SYNTHESIS AND SOME TRANSFORMATIONS OF THIOPHENE SERIES SULFIDES

XII. Action of Sodium in Liquid Ammonia on 3-Ethylmercapto-2-Thiophenaldehyde and 4-Methylmercapto-3-thiophenaldehyde Diethylacetals*

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

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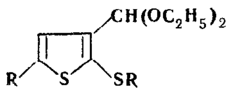
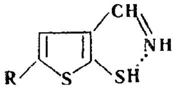
The main products of the reactions of the acetals of 3-ethylmercapto-2-thiophenaldehyde (IIIa) and 4-methylmercapto-3-thiophenaldehyde (IV) with 2 equivalents of sodium are the corresponding mercaptoacetals X, XXII. Reaction of an alkaline solution of mercaptoacetal X with ammonia and HCl at pH ~ 8 led to the isolation of a compound of composition $C_{10}H_7NS_4$ (XIV). The action of 6 equivalents of sodium on the acetals IIIa and IV leads, along with dealkylation of the alkylmercapto group, to reduction of the acetal group to methyl, and formation of 2- and 4-methyl-3-thiophenethiols (V, XVIII) respectively.

Research in this laboratory showed [1, 2] that the action of sodium in liquid ammonia on the diethylacetals of 2-alkylmercapto-3-thiophene-(furan)aldehydes, (I), gives 2-mercapto-5-alkyl-3-thenylidenimines (II) and furfurylidene imines, which are new bifunctional compounds whose stabilities can be explained by formation of an intramolecular hydrogen bond stabilizing the molecule. On the other hand attempts to prepare a compound like the mercaptoaldimine II, from the similarly constituted benzene derivative did not give the desired result [3]. This was put down to the difference between the geometric parameters of the benzene and thiophene or furan rings. Actually, if a hydrogen in the benzene ring is replaced by an atom (e. g. sulfur) of comparatively large radius, it becomes impossible to construct a molecule similar to mercaptoaldimine II, where atoms of nitrogen and sulfur are joined by a hydrogen bond. In the cases of thiophene and furan it is possible because the external valence angles are greater. We will note here that similar kinds of factors often prevail in determining the direction of a chemical reaction. There are many examples of this, so we will limit ourselves to two recent references [4, 5].

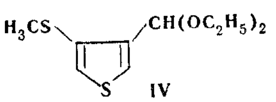
If the geometry of the ring were the ultimate factor in determining the possibility of a type II structure arising, it would be expected that isomeric mercaptoaldimines could be obtained. The acetals of 3-alkylmercapto-2-thiophenaldehyde (III) and 4-alkylmercapto-3-thiophenaldehyde (IV) would be suitable starting compounds, since the external valence angles and interatomic distances with thiophene compounds with substituents at positions 2 and 3 differ but little.



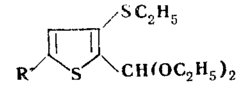
I R = CH_3, C_2H_5



II



IV



IIIa R = H; b R = CH_3

However it is evident that exchange of places between the functional groups (cf. I and III), or their interchange at the 3/4 position can entail change of reactivity. On this basis it was hard to predict the final result of the reactions of III and IV with sodium in liquid ammonia.

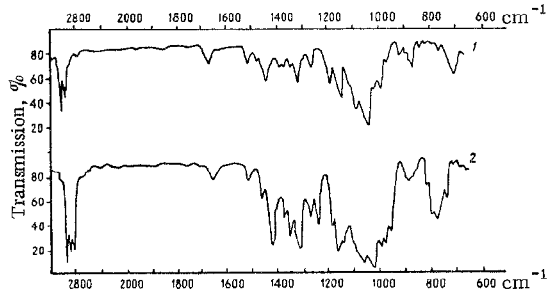


Fig. 1. IR spectra: 1) 3-ethylmercapto-2-thiophenaldehyde diethylacetal (IIIa); 2) 5-ethylmercapto-2-thiophenaldehyde diethylacetal.

The present work was undertaken in order to determine the degree of resemblance or difference between the behaviors of the isomeric acetals III and IV towards sodium in liquid ammonia, and also in the properties of the resultant mercaptoacetals. The necessary alkylmercaptoacetals were synthesized by known methods from the corresponding alkyl(3-thienyl) sulfides. It should be mentioned that the boiling points and melting points of the isomeric 3- and 5-alkylmercapto-2-thiophenaldehydes and their derivatives, acetals, semicarbazones, and other compounds, were close together [6]. However a mixture of their semicarbazones gave a depressed mixed melting point, and the acid obtained by oxidizing 3-ethylmercapto-2-thiophenaldehyde had a markedly different melting point to that of the isomeric 5-ethylmercapto-2-thiophene carboxylic acid [7]. These results showed that we were actually dealing with different compounds. The IR absorption curves given in Fig. 1, also indicate a difference between these acetals.

As we had to study the action of sodium in ammonia on acetals III and IV, containing an alkylmercapto group in the β position in the thiophene ring, it was expedient to first investigate the action of this reagent on 3-ethylmercaptothiophene. An experiment showed

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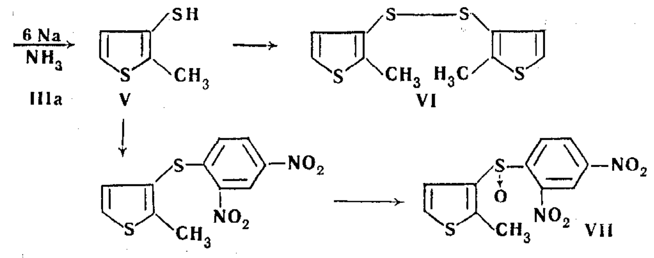
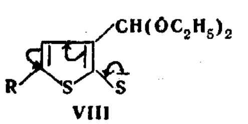
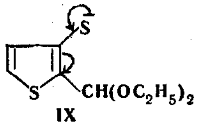
*For Part XI see [18].

that as with 2-alkylmercaptothiophene, reaction stops after adding 2 equivalents of sodium, and gives an 82% yield of 3-thienylmercaptan. In contrast to the reaction with I [1], a blue color is observed when 6 equivalents of sodium have been added to acetal IIIa, and 2-methyl-3-thienylmercaptan V, with an IR spectrum identical with that described in the literature [8], can be isolated in good yield from the reaction products. Mercaptan V is characterized as its disulfide VI and (2,4-dinitrophenyl)-(2-methyl-3-thienyl) sulfoxide (VII). Thus action of sodium in liquid ammonia on acetal IIIa leads not only to dealkylation of the sulfide group, but also to reduction of the acetyl group to methyl, analogous to what obtains with 5-ethylmercapto-2-thiophenaldehyde diethylacetal [6], though not with acetal I.

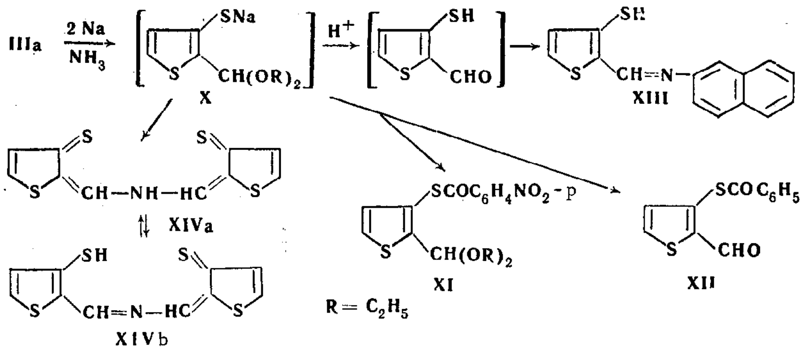


The cause of the difference between the behaviors of acetals IIIa and I towards sodium in liquid ammonia, may be due to the negative charge on the sulfur atom outside the ring being delocalized in mercaptide VIII formed from acetal I, but not in mercaptide IX, neglecting the possibility of spread of the valence cloud of the ring sulfur due to the d-orbital. Hence, the inductive effect due to that charge is less with mercaptide VIII than with mercaptide IX.


VIII


IX

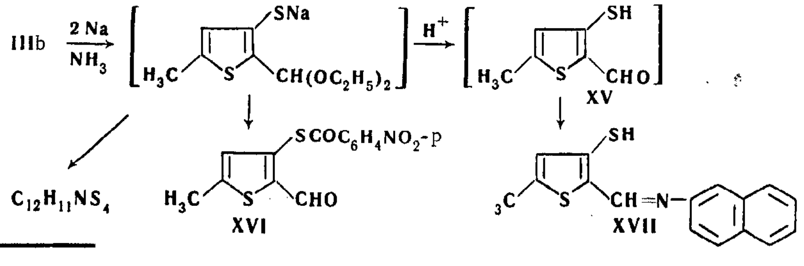
If the amount of sodium added to acetal IIIa, is limited to 2 equivalents, it is possible to isolate from the reaction products, along with 20–30% of the starting acetal, the dealkylation product X, which gives a p-nitrobenzoyl derivative XI, 3-benzoylmercapto-2-thiophenaldehyde XIII, and the Schiff's base XIII.



To sum up it can be said that the main features of the reactions involving 2 equivalents of sodium are similar for acetals I and IIIa (and, as we shall see below, for IIb and IV too). They give identical dealkylation products (mercaptoacetals), but differ quantitatively. Probably this is due to dealkylation being accompanied by reduction of the acetal group in the case of acetal IIIa.

A different picture is found when an alkaline solution of mercaptoacetal X is treated with acid in the presence of ammonia. At pH ~ 8 and under conditions similar to those for formation of mercaptoaldimine II, the mercaptoaldimine is not isolated, but a substance with melting point 179°, whose elementary analysis and molecular weight show that it has the composition $C_{10}H_7NS_4$. Leaving detailed consideration of the problem of the structure of this substance to the next paper, we will only mention that its properties are most fully reflected in formulas XIVa, b, corresponding to two tautomeric forms.

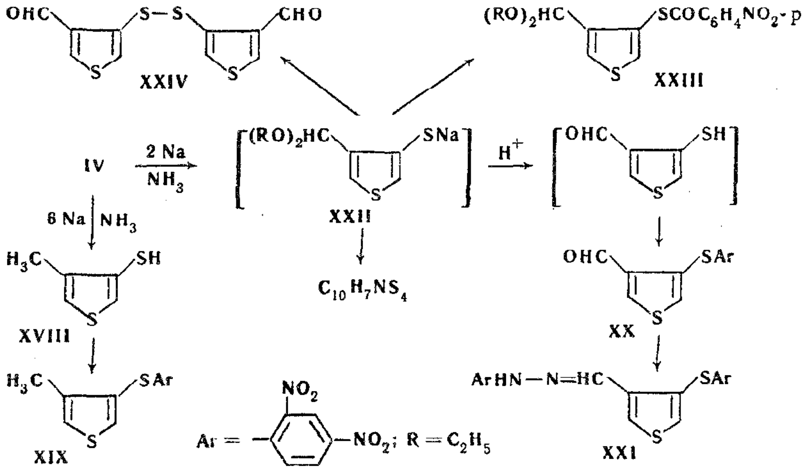
Acetals I and IIIa differing by the presence of an alkyl group at position 5, which can affect the course of the process, it was expedient to investigate the action of 2 equivalents of sodium on acetal IIIb, where position 5 is also substituted. Unfortunately the experimental picture is again complicated to a high degree. 30–40% starting acetal is recovered, and mercaptoaldehyde XV is formed, characterized as derivatives XVI and XVII, along with an insignificant amount of a product of composition analogous to that of amine XIV. It did not prove possible to detect compounds with an unsubstituted aldimine group.



Diethylacetals of Thiophenaldehydes

Diethy-acetal	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D		Formula	Found, %			Calculated, %			Yield, %
				Found	Calculated		C	H	S	C	H	S	
IIIa	107—108 (2)	1.1042	1.5290	68.82	69.09	$C_{11}H_{18}O_2S_2$	53.73 53.94	7.43 7.45	26.45 26.39	53.61	7.36	26.03	88
IIIb	119—121 (2)	1.1009	1.5321	73.33	73.71	$C_{12}H_{20}O_2S_2$	55.10 54.96	7.51 7.57	24.81 24.98	55.34	7.74	24.64	75
IV	125 (2,5)	1.1390	1.5420	64.47	64.20	$C_{10}H_{16}O_2S_2$	51.44 51.54	6.82 6.85	27.87 27.77	51.59	6.94	27.60	57

Only preliminary results regarding conversions of acetal IV can be given. As with acetal IIIa, reaction is incomplete after addition of 2 equivalents of sodium. The action of 6 equivalents of sodium gives 4-methyl-3-thienylmercaptan XVIII, characterized as the sulfide XIX. In a run with 2 equivalents of sodium, acidification to pH ~ 8 of an alkaline solution of the scission product containing ammonia, gave a small amount of a colorless substance which did not melt up to 300°, and which had the same formula $C_{10}H_7NS_4$ as the substance with melting point 179°. It contains one active hydrogen atom, and its IR spectrum lacks a band characteristic of the C≡N group, but has one in the 3295 cm^{-1} region corresponding to NH group vibrations. Because of the inaccessibility of this compound it was not investigated in detail.



The main reaction product was isolated at pH ~ 4, and had the properties of a compound with mercapto and aldehyde groups. With 2, 4-dinitrochlorobenzene it gave the sulfide XX, which in its turn gave the 2, 4-dinitrophenylhydrazone XXI. Here the primary product of dealkylation was the mercaptoacetal XXII, which could be isolated as its p-nitrobenzoyl derivative XXIII. Oxidation of this mercaptoacetal with iodine in alkaline solution gave the disulfite XXIV.

Summing up it can be said that reaction of the isomeric alkylmercaptoacetals in liquid ammonia with 2 equivalents of sodium proceeds similarly in both cases, giving mercaptoacetals. Action of 6 equivalents of sodium on acetals III, IV, and on 5-alkylmercapto-2-thiophenaldehyde reduces the acetal group to methyl. Only acetal I is an exception to this. It was not possible to obtain from acetals III and IV compounds isomeric with the mercaptoaldimine II, but nitrogen compounds with a different structure were obtained.

EXPERIMENTAL

Ethyl-3-thienylsulfide was prepared from 217 g (1.32 mole) 3-bromothiophene, an ether solution of 86.5 g (1.35 mole) n-BuLi, and 167 g (1.32 mole) diethyldisulfide, yield 82%, 80–85° (13 mm), n_D^{20} 1.5802. The literature gives 97–98.5° (22 mm), n_D^{20} 1.5772.

Ethyl(5-methyl-3-thienyl)sulfide was prepared from 200 g (1.15 mole) 4-bromo-2-methylthiophene [10], an ether solution of 75 g (1.17 mole) n-BuLi, and 141 g (1.15 mole) diethyldisulfide, yield 82%, bp 109–110° (17 mm), d_4^{20} 1.0996, n_D^{20} 1.5662. Found: C 53.40; 53.17; H 6.17; 6.44; S 40.47; 40.37%; MR_D 46.97. Calculated for $C_7H_{10}S_2$: C 53.11; H 6.33; S 40.51; MR_D 47.40.

4-Methylmercapto-3-bromothiophene was prepared by the method of [11] from 226.3 g (0.94 mole) 3, 4-dibromothiophene, an ether solution of 60 g (0.94 mole) n-BuLi, and 88.2 g (0.94 mole) dimethyldisulfide, yield 80%, bp 142–146° (28 mm), n_D^{20} 1.6463. The literature gives [11] 116–118° (10 mm), n_D^{20} 1.6474.

3-Ethylmercapto-2-thiophenaldehyde was prepared, as previously described [12], from 144 g (1 mole) ethyl-3-thienylsulfide, 135 g (1 mole) N-methylformanilide, and 153 g (1 mole) $POCl_3$, yield 82%; 106–107° (2 mm); n_D^{20} 1.6350. The literature gives [9] 106–109° (2 mm), n_D^{20} 1.6346. Semicarbazone mp 178.5–179.5° (ex EtOH). Mixed mp with the 5-ethylmercapto-2-thiophenaldehyde semicarbazone (mp 179° [6]), 148–153°. Found: N 17.94; 17.83%. Calculated for $C_8H_{11}N_3OS_2$: N 18.35%.

3-Ethylmercapto-2-thiophene carboxylic acid. A solution of 2.2 g 3-ethylmercapto-2-thiophenaldehyde in ethanol was added with cooling to freshly-prepared silver oxide, and the mixture stirred for 3 hr at room temperature. The precipitate was filtered off, washed with 5% NaOH, the filtrate extracted with ether, and acidified with concentrated HCl. The acid which separated was recrystallized from 50% EtOH and from heptane. It has mp 146–147.5° (decomp). Yield 1.8 g (80%). Found: C 44.70; 44.57; H 4.42; 4.27; S 33.46; 33.65%. Calculated for $C_7H_8O_2S_2$: C 44.65; H 4.28; S 34.06%.

3-Ethylmercapto-5-methyl-2-thiophenaldehyde was prepared from 50 g ethyl(5-methyl-3-thienyl)sulfide, 44 g N-methylformanilide, and 49 g $POCl_3$, yield 78%, bp 125 (2 mm), mp 28–29.5° (ex EtOH). Found: C 51.91; 51.70; H 5.43; 5.33; S 34.08; 34.19%. Calculated for $C_8H_{10}OS_2$: C 51.58; H 5.41; S 34.24%. 2,4-Dinitrophenylhydrazone mp 185.5–186.5°. (ex EtOAc). Found: N 15.58; 15.60%: $C_{14}H_{14}N_4O_4S_2$: N 15.29%.

4-Methylmercapto-3-thiophenaldehyde was prepared by the method of [13] from 115.6 g (0.55 mole) 4-methylmercapto-3-bromothiophene, an ether solution of 35.4 g (0.55 mole) n-BuLi, and 60.5 g (0.83 mole) N, N-dimethylformamide, yield 57%, bp 109–110° (0.1 mm). The literature gives [13] 98–105° (0.3 mm).

Diethylacetals of thiophene aldehydes were prepared by heating the aldehydes with orthoformic ester [1] (see table).

Treatment of thiophene derivatives with sodium in liquid ammonia. A solution of the thiophene derivative in an equal volume of dry ether was mixed with 10 times its volume of ammonia, and the sodium added in small portions at −60°, with stirring and in a current of argon. Completion of the reaction was indicated by appearance of a persistent blue color in the ammonia solution. After stirring for 15–30 min, the undecomposed sodium was decomposed with dry NH_4Cl, the ammonia evaporated off, and benzene and water added to the residue. The aqueous layer was thoroughly extracted with benzene, the benzene layer washed and dried. When 2 equivalents of Na were used, acidification of the aqueous layer to pH ~ 8 gave nitrogen compounds, while rendering it actually acid gave thiophene mercaptoaldehydes, identified as their solid derivatives. Neutrals were obtained from the benzene layer (unreacted acetal).

a) Ethyl-3-thienylsulfide and 2 equivalents of Na. Treatment of 5 g sulfide with 1.6 g Na gave the persistent blue color. Working up in the usual way gave 3.3 g (82.5% yield) 3-thienylmercaptan bp 65° (15 mm), n_D^{20} 1.6200. The literature gives 62–64° (14 mm), n_D^{20} 1.6218. A 90% yield of 2,4-dinitrophenyl-3-thienylsulfide was obtained, mp 133.5–136.5° (ex EtOH). The literature gives [15] 132.5–133°.

b) 3-Ethylmercapto-2-thiophenaldehyde diethylacetal (IIa) and 6 equivalents of Na. After 2.8 g Na had been added to 5 g acetal, a dark color appeared, which disappeared on treatment with NH_4Cl. From the aqueous layer was isolated 2.3 g of a bright mobile liquid with a mercaptan odor, which distilled with resinification at 83–91° (30 mm); n_D^{20} 1.5940. Yield of crude mercaptan 87%. The literature gives [8] for 2-methyl-3-thienylmercaptan (V): bp 71–74° (11 mm), n_D^{20} 1.5978.

Oxidation with iodine in alkaline solution [16] of 0.8 g undistilled 2-methyl-3-thienylmercaptan gave bis(2-methyl-3-thienyl)disulfide (VI) in 62.5% yield, mp 62.5–63° (ex EtOH). Found: C 46.76; H 3.89; 3.98; S 49.14; 49.11%. Calculated for $C_{10}H_{10}S_4$: C 46.47; H 3.90; S 49.63%.

0.8 undistilled mercaptan V and 1.4 g 2, 4-dinitrochlorobenzene gave a sulfide as a viscous oil, and this was oxidized with 4 ml 30% H_2O_2 in glacial AcOH by heating on a water-bath for 1 hr, and the solution was then poured into water. The precipitate of 2, 4-dinitrophenyl(2-methyl-3-thienyl)sulfoxide (VII) which separated on standing was washed with EtOH, and recrystallized from the same solvent, when it had mp 161–163°. Found: C 42.38; 42.14; H 2.61; 2.73; S 20.29; 20.24%. Calculated for $C_{11}H_8O_5N_2S_2$: C 42.30; H 2.58; S 20.53%. The IR spectrum had an intense band in the 1065 cm^{-1} region, characteristic of the sulfoxide group [17].

c) 3-Ethylmercapto-2-thiophenaldehyde diethylacetal (IIIa) and 2 equivalents of Na. 1) When sodium was added to 10 g acetal, the blue color of the ammonia solution rapidly disappeared. From the benzene layer there was isolated 3 g starting acetal, bp 110–111° (3 mm), n_D^{20} 1.5320. The semicarbazone from this acetal had mp 178–179°, mixed mp with authentic 3-ethylmercaptan-2-thiophenaldehyde semicarbazone undepressed. Addition of dilute HCl (1:1) to bring the water-ammonia solution to pH ~ 8 led to precipitation of 2.3 g pale brown solid mp about 165° (decomp). After recrystallizing from benzene, $CHCl_3$, and EtOAc, the almost colorless crystalline material had mp 179–179.5° (decomp), and contained one active hydrogen atom. It was soluble in dioxane, tetrahydrofuran, N, N-dimethylformamide, and dimethylsulfoxide. Found: C 44.38; 44.37; H 2.72; 2.81; N 5.41; 5.49; S 47.49; 47.49%; M 258*, 266.3**. Calculated for $C_{10}H_7NS_4$: C 44.56; H 2.68; N 5.20; S 47.59%; M 269.4. Yield on the acetal reacted 60.5%. A small amount of oil was obtained when the aqueous solution was further acidified to pH ~ 4.

2) The run was repeated with 3.3 g acetal IIIa. The resultant alkaline solution was acidified to pH ~ 4, and the oil which separated extracted with benzene. The benzene solution was washed with water and dried. From it was isolated 1.3 g oil with a mercaptan odor, insoluble in EtOH but soluble in ethanolic alkali. A solution of this oil in 10 ml EtOAc was refluxed with 1.3 g β-naphthylamine in 10 ml EtOH for 1 hr, to give 0.9 g (3-mercapto-2-thenylidene)-β-naphthylamine (XIII), a red crystalline compound, which after recrystallizing from EtOAc and EtOAc benzene had mp 149.5–150.5°. Found: C 66.80; 66.97; H 4.49; 4.33; S 23.70; 23.61%. Calculated for $C_{15}H_{11}NS_2$: C 66.88; H 4.11; S 23.81%. Hence the oil is mainly 3-mercapto-2-thiophenaldehyde.

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*Cryoscopic in dioxane.

**Ebullioscopic in dioxane.

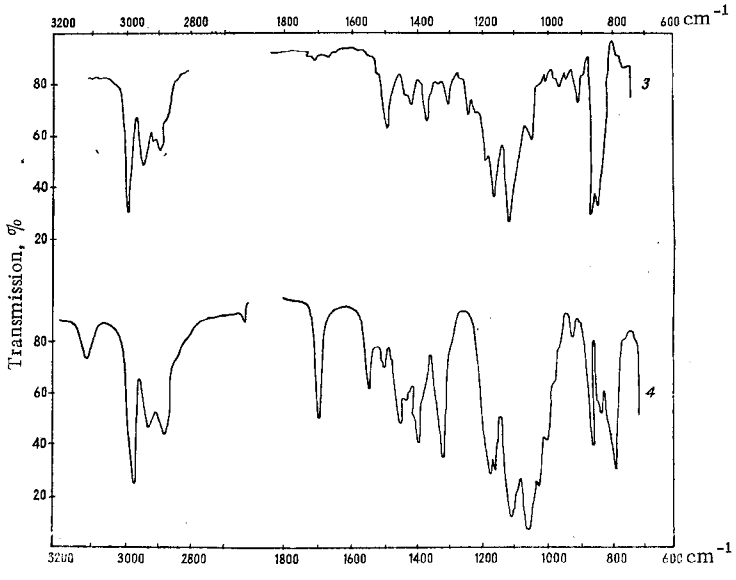

Fig. 2. IR spectra: 3) 2-ethylmercapto-5-ethyl-3-thiophenaldehyde diethylacetal; 4) methylmercapto-3-thiophenaldehyde diethylacetal.

3) 5 g acetal IIIa was treated with 2 equivalents of sodium in the usual way, but the ammonia was carefully vacuum-distilled off. Benzene and water were added to the residue, which was cooled. 1.7 g (34%) of the starting acetal was isolated from the benzene solution. 40 ml aqueous alkaline solution was obtained. 20 ml of it was shaken with 3 g p-nitrobenzoyl chloride, and left overnight. Then the precipitate was filtered off, and recrystallized from EtOH, weight 2 g, mp 108–109°. The yield of 3-(p-nitrobenzoylmercapto)-2-thiophenaldehyde diethylacetal (XI) was 80% (on the acetal which reacted). Found: C 52.37; 52.51; H 4.66; 4.56; S 17.65; 17.55%. Calculated for $C_{16}H_{17}NO_5S_2$: C 55.30; H 4.66; S 17.5%.

10 ml aqueous alkaline solution and 1 ml benzoyl chloride gave, in the way described above, 0.7 g (82% yield on the acetal which reacted) 3-benzoylmercapto-2-thiophenaldehyde (XII), which after recrystallizing from EtOH had mp 90–90.5°. Found: C 57.92; 58.17; H 3.24; 3.23; S 25.81; 25.53%. Calculated for $C_{12}H_8O_2S_2$: C 58.03; H 3.25; S 25.82%.

d) 3-Ethylmercapto-5-methyl-2-thiophenaldehyde diethylacetal (IIIb) and 2 equivalents of sodium. 1) 15 g acetal was treated with sodium in the usual way. From the benzene layer 2.2 g (44%) starting acetal was isolated. It gave a 2, 4-dinitrophenylhydrazone mp 185.5–186°, identical with that of the starting aldehyde (see above). From the aqueous solution at pH ~ 8 was isolated a viscous red oil (1 g) which in treatment with EtOAc gave a small amount of yellow solid containing nitrogen. After recrystallizing from EtOAc it had mp 183–184°, and composition $C_{12}H_{11}NS_4$. It was not further investigated.

0.35 g oil and 0.35 g β-naphthylamine gave 0.2 g (3-mercapto-5-methyl-2-thenylidene)-β-naphthylamine (XVII), as red crystals, which after recrystallizing from EtOAc had mp 165.5–166.5°. Found: C 67.63; 67.39; H 4.84; 4.63; S 22.56; 22.38%. Calculated for $C_{16}H_{13}NS_2$: C 67.80; H 4.62; S 22.63%. The aqueous layer acidified to pH ~ 4 gave a further 0.3 g oil with a mercaptan odor.

2) The run was repeated with 2.5 g acetal IIIb, and the aqueous alkaline solution was treated with 1.2 g p-nitrobenzoyl chloride, as described above, when it gave 1.4 g (68% yield on the acetal which reacted) 3-(p-nitrobenzoyl)mercapto-5-methyl-2-thiophenaldehyde (XVI) which after recrystallizing from EtOAc had mp 166.5–167.5°. Found: C 51.10; 51.10; H 3.04; 3.07; S 20.93; 20.97%. Calculated for $C_{16}H_9NO_4S_2$: C 50.80; H 2.95; S 20.87%.

3) 4-Methylmercapto-3-thiophenaldehyde diethylacetal (IV) and 6 equivalents of sodium. After 1.8 g sodium had been added to 3 g acetal the blue color of the ammonia solution rapidly vanished, indicating that reaction was incomplete. Acidification of the aqueous solution gave 0.9 g oil with a mercaptan odor, bp 85–86° (18 mm), n_D^{20} 1.6020. The literature gives [8] for 4-methyl-3-thienylmercaptan and 0.7 g 2, 4-dinitrochlorobenzene gave 0.6 g 2, 4-dinitrophenyl(4-methyl-3-thienyl)sulfide (XIX), which after recrystallizing from ethanol had mp 87.5–88.5°. Found: C 44.38; 44.16; H 2.84; 2.73; S 21.60; 21.45%. Calculated for $C_{11}H_8N_2S_4O_2$: C 44.58; H 2.72; S 21.64%.

f) 4-Methylmercapto-3-thiophenaldehyde diethylacetal (IV) and 2 equivalents of sodium. 1) After 1.6 g sodium had been added to 7.9 g acetal, the blue color of the ammonia solution rapidly vanished. No reaction products were found in the benzene layer. When the alkaline aqueous solution containing ammonia was acidified with dilute HCl (1:1) and brought to pH ~ 8, 0.2 g white precipitate formed, and was recrystallized from $CHCl_3$. The substance contained nitrogen and one active hydrogen atom, did not melt, but charred when heated to 300°; it was soluble in dioxane, tetrahydrofuran, and hot EtOAc, but did not dissolve in EtOH. Found: N 5.19; 4.96; S 47.36; 47.06%; M 264*. Calculated for $C_{10}H_7NS_4$: C 44.56; H 2.68; N 5.20; S 47.59%; M 269.4. With respect to composition and active hydrogen content, the substance resembles amine XIV. Further acidification of the solution, to pH ~ 4, led to separation of an oil which was extracted with ether. The ether solution was washed with water and dried, and the ether evaporated off to give 4.6 of a pale oil with a mercaptan odor. 15 min refluxing of this oil with 2, 4-dinitrochlorobenzene gave a yellow precipitate of 2, 4-dinitrophenyl(3-formylthienyl-4)sulfide (XX), much contaminated with tar; after recrystallizing from EtOH and EtOAc it had mp 157.5°. Found: C 42.53; 42.47; H 1.95; 2.07; S 20.35; 20.26%. Calculated for $C_{11}H_6N_2O_5S_2$: C 42.57; H 1.95; S 20.66. Hence the starting oil was mainly 4-mercapto-3-thiophenaldehyde. Though the compound contains an aldehyde group, azomethanes could not be obtained with cyclohexylamine and β-naphthylamine. 0.15 g sulfide XX gave 0.15 g 2, 4-dinitrophenylhydrazone XXI, which after recrystallizing from mixed EtOH-tetrahydrofuran had mp 280–281.5°. Found: C 41.77; 41.63; H 2.28; 2.50; S 13.18; 13.11%. Calculated for $C_{17}H_{10}N_6O_8S_2$: C 41.63; H 2.05; S 13.08%.

2) 5.4 g acetal IV was treated in the usual way with 1.1 g sodium, and the blue color rapidly disappeared. The ammonia was carefully vacuum-distilled off. Benzene and water were added, with cooling, to the residue. The colorless benzene solution was removed, and the colored aqueous solution twice extracted with benzene. 50 ml aqueous alkaline solution was obtained. 10 g of this solution and 0.8 g 4-(p-nitrobenzoylmercapto)-2-thiophenaldehyde diethylacetal (XXIII), mp 75.5–76.5° (ex EtOH). Found: C 52.22; 52.13; H 4.72; 4.58; N 4.01; 3.83; S 17.65; 17.86%. Calculated for $C_{16}H_{17}NO_5S_2$: C 52.30; H 4.66; N 3.82; S 17.45%. 15 ml of the alkaline solution was oxidized with 0.8 g iodine. The dark oil which separated was extracted with ether, the ether solution washed with hyposulfite and water, and then dried. 0.6 g oil was obtained, which on refluxing with ethanolic HCl gave 0.3 g yellow powder. After being twice recrystallized from EtOH, bis(3-formyl-4-thienyl)disulfide (XXIV) had mp 119–120.5°. Found: C 41.91; 41.79; H 2.16; 2.32%. Calculated for $C_{10}H_6O_2S_4$: C 41.93; H 2.11%.

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Zelinskii Institute of Organic
Chemistry, AS USSR, Moscow