with the corresponding signals in CCl_4-solution (Table 3) shows that in the former case the signals appear at a considerably higher field, especially the SH and CH_3 (A) signals ($\Delta\delta_{SH}$ = 0·46 ppm and $\Delta\delta_{CH_3(A)}$ = 0·48 ppm). The displacement is presumably due to the formation of a weak complex giving rise to a preferred solute-solvent orientation together with the diamagnetic anisotropy associated with the induced ring currents in the benzene molecules.[24]

The thiolic proton in the NMR spectra of II in CD_3CN solution could not immediately be identified. Therefore, NMR spectra of II, dissolved in different mixtures of CCl_4 and CD_3CN, were recorded. It was found that the thiolic proton signal moves against higher field when the content of CD_3CN in the solvent is increased (Fig. 4). At the same time the coupling constant J_{XZ} decreases, whereas J_{YZ} remains unchanged (Fig. 5). The other signals show only a very small displacement against lower field with increasing CD_3CN concentration. Calculations showed that there is a linear relationship between the square root of the concentration of CD_3CN and the displacement of the thiolic proton signal and the change in J_{XZ}, respectively (Figs 6 and 7). We thus conclude that the described effect is due to a dipole–dipole interaction between the CD_3CN and the thiolester molecules, weakening the intramolecular hydrogen-bonding in the thiolester. A more polar solvent (e.g. CD_3CN) should increase the percentage of the more polar form of the tautomers,[4,8] in this case the

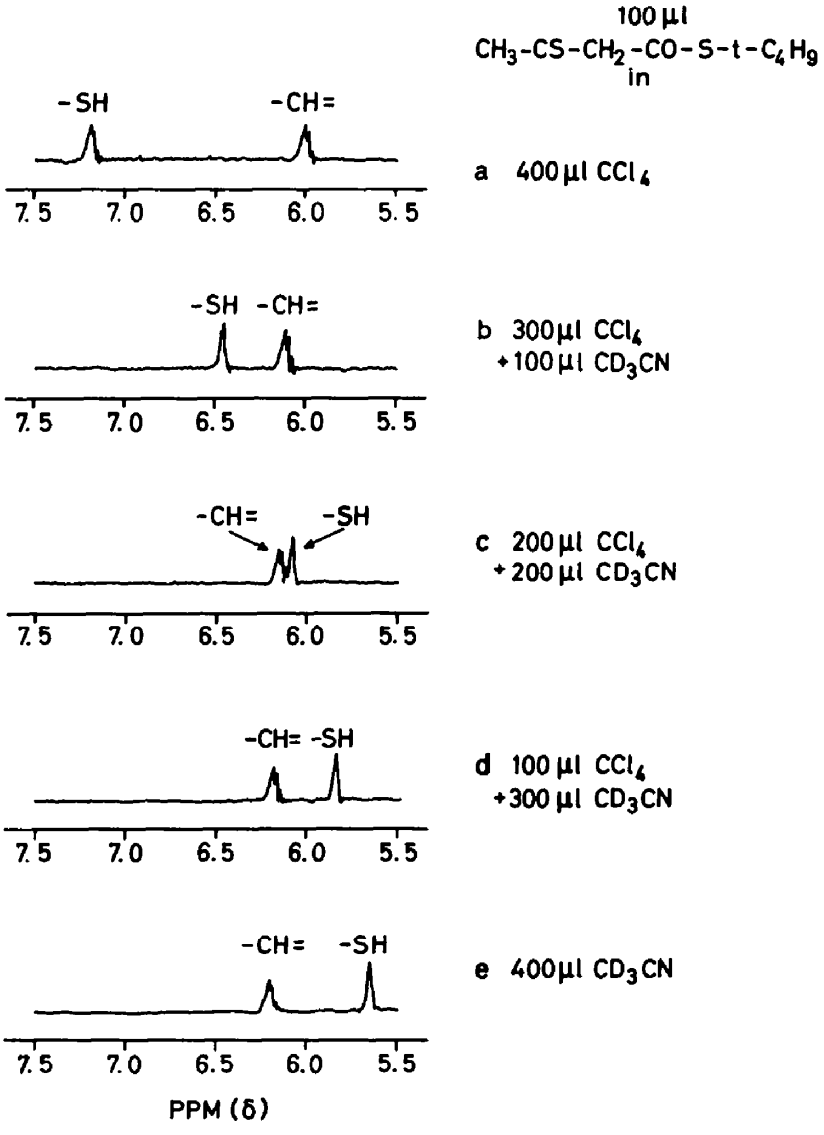


FIG. 4 Chemical shift of the thiolic and the vinyl proton of *t*-butyl thio-acetothiolacetate in mixed CCl_4–CD_3CN solutions.

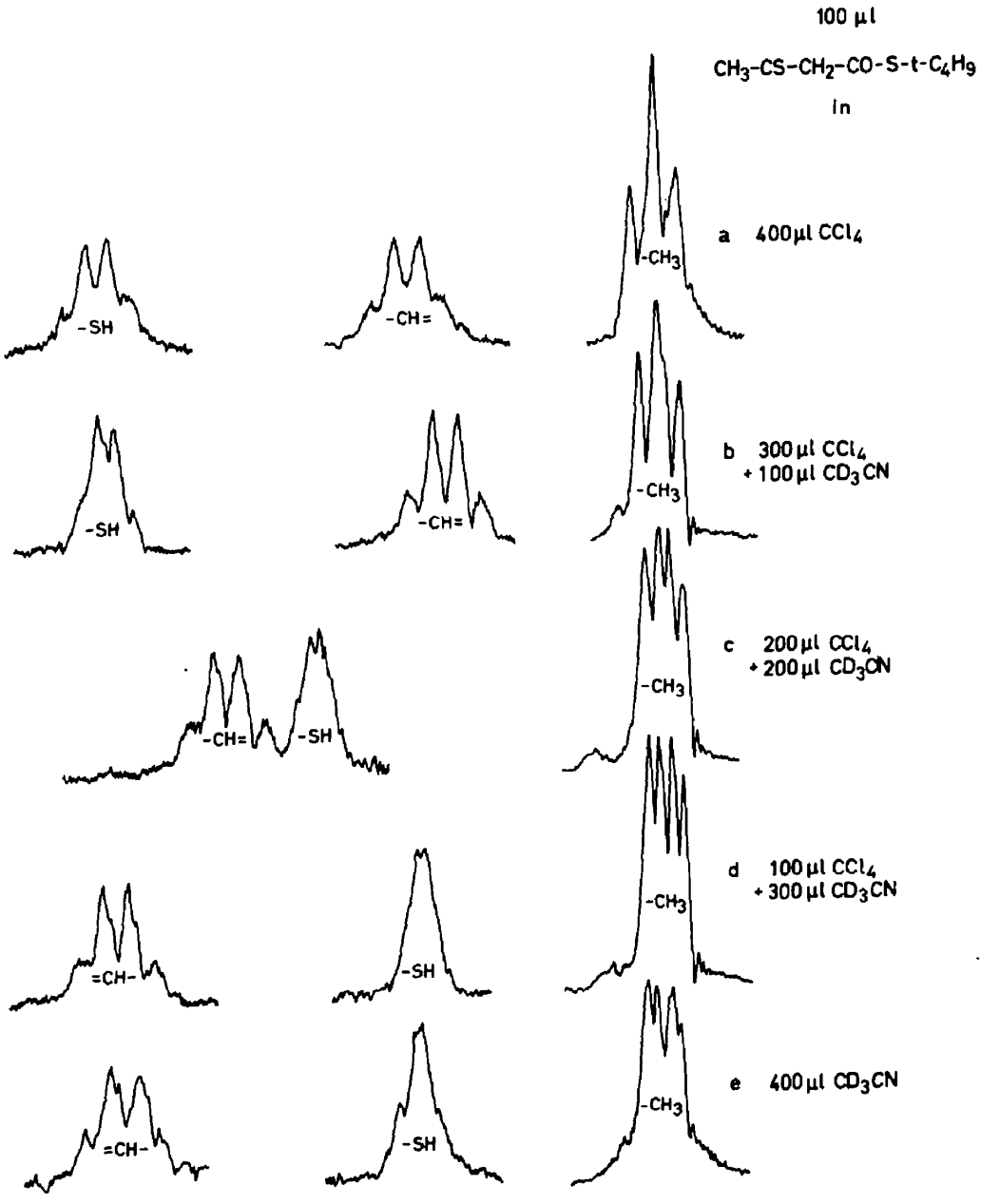


FIG. 5 Influence of varied CD_3CN concentrations on the allylic coupling and the coupling between the thiolic and the allylic protons (Sample: *t*-butyl thioacetothiolacetate).

TABLE 5. CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR *t*-BUTYL THIOACETOTHIOLACETATE DISSOLVED IN DIFFERENT CCl_4-CD_3CN MIXTURES

100 µl IIg dissolved in	δ_{HX}	δ_{HY}	δ_{HZ}	J_{XZ}	J_{YZ}
400 µl CCl_4	7·20	6·01	2·08	1·1	1·1
300 µl CCl_4 + 100 µl CD_3CN	6·47	6·12	2·12	0·8	1·1
200 µl CCl_4 + 200 µl CD_3CN	6·08	6·16	2·15	0·6	1·1
100 µl CCl_4 + 300 µl CD_3CN	5·85	6·18	2·15	0·5	1·1
400 µl CD_3CN	5·67	6·21	2·16	0·4	1·1

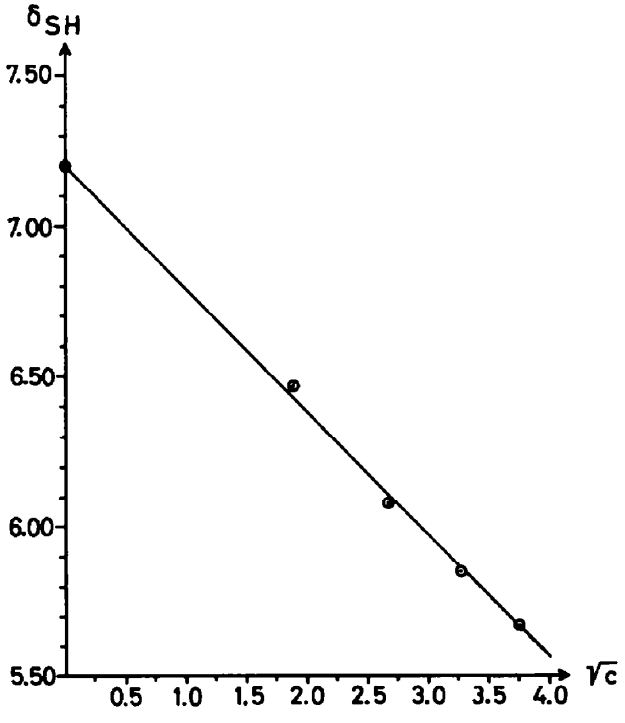


FIG. 6 Plot of δ_{SH} against the square root of the concentration (mol/l solvent) of CD_3CN. (Sample: *t*-butyl thioacetothiolacetate).

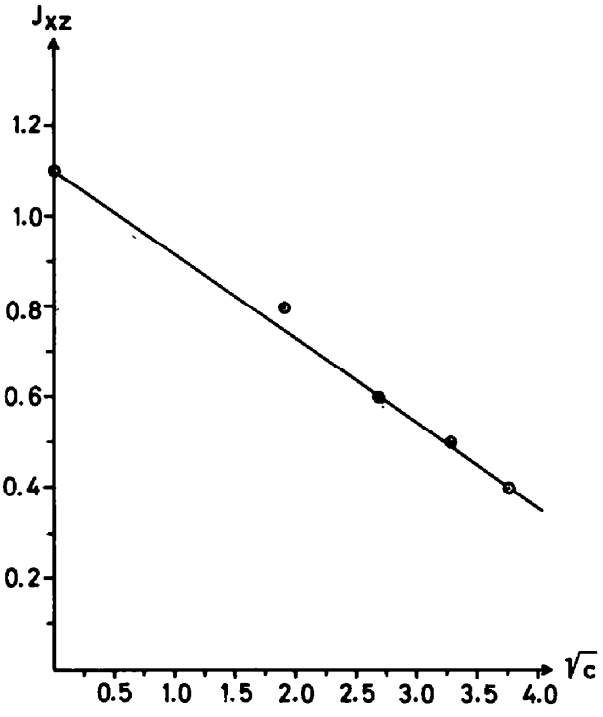


FIG. 7 Plot of J_{XZ} against the square root of the concentration (mol/l solvent) of CD_3CN. (Sample: *t*-butyl thioacetothiolacetate).

thioketo-form. It is suggested that a weak complex between the thiolester and CD_3CN is formed, thus hindering a shift in the thioketo–enethiol equilibrium in the favour of the thioketo-form.

EXPERIMENTAL

NMR spectra were recorded at 60 Mc/s on a Varian A-60 spectrometer. Unless stated to the contrary, the temps of the 15–20% solns (w/w) were 33° ± 1. TMS was used as internal reference standard and the chemical shifts are expressed in δ-values (ppm) downfield from TMS and are believed to be correct within ±0·02 ppm. The coupling constants were measured with an accuracy of ±0·1 c/s on the 50 c/s scale.

IR spectra were recorded as 5% soln in CCl_4 on either a Perkin–Elmer 521 spectrophotometer or a Beckmann IR 10 spectrophotometer.

UV spectra were measured on a Bausch & Lomb Spectronic 505 spectrophotometer.

The analyses were carried out by Dr. Alfred Bernhardt, Mülheim (Ruhr), Germany. B.ps are uncorrected.

Owing to the similarity of the syntheses of the compounds Ia–g, only one detailed working-up procedure will be given as an example. For the same reason only one of the syntheses of the compounds IIa–g will be described in detail. Experimental data for Ia–g and IIa–g are given in Tables 6 and 7. It should be noted that no attempts have been made to find the conditions for obtaining maximum yields.

TABLE 6. EXPERIMENTAL DATA FOR β-KETOTHIOLESTERS

Compound	b.p. °C/mm Hg	n_D^{25}	Yield %		Analyses % C	Analyses % H	Analyses % S
Ia	88/13	1·4985	26	Calc.	49·29	6·83	21·93
				Found	48·44	6·95	21·51
Ib	102–3/12	1·4944	41	Calc.	52·48	7·55	20·02
				Found	52·40	7·24	18·63
Ic	94/13	1·4890	38	Calc.	52·48	7·55	20·02
				Found	52·06	6·89	19·66
Id	113–15/12	1·4886	10	Calc	55·13	8·10	18·39
				Found	55·14	8·26	18·32
Ie	107–8/10	1·4849	39	Calc.	55·13	8·10	18·39
				Found	55·08	7·95	18·44
If	108/11	1·4876	38	Calc.	55·13	8·10	18·39
				Found	54·88	7·92	17·60
Ig	100/15	1·4818	17	Calc.	55·13	8·10	18·39
				Found	54·91	8·11	17·90

TABLE 7. EXPERIMENTAL DATA FOR β-THIOKETOTHIOLESTERS

Compound	gas supply	b.p. °C/mm Hg	n_D^{25}	Yield %		Analyses % C	Analyses % H	Analyses % S
IIa	H_2S: 2 hrs HCl: 1 hr	107–9/10	1·5796	61	Calc.	44·44	6·22	39·47
					Found	44·25	6·05	39·34
IIb	H_2S: 2 hrs HCl: 1 hr	123–6/10	1·5686	43	Calc.	47·72	6·87	36·33
					Found	47·53	6·69	36·43
IIc	H_2S: 1½ hr HCl: ½ hr	114/11	1·5622	80	Calc.	47·72	6·87	36·33
					Found	47·71	6·87	36·25
IId	H_2S: 2½ hr HCl: 1½ hr	137–8/12	1·5607	72	Calc.	50·52	7·42	33·66
					Found	50·34	7·40	33·91
IIe	H_2S: 1½ hr HCl: 1 hr	128–9/10	1·5592	72	Calc.	50·52	7·42	33·66
					Found	50·38	7·18	33·72
IIf	H_2S: 2½ hr HCl: 1 hr	127–8/11	1·5608	66	Calc.	50·52	7·42	33·66
					Found	50·45	7·30	33·90
IIg	H_2S: 2 hrs HCl: 1 hr	114–5/10	1·5558	75	Calc.	50·52	7·42	33·66
					Found	50·37	7·24	33·65

Iso-*butyl acetothiolacetate* (Ie): 12·6 g (0·14 mole) of *iso*-butyl mercaptan† were placed in a 100 ml 3-necked flask equipped with a stirrer, a dropping funnel, and a reflux condenser and warmed on a water bath at 50°, 0·2 g anhyd NaOAc was added under stirring and then 15·2 g (0·18 mole) of diketene were added dropwise during 1 hr also under stirring. The temp was kept below 60° during the addition of diketene. Stirring was continued for 2 hr at 40–50°. The reaction mixture was distilled and a fraction boiling at 108–115°/11 mm Hg collected and redistilled. Colourless liquid, b.p.$_{10}$: 107–108°, n_D^{25}: 1·4849, yield: 9·4 g (38·6%). (Found: C, 55·08; H, 7·95; S, 18·44. $C_8H_{14}O_2S$ requires: C, 55·13; H, 8·10; S, 18·39%).

t-*Butyl thioacetothiolacetate* (IIg). 14·7 g (0·085 mole) of *t*-butyl acetothiolacetate were dissolved in 150 ml MeCN and the soln was cooled to −60°. Keeping the temp constant, H_2S gas was passed through the soln for 2 hr followed by dry HCl gas for 1 hr. The cooling-bath was removed and after standing for 15 min, the yellow reaction mixture was poured into ice-water and extracted with benzene. The benzene layer was first washed with a diluted Na_2CO_3 aq, then with water and subsequently dried (Na_2SO_4). The benzene was removed and the remaining oil distilled to give the desired *t*-butyl thioacetothiolacetate as a wine-red oil, yield: 12·2 g (75%). B.p.$_{10}$: 114–115°, n_D^{25}: 1·5558. (Found: C, 50·37; H, 7·24; S, 33·65. $C_8H_{14}S_2$ requires: C, 50·52; H, 7·42; S, 33·66%).

Iso-*propyl β-(ethylmercapto)thiolcrotonate* (IIIc). A soln of 5·6 g of IIc (0·035 mole) in 50 ml dry benzene was added dropwise to a stirred suspension of 0·9 g NaH (0·0375 mole) in 100 ml dry benzene during 45 min. Stirring was continued until the evolution of H_2 had ceased (about 1 hr). Then a soln of 5·5 g EtI (0·035 mole) in 25 ml dry benzene was added and the reaction mixture was refluxed for 5 hr. The precipitated NaI was filtered off, the benzene removed from the filtrate, and the remaining oil distilled. The title compound is a colourless liquid, b.p.$_{10}$: 140°, n_D^{25}: 1·5609, yield: 2·7 g (38%). (Found: C, 52·97; H, 8·01; S, 31·25. $C_9H_{16}OS_2$ requires: C, 52·93; H, 7·90; S, 31·32).

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