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STUDIES ON ENETHIOLS—VI*

REARRANGEMENT OF α-THIOACYLLACTONES AND α-THIOACYLTHIOLLACTONES IN ACID ALCOHOLIC SOLUTION

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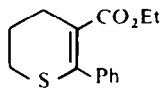
Abstract—α-Thioacyl-γ-thiollactones and -δ-thiollactones rearrange almost quantitatively in acid alcoholic solution to give 2-alkyl-3-alkoxycarbonyl-4,5-dihydrothiophenes and 2-alkyl-3-alkoxycarbonyl-Δ^2-dihydrothiopyrans, respectively. Similarly α-thioacyl-γ-lactones rearrange to give 2-alkyl-3-alkoxycarbonyl-4,5-dihydrofurans, but the yields are generally lower and by-products are obtained. The relative amounts of the products are strongly dependent on the reaction time. The mechanism of the thioacyllactone rearrangement is discussed on the basis of experimental facts.

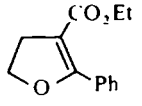
The NMR spectra of the cyclic rearrangement products are described and discussed. The ABX system appearing in the NMR spectrum of 2,5-dimethyl-3-ethoxycarbonyl-4,5-dihydrofuran has been analysed.

INTRODUCTION

IN CONNECTION with the study of the tautomerism of α-thioacyllactones it seemed desirable to synthesize α-thiobenzoyl-δ-valerothiollactone and α-thiobenzoyl-γ-butyrolactone.[1] Following a usual method,[1] α-benzoyl-δ-valerothiollactone was treated with H_2S in ethanolic solution in the presence of HCl at room temperature. However, the reaction product was not the desired α-thiobenzoyl-δ-valerothiollactone, instead the dihydrothiopyran I was obtained in 83% yield. Lower reaction temperatures resulted only in reduced yields of I and increasing amounts of unreacted starting material. The



I



II

reaction of α-benzoyl-γ-butyrolactone with H_2S afforded the desired α-thiobenzoyl-γ-butyrolactone only under crucial conditions, otherwise the reaction product was identified as the 4,5-dihydrofuran II. It has been suggested[1] that a rearrangement of preliminarily formed α-thiobenzoyllactones took place in both cases. In order to prove the existence of this rearrangement, which is formally analogous with the well-known acyllactone rearrangement,[2] several stable α-thioacyllactones and γ-thiollactones were subjected to the rearrangement conditions.

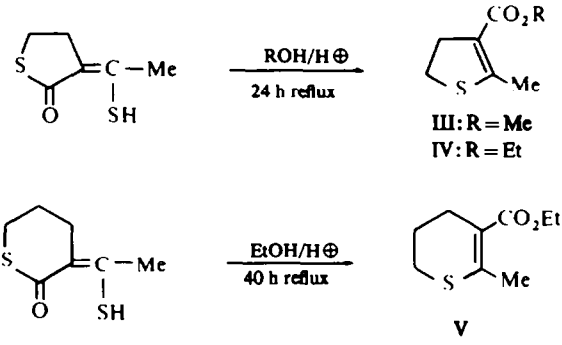
RESULTS AND DISCUSSION

Rearrangement of α-thioacylthiollactones

When refluxed for 24-40 h in 0·5 N alcoholic HCl solutions, α-thioacylthiollactones

* Part V, see ref. 1

(existing in the enethiol form)[1] are readily converted to 4,5-dihydrothiophenes or Δ^2-dihydrothiopyrans:



III: R = Me
IV: R = Et
V

These reactions proceed with the evolution of H_2S. The yields of the rearrangement products are practically quantitative, thus demonstrating the insignificance of a subsequent decomposition. Rearrangement of the corresponding α-acylthiollactones under similar conditions gives the same products, also in good yields.[2, 3, 4]

Rearrangement of α-thioacyllactones

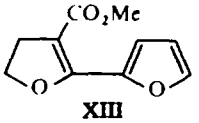
α-Thioacyl-γ-lactones can, when refluxed in 0·5 N alcoholic HCl solution, rearrange to 4,5-dihydrofurans, but the yields are generally low. On the other hand, lower-boiling by-products in appreciable amounts together with unreacted starting material can also be isolated. It turns out that the best yields of the dihydrofurans are obtained with reaction times between 12 and 24 h. Shorter reaction times result in reduced yields of the dihydrofurans as well as of the lower-boiling by-products. Longer reaction times give reduced yields of the dihydrofurans, but increased yields of the by-products. Unreacted α-thioacyllactone is isolable even after 48 h. Moreover, the alcohol also seems to influence the yield of the dihydrofuran.

VI–X

	R	R'	Yield (%)
VI	Me	H	40
VII	Et	H	34
VIII	iPr	H	20
IX	allyl	H	20
X	Et	Me	28

The lower-boiling by-products can be separated from the dihydrofurans by simple distillation as a forerun (a similar forerun was also observed in the rearrangement of α-acetyl-γ-butyrolactone in methanolic HCl-solution,[5] but it was not further charac-

terized). In all cases the forerun was investigated by NMR, but the spectra were complex, showing the presence of at least two compounds, not separable by distillation. However, in one case (R = Et, R′ = H) the two open-chain compounds XI and XII were isolated by means of preparative GLC. The ketones XI and XII are the only products obtained, when α-thioacetyl-γ-butyrolactone is refluxed for 48 h in 2N ethanolic HCl. α-(2-Thiofuruyl)-γ-butyrolactone is especially sensitive towards rearrangement. When refluxed in 0·5 N methanolic HCl, the reaction mixture becomes dark in colour almost immediately, and when the reaction is stopped within 4 h, the dihydrofuran XIII may be isolated from the reaction mixture, otherwise the only isolable products are the open-chain ketones XIV and XV. All rearrangement reactions are attended by evolution of H_2S.



XIII

	R—CO—$(CH_2)_3$—X	
	R	X
XI	Me	Cl
XII	Me	OEt
XIV	2-furyl	Cl
XV	2-furyl	OMe

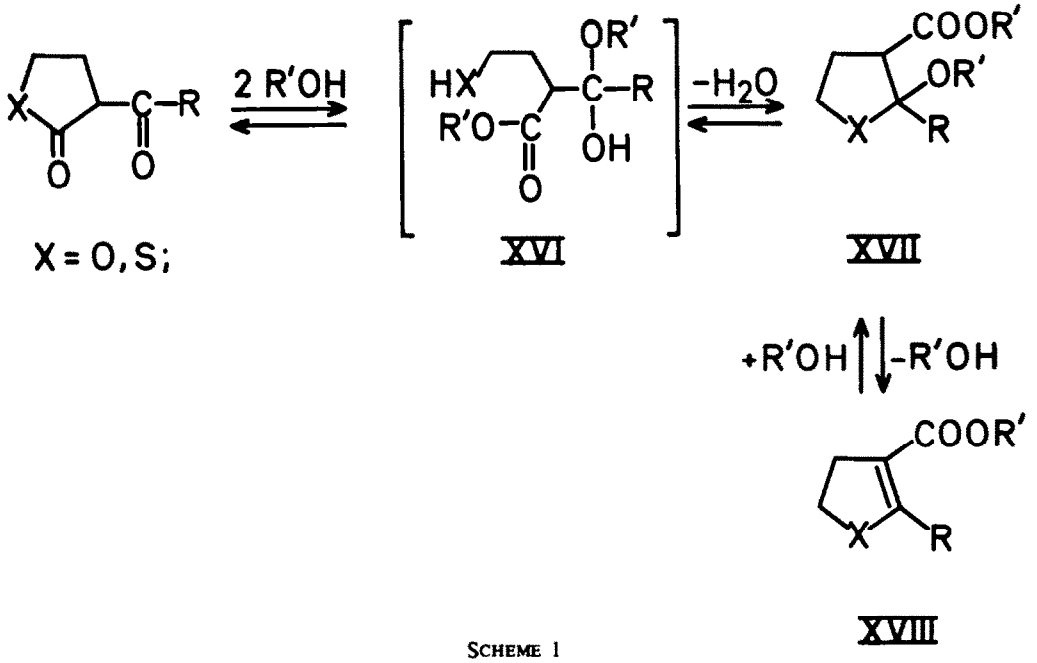
Since increased reaction times simultaneously lead to decreasing yields of the dihydrofurans and increasing yields of the open-chain by-products, it seems reasonable to regard the latter compounds as being decomposition products of the dihydrofurans. This conclusion is further supported by the following experimental facts. When XIII is refluxed in 0·5 N methanolic HCl for 48 h, the only isolable products are the ketones XIV and XV. Reflux of the dihydrofuran VI in 0·5 N ethanolic HCl for 48 h results in a mixture consisting of VII (ester-interchange), XI, and XII.

Mechanism

In their studies on the acyllactone rearrangement, Korte *et al.* operated with the following mechanism (scheme 1):[2]

The first step involves ring-opening and hemiketal formation to give the intermediate XVI. The second step consists of a nucleophilic attack of the HX-group on the hemiketal carbon atom to give the cyclic compound XVII, which then in the third step loses alcohol to yield XVIII. It should be noted that, for X=O, XVII has been isolated in some cases,[2] and very often a mixture of XVII and XVIII is obtained.[2,5] The reversibility of the rearrangement reaction has also been proved for X=O.[2] For X=S, the dihydrothiophene XVIII is always the only isolable product.[2, 3, 4]

A similar reaction mechanism would immediately be expected for the thioacyllactone rearrangement. However, in this case two additional facts must be taken into consideration. Firstly, XVII is never isolated, nor is it with certainty detected by NMR in the crude reaction mixture (see Experimental). Secondly, rearrangement of α-acetyl-γ-butyrolactone and α-thioacetyl-γ-butyrolactone under identical conditions showed that practically all acyllactone is consumed after 24 h, whereas a small percentage of thioacyllactone is still present in the reaction mixture after 48 h (measured by NMR).



SCHEME 1

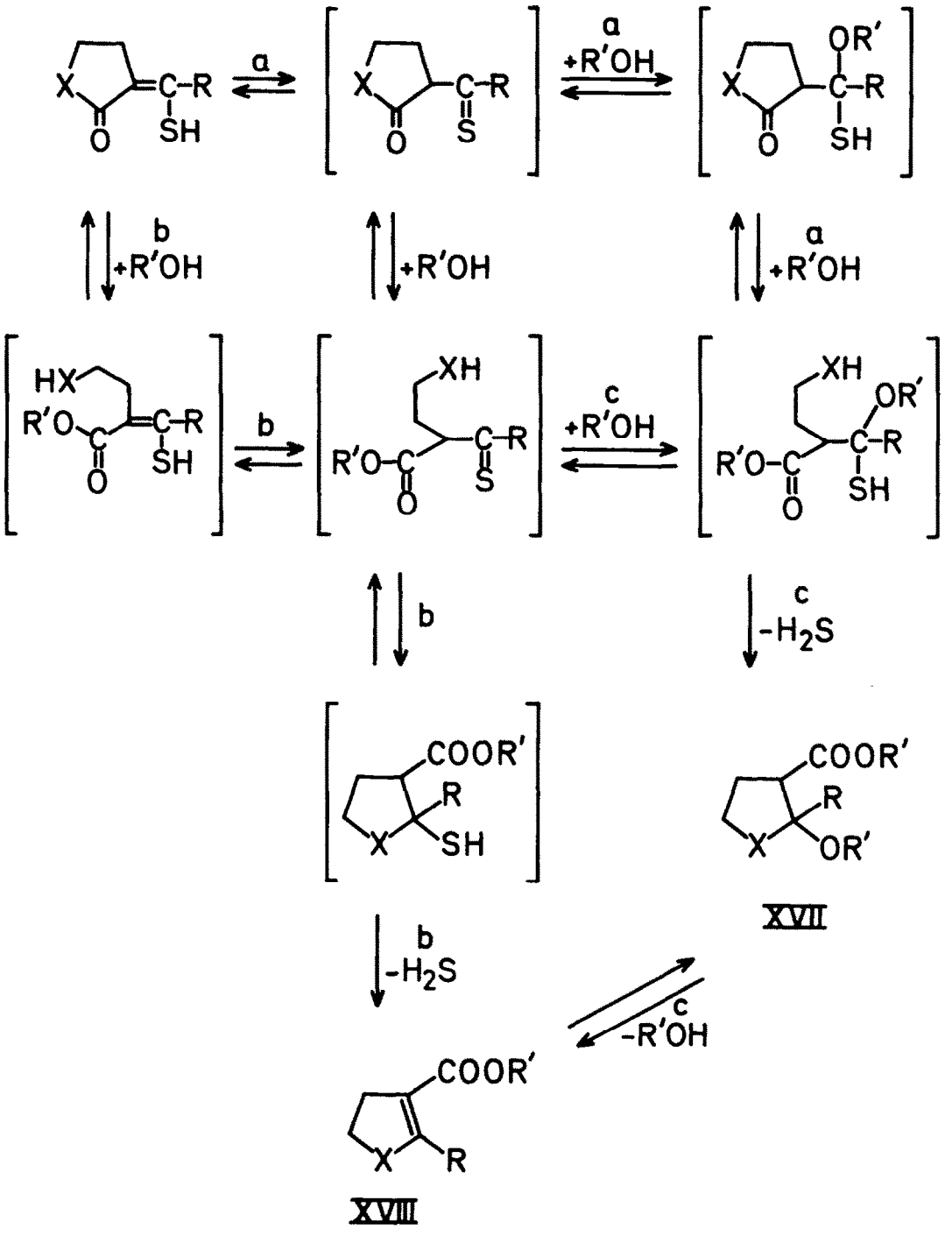
This difference in rearrangement rate is doubtless a consequence of the structural dissimilarity between the two participants: α-Thioacetyl-γ-butyrolactone is completely enethiolized,[1] whereas α-acetyl-γ-butyrolactone exists almost exclusively in the keto-form.[6,7] It is therefore concluded that the rearrangement proceeds *via* a thioketonic intermediate, and that the shifting in the enethiol-thioketo equilibrium exerts a considerable influence on the rearrangement rate. Scheme 2 gives a survey of the theoretically possible reaction paths. Direct addition of the alcohol or the XH-group to the C=C-bond seems most unlikely,[2] and this possibility is omitted in the scheme.

A reaction path following route **a** or **c** seems to be of less importance due to the lack of appreciable amounts of the tetrahydrofuran XVII in the reaction mixtures (X=O). A reaction mechanism proceeding through the thioketo-form of the thioacyllactone with subsequent lactone-ring-opening and otherwise following route **b** is regarded as being of minor probability due to the well-known high reactivity of the thioketo-function. Thus, route **b** is left as the most probable reaction path.

The appearance of the lower-boiling by-products only in the case where X=O is in agreement with the concept that they are decomposition products of XVIII. If their formation is due to an open-chain intermediate, decomposition products should be expected also for X=S. Ring-opening of 4,5-dihydrofurans by an attacking nucleophilic reagent, apparently *via* an intermediate like XVII,[9] is well known.[8,9] For X=S, addition of alcohol to the dihydrothiophene XVIII to give the tetrahydrothiophene XVII is less favourable, due to the much stronger participation of the free electron pair of the S-atom in a mesomeric system, giving rise to greater stability of XVIII.

NMR spectra

The NMR spectra of the cyclic rearrangement products III–X are all characterized by



SCHEME 2

a homo-allylic long-range coupling between the 2-methyl group protons and the ring 4-protons. In the dihydrofurans VI–X the methyl signal appears as a well-defined triplet (Fig 1), whereas in the dihydrothiophenes III and IV it has a more complex appearance (Fig 2). This dissimilarity is ascribed to the occurrence of "virtual coupling"[10] between the methyl protons and the ring 5-protons in the latter case. From the representative spectra (Figs 1 and 2) it is seen that in the case of the dihydrofurans the difference in chemical shift between the 4- and 5-protons is large compared with the relevant coupling constants,[11, 12] but in the dihydrothiophenes the 4- and 5-protons have approximately the same chemical shifts and are apparently sufficiently strongly coupled.[11, 12] The extra ring

TABLE 1. NMR DATA FOR THE CYCLIC REARRANGEMENT PRODUCTS III-X, AND XIII[a]

Chemical shifts are expressed as δ-values (ppm), coupling constants in Hz. The following abbreviations are used: d (doublet), t (triplet), m (multiplet), dd (double doublet), and tm (triplet with less well-defined fine-structure). Unless stated to the contrary, the solvent is CCl_4.

	δ_{H^4}	δ_{H^5}	δ_{H^5}	$\delta_{2\text{-Me}}$	$J_{\text{Homo-allylic}}$
III	3·05–3.18 m		—	~2·28 m	?
IV	3·07–3·20 m		—	~2·29 m	?
V	2·25–2·6 m	1·8–2·25 m	2·7–2·95 m	2·21 t	1·50
VI	2·82 tm	4·38 tm	—	2·13 t	1·60
VII	2·82 tm	4·35 tm	—	2·12 t	1·55
VIII	2·80 tm	4·35 tm	—	2·12 t	1·60
IX	2·81 tm	4·34 tm	—	2·10 t	1·60
X[b]	2·37[c] 2·88[d]	1·32[e] d 4·61[f] m	—	2·06 t	1·60
XIII	3·00 tm	4·46 tm	—	—	—

[a] Data for the ester groups are trivial, and are therefore omitted
[b] Solvent is CS_2
[c] H^B of ABX system, see text
[d] H^A of ABX system, see text
[e] 5-methyl protons
[f] H^X of ABX system, see text

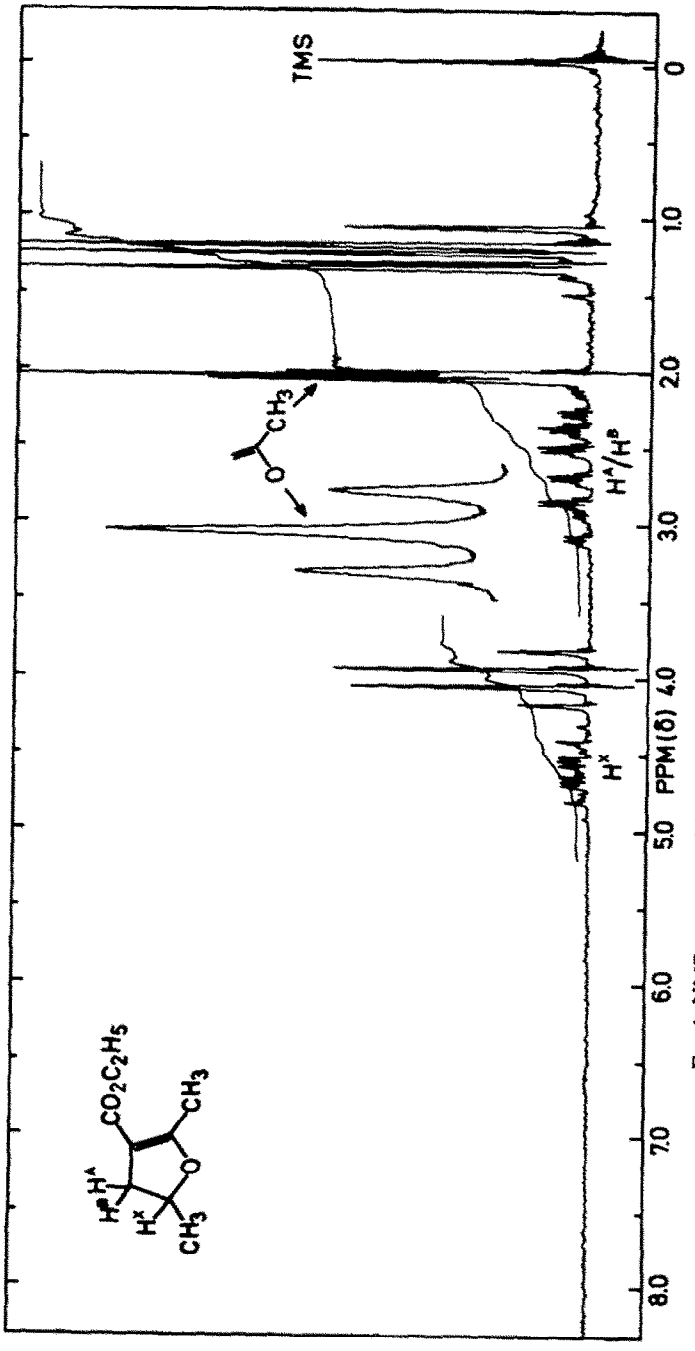


FIG 1. NMR spectrum of 2,5-dimethyl-3-ethoxycarbonyl-4,5-dihydrofuran (X) in CS_2.

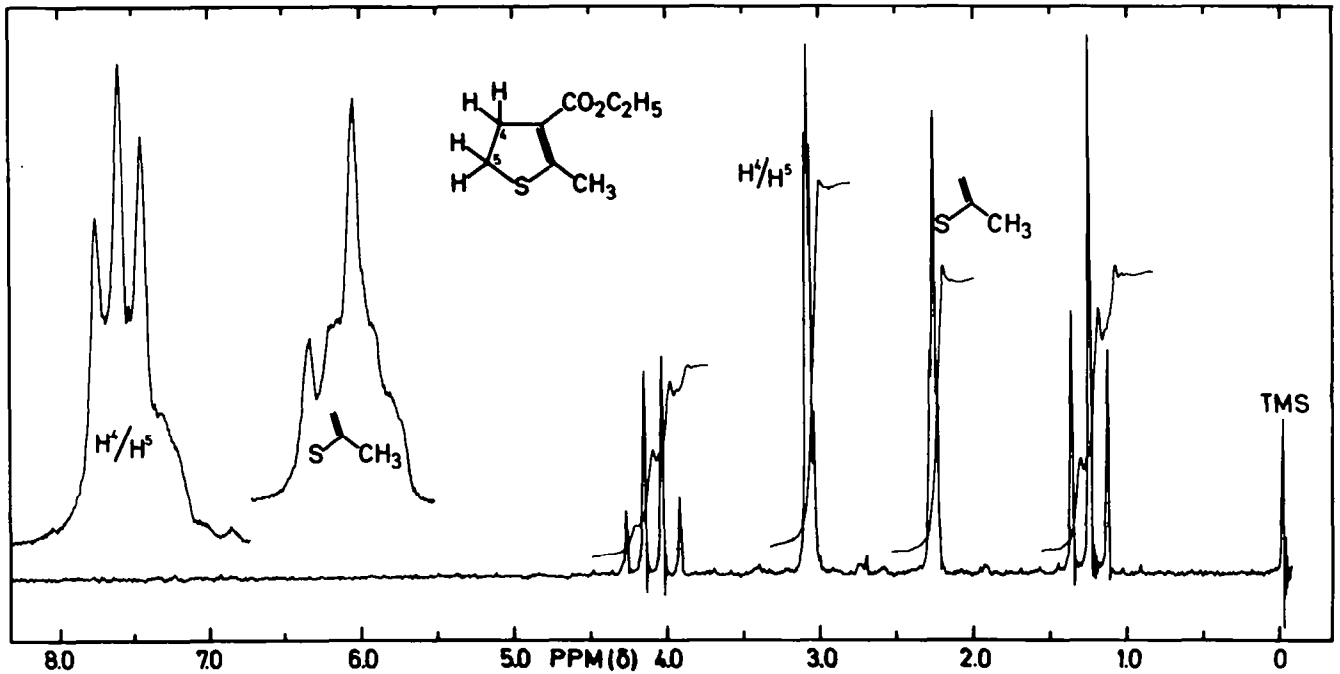


FIG 2. NMR spectrum of 2-methyl-3-ethoxycarbonyl-4,5-dihydrothiophene (IV) in CCl_4.

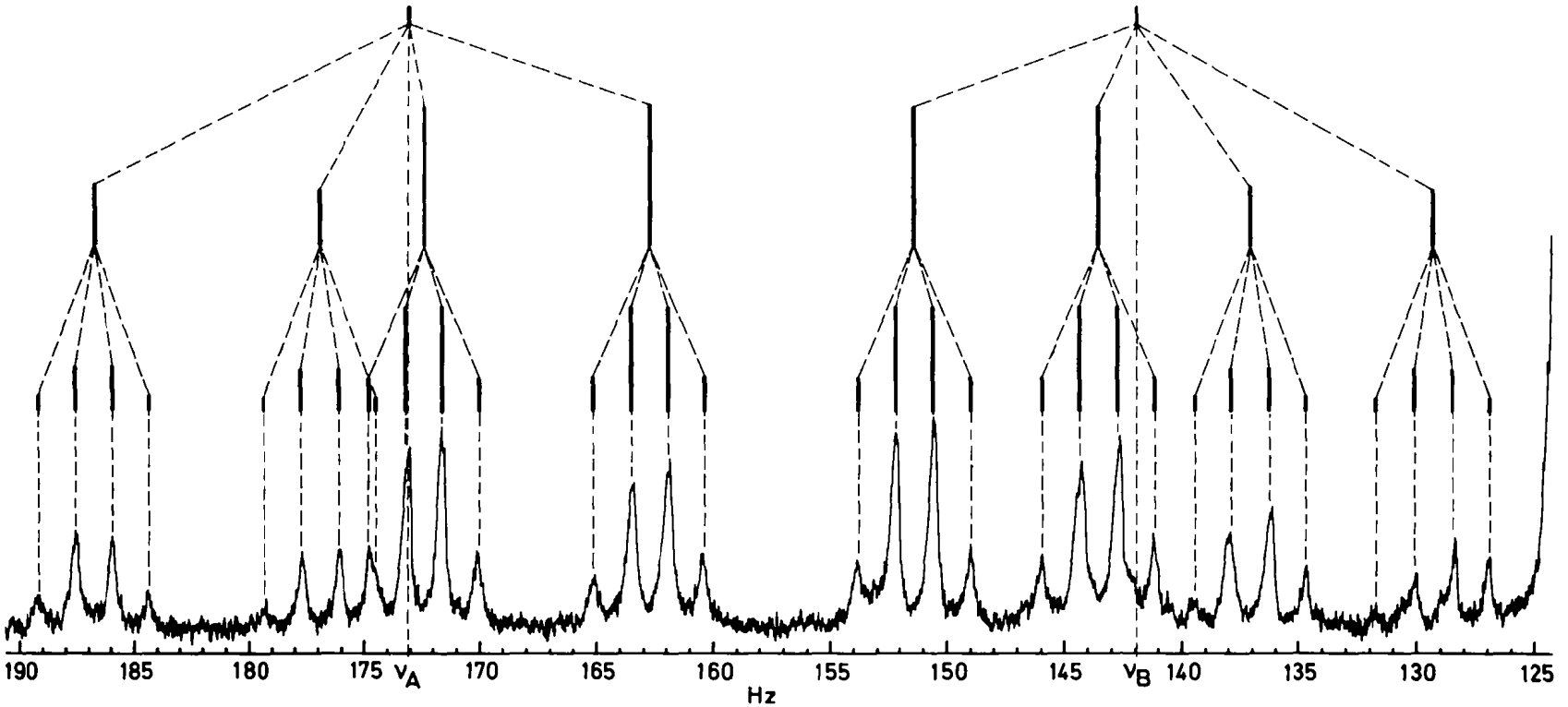


FIG 3. AB part of the ABX system of the NMR spectrum of X.

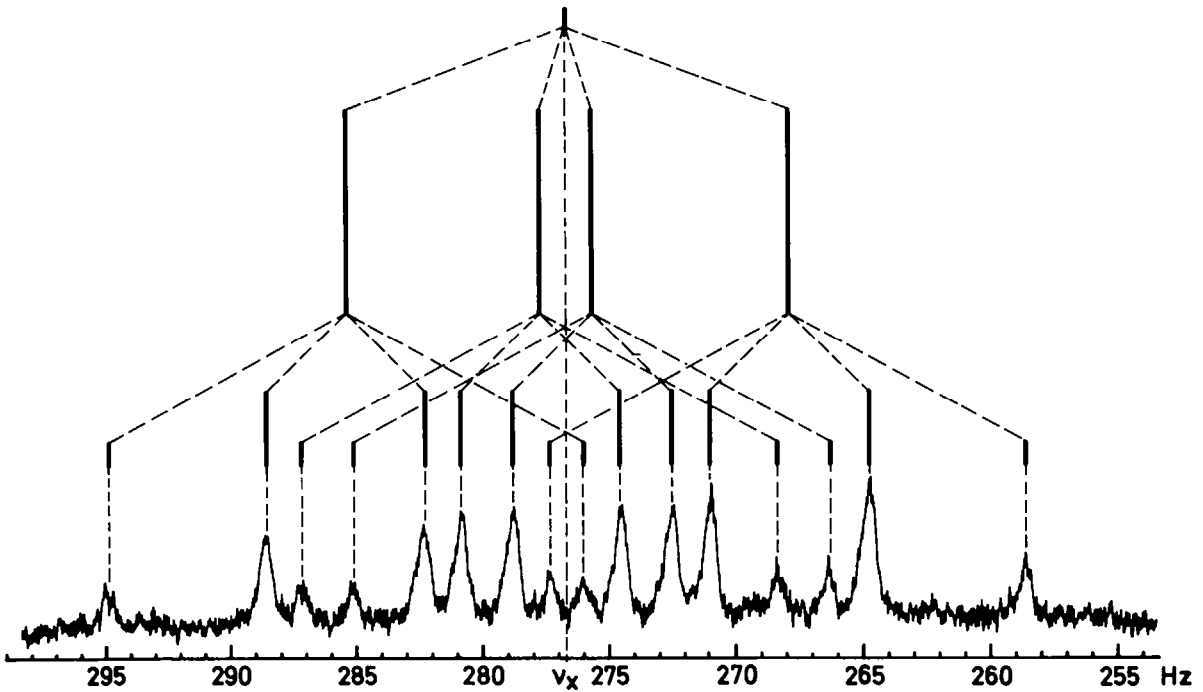


FIG 4. X part of the ABX system of the NMR spectrum of X.

methylene group of the dihydrothiopyran V reduces the possibility of "virtual coupling", and again the 2-methyl signal appears as a well-defined triplet (Table 1).

The three ring protons of the dihydrofuran X constitute an ABX system, where the A- and B-protons are homo-allylicly coupled to the 2-methyl protons, and the X-proton is coupled to the vicinal protons of the 5-methyl group (Figs 1, 3 and 4). Analysis of this system gave the following chemical shift values (in Hz, relative to TMS), and coupling constants (Hz): $\nu_X = 276{\cdot}70$, $\nu_A = 173{\cdot}08$, $\nu_B = 141{\cdot}91$, J_X Me $= 6{\cdot}27$, $J_{AB} = 14{\cdot}19$ (Sign presumably negative[13]), $J_{AX} = 9{\cdot}80$, and $J_{BX} = 7{\cdot}68$ (same relative signs, presumably positive[13]). From the sizes of J_{AX} and J_{BX} it is concluded that H^X and H^A are situated *cis* to each other. This conclusion is based on the Karplus $\cos^2\phi$ law, and on the assumption of a near-planar ring for the dihydrofuran. According to the law in question, J_{BX} is nevertheless anomalously large. However, the phenomenon is not unknown, and is presumably connected with the presence of the lone pairs of electrons on the ring-hetero-atom.[11, 12]

The furan ring protons of XIII give rise to three signals (numbers refer to the ring positions): $\delta_3 = 7{\cdot}79$ ppm (dm, $J_{3,4} = 3{\cdot}55$ Hz), $\delta_4 = 6{\cdot}45$ ppm (dd, $J_{3,4} = 3{\cdot}55$ Hz, $J_{4,5} = 1{\cdot}70$ Hz), and $\delta_5 = 7{\cdot}44$ ppm (dm, $J_{4,5} = 1{\cdot}70$ Hz). The assignments are based on the measured coupling constants.[14] The remarkable deshielding of H^3 is probably a consequence of the neighbourhood with the ester group situated at 3-position of the dihydrofuran ring. The diamagnetic anisotropy effect of the carbonyl group is possibly further enhanced due to the potential presence of a hydrogen-bonding between H^3 and the ester-carbonyl O-atom.

EXPERIMENTAL

NMR spectra were recorded at 60 MHz on a Varian A-60 spectrometer. The temps of the 15–20% solns (w/w) were 33° ±2. 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 are expressed in Hz with an accuracy within ±0·1 Hz. All measurements were carried out on the 50 Hz scale.

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

IR spectra were recorded as 5% solns in CCl_4 on a Beckmann IR 10 spectrophotometer or a Perkin–Elmer Infracord spectrophotometer.

M.ps. and b.ps. are uncorrected. The yields refer to the pure products. The purity was checked by NMR, TLC, and for the new compounds also by elementary analysis.

General rearrangement procedure. The thioacyllactone (-thiollactone) was refluxed for a certain period of time in the acid (HCl) alcoholic solution. After standing at room temp for 0–6 days the solvent was removed, and the composition of the residual oil was determined by NMR. The oil was dissolved in Et_2O, the soln washed several times with dil $NaHCO_3$ aq, and dried. The ether was removed, and again the composition of the remnant was determined by NMR. After distillations or recrystallizations or use of PLC or prep GLC, the yields of the pure products were determined together with physical and spectroscopic data.

2-Methyl-3-methoxycarbonyl-4,5-dihydrothiophene (III). 3·2 g (20 mmole) of 2-thioacetyl-γ-butyrothiollactone[1] was refluxed for 24 h in 70 ml of 0·5 N methanolic HCl, and worked up after standing for 4 days. Purification by PLC (SiO_2, 50% ether/50% light petr.). Yield of III: 2·6 g (82%). Colourless oil, b.p.$_{12}$: 96° $n_D^{25} = 1{\cdot}5447$. ν[C=O]: 1705 cm^{-1}, ν[C=C]: 1600 cm^{-1}. λ_{max}: 296, mμ. log ε_{max}: 4·05. (lit[3] b.p.$_{0.5}$: 52–54°, λ_{max}: 294 mμ, log ε_{max}: 4·09).

2-Methyl-3-ethoxycarbonyl-4,5-dihydrothiophene (IV). 3·2 g (20 mmole) of 2-thioacetyl-γ-butyrothiollactone was refluxed for 24 h in 60 ml of 0·5 N ethanolic HCl, and worked up after standing for 2 days. Purification as described above. Yield for IV: 3·44 g (90%). Colourless oil, b.p.$_{13}$: 102°, n_D^{25}: 1·5300. ν[C=O]: 1700 cm^{-1}, ν[C=C]: 1610 cm^{-1}. $\lambda_{max} = 295$ mμ, log ε_{max}: 4·13. (Found: C, 55·68; H, 6·94; S, 18·74. $C_8H_{12}O_2S$ requires: C, 55·80; H, 7·03; S, 18·59%).

2-Methyl-3-ethoxycarbonyl-Δ²-dihydrothiopyran (V). 4·35 g (25 mmole) of 2-thioacetyl-δ-valerothiol-lactone[1] was refluxed for 40 h in 65 ml of 0·5 N ethanolic HCl. Standing at room temp for 60 h. Following the usual working-up procedure V was obtained as a colourless oil. Yield: 3·80 g (82%), $b.p._{10}$: 128°, n_D^{25}: 1·5320. ν[C=O]: 1695 cm^{-1}, ν[C=C]: 1585 cm^{-1}. λ_{max}: 284 mμ, log ε_{max}: 3·98 (lit[15] $b.p._{0·05}$; 69°, n_D^{20}: 1·5350. ν[C=O]: 1695 cm^{-1}. λ_{max}: 283 mμ, log ε_{max}: 4·18).

2-Methyl-3-methoxycarbonyl-4,5-dihydrofuran (VI). 10·0 g (70 mmole) of 2-thioacetyl-γ-butyrolactone[1] was refluxed for 24 h in 60 ml of 0·5 N methanolic HCl. Standing for 6 days. Yield of VI: 4·0 g (40%). Colourless oil, which solidifies on standing, $b.p._{10}$: 77°. ν[C=O]: 1700 cm^{-1}, ν[C=C]: 1645 cm^{-1}. λ_{max}: 257 mμ, log ε_{max}: 4·09 (lit[5] $b.p._{11}$: 72–73°, m.p. 31·5–32·5°. λ_{max}: 257 mμ, log ε_{max}: 4·15).

2-Methyl-3-ethoxycarbonyl-4,5-dihydrofuran (VII). 10·0 g (70 mmole) of 2-thioacetyl-γ-butyrolactone was refluxed for 24 h in 70 ml of 0·5 N ethanolic HCl. Standing for 5 days. Yield of VII: 3·7 g (34%). Colourless oil, $b.p._9$: 86–87°, n_D^{25}: 1·4719. ν[C=O]: 1700 cm^{-1}, ν[C=C]: 1650 cm^{-1}. λ_{max}: 257 mμ, log ε_{max}: 4·03 (lit[16] $b.p._{10}$: 86–88°).

2-Methyl-3-isopropoxycarbonyl-4,5-dihydrofuran (VIII). Reflux of 14·4 g (0·1 mole) of 2-thioacetyl-γ-butyrolactone for 24 h in 65 ml of 0·5 N isopropanolic HCl gave after standing for 3 days 3·4 g (20%) of VIII. The product was purified by prep GLC. Colourless oil, $b.p._{10}$: 94–96°, n_D^{25}: 1·4662. ν[C=O]: 1695 cm^{-1}, ν[C=C]: 1650 cm^{-1}. λ_{max}: 258 mμ, log ε_{max}: 3·98 (Found: C, 63·59; H, 8·11. $C_9H_{14}O_3$ requires: C, 63·51; H, 8·29%).

2-Methyl-3-allyloxycarbonyl-4,5-dihydrofuran (IX). 14·4 g (0·1 mole) of 2-thioacetyl-γ-butyrolactone was refluxed for 24 h in 65 ml of an 0·5 N soln of HCl in allyl alcohol. Standing at room temp for 2 days. Yield of IX: 3·4 g (20%). Colourless oil, $b.p._{10}$: 105–106°, n_D^{25}: 1·4860. ν[C=O]: 1700 cm^{-1}, ν[C=C]: 1645 cm^{-1}. λ_{max}: 258 mμ, log ε_{max}: 4·02 (Found: C, 64·40; H, 7·09. $C_9H_{12}O_3$ requires: C, 64·27; H, 7·19%).

2,5-Dimethyl-3-ethoxycarbonyl-4,5-dihydrofuran (X). 7·3 g (46 mmole) of 2-thioacetyl-γ-valerolactone[1] was refluxed for 24 h in 65 ml of 0·5 N ethanolic HCl. Standing for 4 days. Yield of X: 2·2 g (28%), $b.p._{11}$: 93–94°, n_D^{25}: 1·4632. ν[C=O]: 1695 cm^{-1}. ν[C=C]: 1645 cm^{-1}. λ_{max}: 258 mμ, log ε_{max}: 4·08 (Found: C, 63·17; H, 8·42. $C_9H_{14}O_3$ requires: C, 63·51; H, 8·29%).

2-(2-Furyl)-3-methoxycarbonyl-4,5-dihydrofuran (XIII). 4·9 g (25 mmole) of 2-(2-thiofuroyl)-γ-butyrolactone[1] was refluxed for 4 h in 70 ml of 0·2 N methanolic HCl. Standing for 36 h. Yield of XIII: 0·8 g (16%), m.p.: 70° (EtOH). ν[C=O]: 1700 cm^{-1}, ν[C=C]: 1610 cm^{-1}, 1560 cm^{-1}. λ_{max}: 262 mμ, 313 mμ, log ε_{max}: 3·57, 4·19 (Found: C, 61·78; H, 5·23. $C_{10}H_{10}O_4$ requires: C, 61·85; H, 5·19%).

1-Chloropentane-4-on (XI) *and 1-ethoxypentane-4-on* (XII). (a) Reflux of 14·4 g (0·1 mole) of 2-thioacetyl-γ-butyrolactone for 48 h in 2 N ethanolic HCl gave after distillation 3·1 g of a mixture consisting of 80% of XI and 20% of XII. The two products were separated by prep GLC. XI: Colourless oil, $b.p._{12}$: 59°. ν[C=O]: 1725 cm^{-1}. δ (ppm): 1·7–2·2 (m, 2H); 2·10 (s, 3H); 2·4–2·7 (m, 2H); 3·54 (tm, 2H) (lit[17] $b.p._{12}$: 57–60°). XII: Colourless oil, $b.p._{12}$: 55°. ν[C=O]: 1725 cm^{-1}. δ (ppm): 1·12 (5, $J \sim 7$ Hz, 3H); 1·5–2·1 (m, 2H); 2·05 (s, 3H); 2·2–2·7 (m, 2H); 3·1–3·6 (m, 4H) (lit[18] $b.p._{763}$: 170·5–171°).

(b) Reflux of 3·55 g (25 mmole) of VI for 48 h in 0·5 N ethanolic HCl gave 1·2 g of a mixture consisting of VII (30%), XI (40%), and XII (30%) (determined by NMR).

4-Chloro-1(2-furyl)-butane-1-on (XIV) *and 4-methoxy-1(2-furyl)-butane-1-on* (XV). (a) 5·88 g (30 mmole) of 2-(2-thiofuroyl-γ-butyrolactone was refluxed for 48 h in 70 ml of 0·5 N methanolic HCl. After standing for 3 days, the reaction mixture was worked up according to the general procedure. Distillation gave a mixture of XIV and XV, $b.p._{10}$: 128–135°. XIV and XV were separated by means of PLC (SiO_2, 5% acetone/45% benzene/50% light petr). Yield of XIV: 1·1 g (21%). Colourless oil, which darkens on standing, $b.p._{11}$: 127–128°, n_D^{25}: 1·5220. ν[C=O]: 1680 cm^{-1}. δ (ppm): 2·18 (quint., $J \sim 6$ Hz, 2H); 2·98 (t, $J \sim 6$ Hz, 2H); 3·62 (t, $J \sim 6$ Hz, 2H); 6·50 (dd, $J = 3·5$, 1·7, 1H); 7·13 (dd, $J = 3·5$, 0·75, 1H); 7·56 (dd, $J = 1·7$, 0·75, 1H) (Found: C, 56·02; H, 5·21; Cl, 19·81. $C_8H_9O_2Cl$ requires: C, 55·66; H, 5·26; Cl, 20·54%). Yield of XV: 0·6 g (12%). Light yellow oil, $b.p._{12}$: 120–122°, n_D^{25}: 1·4940. ν[C=O]: 1680 cm^{-1}. δ (ppm): 1·94 (quint., $J \sim 6$ Hz, 2H); 2·87 (t, $J \sim 7$ Hz, 2H); 3·26 (s, 3H); 3·34 (t, $J \sim 6$ Hz, 2H); 6·49 (dd, $J = 3·5$, 1·7, 1H); 7·11 (dd, $J = 3·5$, 0·75, 1H); 7·55 (dd, $J = 1·7$, 0·75, 1H) (Found: C, 64·54; H, 7·17. $C_9H_{12}O_3$ requires: C, 64·27; H, 7·19%).

(b) Reflux of 1·41 g (7·3 mmole) of XIII for 48 h in 50 ml of 0·5 N methanolic HCl gave 0·68 g of a mixture of XIV (80%) and XV (20%) (determined by NMR).

Thioacyllactone rearrangement at room temp. 5·04 g (35 mmole) of α-thioacetyl-γ-butyrolactone was dissolved in 50 ml of 0·5 N methanolic HCl, and the soln was allowed to stand for 48 h. After removal of solvent, the residual oil was examined by NMR and found to consist of 14% of VI and 86% of unreacted starting material.

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