SYNTHESIS AND SEVERAL TRANSFORMATIONS OF SULFIDES OF THE THIOPHENE SERIES

XXIII.* PREPARATION OF N-SUBSTITUTED 2,5-BIS(MERCAPTO)-3,4-BIS(IMINOMETHYL)THIOPHENES

Ya. L. Gol'dfarb and M. A. Kalik

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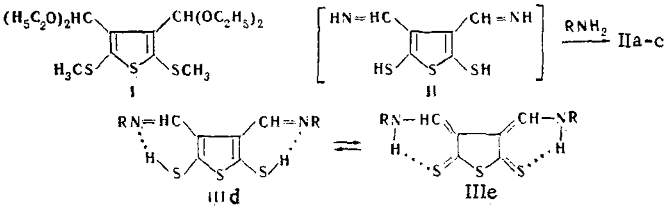
Several new N-substituted 2,5-bis(mercapto)-3,4-bis(iminomethyl)thiophenes, which are new tetradentate ligands of the thiophene series, were obtained by the reaction of primary amines with the product formed during the successive action of four equivalents of sodium in liquid ammonia and HCl on the tetraethylacetal of 2,5-bis(methylmercapto)-3,4-thiophenedialdehyde.

We have previously shown [1] that mercaptoaldimines form during the action of sodium in liquid ammonia on the acetals of the corresponding alkylmercaptoaldehydes and subsequent treatment of the reaction mixture with acid and ammonia. It was of interest to obtain further information regarding the limits of applicability of this reaction, particularly the possibility of the formation, under the same conditions, of a compound of composition II from the diacetal of 2,5-bis(methylmercapto)-3,4-thiophenedialdehyde (I); in contrast to the previously described mercaptothienylidenimines [1,2], II has four coordination centers attached to one thiophene ring.



III a, $R = C_4H_9$; b, R = cyclohexyl; c, $R = C_6H_5$

The external picture of the process occurring during the addition of sodium to a suspension of I in liquid ammonia does not differ in general from that which is observed in experiments with monoacetals, but in this case four equivalents of metal were necessary to complete the reaction (appearance of a stable blue solution). After the usual treatment of the reaction mixture and acidification of the aqueous alkaline solution of the reaction product to pH 7-8, we isolated an infusible powder that contains nitrogen and gives a reaction for mercapto and aldehyde groups and is insoluble in the usual organic solvents. It is probably polymer II. The action on this product of primary amines results in the formation of tetrafunctional compounds IIIa-c with ammonia evolution. These are brightly colored crystalline compounds with definite melting points and can be purified by recrystallization or reprecipitation from organic solvents.

The results of an investigation of the IR and PMR spectra of these compounds make it possible to assume the existence of tautomeric equilibrium IIId $\rightleftharpoons$ IIIe. The PMR spectrum of IIIa obtained in dimethyl sulfoxide has multiplets of protons from the NH groups ($\delta = 13.15$ ppm relative to TMS) and doublets of the protons of $=CH$ groups ($\delta = 8.27$ ppm) with a relative integral intensity of 1 : 1. The IR spectrum of IIIa (Fig. 1) also corroborates the assumption of the existence of III in form IIIe. A broad band which can be

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*For Communication XXII, see [4].

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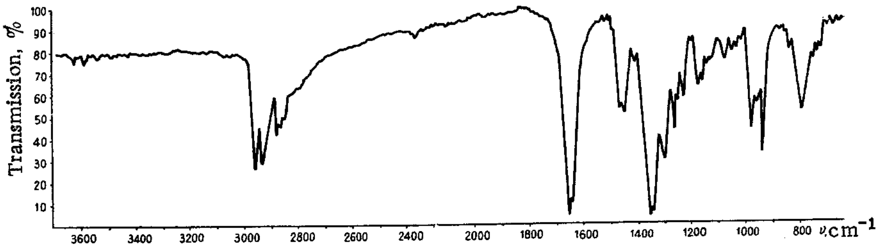

Fig. 1. IR spectrum of 2,5-bis(mercapto)-3,4-bis(n-butyliminomethyl)-thiophene (IIIa) (pressing with KBr).

TABLE 1. N-Substituted 2,5-Bis(mercapto)-3,4-bis(iminomethyl)-thiophenes IIIa-c

Compound	R	mp (solvent)	Empirical formula	Found, %			Calc., %			Yield, %
				C	H	S	C	H	S	
IIIa	C_4H_9	165—166,5 (alcohol)	$C_{14}H_{22}N_2S_3$	53,56 53,33	7,08 6,95	30,41 30,69	53,46	7,05	30,58	55
IIIb	Cyclohexyl	208—211 (dimethylformamide)	$C_{18}H_{26}N_2S_3$	58,85 58,79	7,19 7,15	26,42 26,16	58,97	7,15	26,24	54
III	C_6H_5	200—202 (dimethylformamide + ethyl acetate)	$C_{18}H_{14}N_2S_3$	60,43 60,38	4,00 4,08	27,07 26,97	60,98	3,98	27,13	52

assigned to the vibrations of the associated NH group is observed from 2900 to 3000 cm^{-1}. Bands corresponding to a tetrasubstituted thiophene ring are appreciably weakened in the spectrum; the band from 1640 to 1650 cm^{-1} corresponds to the vibrations of the system of conjugated S = C – C = C bonds. However, the presence of a small shoulder on the intense band at 1640 cm^{-1} does not exclude the presence of small amounts of form IIId.

A more detailed discussion of the spectral data from a study of the mercaptoaldimines of the thiophene series will be published separately [4].

EXPERIMENTAL

2,5-Bis(methylmercapto)-3,4-thiophenedialdehyde Tetraethylacetal (I). A mixture of 30 g of 2,5-bis-(methylmercapto)-3,4-thiophenedialdehyde [3], 150 ml of absolute ethanol, 46 g of orthoformic ester, and four drops of concentrated HCl was refluxed for 5 h. The solution was neutralized with methanolic KOH, the alcohol was distilled off, and the residue was diluted with water and thoroughly extracted with ether. The ether solution was washed with water and dried with magnesium sulfate. After removal of the ether, 29.7 g (60.5%) of bright yellow crystals of I with mp 59.5-60° (from heptane) were obtained. Found %: C 50.85, 50.78; H 7.52, 7.38; S 25.26; 25.04. $C_{16}H_{28}O_4S_3$. Calculated %: C 50.49; H 7.41; S 25.28.

Action of Sodium in Liquid Ammonia on 2,5-Bis(methylmercapto)-3,4-thiophenedialdehyde Tetraethylacetal (I). Sodium [2.45 g, (4 equivalents)] was added in small portions with stirring under argon to a suspension of 10 g of I in 150 ml of liquid ammonia and 20 ml of dry ether at −60° until the appearance of a stable blue color. Ammonium chloride was then added to the solution, the ammonia was evaporated, and benzene and water were added to the residue with cooling. The aqueous layer was separated, thoroughly extracted with benzene, and acidified with dilute HCl (1 : 1) to pH 7-8. The precipitate was separated by centrifugation, washed with water and alcohol, and dried in vacuo to give 4.5 g (88%) of bisimine II in the form of a brown powder which did not melt on heating to 360° and did not dissolve in the usual organic solvents. A satisfactory analysis could not be obtained after reprecipitation from dimethylformamide solution with heptane. Another 0.7 g of infusible, amorphous product which gives a reaction for aldehyde and mercapto groups was isolated by acidification of the mother liquor.

N-Substituted 2,5-Bis(mercapto)-3,4-bis(iminomethyl)thiophenes (IIIa). A suspension of 0.01 mole of unpurified II and 0.03 mole of primary amine in 10 ml of alcohol or ethyl acetate was heated for several minutes on a water bath (during which the bisimine went into solution), cooled, and the precipitate was filtered, washed with alcohol, and recrystallized from suitable solvents (see Table 1).

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