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ENAMINE CHEMISTRY—XIV*
THE REACTION OF ENAMINES WITH THIOLACIDS AND α-MERCAPTOACIDS†

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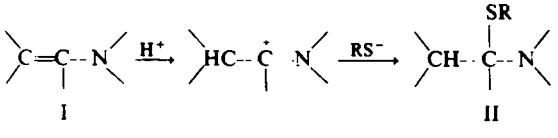
Abstract—Enamines, derived from β-dicarbonyl compounds and secondary amines, react with thiolacids to give enethiols, stabilized by H-bonding to CO groups in the β-positions. At −40° 1-morpholinocyclopentene and thiolacetic acid react to give a 1:1 addition product, which can be isolated and characterized. By allowing the addition product to reach room temperature an S → N acetyl-migration occurs producing N-acetylmorpholine in quantitative yields and thiocyclopentanone polymers. Reactions of enamines from cyclic ketones with α-mercaptocarboxylic acids at 80° produced 1,3-oxathiolan-5-one-2-spiro-1′-cycloalkanes, which also can be prepared from cycloalkanones and α-mercaptocarboxylic acids. Enamines, derived from β-ketoesters and ammonia or methylamine, produce thiazolidones, when refluxed with α-mercaptocarboxylic acids in benzene.

INTRODUCTION

IT HAS been shown[1,2] that thiophenols add smoothly to certain enamines, I, under mild conditions to give N,S-ketals, II. These products, II, are thermally unstable and can only be isolated and characterized when they are solids.[2] As reaction mechanism it is suggested that protonation takes place at the β-carbon[3,4] and the protonated enamine can then undergo nucleophilic reactions at the α-carbon.

The reaction between enamines and thiols has now been extended with the reactions of thiolacids and α-mercaptocarboxylic acids.[5]



Enamines and thiolacids

When thiolacetic (or thiolbenzoic) acid was added to 1-morpholinocyclopentene at room temperature, a very violent reaction occurred. Quantitative yield of N-acetyl (or N-benzoyl) morpholine was isolated besides tarry products. The tar is suggested to consist of trimers or polymers[6] of formed thiocarbonyl compounds, but no attempts to isolate these compounds have been made. The same exothermic reaction was

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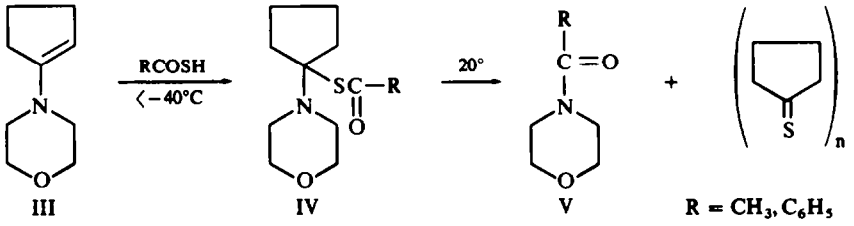
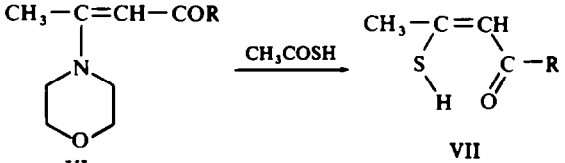
observed when reacting enamines, III, derived from cyclopentanone and different amines, with thiolacids. In all other cases with enamines derived from cyclohexanone or aldehydes no exothermic reaction was observed and the two reactants had to be heated in benzene for 2–6 hours to give quantitative yields of N-acylamines. With the above procedure no intermediate could be trapped, but by running the reaction with 1-morpholino-cyclopentene and a thiolacid at $-40°$ the addition product could be isolated and was found to be stable at temperatures below $-40°$. When allowing IV to reach room temperature, only V could be isolated. That the addition compound IV



III IV V $R = CH_3, C_6H_5$

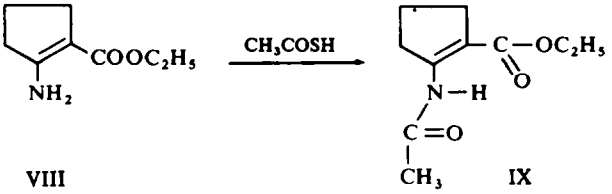
had the suggested structure is proved by its NMR-spectrum, which is devoid of signals attributable to olefinic protons. To prove directly that a thione is formed during this reaction is met with difficulties as aliphatic and alicyclic thioketones are quite unstable under these reaction conditions.[6–8] However, enethiolizable monothio-β-dicarbonyl compounds are quite stable due to H-bonding and have therefore received much attention[9] in recent years. We therefore reacted some enamines, VI, derived from β-dicarbonyl compounds and secondary amines (in one case also aniline), with a thiolacid, and the corresponding thiocarbonyl compounds (as enethiols), VII, could be isolated in fair to high yields, e.g.



VI VII

The method for the preparation of enethiols seems to be quite general and is in certain cases superior to the hitherto known ones.[9–14] Pure enethiols are obtained without admixture of gem. dithiols or of the original carbonyl compounds which simplifies the final working-up procedure extensively.

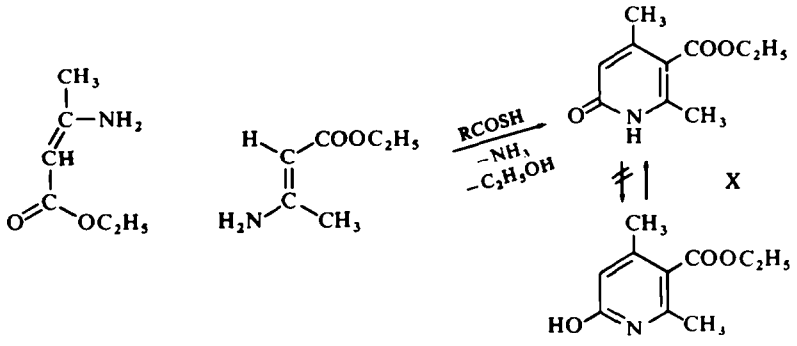
Enamines derived from β-dicarbonyl compounds and ammonia or primary amines showed other types of reactions with thiolcarboxylic acids. Thus, 2-ethoxycarbonyl-1-aminocyclopentene, VIII, underwent an N-acylation to give IX:



VIII IX

This is not unexpected, as thiolacetic acid is known as an acetylation reagent for special amines.[15–18]

On the other hand, no N-acylation of ethyl 3-amino-crotonate was observed, but instead 2 moles of the enamine condensed and gave 2,4-dimethyl-3-ethoxycarbonyl-6-oxopyridine, X:

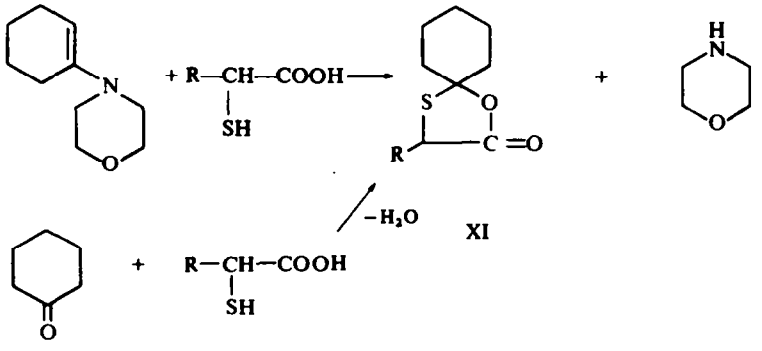


The same pyridone derivative has earlier been prepared by heating the hydrochloride of ethyl 3-aminocrotonate,[19–21] although no mechanistic considerations have been made.

As stated above, ethyl 3-phenylaminocrotonate produces ethyl 3-mercaptocrotonate when reacted with a thiolacid. Strange enough, ethyl 3-methylaminocrotonate gave a completely different product with thiolbenzoic acid, namely N-methylbenzamide in quantitative yields.

Enamines and α-mercaptoacids

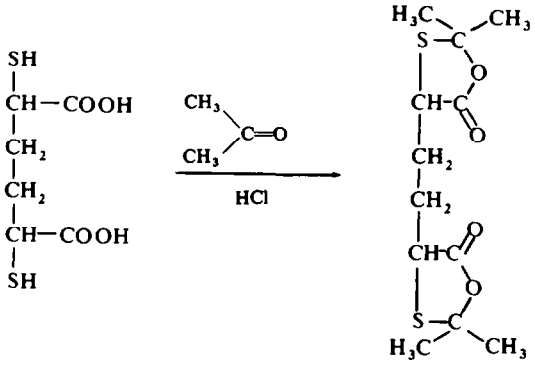
Enamines, derived from aldehydes or cyclic ketones, gave no products when reacted with α-mercaptocarboxylic acids at room temperature. However, when heating the reactants in benzene, spiro compounds derived from 1,3-oxathiolan-5-ones, XI, were formed in high yields:



A search in the literature reveals that there is no general method for the preparation of 1,3-oxathiolan-5-ones. Bistrzycki and Brenken[22] were able to show that thio-

benzilic acid reacted with aldehydes to give 4,4-diphenyl-1,3-oxathiolan-5-ones. The same method has later been used successfully both with aldehydes and ketones, but only in reactions with thiobenzilic acid.[23–26] Other α-mercaptocarboxylic acids gave no ring-closure products when hydrogen chloride was present, but only the corresponding thioketals.

To our knowledge there is one exception: Fredga[27] succeeded in reacting acetone with dimercaptoadipic acid to give XII.



IIX

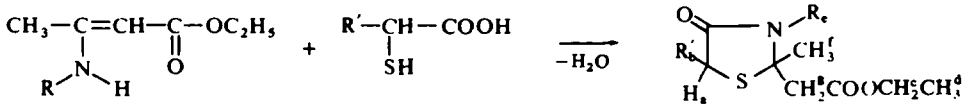
The inconvenience of the very time-consuming route to XI via enamines prompted us to find another method. We therefore reacted cyclohexanone with thioglycollic acid in benzene and the formed water removed by a water-separator. No thioketal was formed, but 95% yield of XI was isolated after a reaction time of 24 hours. This should now become the method of choice for the preparation of 1,3-oxathiolan-5-ones

TABLE 1. CHEMICAL SHIFTS (δ-VALUES, ppm) AND COUPLING CONSTANTS (c/s) OF THE THIAZOLIDONES (XIV). SOLVENT: CCl_4. THE FOLLOWING ABBREVIATIONS ARE USED: s (SINGLET), d (DOUBLET), t (TRIPLET), q (QUARTET), m (MULTIPLET), AND br (BROAD).

	H_a	H_b	H_c	H_d	H_e	H_f	H_g
XIVa	3·54 (s)	3·54 (s)	4·15 (q) J_{cd} = 7·2 c/s	1·26 (t) J_{cd} = 7·2 c/s	8·36 (br)	1·71 (s)	2·84 (s)
XIVb	3·84 (q) J_{ab} = 7·0 c/s	1·47 (d) J_{ab} = 7·0 c/s	4·16 (q) J_{cd} = 7·2 c/s	1·28 (t) J_{cd} = 7·2 c/s	8·47 (br)	1·73 (s)	2·82 (s)
XIVc	3·39 (s)	3·39 (s)	4·03 (q) J_{cd} = 7·2 c/s	1·17 (t) J_{cd} = 7·2 c/s	2·72 (s)	1·61 (s)	2·72 (s)
XIVd	3·72 (q) J_{ab} = 7·0 c/s	1·43 (d) J_{ab} = 7·0 c/s	4·09 (q) J_{cd} = 7·2 c/s	1·25 (t) J_{cd} = 7·2 c/s	2·81 (s)	1·68 (s)	2·76 (s)

from carbonyl compounds (aldehydes, ketones) and α-mercaptocarboxylic acids. The generality of this reaction has also been proved, but only four examples are described here as similar results have been published in a recent patent.[28]

Enamines derived from ethyl acetoacetate and ammonia or methylamine undergo a smooth reaction with α-mercaptocarboxylic acids to give thiazolidones,



XIV a: R = R′ = H
b: R = H; R′ = CH_3
c: R = CH_3; R′ = H
d: R = R′ = CH_3

When R = H or CH_3, high yields of XIV are found. From the structure of XIV it is noted that both an addition of the thiol to the double bond and an amide formation between the amine and acid have occurred. It is impossible at the present time to advance an unquestionable reaction mechanism as the used enamines are known to react as nucleophiles having nucleophilic centers either at the α-carbon or at the N atom.[29, 30]

The UV and IR data of XIV are found in the experimental part and the NMR data tabulated in Table 1 need no comments.

EXPERIMENTAL

NMR spectra were recorded at Mc/s on a Varian A-60 spectrometer. TMS was used as internal reference standard and the chemical shifts are expressed in δ-values (ppm) downfield from TMS = 0 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. The 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 with sodium chloride optics throughout. UV spectra were measured on a Bausch & Lomb Spectronic 505 spectrophotometer with EtOH as solvent. M.ps and b.ps are uncorrected. The microanalyses were performed by Drs. G. Weiler and F. B. Strauss, Oxford, England.

Starting materials. Thiolacetic acid (Schuchardt), n_D^{20} = 1·4630; thiolbenzoic acid (Aldrich), n_D^{20} = 1·6040; 2-mercaptopropionic acid (Aldrich), n_D^{20} = 1·4809; thioglycolic acid (Aldrich), n_D^{20} = 1·5030; and ethylthioglycolate (Fluka), n_D^{20} = 1·4575.

The enamines were prepared according to Szmuzkoviecz[31] by refluxing the amine with the corresponding CO compound in benzene soln, and the water formed is removed continuously.

1-(N-*morpholino*)-1-*acetylthiocyclopentane* (IVa). 1-Morpholino-cyclopentene (15·3 g; 0·1 mole) in 25 ml ether were put in a 250 ml 3-necked flask, equipped with a stirrer, a reflux-condenser, and a dropping funnel. After cooling to < 40°, 7·6 g (0·1 mole) thiolacetic acid in 25 ml dry ether were added dropwise during 30 min. The ppt was filtered off and dried in a cooled desiccator (< −40°), yield: approximately 50°. It is very important that the temp under no circumstances raises over −40°. (NMR spectra ($CDCl_3$): 3·7 (4H, m); 2·8 (4H, m); 2·29 (3H, s); 2·4–1·5 (8H, m).

1-(N-*morpholino*)-1-*benzoylthiocyclopentane* (IVb). The title compound was obtained as for IVa from 15·3 g (0·1 mole) 1-morpholino-cyclopentene and 13·8 g (0·1 mole) thiolbenzoic acid in 50 ml ether, yield: approximately 80%; NMR spectra ($CDCl_3$): 4·0 (4H, m); 2·9 (4H, m); 8·4–7·5 (5H, m); and 2·5–1·7 (8H, m).

N-*acylamines.* Equiv amounts of an enamine (derived from cyclopentanone, cyclohexanone, isobutyraldehyde, and various secondary amines) and thiolacetic (thiolbenzoic) acid were mixed, dissolved in benzene, and refluxed for 2–6 hr. Quantitative yields of the corresponding N-acylamines were isolated; N-acetylmorpholine, b.p. 113–115°/10 mm Hg, n_D^{25} = 1·4833;[32] N-acetylpiperidine, b.p. 55–56°/0·6 mm Hg, n_D^{25} = 1·4800;[33] N-benzoylpiperidine, m.p. 66°;[34] N-acetylpyrrolidine, b.p. 59–60 /0·3 mm Hg, n_D^{25} = 1·4758,[35] and N-benzoylmorpholine, b.p. 124–125°/0·1 mm Hg, m.p. 74–75°.[36] The spectroscopic data are

concurrent with those found in the literature. In IR the CO group was found to absorb between 1720 and 1775 cm^{-1}.

Compound VIIa. A soln of 39·8 g (0·2 mole) ethyl-β-(N-morpholino)crotonate and 19·0 g (0·25 mole) thiolacetic acid in 100 ml benzene was refluxed for 3 hr. Immediate distillation gave two products: a pink oil with b.p. 68–76°/10 mm Hg; yield 17·2 g (55%) identified as ethyl-β-mercaptocrotonate,[37] and a colourless liquid with b.p. 96–98°/0·2 mm Hg; n_D^{25} = 1·4840, yield: 25·8 g (100%) identified as N-acetyl-morpholine.

Compound VIIb. A soln of 30·6 g (0·2 mole) 2-(N-pyrrolidino)-2-pentene-2-one and 19 g (0·25 mole) thiolacetic acid in 100 ml benzene was refluxed for 30 min. Distillation gave two products, a dark-yellow oil with b.p. 62–68°/10 mm Hg; yield: 11·6 g (50%) identified as VIIb,[37] and a liquid with b.p. 56–57°/0·1 mm Hg; n_D^{25} = 1·4760, yield: 20·3 g (90%) identified as N-acetyl-pyrrolidine.[35]

Compound VIIc. A mixture of 43·1 g (0·2 mole) 2-(N-pyrrolidino)-4-phenyl-2-butene-4-one and 19 g (0·25 mole) thiolacetic acid in 100 ml benzene was refluxed for 30 min. Then approximately 80 ml of the benzene were stripped off, and the residue was placed in a refrigerator. Dark-red crystals precipitated, and they were characterized as the title compound by comparison with an authentic sample,[37] m.p. 26° (recrystallized from light petroleum), yield: 19·5 g (55%). Distillation of the mother liquid gave an oil with b.p. 56–57°/0·1 mm Hg; yield: 21·5 g (95%); n_D^{25} = 1·4758, identified as N-acetyl-morpholine.[32]

2-*Ethoxycarbonyl-2-mercapto-1-cyclopentene.* 1-ethoxycarbonyl-2(N-piperidino)-1-cyclopentene and 34·5 g (0·25 mole) thiobenzoic acid in 100 ml benzene were refluxed for 2 hr. Distillation gave two products, a pink oil with b.p. 111–113°/11 mm Hg; yield: 18·2 g (53%) identified as the title compound[37] and a bright oil with b.p. 125–126°/0·1 mm Hg, m.p. 66° (benzene), yield: 34·0 g (92%) identified as N-benzoyl-piperidine.[34]

2-*Ethoxycarbonyl-1-acetylaminocyclopentene* (IX). A soln of 0·2 mole (31·8 g) 2-ethoxycarbonyl-1-aminocyclopentene and 15·2 g (0·2 mole) thiolacetic acid in 75 ml ether was refluxed for 5 hr. Distillation gave a main fraction with b.p. 101–102°/0·3 mm Hg which crystallized on standing; m.p. 52·5–53°, yield: 31·8 g (81%), (lit.[38]: m.p. 53–54°). The IR and NMR spectra were consistent with the proposed structure. In the IR the following absorptions were found (cm^{-1}): 3270 (m), 2990–2840 (m), 1703 (s), 1658 (s), 1623 (s), 1450 (m, broad), 1352 (m), 1295 (m), 1245 (s), 1150 (s), 1040 (s), and 765 (m). NMR (CCl_4): 10·23 (1H, broad); 4·13 (2H, q, J = 7·5 c/s); 3·1 (2H, m); 2·3 (2H, m); 2·06 (3H, s); 1·9 (2H, m); 1·27 (3H, t, J = 7·5 c/s).

2,4-*Dimethyl-3-ethoxycarbonyl-6-oxopyridine* (X). A soln of 26 g (0·2 mole) ethyl β-aminocrotonate and 15·2 g (0·2 mole) thiolacetic acid in 100 ml benzene was refluxed for 6 hr. The benzene and excess thiolacetic acid were distilled off and after leaving the residue overnight in a refrigerator, white crystals precipitated, m.p. 138–139° (lit: m.p. 138–139°),[19–21] yield: 35·8 g (92%). Spectroscopical data: IR ($CHCl_3$): 3100 cm^{-1} (s); 1740 cm^{-1} (s) (alkoxy) CO stretching vibration; 1690 cm^{-1} (s) stretching vibration of the ring CO adjacing the N atom; 1420 cm^{-1} (m); 1280 cm^{-1} (s); 1204 cm^{-1} (m); 1110 cm^{-1} (s). NMR ($CDCl_3$): 13·33 (1H, broad); 6·28 (1H, s); 4·34 (2H, q, J = 7·5 c/s); 2·5 (3H, s); 2·29 (3H, s); 1·37 (3H, t, J = 7·5 c/s).

1,3-*Oxathiolan-5-one-2-spiro-1'-cyclohexane* (XI, R = H). A soln of 50·7 g (0·3 mole) 1-morpholino-cyclohexene and 55·2 g (0·6 mole) thioglycollic acid in 250 ml benzene was refluxed for 14 days. After cooling to room temp the soln was shaken with dil NaOH aq to remove excess acid and dried (K_2CO_3). Benzene was removed and fractional distillation gave the title compound: b.p. 70–72°/0·1 mm Hg; n_D^{25} = 1·5180, yield: 60 g (90%). (Found: C, 55·67; H, 7·00; S, 18·49; $C_8H_{12}O_2S$ requires: C, 55·80; H, 7·03; S, 18·58%; IR (CCl_4): 2918 (s), 2840 (m), 1865 (s), 1438 (m), 1245 (s), and 1190 (s) cm^{-1}; NMR (CCl_4): 3·68 (2H, s); 2·2–1·3 (10H, m).

The same compound was also obtained by refluxing 39·2 g (0·4 mole) cyclohexanone and 36·8 g (0·4 mole) thioglycollic acid in 200 ml benzene in a flask connected to a water separator. Quantitative amounts of water were isolated. The benzene phase was shaken with 1M NaOH, washed with water, and dried (K_2CO_3), yield: 63 g (95%).

4-*Methyl*-1,3-*oxathiolan-5-one-2-spiro-1'-cyclohexane* (XI; R = CH_3). This was obtained from 50·7 g (0·3 mole) 1-morpholino-cyclohexene and 63·3 g (0·6 mole) thiolacetic acid according to the above procedure, b.p. 131–132°/13 mm Hg; n_D^{25} = 1·5061, yield: 50·8 g (91%). (Found: C, 57·89; H, 7·51; S, 16·98; $C_9H_{14}O_2S$ requires: C, 58·05; H, 7·58; S, 17·19%); IR (CCl_4): 2918 (s), 1759 (s), 1440 (m), 1250 (m), 1200 (s), and 1035 cm^{-1} (m); NMR (CCl_4): 3·98 (1H, q, J = 7·0 c/s); 2·33–1·33 (10H, m); 1·59 (3H, d, J = 7·0 c/s). The same compound was prepared in 94% yield from cyclohexanone and thiolacetic acid, as described.

1,3-*Oxathiolan-5-one-2-spiro-1'-(2'-methyl)-cyclohexane.* This was obtained from 21·0 g (0·2 mole) 2-methylcyclohexanone and 18·4 g (0·2 mole) thioglycollic acid in 100 ml benzene; time: 100 hr, b.p. 146–147°/17 mm Hg; n_D^{25} = 1·5138, yield: 27 g (77%). (Found: C, 58·23; H, 7·65; S, 17·35; $C_9H_{14}O_2S$ requires: C, 58·09; H, 7·53; S, 17·19%).

1,3-*Oxathiolan-5-one-2-spiro-1'-(3'-methyl)-cyclohexane.* This was obtained from 21·0 g (0·2 mole) 3-methylcyclohexanone and 18·4 g (0·2 mole) thioglycollic acid in 140 ml of benzene, time: 100 hr, b.p. 157–158°/25 mm Hg, n_D^{25} = 1·5084, yield: 28 g (80%). (Found: C, 57·95; H, 7·54; S, 17·05; $C_9H_{14}O_2S$ requires: C, 58·09; H, 7·53; S, 17·19%).

2-*Methyl-2(ethoxycarbonylmethyl)-thiazolidone-4* (XIVa). A soln of 25·8 g (0·2 mole) ethyl β-aminocrotonate, 18·4 g (0·2 mole) thioglycollic acid, and 0·1 g *p*-toluenesulphonic acid in 250 ml benzene was refluxed for 10 hr in a flask connected to a water separator. Quantitative amounts of water were separated, yielding XIVa b.p. 135–136°/0·3 mm Hg, n_D^{25} = 1·5111, yield: 25·5 g (64%). (Found: C, 47·58; H, 6·40; N, 7·17; S, 16·08; $C_8H_{13}NO_3S$ requires: C, 47·29; H, 6·45; N, 6·89; S, 15·72%); λ_{max} (EtOH) (ε_{max}) = 211 nm ($4 \cdot 10^3$).

2,5-*Dimethyl-2(ethoxycarbonylmethyl)-thiazolidone-4* (XIVb). This was obtained from 25·8 g (0·2 mole) ethyl β-aminocrotonate and 21·2 g (0·2 mole) thiolactic acid, b.p. 120–121°/0·4 mm Hg, n_D^{25} = 1·5008, yield: 30 g (70%). (Found: C, 49·70; H, 6·89; N, 6·40; S, 14·64. $C_9H_{15}NO_3S$ requires: C, 49·76; H, 6·96; N, 6·45; S, 14·76%); λ_{max} (EtOH) (ε_{max}) = 217 nm ($4 \cdot 10^3$). The same compound was also prepared in 10% yield from ethyl β-aminocrotonate and ethyl α-mercaptopropionate after heating under reflux for 40 hr in benzene.

2,3-*Dimethyl-2(ethoxycarbonylmethyl)-thiazolidone-4* (XIVc). This was obtained from 28·6 g (0·2 mole) ethyl β-methylaminocrotonate and 18·4 g (0·2 mole) thioglycollic acid by heating under relux for 10 hr, b.p. 115°/0·4 mm Hg; n_D^{25} = 1·5058, yield: 24·5 g (57%). (Found: C, 49·67; H, 7·04; N, 6·76; S, 14·53. $C_9H_{15}NO_3S$ requires: C, 49·76; H, 6·96; N, 6·45; S, 14·76%); λ_{max} (EtOH) (ε_{max}) = 210 nm ($3 \cdot 10^3$).

2.3.5-*Trimethyl-2(ethoxycarbonylmethyl)-thiazolidone-4* (XIVa). This was obtained from 28·6 g (0·2 mole) ethyl β-methylaminocrotonate and 21·2 g (0·2 mole) thiolactic acid, b.p. 140°/0·7 mm Hg. n_D^{25} = 1·4966, yield: 20 g (49%). (Found: C, 51·54; H, 7·34; N, 6·22; S, 13·90. $C_{10}H_{17}NO_3S$ requires: C, 51·94; H, 7·41; N, 6·06; S, 13·84; λ_{max} (EtOH) (ε_{max}) = 220 nm ($4 \cdot 10^3$).

The IR spectra of XIVa–d in CCl_4 show the following absorptions (cm^{-1}): 3005–3000 (m); 1740–1735 (s); 1690–1675 (s); 1410–1400 (m); 1380–1370 (s); 1340–1330 (m); 1300 (s, broad); 1120–1110 (w); 1080–1070 (m), and 1070–1060 (s).

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