SYNTHESIS OF 4-ETHOXYCARBONYLMETHYL-, 4-N-PHENYLCARBAMOYLMETHYL-, AND 4-CARBOXYMETHYL-1,3-DITHIOLE-2-THIONES AND THE CORRESPONDING 1,3-DITHIOLIUM SALTS

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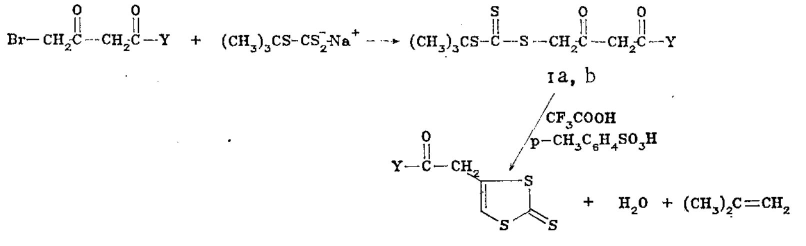
A method for the preparation of 4-ethoxycarbonylmethyl-, 4-N-phenylcarbamoylmethyl-, and 4-carboxymethyl-1,3-dithiole-2-thiones and the corresponding 1,3-dithiolium salts from γ-bromoacetoacetic ester, γ-bromoacetoacetanilide, and sodium tert-butyltrithiocarbonate was developed. The compounds were characterized by their IR and PMR spectra.

1,3-Dithiole-2-thiones and the 1,3-dithiolium salts synthesized from them are starting compounds for the preparation of tetrathiafulvalenes [1]. We set out to obtain 4-carboxymethyl-substituted 1,3-dithiole-2-thiones and the corresponding 1,3-dithiolium salts.

γ-Bromoacetoacetic ester [2] and γ-bromoacetoacetanilide [3] served as the starting compounds. To obtain the corresponding 4-substituted 1,3-dithiole-2-thiones we used a modified method [4] that consists in the reaction of the halocarbonyl compound with sodium tert-butyltrithiocarbonate and cyclization of the resulting s-substituted tert-butyltrithiocarbonates in the presence of trifluoroacetic and p-toluenesulfonic acids.

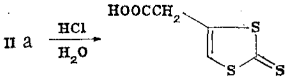


Ia, b

II a, b

I, II a $Y=OC_2H_5$; b $Y=NHC_6H_5$

We used this method to obtain acetoacetic ester derivatives (Ia, b) in the form of yellow oils, which were subjected without purification to cyclization. We obtained yellow stable (during storage) 4-ethoxycarbonylmethyl-1,3-dithiole-2-thione (IIa) and 4-N-phenylcarbamoylmethyl-1,3-dithiole-2-thione (IIb) in 35-40% yields. The acidic hydrolysis of IIa gave 4-carboxymethyl-1,3-dithiole-2-thione (IIc) in good yield.



II c

We obtained thione IIa for the first time from ethyl 3-pyrrolidinocrotonate and tetramethylthiuram disulfide [5].

To obtain 1,3-dithiolium salts we checked two methods described in the literature, viz., oxidation of 1,3-dithiole-2-thiones [6] and alkylation with subsequent reduction of the 5-alkyl product and treatment with acid [7].

Oxidation with peracetic acid was successful in the case of thiones IIa and IIc. Oxidation of thione IIa with hydrogen peroxide in acetic acid followed by precipitation of per-

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TABLE 1. PMR and IR Spectra of 4-Substituted 1,3-Dithiole-2-thiones and 4-Substituted 1,3-Dithiolium Salts

Compound	PMR spectrum in $CDCl_3 + d_6$-DMSO, δ, ppm				IR spectrum,[a] cm^{-1}
	2-H	5-H	$COCH_2$	remaining protons	
IIa[b]	—	6,89 (t)	3,60 (d)	1,29 (m, CH_3), 4,20 (q, CH_2O)	1748
IIb	—	7,13 (s)	3,75 (s)	7,06—7,65 (m Ph), 10 (s., $\mathrm{C{-}\underset{\substack{\vert\\H}}{N}}$)	1546, 1609, 1643, 3036, 3059, 3364
IIc	—	6,90 (t)	3,64 (d)	—	1645, 1691, 3044
IIIa	11,65 (d)	9,25 (m)	4,47 (d)	1,32 (t, CH_3), 4,28 (q, OCH_2)	1719
IIIb	11,63 (d)	9,17 (d)	4,49 (s)	7,0—7,6 (m, Ph), 10,23 (broad $\mathrm{C{-}\underset{\substack{\vert\\H}}{N}}$)	1540, 1604, 1682
IIIc	11,90 (s)	9,35 (s)	4,44 (s)	—	1716, 2584, 2630, 2933, 3045, 3091

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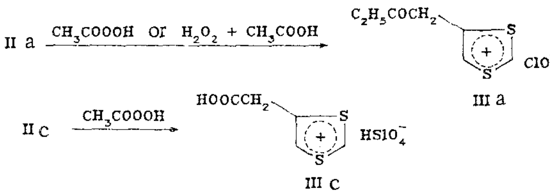
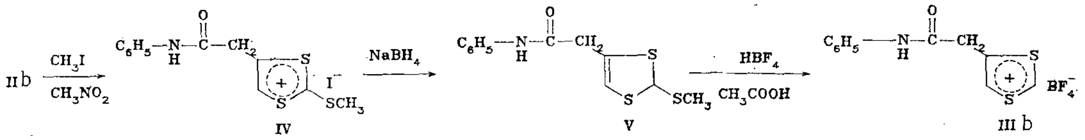
[a] The spectra at 1500-1800 cm^{-1} were recorded from suspensions in mineral oil, and the spectra at 2400-3600 cm^{-1} were recorded from suspensions in hexachlorobutadiene.
[b] PMR spectrum of IIa in CCl_4 [5]: 6.95 (5-H), 3.59 ($COCH_2$), 4.22 (CH_2O), and 1.35 ppm (CH_3).

chlorate IIIa by the addition of perchloric acid and ether is a fast and simple method for the preparation of 4-ethoxycarbonylmethyl-1,3-dithiolium perchlorate. Oxidation proceeds similarly under the influence of peracetic acid. Thione IIc is oxidized by peracetic acid in acetic acid, and 4-carboxymethyl-1,3-dithiolium bisulfate is precipitated by the addition of ether.



Dithiolium salts IIIa and IIIc are unstable colorless substances that are soluble in polar solvents.

The oxidation of thione IIb did not give the desired results. Thione IIb was methylated with methyl iodide, and the resulting 2-methylthio-4-N-phenylcarbamoylmethyl-1,3-dithiolium iodide (IV) was reduced with sodium borohydride to give 2-methylthio-4-N-phenylcarbamoylmethyl-1,3-dithiole (V). Treatment of V with tetrafluoroboric acid in acetic acid gave 4-N-phenylcarbamoylmethyl-1,3-dithiolium tetrafluoroborate (IIIb).



The structures of thiones IIa-c and dithiolium salts IIIa-c were confirmed by data from the IR and PMR spectra, which are correlated in Table 1.

The chemical transformations of 1,3-dithiolium salts III to obtain substituted tetrathiafulvalenes are currently under investigation.

EXPERIMENTAL

The IR spectra were recorded with IKS-14 and Specord 75-IR spectrometers. The PMR spectra were recorded with a Tesla 75-IR spectrometer with tetramethylsilane as the internal standard.

4-Ethoxycarbonylmethyl-1,3-dithiole-2-thione (IIa). A 6.97-g (0.03 mole) sample of γ-bromoacetoacetic ester [2] was dissolved in 75 ml of acetone, 6.72 g (0.03 mole) of sodium tert-butyltrithiocarbonate dihydrate was added in small portions at 8-10°C, and the mixture was stirred at room temperature for 2 h. Water (100 ml) was added, and the mixture was extracted with 75 ml of ether. The ether solution was dried with anhydrous magnesium sulfate, and the ether was removed by distillation to give a residual yellow oil. The yield of crude Ia was 8 g (95%).

A 2.8-g (0.01 mole) sample of Ia was dissolved in a mixture of 10 ml of acetic acid and 10 ml of trifluoroacetic acid, 0.1 g of p-toluenesulfonic acid was added, and the mixture was heated on a steam bath for 30 min and refluxed for 20 min. The solution was cooled and treated with 150 ml of water, and the precipitate was removed by filtration and crystallized from hexane to give 0.90 g (41%) of yellow crystals of IIa with mp 54-55°C (mp 54°C [5]). Found: S 43.9%. $C_7H_6O_2S_3$. Calculated: S 43.7%.

4-N-Phenylcarbamoylmethyl-1,3-dithiole-2-thione (IIb). The reaction of 5.12 g (0.02 mole) of γ-bromoacetoacetanilide and 4.48 g (0.02 mole) of sodium tert-butyltrithiocarbonate dihydrate by a procedure similar to that used to obtain Ia gave 4.65 g (72%) of Ib.

The cyclization of 3.41 g (0.01 mole) of Ib by a procedure similar to that used to obtain IIa gave 1 g (37%) of thione IIb, with mp 151-153°C (from aqueous ethanol), in the form of dark-yellow crystals. Found: S 33.9%. $C_{11}H_9ONS_3$. Calculated: S 36.0%.

4-Carboxymethyl-1,3-dithiole-2-thione (IIc). A mixture of 1.76 g (8 mmole) of thione IIa, 6 ml of acetic acid, 12 ml of concentrated HCl, and 35 ml of water was refluxed, during which the solid material dissolved. The mixture was distilled to remove ~40 ml of water, and the residual mixture was cooled to precipitate IIc. Recrystallization of the precipitate from benzene gave 1.25 g (81%) of IIc with mp 105-107°C. Found: S 49.8%. $C_5H_4O_2S_3$. Calculated: S 50.1%.

4-Ethoxycarbonylmethyl-1,3-dithiolium Perchlorate (IIIa). A) A 0.44-g (4 mmole) sample of IIa was dissolved in 5 ml of acetic acid, and 0.6 ml of 30% hydrogen peroxide was added dropwise while maintaining the temperature of the solution at 40-45°C. After spontaneous heating of the solution had ceased, 0.2 ml of perchloric acid was added, and the mixture was cooled and treated with 100 ml of ether to give 0.12 g (21%) of crystals of IIIa. Found: Cl 12.6; S 23.9%. $C_7H_9ClO_6S_2$. Calculated: Cl 12.3; S 22.2%.

B) A 2.2-g (0.01 mole) sample of IIa was added in small portions to 23 ml (0.04 mole) of a 12% solution of peracetic acid in acetic acid in the course of 10-15 min while maintaining the temperature at 10-15°C. After spontaneous heating of the solution had ceased, 1 ml of perchloric acid and 20 ml of ether were added to give 2.05 g (71%) of crystals of salt IIIa. Recrystallization was impossible because of the instability of the product. Found: Cl 13.1; S 22.7%. $C_7H_4ClO_6S_2$. Calculated: Cl 12.3; S 22.2%.

4-Carbomethoxymethyl-1,3-dithiolium Bisulfate (IIIc). A 0.38-g (5 mmole) sample of thione IIc was added in small portions to 5 ml (~8 mmole) of a 12% solution of peracetic acid in acetic acid in the course of 10 min at 10-15°C. At the end of the oxidation crystals precipitated; the amount of crystals was increased by the addition of 5 ml of ether. The precipitate was removed by filtration, washed on the filter with ether, and dried *in vacuo* to give 0.40 g (79%) of salt IIIc with mp 110-112°C (dec.). Found: S 36.4%. $C_5H_6OS_3$. Calculated: S 37.2%.

4-N-Phenylcarbamoylmethyl-2-methylthio-1,3-dithiolium Iodide (IV). A 0.52-g (2 mmole) sample of thione IIb was dissolved in 6 ml of nitromethane, 2 ml of methyl iodide was added, and the mixture was allowed to stand at room temperature for 24 h to precipitate 0.81 g (100%) of dark-yellow crystals of IV (not crystallized because of its instability) with mp 128-130°C. Found: I 31.5; S 24.1%. $C_{11}H_{12}INOS_3$. Calculated: I 31.1; S 23.4%.

4-N-Phenylcarbamoylmethyl-2-methylthio-1,3-dithiole (V). A 0.81-g (2 mmole) sample of IV was suspended in ethanol and reduced with 0.30 g of sodium borohydride at 10-15°C, during which the solid gradually dissolved. Water was added to the solution to precipitate while crystals (not recrystallized because of their instability), which were dried in a vacuum desiccator to give 0.40 g (71%) of V with mp 110-115°C. Found: S 33.3%. $C_{12}H_{13}NOS_3$. Calculated: S 33.9%.

4-N-Phenylcarbamoylmethyl-1,3-dithiolium Tetrafluoroborate (IIIb). A 3-ml sample of acetic anhydride was added to 0.40 g (14 mmole) of V, and 1.4 ml (1.4 mmole) of a solution of tetrafluoroboric acid in acetic acid was added dropwise at –5°C, during which the solid gradually dissolved. Ether was added to precipitate 0.40 g (90%) of salt IIIb with mp 118-120°C. Found: S 20.9%. $C_{11}H_{10}BF_4NOS_2$. Calculated: S 20.0%.

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2-ETHYNYLAZIRIDINES

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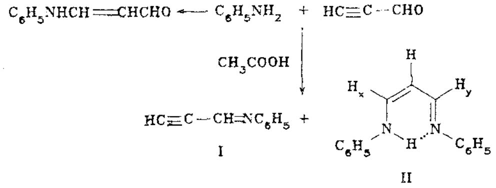
Methods for the synthesis of 2-ethynylaziridines by the cycloaddition of carbene to an α-ethynyl imine, cyclization of acetylenic β-amino alcohols in the presence of triphenylphosphine, and by means of the Gabriel reaction were developed.

2-(Phenylethynyl)aziridines were obtained in [1] by the cycloaddition of carbenes to N-(phenylpropynylidene)aniline and by cyclization of acetylenic β-amino alcohols by means of the $(C_6H_5)_3P{-}CCl_4$ complex in the presence of triethylamine.

In the present research we attempted to increase the number of ethynylaziridines by previously described methods [1] and carried out a search for other methods for the preparation of such compounds. Unsubstituted 2-ethynylaziridines are of particular interest. Only one representative of this series, viz., 2-vinyl-3-ethynylaziridine, has been described thus far [2].

α-Ethynyl imine I is necessary for the synthesis of 2-ethynylaziridines by the cycloaddition of carbenes to imines. It was established in [3] that the reaction of 2-propynal with aniline does not lead to the expected imine but rather to the product of addition of aniline to the triple bond, viz., an enamino aldehyde:



We obtained imine I by carrying out this reaction in the presence of acetic acid, which evidently facilitates dehydration of the initially formed unstable amino carbinol. In neutral media the latter decomposes to give the starting component with subsequent addition of aniline to the triple bond. The structure of imine I was confirmed by the IR and PMR spectra. N-(3-Phenylamino-2-propenylidene)aniline (II) — the product of the addition of aniline to the triple bond of imine I — is formed in addition to acetylenic imine I. The magnetic equivalence of the H_x and H_y protons in II is explained by rapid intramolecular transfer of the N–H proton [4], which constitutes evidence for the formation of the cis-s-cis form. It should be noted that the yield of II increases as the time that the reaction mixture is allowed to stand is increased.

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