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STUDIES ON ENETHIOLS—V*
SYNTHESES OF α-THIOACYLLACTONES AND α-THIOACYLTHIOLLACTONES. STRUCTURE DETERMINATION BY NMR SPECTROSCOPY

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Abstract—α-Thioacyllactones and α-thioacylthiollactones have been prepared in moderate to good yields by action of H_2S and HCl on the α-acyl-analogues. NMR and IR studies show that the aliphatic thioacyl compounds exist as equilibrium mixtures of the *cis*- and the *trans*-enethiol forms, whereas the thioaroyllactones are present exclusively as intramolecularly H-bonded *cis*-enethiols. The NMR spectra are discussed and the influence of different solvents on chemical shifts and coupling constants are also described and discussed. The syntheses and properties of some methylated and acetylated α-thioacyllactones are presented, and their absolute configurations determined by NMR spectroscopy.

INTRODUCTION

DURING the last few years an increasing interest has been shown in the field of enethiolizable thiocarbonyl compounds.[1, 2] Due to their instability simple aliphatic and alicyclic thiones have been synthesized[3–5] and studied[4, 5] only to a limited extent. Enethiolizable monothio-β-dicarbonyl compounds,[6–19] however, have received much attention owing to their greater stability and their ability to form stable metal chelates.[17–22] Both of these properties are related to the fact that in these compounds the thioketo-enethiol equilibrium is shifted strongly to the enethiol side, so that the *cis*-enethiol form, stabilized by an intramolecular H-bonding, is highly predominant, as recently demonstrated in the cases of β-thioketoesters[6,16] and β-thioketothiolesters.[8, 23]

As a continuation of our studies on enethiols[6–9] we have synthesized a number of the hitherto unknown α-thioacyllactones and α-thioacylthiollactones and studied them by NMR and IR spectroscopy. The α-acyl analogues have been thoroughly investigated for a number of years by Korte *et al.* with special regard to their preparation and the so-called acyllactone rearrangement,[24, 28] but the tautomerism of these compounds have also been studied.[24–26] The α-acyllactones and α-acylthiollactones exist mainly as the keto-tautomers,[24, 26] but in many cases the *cis*-enol form is also present, the amount being strongly dependent on the solvent used.[24] Halometric titrations[26] gave evidence for the existence of a *trans*-enol form in some cases, but according to a recent paper[24] this tautomer is non-existent, supposedly because of its relative instability. This is in good agreement with the result obtained by Yoffe *et al.* from studies on 2-formyl-2-phenylacetic esters.[27]

RESULTS AND DISCUSSION

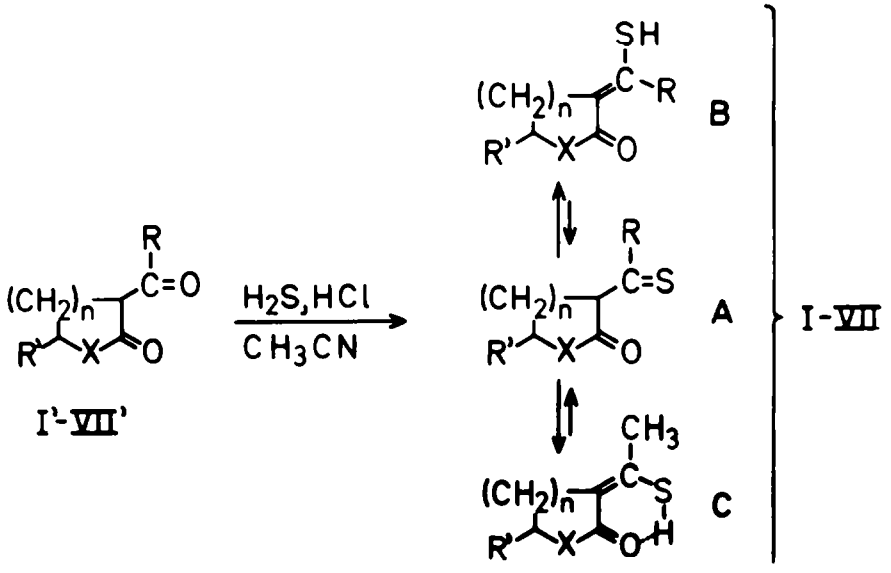
Syntheses of α-thioacyllactones and α-thioacylthiollactones

The conversion of a CO group into the corresponding CS group by treatment of the former with hydrogen sulphide has been successfully demonstrated in the cases of β-thioketoesters[6, 7] and β-thioketothiolesters.[8] These reactions were carried out in

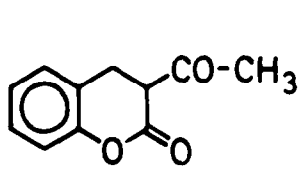
* Part IV: see Ref. 9.

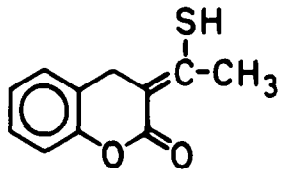
the presence of hydrogen chloride at low temperatures and in polar solvents. The yields were good, although apparently strongly dependent on the reaction temperature.[6, 8, 10]

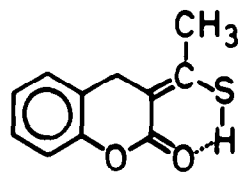
Using acetonitrile as solvent the thioacyllactones I–V and VIII and the thioacylthiollactones VI–VIII were synthesized from the oxygen analogues I'–VIII' under the above-mentioned conditions. The yields were generally good, varying from 38 to 82%. Rather surprisingly it turned out that variations in the reaction temperature affected the yields only to a very small degree. Further, no by-products such as *gem*-dithiols or *sym*-trithianes could be isolated or detected even at reaction temperatures up to about 40°. This contrasts sharply with the case where a β-ketoester or a β-ketothiolester is the reaction participant.[6, 8, 10] Prolonged reaction times had no other effect than to increase the otherwise negligible amount of thioacetamide



	R	R'	X	n
I	CH_3	H	O	1
II	CH_3	CH_3	O	1
III	C_2H_5	H	O	1
IV	*n*-C_3H_7	H	O	1
V	*iso*-C_3H_7	H	O	1
VI	CH_3	H	S	1
VII	CH_3	H	S	2

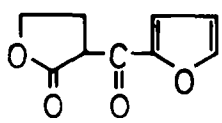

VIII'

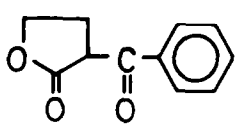

VIII B

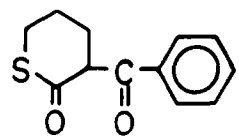

VIII C

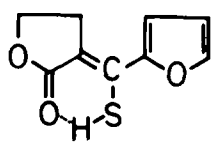
hydrochloride formed by the action of hydrogen sulphide on the solvent. This competitive reaction is of no importance if the reaction time is shorter than about 8 hr and the reaction temperature is kept below about −20°.

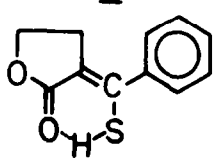
Attempts to react the compounds IX′–XI′ in acetonitrile were rather unsuccessful. A small yield of IX was obtained, but neither X nor XI could be isolated.

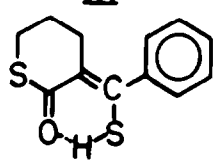

IX'


X'

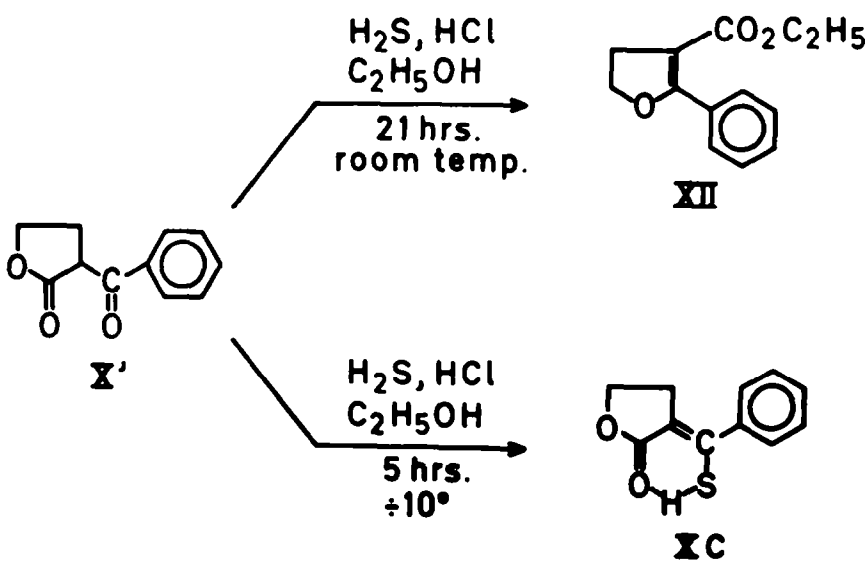

XI'


IX C

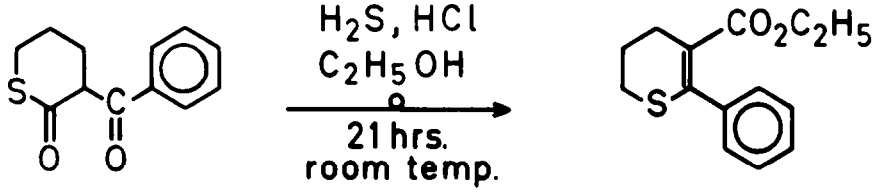

X C


XI C

However, when ethanol was used as solvent, IX could be obtained in 50% yield after treatment of IX′ with hydrogen sulphide and hydrogen chloride for 21 hr at room temperature. The same conditions failed to give X in a satisfactory yield. The reaction resulted in a complex mixture, from which the main product, the rearranged compound XII, could be isolated.

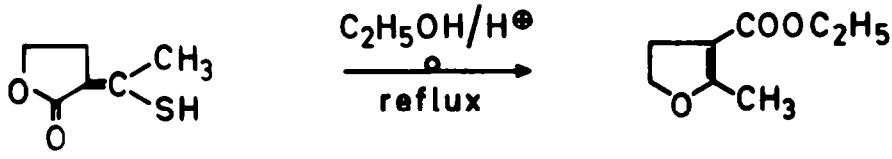


A lower reaction temperature (about $-10°$) afforded, however, a better yield of X. This temperature seems to be crucial for the formation of X, as reactions carried out below $-20°$ result in the regeneration of the starting material, and reactions carried out above $-10°$ result in rapidly increasing amounts of XII. When XI′ was reacted at room temperature, only the rearranged compound XIII could be isolated in a yield of 83%. Reaction at lower temperatures still afforded formation of XIII, although in reduced yields. Even at $-40°$ no XI could be isolated, the reaction mixture containing only XIII and unreacted XI′.



XI′ XIII

It is well-known that α-acyllactones and α-acylthiollactones on warming in acid alcoholic solutions may undergo the acyllactone rearrangement,[24, 28] thereby being converted to products like XII and XIII. It could be assumed that simple rearrangements of X′ and XI′ actually take place, but the violet colour (from the thioaroyl chromophore) of the reaction mixture in both cases, together with the fact that under critical conditions X can be isolated leads us to suppose that it is the thioacyl compounds which rearrange. In this connection it should be noted that several α-thioacyllactones have been found to undergo what could be called the thioacyllactone rearrangement, e.g.



Further investigations of this new rearrangement are in progress and will be the subject of a separate paper.[29]

Spectroscopic studies

The advantageous application of NMR spectroscopy in studies of tautomeric phenomena has been amply demonstrated, particularly in the case of keto-enol tautomerisms.[30] Also in thioketo-enethiol equilibria, in which the tautomers are relatively slowly interconverted, the proton signals of the individual isomers may be expected to be clearly distinguishable. This has, in fact, been found to be the case.[5, 6, 8] Thus it was found that β-thioketoesters and β-thioketothiolesters[8] exist to a very high degree as intramolecularly chelated enethiols, whereas the thioketo form represents only a small percentage and a nonchelated enethiol form is either non-existent or present to a negligible extent.

On the basis of these experiences we also expected to find a predominance of the chelated enethiol form (C) among the lactones. However, the NMR spectra of I–VIII

showed in addition the presence of considerable amounts of another tautomer, (Figs 1–4), which could be unambiguously identified as the *trans*-enethiol form (B).

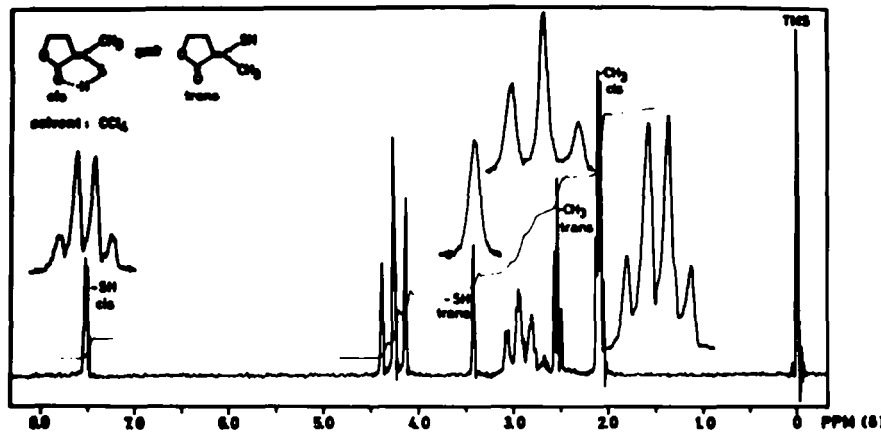


FIG. 1 NMR spectrum of α-thioacetyl-γ-butyrolactone (I) showing the co-existence of the two enethiol forms, B and C (solvent: CCl_4).

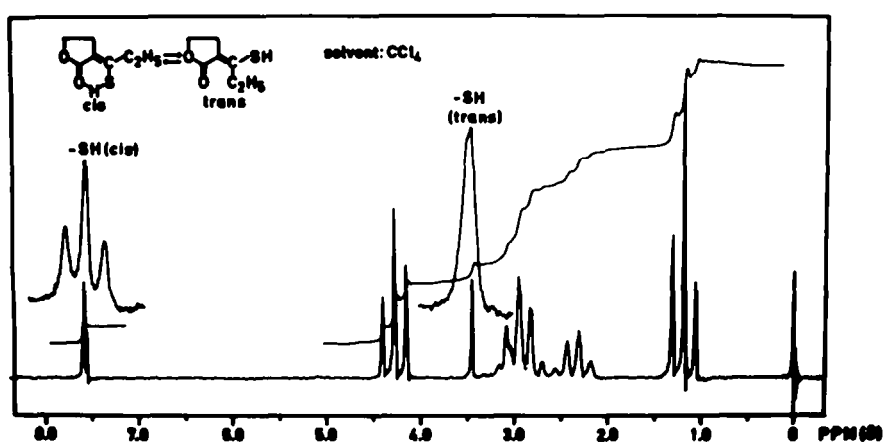


FIG. 2 NMR spectrum of α-thiopropionyl-γ-butyrolactone (III) (solvent: CCl_4).

In spite of the pink colour (believed to be due to the thioacetyl chromophore), which characterizes several of the thioacyllactones, the thioketo form is never detectable in the NMR spectra, even at temperatures up to 120° although an unmistable thermochromatic effect, being reflected in an increase in the intensity of the pink colour, is observed.

The existence of a true tautomeric equilibrium between the *cis*-enethiol form (C) and the *trans*-enethil form (B) has been firmly established in the present studies. Firstly, the *cis*-trans ratio was found to be solvent-dependent to some degree. Secondly, on standing for a few days, all lactones increased their *trans*-percentage, until an equilibrium position was reached. The latter effect was most pronounced in the case of VI, which after several recrystallizations could be obtained as almost pure

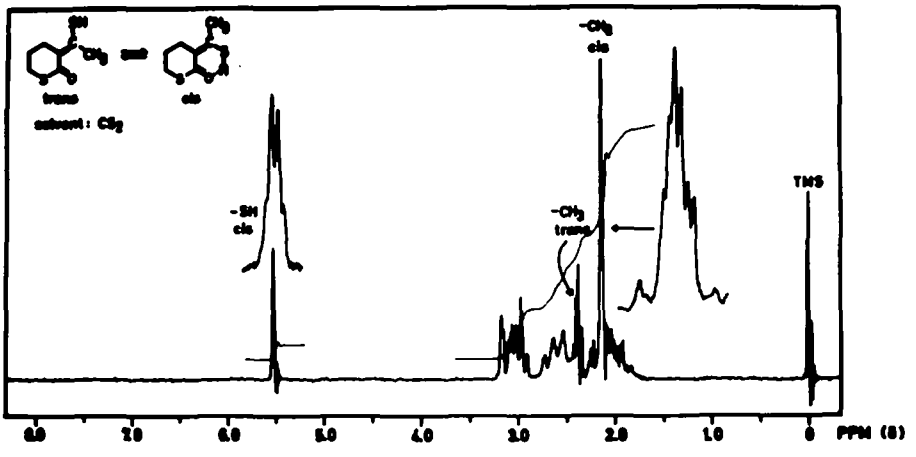


FIG. 3 NMR spectrum of α-thioacetyl-δ-valerothiollactone (VII) (solvent: CS_2).

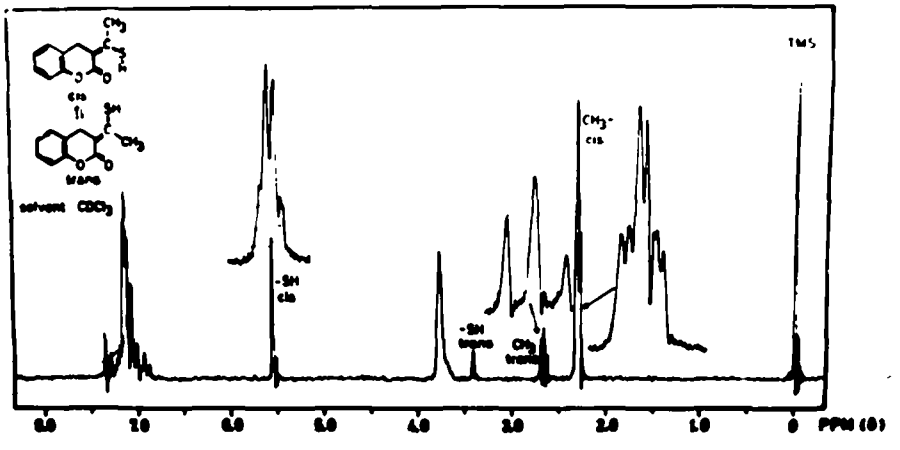


FIG. 4 NMR spectrum of 3-thioacetyl-3.4-dihydrocoumarin (VIII) (solvent: $CDCl_3$).

VI C. The NMR spectrum of a freshly prepared solution of recrystallized VI in CCl_4 showed a VI B-percentage of about 5–6. After standing for a week, the VI B tautomer was found to be present to about 31%.

The thioaroyllactones IX and X exist exclusively as chelated *cis*-enethiols, as seen in Figs 5 and 6. No other tautomer could be detected, even if the solutions were allowed to stand for a week. The equilibrium percentages of the *trans*-enethiol form for all thioacyllactones under investigation are tabulated below (Table 1).

The relatively lower *trans*-form percentages of II, VI, and VII are not immediately explainable, but may be considered in relation to observations made by Korte and Wüsten,[26] according to whom unsubstituted 5-membered-ring α-acyllactones are enolized to a lesser extent than the corresponding alkyl-substituted compounds regardless of the position of the alkyl substituent (β- or γ-position). Further, the same authors found[26] that α-acylthiollactones are generally more enolized than the oxygen-analogues.

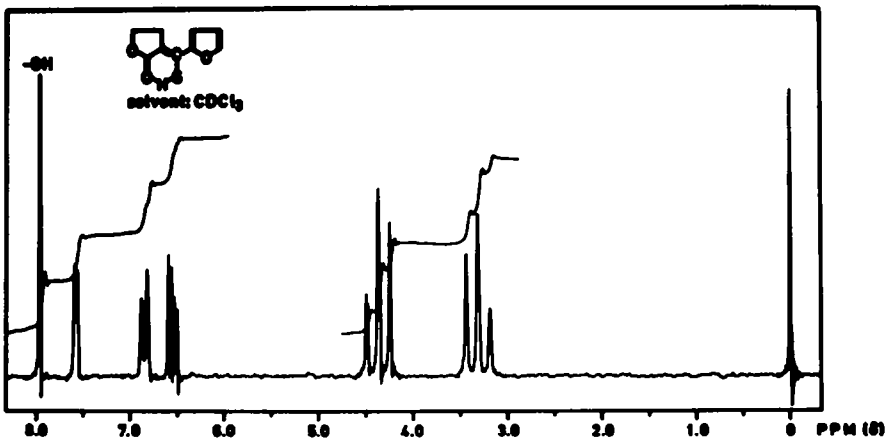


FIG. 5 NMR spectrum of α-thiofuroyl-γ-butyrolactone (IX) (solvent: $CDCl_3$).

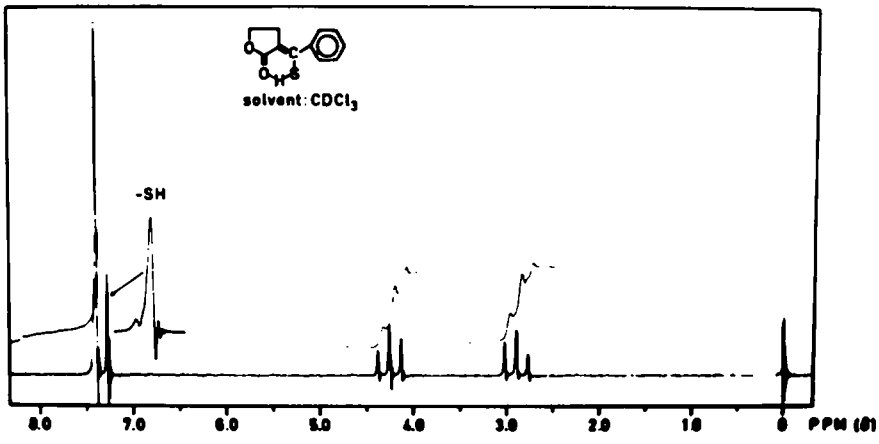


FIG. 6 NMR spectrum of α-thiobenzoyl-γ-butyrolactone (X) (solvent: $CDCl_3$)

TABLE 1. PERCENTAGES OF *trans*-ENETHIOL FORMS AFTER STANDING IN SOLUTION FOR A WEEK

Compound	Solvent	*trans*-%	Compound	Solvent	*trans*-%
I	CCl_4	45 ± 1	VI	CCl_4	31 ± 2
II	CCl_4	34 ± 1	VII	CCl_4	35 ± 2
III	CCl_4	42 ± 1	VIII	$CDCl_3$	40 ± 1
IV	CCl_4	43 ± 2	IX	$CDCl_3$	0
V	CCl_4	24 ± 2	X	$CDCl_3$	0

The non-existence of a *trans*-form in the cases of IX and X is presumably due to the otherwise unfavourable sterical interaction between the aryl group and the lactone CO group, which may also account for the lower *trans*-form percentage of V. This is fully confirmed from model studies.

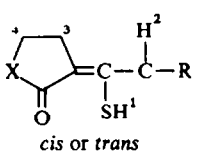
The striking difference in chemical shift between the thiolic protons of the two forms, B and C (see Figs 1–4 and Table 2), is explained by the presence of an intramolecular H-bonding in C, keeping the thiolic proton in a more fixed position. The anisotropic effect from the CO group, in connection with the changed electronic environment caused by the H-bonding, is then responsible for the observed displacement against lower field.

The chemical shift of the side-chain protons in the α-position to the enethiol-function (H^2) is also clearly dependent on the molecular structure, i.e. on whether it is the B or the C form. If in the B form, such protons are exposed to deshielding due to the anisotropy of the lactone CO group, which has only a negligible effect on the corresponding C-form protons. The resulting difference in chemical shift is demonstrated most clearly by the Me protons in I, VII and VIII (Figs 1, 3 and 4), although it is most pronounced in V, due to the special steric properties of the isopropyl group.

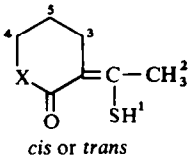
The correct determination of the chemical shifts of the β-protons of the lactone ring (H^3) is verified by spin-decoupling experiments.

TABLE 2. CHEMICAL SHIFTS (δ-VALUES, PPM) AND COUPLING CONSTANTS (C/S) OF α-THIOACYLLACTONES AND -THIOLLACTONES*

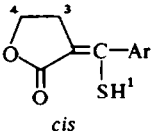
* The following abbreviations are used: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br. (broad). Unless stated to the contrary, the solvent is CCl_4.



cis or *trans*
I–VI



cis or *trans*
VII, VIII



cis
IX, X

	SH^1	H^2	R	Ar	H^3	H^4	H^5	J_{12}	J_{23}
IB	3·43 3·17[a] s	2·54 t	—	—	2·81 br. t	4·27 t	—	—	2·1
IC	7·53 7·82[a] q	2·11 q	—	–	2·93 br. t	4·27 t	—	1·1	1·5
IIB	3·47 3·18[a] s	2·54 t	—	—	2·2–3·4 m	4·54 m 1·40[b] d	—	—	2·1
IIC	7·57 7·84[a] q	2·07 q	—	—	2·2–3·4 m	4·54 m 1·40[b] d	—	1·15	1·5

TABLE 2—*continued*

	SH[1]	H[2]	R	Ar	H[3]	H[4]	H[5]	J_{12}	J_{23}
IIIB	3·45 3·17[a] s	~2·96 br. q	1·19[b] t	—	2·82 br. t	4·26 t	—	—	?
IIIC	7·57 7·85[a] t	2·37 br. q	1·19[b] t	—	2·95 br. t	4·26 t	—	1·25	?
IVB	3·43 3·20[a] s	~2·97 br. t	1·65[c] m 1·00[b] t	—	~2·83 br. t	4·27 t	—	—	?
IVC	7·65 7·90[a] t	~2·34 br. t	1·65[c] m 1·00[b] t	—	~2·97 br. t	4·27 t	—	1·3	?
VB	3·37 3·20[a] s	~4·47 br. m	1·13[b] d	—	2·84 br. t	4·28 t	—	—	?
VC	7·89 8·04[a] d	~2·7 br. m	1·17[b] d	—	2·97 br. t	4·28 t	—	~1	?
VIB	3·30 3·16[a] s	2·49 t	—	—	2·8–3·4 m	2·8–3·4 m	—	—	1·8
VIC	7·37 7·75[a] q	2·12 q	—	—	2·8–3·4 m	2·8–3·4 m	—	1·0	1·0
VIIB	3·14 2·93[a] s	2·45 t	—	—	2·4–2·8 br. m	2·9–3·2 br. m	1·9–2·2 br. m	—	1·5
VIIC	5·72 6·33[a] q	2·18 d, t	—	—	2·4–2·8 br. m	2·9–3·2 br. m	1·9–2·2 br. m	0·4	0·8
VIIIB*	3·42 3·34[a] s	2·67 t	—	—	3·71 br. q	6·8–7·4[d] m		—	1·8
VIIIC*	5·55 5·68[a] q	2·31 d, t	—	—	3·77 br. q	6·8–7·4[d] m		0·5	1·1
IXC†	8·44 s	—	—	see text	3·32 t	4·32 t	—	—	—

TABLE 2—*continued*

	SH^1	H^2	R	Ar	H^3	H^4	H^5	J_{12}	J_{23}
IXC*	7·99 8·07[a] s	—	—	see text	3·32 t	4·37 t	—	—	—
XC†	7·79 7·95[a] s	—	—	7·38 s	2·90 t	4·22 t	—	—	—
XC*	7·28 s	—	—	7·40 s	2·89 t	4·26 t	—	—	—

* in $CDCl_3$-soln † diluted CCl_4-soln
[a] at infinite dilution[6] [b] Me protons [c] methylene protons [d] aromatic protons.

In agreement with earlier observations[6,8] the signal of the chelated enethiolic proton, in all cases except IX C and X C, exhibits a fine-structure being due to the coupling between the enethiolic proton and the allylic protons (H^2). Further, a good qualitative agreement is found between the size of the coupling constants (J_{12}) and the chemical shift of the enethiolic protons. The displacement of chelated enolic[31] and enethiolic[6,8] proton signals against lower field is generally accepted as a measure of the strength of the H-bond. It therefore seems reasonable to postulate that the size of the coupling constant J_{12} reflects the strength of the H-bond. When CD_3CN is used as solvent, a displacement of the chelated enethiolic proton signal against higher field (relative to that obtained in CCl_4-solution) is observed, together with a decrease in J_{12}. This effect has also been observed recently for β-mercaptothiol-crotonic esters[8] (β-thioketothiolesters), and has been explained by a dipole–dipole interaction between the enethiol and the CD_3CN molecules, thus weakening or disturbing the intramolecular H-bonding.

Characteristic for all the enethiols under consideration (with the natural exception of IX C and X C), is the homoallylic long-range coupling between the side-chain protons in α-position to the enethiol-function (H^2) and the β-protons of the lactone ring (H^3). As seen in Table 2, this coupling is observed for *cis*- as well as for *trans*-forms. Although the size of the coupling constant (J_{23}) is somewhat variable, the *trans*-coupling is always greater than the corresponding *cis*-coupling. It should be noted that the tabulated values of J_{23} are based on the assumption of an approximately first order spin–spin coupling system.

Other couplings seem trivial and do not need further discussion. However, the furanoic protons of IX C should be mentioned. The chemical shifts and the coupling constants are ($CDCl_3$-solution, numbers refer to ring-positions!): $\delta_3 = 6{\cdot}86$ (d), $\delta_4 = 6{\cdot}56$ (dd), $\delta_5 = 7{\cdot}59$ (d), $J_{34} = 3{\cdot}6$ c/s, and $J_{45} = 1{\cdot}75$ c/s. Thus the couplings are quite typical.[32] The solvent CCl_4 afforded no alterations of significance.

NMR spectra of the thioacyllactones dissolved in C_6D_6 show a greater or lesser displacement of all proton signals against higher field, as compared to when CCl_4 (or $CDCl_3$) is the solvent. This displacement can be explained by the formation of

collision complexes between the solute molecules and the C_6D_6 molecules. As pointed out by Ledaal,[33] dipole solute molecules will orientate themselves in such a way that the dipole axis of the solute molecule is located along the sixfold symmetry axis of a benzene nucleus, with the positive end of the dipole nearest, and the negative end farthest away from it. Once orientated, the solute molecule will be exposed to the diamagnetic anisotropy associated with the induced ring current in the benzene molecule,[34] resulting in shielding (or deshielding) of the solute protons. As an example the chemical shifts of I in C_6D_6 solution together with the solvent shifts $\Delta\delta = \delta^{CCl_4} - \delta^{C_6D_6}$ are seen in Table 3.

TABLE 3. CHEMICAL SHIFTS (δ-VALUES, PPM) OF IB AND IC IN C_6D_6-SOLUTION AND CALCULATED SOLVENT SHIFTS $\Delta\delta = \delta^{CCl_4} - \delta^{C_6D_6}$

	IB				IC			
	H^1	H^2	H^3	H^4	H^1	H^2	H^3	H^4
$\delta^{C_6D_6}$	2·71 s	2·71 t	1·87 m	3·43 t	7·36 q	1·38 q	1·87 m	3·43 t
$\Delta\delta$	0·72	0·37	0·94	0·84	0·17	0·73	1·06	0·84

The formation and cleavage of collision complexes can be assumed to take place at a much faster rate than that with which B rearranges to C (or vice versa). Therefore, it seems reasonable to explain the solvent shifts listed in Table 3 by the existence of two kinds of collision complexes, one for each of the tautomeric forms, B and C. This is demonstrated in Fig. 7.

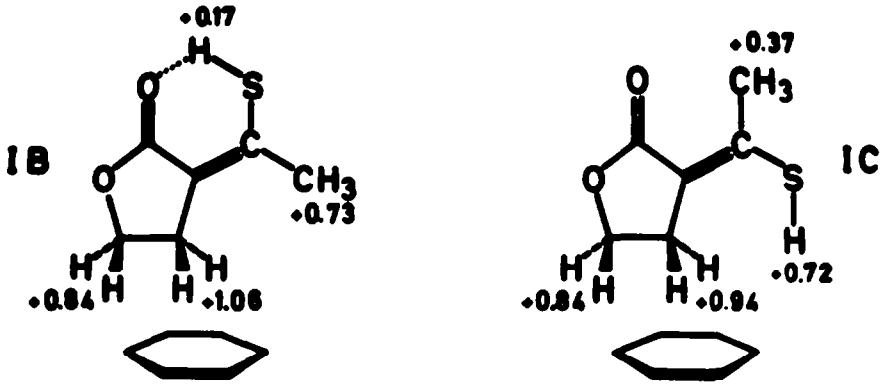


FIG. 7 Models of collision complexes between the C_6D_6 molecule and *cis*- and *trans*-α-[1-mercaptoethylidene]-γ-butyrolactone molecules (IC and IB). The solvent shifts are expressed in ppm.

The IR spectra of I–X give further support to the conclusions derived from the NMR spectra. Those of the aliphatic compounds I–VIII all show two CO stretching absorption bands and two C=C stretching absorption bands, thus indicating the presence of both B and C. Broad bands in the SH-region and bands about 680 cm^{-1} arising from the C—S single bond stretchings are also seen. The IR spectra of the

aromatic compounds IX and X show, as expected, only a single absorption band in the CO region as well as in the region of olefinic stretchings. A typical IR spectrum is seen in Fig. 8, and IR absorption bands of interest for all compounds I–X are tabulated in Table 4.

TABLE 4. IR ABSORPTION BANDS OF α-THIOACYLLACTONES AND -THIOLLACTONES

	ν[S—H] C	ν[C=O] B	ν[C=O] C	ν[C=C] B	ν[C=C] C	ν[C—S—]
I	2449 m, br.	1748 s	1715 s	1634 s	1613 s	684 w
II	2440 m, br.	1742 s	1710 s	1631 s	1610 s	679 s
III	2438 m, br.	1746 s	1710 s	1627 s	1607 s	685 w
IV	2435 m, br.	1744 s	1709 s	1624 s	1603 s	689 w
V	2428 m, br.	1747 s	1712 s	1614 s	1596 s	683 w
VI	2425 m, br.	1671 sh	1632 s	1584 w, sh	1565 s	670 w 693 w
VII	—	—	1617 m	1590 sh	1535? m, br.	655 w 692 w
VIII*	2434 m, br.	1723 sh	1699 s	—	1595 m	669 m
IX*	2432 m, br.	—	1697 s	—	1590 m	667 w
X	2432 m, br.	—	1701 s	—	1577 s	673 m

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

* solvent: $CHCl_3$.

Alkylation and acylation of α-thioacyllactones

Methylation and acetylation of α-thiofuroyl-γ-butyrolactone (existing exclusively as IX C) afforded, as expected, only the *cis*-products XIV C and XV C:

Surprisingly, however, it turned out that methylation of I (existing as an equilibrium mixture of I B and I C) gave only XVI B in a low yield. Although acetylation of I

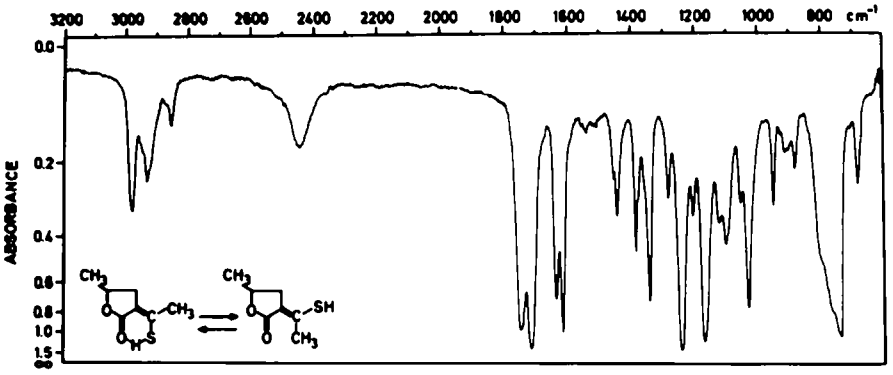
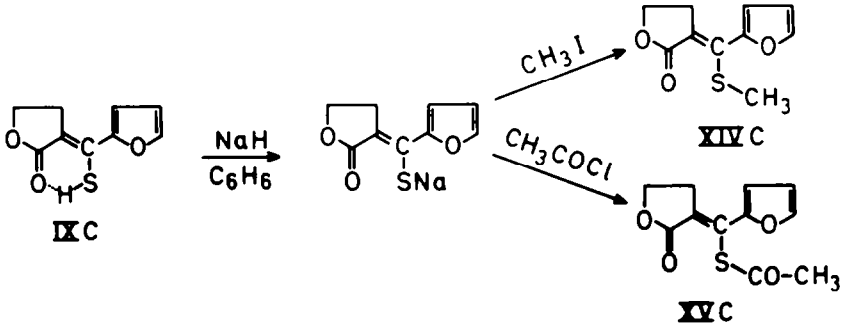


FIG. 8 IR spectrum of α-thioacetyl-γ-valerolactone (II).

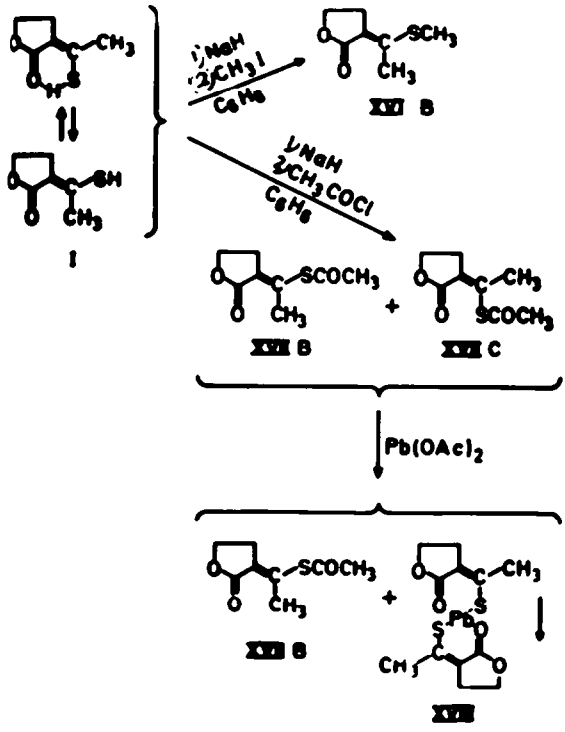


afforded the expected mixture of XVII B and XVII C, the lesser stability of the *cis*-form is demonstrated by the reaction of this mixture with lead acetate. XVII B was regenerated, but XVII C reacted under formation of the lead complex XVIII. Examples of cleavage of thiolesters by mercury (II)- and silver(I)-salts are known,[35] but, so far known, no such cleavage has been performed with a lead salt. Fig. 9 shows

TABLE 5. NMR DATA OF METHYLATED AND ACETYLATED α-THIOACYL-γ-BUTYROLACTONES

	H^2	H^3	H^4	CH_3	J_{23}
XIVC†	—	3·18	4·33	2·29	—
XVC†	—	3·53	4·38	2·44	—
XVIB*	2·50	2·74	4·23	2·42	2·2
XVIIB*	2·50	2·92	4·28	2·39	2·4
XVIIC*	2·23	3·04	4·31	2·37	1·8

* solvent: CCl_4
† solvent: $CDCl_3$.



the NMR spectrum of the *cis-trans*-mixture of XVII as well as the NMR spectrum of the pure *trans*-isomer, XVII B, obtained after treatment of the isomer-mixture with lead acetate.

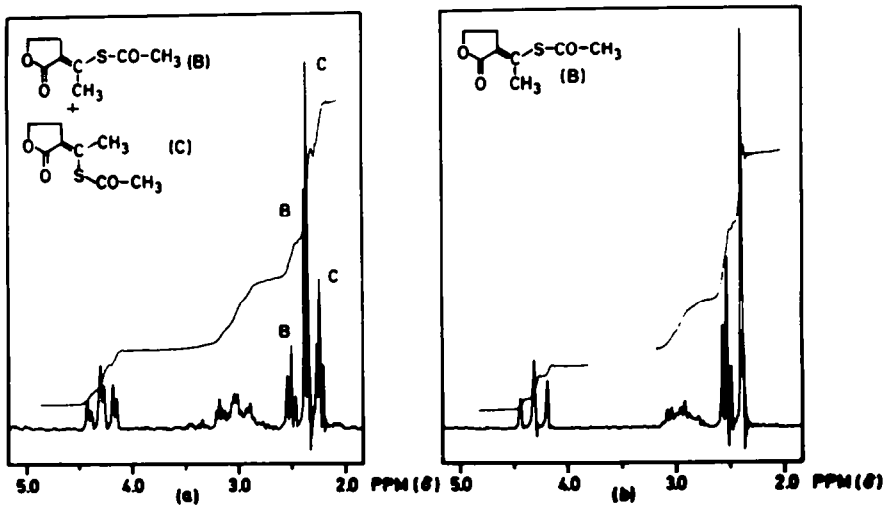


FIG. 9 a: NMR spectrum of the *cis-trans*-mixture of XVII, obtained after acetylation of I.
b: NMR spectrum of pure XVIIB.

NMR data of the methylated and acetylated α-thioacyllactones are seen in Table 5. The size of the coupling constant J_{23} in XVI B and XVII B agrees well with that observed in I B, and a similar good agreement is found between J_{23}'s in XVII C and I C. The signals from the *trans*-allylic Me protons (H^2) assume approximately the same chemical shift in I B, XVI B, and XVII B, whereas a small displacement against lower field is observable for the corresponding *cis*-form signal in XVII C relatively to that of I C. This chemical shift difference is probably a consequence of the hydrogen-bonding present in I C.

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, expressed numerically in c/s, were measured with an accuracy of ±0·1 c/s on the 50 c/s scale.

IR spectra were recorded as 5% solns in CCl_4 or $CHCl_3$ 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 solvent was EtOH.

M.ps are corrected, b.ps are uncorrected. The yields refer to the pure products.

The acyllactones II′–V′, IX′ and X′ were all prepared after a method described by Korte and Wüsten.[26] Some of them are known (II′,[36] IV′,[37] and X′[38]), but III′, V′, and IX′ are new compounds and will therefore be characterized below. Known procedures were also employed by the syntheses of VI′,[39] VII′,[40] VIII′[41] and XI′.[40] I′ is a commercial sample.

α-*Propionyl-γ-butyrolactone* (III′). Yield: 15%, b.p.$_{13}$: 139–140°, n_D^{25}: 1·4622. (Found: C, 59·27; H, 7·19. $C_7H_{10}O_3$ requires: C, 59·14; H, 7·09%).

α-(iso-*Butyryl-γ-butyrolactone* (V′). Yield: 12%, b.p.$_{10}$: 125–127°. (Found: C, 62·18; H, 8·20; $C_8H_{12}O_3$ requires: C, 61·52; H, 7·75%).

α-*Furoyl-γ-butyrolactone* (IX′). Yield: 43%, m.p.: 70–72°. (Found: C, 60·01; H, 4·50. $C_9H_8O_4$ requires: C, 60·00; H, 4·48%).

It should be noted that no attempts have been made to find conditions leading to optimum yields of III′, V′, and IX′.

α-*Thioacetyl-γ-butyrolactone* (I). 32·0 g (0·25 mole) of I′ were dissolved in 300 ml MeCN and the soln was cooled to −60°. Keeping the temp constant, H_2S gas was passed through the soln for 1 hr followed by dry HCl gas also for 1 hr. The cooling-bath was removed, and the reaction mixture was allowed to stand for 5–6 hr while H_2S gas was supplied very slowly. The reaction mixture was then poured into a benzene–ice-water mixture under stirring. The benzene-layer was separated, washed with water, and dried (Na_2SO_4). The benzene was removed and the residue oil distilled. The destillate solidified, and recrystallization from a light petroleum–benzene mixture gave pure I as white crystals, yield: 27·1 g (75%), m.p. 34–39°, b.p.$_{13}$: 154–156°. λ_{max} (log ε_{max}): 278 mμ (3·98); 326 mμ (3·24). (Found: C, 49·92; H, 5·60; S, 21·98. $C_6H_8O_2S$ requires: C, 49·97; H, 5·59; S, 22·24%).

α-*Thioacetyl-γ-valerolactone* (II). 14·2 g (0·1 mole) of II′ were dissolved in 150 ml MeCN and treated as above, yield: 12·3 g (78%); pale pink oil, b.p.$_{0·15}$: 82–84°, n_D^{25}: 1·5460; λ_{max} (log ε_{max}): 281 mμ (4·05); 348 mμ (3·61). (Found: C, 53·18; H, 6·42; S, 19·94. $C_7H_{10}O_2S$ requires: C, 53·16; H, 6·37; S, 20·24%).

α-*Thiopropionyl-γ-butyrolactone* (III). 15·6 g (0·11 mole) of III′ dissolved in 200 ml MeCN were treated with H_2S and HCl as described under I, yield: 14·3 g (82%); pink oil, b.p.$_{0·5}$: 115–116°, n_D^{25}: 1·5545; λ_{max} (log ε_{max}): 279 mμ (4·03); 332 mμ (2·90). (Found: C, 53·32; H, 6·42; S, 19·88. $C_7H_{10}O_2S$ requires: C, 53·16; H, 6·37; S, 20·24%).

α-*Thiobutyryl-γ-butyrolactone* (IV). 15·6 g (0·1 mole) of IV′ dissolved in 200 ml MeCN were treated with H_2S and HCl as described under I, yield: 6·5 g (38%); pink oil, b.p.$_{0·3}$: 109–110°, n_D^{25}: 1·5437; λ_{max} (log ε_{max}): 281 mμ (3·97); 332 mμ (2·90). (Found: C, 56·22; H, 7·12; S, 18·25. $C_8H_{12}O_2S$ requires: C, 55·80; H, 7·03; S, 18·59%).

α-*Thio*-iso-*butyryl-γ-butyrolactone* (V). 15·6 g (0·1 mole) of V′ dissolved in 250 ml MeCN were reacted

with H_2S and HCl as described under I, yield: 8·4 g (49%); pink oil, b.p.$_{0·1}$: 87–89°, n_D^{25}: 1·5406; λ_{max} (log ε_{max}): 285 mμ (3·85); 339 mμ (2·79). (Found: C, 55·77; H, 7·09; S, 18·46. $C_8H_{12}O_2S$ requires: C, 55·80; H, 7·03; S, 18·59%).

α-*Thioacetyl-γ-butyrothiollactone* (VI). 10·8 g (0·075 mole) of VI′ were dissolved in 200 ml MeCN. H_2S gas was passed through the soln for 1 hr at −60° followed by dry HCl gas also for 1 hr at −60°. The temp was raised to about −30° and kept constant for 3 hr, meanwhile H_2S gas was passed very slowly through the soln. The reaction mixture was then poured into a benzene–ice-water mixture and worked up as described under I, yield: 8·7 g (72%). Pale yellow crystals, m.p. 59–61°, b.p.$_{0·2}$: 118–122°, λ_{max} (log ε_{max}): 305 mμ (4·06); 366 mμ (2·57). (Found: C, 44·72; H, 5·00; S, 39·29. $C_6H_8OS_2$ requires: C, 45·00; H, 5·04; S, 39·97%).

α-*Thioacetyl-δ-valerothiollactone* (VII). 7·3 g (0·046 mole) of VII′ dissolved in 150 ml MeCN were successively treated with H_2S gas at −60° for 1 hr, with HCl gas at −60° for 1 hr, and with H_2S gas (very slow stream) at about −20° for 5 hr. Otherwise following the working-up procedure described under I, VII was obtained as a yellow oil, which partly crystallized on standing, yield: 5·2 g (65%), b.p.$_{0·1}$: 110–113°, λ_{max} (log ε_{max}): 304 mμ (4·02); 365 mμ (3·02). (Found: C, 48·11; H, 5·74; S. 36·75. $C_7H_{10}OS_2$ requires: C, 48·27; H, 5·79; S, 36·75%).

3-*Thioacetyl-3.4-dihydrocoumarin* (VIII). 5·7 g (0·03 mole) of VIII′ dissolved in 100 ml MeCN were treated with H_2S (1 hr, −60°), with HCl (1 hr, −60°), and finally again with H_2S (2–3 hr, room temp). The working-up procedure was identical with that described for I except that no distillation was carried out after the removal of the benzene. Direct crystallization of the residue gave pure VIII as yellowish crystals, m.p. 110–114°, yield: 2·6 g (42%); λ_{max} (log ε_{max}): 281 mμ (3·96); 352 mμ (3·48). (Found: C, 64·04; H, 4·91; S, 15·67. $C_{11}H_{10}O_2S$ requires: C, 64·07; H, 4·89; S, 15·92%).

α-*Thiofuroyl-γ-butyrolactone* (IX). 14·4 g (0·08 mole) of IX′ were dissolved in 300 ml 99% EtOH. A stream of H_2S gas was passed through the soln for 1 hr at room temp followed by a stream of dry HCl gas also for 1 hr at room temp. The soln was allowed to stand for 20 hr while H_2S gas was bubbled through it very slowly. The reaction mixture was then poured into a benzene–ice-water mixture under stirring, the benzene-layer was separated, washed twice with water, and dried (Na_2SO_4). The benzene was removed leaving a dark green, crystalline substance (12·7 g), which was dissolved in MeCN and treated with an excess of $Pb(OAc)_2$ dissolved in 50% aqueous EtOH. The resulting yellow ppt was washed successively with H_2O, EtOH, and ether, and finally dried. It was then suspended in ether, and H_2S gas was passed through the suspension for 1½ hr. After filtration, the filtrate was dried (Na_2SO_4), the ether evaporated, and the remaining greenish substance recrystallized (benzene), yield: 7·8 g (50%); pale yellow-green crystals, m.p. 80–81°; λ_{max} (log ε_{max}): 318 mμ (4·14). (Found: C, 55·06; H, 4·13; S, 16·24. $C_9H_8O_3S$ requires: C, 55·10; H, 4·11; S, 16·31%).

α-*Thiobenzoyl-γ-butyrolactone* (X). 250 ml EtOH was cooled to −15° and saturated with dry HCl and H_2S. 10 g (53 mmole) of X′ were added, and a moderate stream of H_2S gas was passed through the soln for 5 hr. The temp was kept constant at −15°. EtOH was evaporated, and the precipitated crystals recrystallized (ether), yield: 6·6 g (61%); white crystals, m.p. 93–94°, λ_{max} (log ε_{max}): 298 mμ (3·96). (Found: C, 64·14; H, 4·72; S, 15·66. $C_{11}H_{10}O_2S$ requires: C, 64·07; H, 4·89; S, 15·52%).

2-*Phenyl-3-ethoxycarbonyl-4,5-dihydrofuran* (XII). 11·4 g (60 mmole) of X′ dissolved in 250 ml EtOH were treated with H_2S and HCl as described under X, but at 0°. The reaction mixture was poured into a benzene–ice-water mixture (stirring), the benzene layer was separated, washed with water, with excess of 1N NaOH, and finally again with water. The soln was dried (Na_2SO_4), the solvent removed, and the residue oil distilled to give XII as a colourless oil, b.p.$_{0·4}$: 140°, n_D^{25}: 1·5636, yield: 6·3 g (47%). (Found: C, 71·35; H, 6·51. $C_{13}H_{14}O_3$ requires: C, 71·54; H, 6·47%).

2-*Phenyl-3-ethoxycarbonyl-Δ²-dihydrothiopyran* (XIII). 3·0 g of XI′ (13·5 mmole) dissolved in 150 ml EtOH were treated with H_2S and HCl as described under IX. Following the usual working-up procedure, a colourless oil was obtained after removal of the benzene and distillation, yield: 2·8 g (83%), b.p.$_{0·1}$: 118–119°, n_D^{25}: 1·5872 (lit.[40]: b.p.$_{0·05}$: 120°, n_D^{25}: 1·5905).

cis-α-[(α′-*Methylmercapto*)-2-*furfurylidene*]-γ-*butyrolactone* (XIVC). A soln of 2·94 g of IX (15 mmole) in 50 ml dry benzene was added dropwise to an ice-cooled stirred suspension of 0·36 g NaH (15 mmole) in 50 ml dry benzene during 1 hr. Stirring was continued until the evolution of H_2 had ceased (1 hr). A soln of 2·13 g MeI (15 mmole) in 20 ml dry benzene was then added, and the reaction mixture refluxed for 18 hr. The precipitated NaI was filtered off, the benzene removed from the filtrate, and the residue crystalline substance recrystallized (MeOH) to give pure XIVC as yellow-brown needles, yield: 1·8 g (57%), m.p. 99–100°. ν[C=O]: 1755 cm^{-1}, ν[C=C]: 1590 cm^{-1}, λ_{max}: 317 mμ. (Found: C, 57·10; H, 4·79; S, 15·10. $C_{10}H_{10}O_3S$ requires: C, 57·14; H, 4·80; S, 15·23%).

cis-α-[(α'-*Acetylmercapto*)-2-*furfurylidene*]-γ-*butyrolactone* (XVC). A soln of 4·9 g of IX (25 mmole) in 70 ml dry benzene was added dropwise to an ice-cooled, stirred suspension of 0·75 g NaH (>25 mmole) in 70 ml dry benzene over a period of ½ hr. Stirring was continued for 1½ hr (water-bath). A soln of 2·0 g AcCl in 25 ml dry benzene was added and the reaction mixture was refluxed for 1 hr. After standing overnight, precipitated NaI was filtered off, benzene removed from the filtrate, and the residue substance recrystallized twice (MeOH), yield of pure XVC: 1·8 g (30%), white needles, m.p. 109°, ν[C=O]: 1745 cm^{-1}, ν[C=O]: 1710 cm^{-1}, ν[C=C]: 1595 cm^{-1}, λ_{max}: 328 mμ. (Found: C, 55·31; Hm 4·06; S, 13·37. $C_{11}H_{10}O_4S$ requires: C, 55·46; H, 4·23; S, 13·43%).

trans-α-[1-*Methylmercaptoethylidene*]-γ-*butyrolactone* (XVIB). 10·1 g of I (0·07 mole), 2·1 g of NaH, and 9·9 g of MeI were reacted and worked-up as described under XIVC. After removal of benzene, the remaining oil was distilled and the solidified distillate recrystallized (light petroleum), white crystals, yield: 1·6 g (14%), $b.p._1$: 108–109°, m.p. 52–53°, ν[C=O]: 1745 cm^{-1}, ν[C=C]: 1620 cm^{-1}, λ_{max}: 291 mμ. (Found: C, 53·54; H, 6·41; S, 19·50. $C_7H_{10}O_2S$ requires: C, 53·16; H, 6·37; S, 20·24%).

α-[1-*Acetylmercaptoethylidene*]-γ-*butyrolactone* (XVII). 10·1 g of I (0·07 mole), 2·1 g of NaH, and 5·5 g of AcCl were reacted and worked-up as described under XIVC. After removal of benzene, the remaining oil was distilled twice to give XVII as a colourless liquid, yield: 6·4 g (48%), $b.p._{0·15}$: 108–112°. (Found: C, 51·58; H, 5·45; S, 17·09. $C_8H_{10}O_3S$ requires: C, 51·61; H, 5·41; S, 17·19%).

trans-α-[1-*Acetylmercaptoethylidene*]-γ-*butyrolactone* (XVIIB). 6·0 g of XVII was dissolved in 25 ml EtOH and 150 ml of a saturated soln of lead acetate in 50% EtOH was added under stirring. Stirring was continued for 30 min. The yellow ppt (XVIII) was filtered off, washed carefully with EtOH and water, and the combined liquid phases extracted with ether. The ether-layer was dried (Na_2SO_4), and the ether removed, leaving a colourless oil, which after distillation solidified. Recrystallization (n-pentane) gave pure XVIIB as white crystals, yield: 2·9 g, $b.p._{0·1}$: 105°, m.p. 45°. ν[C=O]: 1760 cm^{-1}, ν[C=O]: 1710 cm^{-1}, ν[C=C]: 1640 cm^{-1}, λ_{max}: 269 mμ. (Found: C, 51·65; H, 5·30; S, 17·07. $C_8H_{10}O_3S$ requires: C, 51·61; H, 5·41; S, 17·19%).

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