

SYNTHESIS AND SOME TRANSFORMATIONS OF SULFIDES
OF THE THIOPHENE SERIES

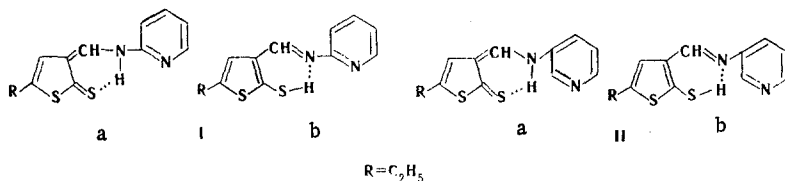
XXIV.* ACTION OF METHYL IODIDE ON SOME CHELATES OF 5-ETHYL-
3-(α -PYRIDYLAMINOMETHYLENE)-4-THIOLENE-2-THIONE

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UDC 547.732'829.07+541.49

The action of methyl iodide on N-(2-mercapto-5-ethyl-3-thienylidene)- α -aminopyridine and its Zn(II), Co(II), and Ni(II) chelates was studied. S-Alkylation and the formation of chelates of the VII and VIII type occur in the case of Zn and Co chelates (III and IV). This fact, together with a consideration of volume and skeleton models of the compounds obtained, makes it possible to arrive at the conclusion that the nitrogen atom of the pyridine ring is coordinated in chelates III and IV (structure C).

In developing our research on the synthesis and investigation of the reactivities of mercaptoaldimines of the thiophene series and of the chelates formed by them, we undertook the synthesis of compounds of the Ia,b and IIa,b types.



In contrast to mercaptoaldimines [2], these compounds contain three atoms capable of coordination with metal ions. However, judging from the results in [3], the Schiff bases formed by salicylaldehyde and α -aminopyridine, i.e., derivatives that have structural fragments similar to I, can function as bidentate compounds, since only the exocyclic nitrogen atom participates in coordination in Co(II) and Zn(II) chelates. In addition, a number of complexes with an S, N, N chelate node are known [4].

We obtained Schiff bases I and II† in 60% yield by the reaction of 2-mercapto-5-ethyl-3-thienylidene-amine with α - or, respectively, β -aminopyridine. According to the PMR spectra, they exist, like mercaptoaldimines [5], primarily in the thionamine form (Ia), which includes an NH...S hydrogen bond.

Schiff bases I form good yields of colored chelates III-V‡ with sharp melting points on reaction with zinc, cobalt, and nickel acetates. Chelates III-V are soluble in chloroform or dimethylformamide (DMF). The metal to ligand ratio in them is 1:2. In principle, their structure can be represented by one of the following formulas:

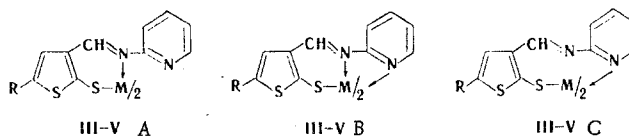
*See [1] for communication XXIII.

† Here and elsewhere we name these compounds (2-mercapto-5-ethyl-3-thienylidene)aminopyridines with respect to one of the possible tautomeric forms.

‡ All of the discussion pertaining to the complexes designated by formulas III-V remains in force if their structures correspond to the thionamine form.

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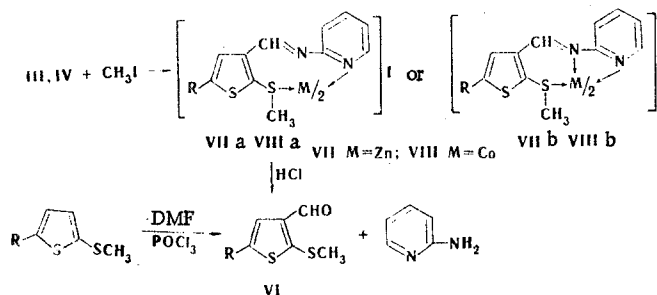
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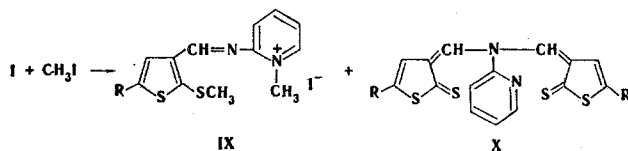
III M = Zn; IV M = Co; V M = Ni

The character of the coordination in the chelates under discussion naturally depends on a number of factors – the nature of the metal and ligand, the degree of strain of the developing chelate rings, and the distribution of the electron density on the donor atoms of the ligand – and can be explained only from a series of data from an investigation of their chemical and physical properties. We will discuss the geometry of these compounds later; here, however, we will be concerned with only one side of the problem – the participation in the coordination of the pyridine and (or) exocyclic nitrogen atoms. For this, it seemed expedient to study the reaction of the chelates with methyl iodide or some other alkyl halide. Actually, when the electron pair of nitrogen is involved in coordination, the site of attack of the electrophilic agent should change, as occurs, for example, in the reactions of metalloporphines [6]. In addition, it is known that a coordinated sulfur atom is capable of reacting with alkyl halides to form complexes of the corresponding thio ethers [7-12]; moreover, the alkylation proceeds without cleavage of the S-metal bond [7, 10]. It has also been shown in a number of studies pertaining to the reactions of aminomercaptan and mercaptoimine complexes with alkyl halides [7, 9, 11] that the coordinated nitrogen atom is not involved in the reaction.

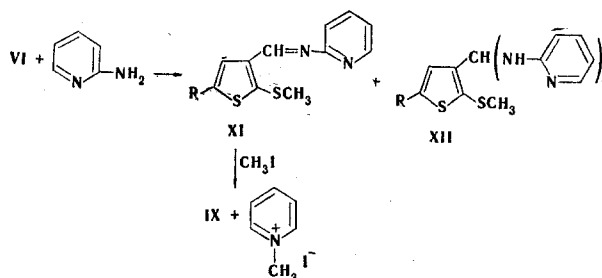
Zinc and cobalt chelates III and IV react with excess methyl iodide to give high yields of colored, crystalline substances VII and VIII, the composition of which corresponds to the products of the addition of 2 mole of CH_3I to 1 mole of the chelate. The hydrolysis of these compounds by dilute hydrochloric acid, during which 2-methylmercapto-5-ethyl-3-formylthiophene (VI) and α -aminopyridine are formed, and the shift in the absorption maxima in the UV spectra to the short-wave region as compared with the starting chelates III and IV indicate alkylation of the coordinated sulfur atom rather than of the nitrogen atoms. This makes it possible to propose a structure of the VIIa,b or VIIIa,b type with a coordinated pyridine ring nitrogen atom for the products of the addition of methyl iodide.



Turning again to the problem of the character of the coordination in chelates III and IV, it should be taken into account that the ring nitrogen atom in α -aminopyridine, which has an amide grouping of atoms, is more basic [13]. It might have been assumed that similar relationships are retained for Schiff bases I. In fact, in the reaction of ligand I – a system with a genuinely uncoordinated pyridine nitrogen atom – with excess methyl iodide the products were methiodide IX and X; the latter could arise as a result of subsequent transformations of azomethine I.



The structure of methiodide IX is confirmed by the fact that it hydrolyzes to give aldehyde VI and α -aminopyridine methiodide. Methiodide IX is also formed in the reaction of methyl iodide with Schiff base XI. The presence of a small amount of α -aminopyridine methiodide in the product of this reaction apparently attests to the facile hydrolysis of XI or IX under the influence of traces of acid, probably introduced by the methyl iodide. We note here that ligands I and II are also readily cleaved on reaction with picric acid. We synthesized azomethine XI from VI and α -aminopyridine; in the process, we also isolated XII – the product of the condensation of aldehyde VI with 2 mole of α -aminopyridine. Compounds similar to XII were previously described in [14].



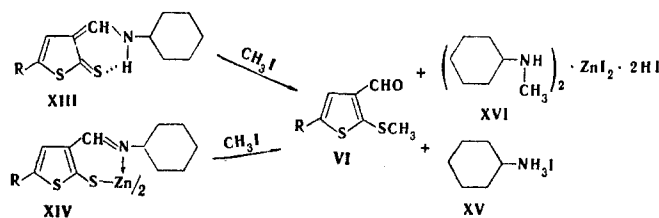
The formation of methiodide IX in the reaction of Schiff bases I and XI with methyl iodide is in complete agreement with the concept of the high nucleophilicity of the ring nitrogen atom in these azomethines.

The data set forth above and an examination of Stuart-Briegleb models of III-V, which demonstrate considerable steric hindrance during the formation of the metal bond simultaneously with the ring and exocyclic nitrogen atoms in the type-B structure,* make it possible to assume for them a more probable structure with an unstrained eight-membered ring - type C. However, one cannot exclude the possibility that if the ring nitrogen atom participates in intermolecular coordination in the starting chelates, the possibility for the realization of a structure with a six-membered ring - type A - also remains.

Dimethylformamide has a substantial effect on the course of the reaction of chelate IV with CH₃I. The presence of even a small amount of it leads to the rapid formation of a double methylation product - methiodide IX. Whether this is the result of subsequent transformations of the VIII formed (for example, with the starting chelate or excess CH₃I) or the specific influence of DMF still remains unclear. For comparison only, we will present the indication [15] of a complex with the composition NiI₂(H₂NCH₂CH₂SCH₃)₂; in DMF it dissociates completely to form [Ni(H₂NCH₂CH₂SCH₃)₂DMF₂]²⁺.

A different pattern than in the case of zinc and cobalt chelates is observed in the reaction of Ni chelate V with methyl iodide. Methiodide IX rather than a chelate of the VII-VIII type can be isolated from the mixture by repeated crystallization. This same compound is isolated in yields up to 80% along with α -aminopyridine methiodide in the reaction of Ni chelate with methyl iodide in DMF. Whether this should be considered to be a consequence of the fact that chelate V differs in the character of its coordination from Zn(II) and Co(II) chelates cannot be stated at present. As already noted, we expect to return to an examination of the geometry of the chelates later after an investigation of their physical properties.

In the light of the data set forth, it seemed of interest to follow the action of methyl iodide on ligand XIII, which does not have a third coordination center and is formed by cyclohexylamine - a base that is stronger than α -aminopyridine - and on its zinc chelate XIV. We found that in both cases the process develops in one direction: the chief reaction products are aldehyde VI and cyclohexylamine (or its methylation product), which is isolated as a salt (XV) in the first case or as a complex (XVI) with zinc iodide in the second case. Thus the character of the action of methyl iodide on chelates XIV and V coincides in many respects. In addition, it should be noted that since this pertains to the examined chelates, the strength of the basic fragment per se does not have a stabilizing effect on the chelates during their interaction with electrophilic agents. This factor apparently takes on significance in the presence of a second basic coordination center, as occurs in chelates with an α -aminopyridine fragment; i.e., when competition is possible between the two basic centers that are capable of coordination.



*Judging from the skeletal models developed in our laboratory by F. D. Alashev, the realization of this sort of structure would distort the valence angles too markedly.

EXPERIMENTAL

N-(2-Mercapto-5-ethyl-3-thienylidene)- α -aminopyridine (I). A solution of 5.5 g (0.058 mole) of α -aminopyridine in 30 ml of absolute alcohol was added to a solution of 5 g (0.029 mole) of 2-mercapto-5-ethyl-3-thienylideneamine [2] in 30 ml of absolute alcohol, and the mixture was refluxed for 3 h. The alcohol was removed by vacuum distillation to dryness, and 30 ml of alcohol was added to the residue. The alcohol was again removed by distillation to dryness (this treatment was repeated three times). The residual dark oil or crystalline precipitate was treated with a small amount of cold alcohol, and the precipitate was removed by filtration, washed with water and alcohol, and vacuum-dried to give 4.17 g (58%) of Schiff base I with mp 98–99°. Two recrystallizations from ethyl acetate gave red needles with mp 101–102°. PMR spectrum (in dioxane): δ 15.33 (NH), 9.3 (β -CH), 6.92 (4H) ppm, $J_{\text{NH,CH}} = 13$ Hz. Found: C 58.0; H 4.9; S 25.8%. $\text{C}_{12}\text{H}_{12}\text{N}_2\text{S}_2$. Calculated: C 58.0; H 4.9; S 25.8%. One mole of 2-aminopyridine gave 50–52% of I with mp 96°.

N-(2-Mercapto-5-ethyl-3-thienylidene)- β -aminopyridine (II). This compound was similarly obtained in 62% yield from 2 g (0.012 mole) of 2-mercapto-5-ethyl-3-thienylideneamine and 2.25 g (0.024 mole) of β -aminopyridine in 25 ml of alcohol. Two recrystallizations from ethyl acetate gave a product with mp 134–135°. Found: C 58.1; H 4.0; S 25.6%. $\text{C}_{12}\text{H}_{12}\text{N}_2\text{S}_2$. Calculated: C 58.0; H 4.9; S 25.8%.

Reaction of I with Picric Acid. A solution of 0.1 g of picric acid was added to a solution of 0.1 g of I in absolute alcohol, and the mixture was heated for several minutes and cooled. The resulting yellow crystals were removed by filtration and recrystallized from ethyl acetate and from alcohol to give 0.07 g of the picrate of α -aminopyridine with mp 219–220° (mp 216–217° [16], 224–225° [17]). This product did not depress the melting point of the picrate obtained from α -aminopyridine and picric acid (mp 219–220°).

Zinc Chelate of N-(2-Mercapto-5-ethyl-3-thienylidene)- α -aminopyridine (III). A solution of 2.65 g (0.012 mole) of zinc acetate in 15 ml of methanol was added to a hot solution of 3 g (0.012 mole) of I in 50 ml of methanol, and the mixture was heated for 20 min. The orange precipitate was removed by filtration, washed with methanol, and dried to give 2.67 g (79%) of chelate III. Two reprecipitations from chloroform by the addition of methanol gave a product with mp 206–207°. Found: C 51.5; H 3.8; S 22.7; Zn 11.4%. $\text{C}_{24}\text{H}_{22}\text{N}_4\text{S}_4\text{Zn}$. Calculated: C 51.6; H 4.0; S 22.9; Zn 11.6%.

Cobalt Chelate of I (IV). This chelate was obtained in 70% yield as described above from 3 g of I and 3 g of cobalt (II) acetate in methanol. Three reprecipitations from chloroform by the addition of methanol gave a product with mp 234.5–236.5°. Found: C 51.9; H 3.9; Co 10.2; S 23.4%. $\text{C}_{24}\text{H}_{22}\text{CoN}_4\text{S}_4$. Calculated: C 51.1; H 4.0; Co 10.6; S 23.2%.

Nickel Chelate of I (V). This chelate was similarly obtained in 80% yield from 3 g of I and 3 g of nickel acetate in methanol. Reprecipitation from chloroform and from dimethylformamide by the addition of methanol gave a product with mp 216–218°. Found: C 52.3; H 4.0; Ni 10.7; S 23.0%. $\text{C}_{24}\text{H}_{22}\text{NiS}_4$. Calculated: C 52.1; H 4.0; Ni 10.6; S 23.2%.

2-Methylmercapto-5-ethyl-3-formylthiophene (VI). This compound was obtained in 80% yield via the method in [18] from 5-methylmercapto-2-ethylthiophene [19] and had bp 137° (4 mm) and n_D^{20} 1.6120. Found: C 51.9; H 5.4; S 34.6%. $\text{C}_8\text{H}_{10}\text{OS}_2$. Calculated: C 51.6; H 5.4; S 34.4%. The 2,4-dinitrophenylhydrazone had mp 203–205° (from chloroform and from ethyl acetate). Found: C 45.8; H 4.0; S 17.3%. $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_4\text{S}_2$. Calculated: C 45.8; H 3.9; S 17.5%.

Action of Methyl Iodide on the Chelates of N-(2-Mercapto-5-ethyl-3-thienylidene)- α -aminopyridine (III–V). A. On Zinc Chelate III. A 0.2-g sample of zinc chelate III was dissolved by heating in 2 ml of methyl iodide, and the solution was allowed to stand overnight. The excess methyl iodide was removed by vacuum distillation to give 0.25 g (80%) of a yellow powder bis[N-(2-methylmercapto-5-ethyl-3-thienylidene)- α -aminopyridine]zinc iodide (VII), which melted at 197–198° after two reprecipitations from chloroform by the addition of heptane and after recrystallization from ethyl acetate. Found: C 37.1; H 3.2; I 29.7; S 14.9; Zn 7.8%. $\text{C}_{26}\text{H}_{28}\text{I}_2\text{N}_4\text{S}_4\text{Zn}$. Calculated: C 37.0; H 3.3; I 30.1; S 15.2; Zn 7.8%.

B. On Cobalt Chelate IV. A 0.5-g sample of chelate IV and 5 ml of CH_3I were heated for several minutes until the chelate had dissolved completely, and the mixture was allowed to stand overnight (it began to partially crystallize). The excess CH_3I was removed by distillation, and the residue was washed with heptane and dried to give 0.7 g (92%) of green crystals of bis[N-(2-methylmercapto-5-ethyl-3-thienylidene)- α -aminopyridine]cobalt iodide (VIII). Three recrystallizations from CHCl_3 –ethyl acetate gave a product with mp 195–196.5° that was soluble in hot water and slightly soluble in alcohol and ethyl acetate. Found: C 37.3; H 3.2; Co 7.1; I 29.9; S 15.1%. $\text{C}_{26}\text{H}_{28}\text{N}_4\text{CoI}_2\text{S}_4$. Calculated: C 37.3; H 3.4; Co 7.0; I 30.3; S 15.3%.

C. On Cobalt Chelate IV in the Presence of DMF. A 0.25-g sample of chelate IV, 3 ml of CH_3I , and 1 ml of DMF were heated for several minutes until the chelate had dissolved completely, during which an orange precipitate began to appear immediately. The mixture was allowed to stand overnight, and the excess CH_3I was removed by distillation. The solid was removed by filtration and washed with alcohol to give 0.15 g of N-(2-methylmercapto-5-ethyl-3-thienylidene)-2-aminopyridine methiodide (IX) with mp 224-226°. The product did not depress the melting point of a sample of methiodide IX (see below).

D. On Nickel Chelate V without a Solvent. A 0.5-g sample of chelate V was heated for 10-15 min with 10-15 ml of CH_3I , and the mixture was allowed to stand for 30 min. The insoluble material was removed by filtration, and the filtrate was evaporated to give 0.24 g of an orange Ni-containing powder with mp 200-206°. Recrystallization from alcohol and from chloroform-heptane gave a small amount of methiodide IX with mp 217°. This product did not depress the melting point of a genuine sample of methiodide IX (see below).

E. On Nickel Chelate V in the Presence of DMF. A 0.5-g sample of V, 15 ml of CH_3I , and 3 ml of DMF were heated for several minutes on a water bath. The chelate dissolved rapidly, and the color changed from dark-brown to orange, and orange crystals appeared. The mixture was allowed to stand overnight, the excess CH_3I was removed by distillation, and the residue was filtered and dried to give 0.58 g (79%) of methiodide IX, which, after two recrystallizations from alcohol, did not contain nickel, melted at 222-223°, and did not depress the melting point of a sample of IX obtained by an independent method (see below). The mother liquor from the crystallization of IX yielded a small amount of α -aminopyridine methiodide with mp 145-147°. This product did not depress the melting point of a genuine sample of α -aminopyridine methiodide (mp 149-150°).

Hydrolysis of Co-Iodide VIII. A 0.5-g sample of iodide VIII was heated for several minutes with dilute (1:1) hydrochloric acid, and the resulting oil was extracted with ether. The ether extract was washed with water and dried with MgSO_4 . The ether was removed by distillation to give 0.17 g of a red oil from which 0.3 g of 2-methylmercapto-5-ethyl-3-formylthiophene 2,4-dinitrophenylhydrazine (2,4-DNP)* with mp 202-204° was obtained. This product did not depress the melting point of a genuine sample of the 2,4-DNP of this aldehyde (see above). The acidic aqueous solution was made alkaline with 20% NaOH solution, salted out with potassium carbonate, and extracted with ether. The extract was dried with KOH, and the ether was removed by distillation to give 0.09 g of an oil, which crystallized on trituration. The crystals were washed with heptane to give a product with mp 55-56°. The product did not depress the melting point of a genuine sample of α -aminopyridine (mp 56-58°).

Hydrolysis of Zn-Iodide VII. A 0.5-g sample of VII was treated with 5 ml of hydrochloric acid (1:1) as described above. The solvent was removed by distillation, the residue was treated with 2,4-dinitrophenylhydrazine, and 0.3 g of the 2,4-DNP of aldehyde VI with mp 203-205° (from ethyl acetate) was isolated from the ether layer. Alkalization of the aqueous solution gave 0.06 g of α -aminopyridine with mp 56-57°, which did not depress the melting point of a genuine sample of α -aminopyridine.

N-(2-Methylmercapto-5-ethyl-3-thienylidene)- α -aminopyridine (XI). A mixture of 10 g (0.054 mole) of aldehyde VI, 5.2 g (0.055 mole) of α -aminopyridine, and 120 ml of o-xylene was refluxed for 4 h with a Dean-Stark adapter, after which the xylene was removed by vacuum distillation, and the residue was dissolved in 40 ml of ether. The ether solution was washed with water and dried with MgSO_4 . The ether was removed by distillation, and the residue (13 g of a brown oil) was dissolved in 100 ml of hot heptane. The solution was cooled, and the resulting oil began to crystallize on trituration. The crystals were removed by filtration and washed with heptane to give 1.55 g of 2-methylmercapto-5-ethyl-3-[di(2-pyridylamino)]-methylthiophene (XII) with mp 69-70° (after two recrystallizations from heptane). Found: C 60.5; H 5.8; N 16.1; S 18.5%. $\text{C}_{18}\text{H}_{20}\text{N}_4\text{S}_2$. Calculated: C 60.6; H 5.7; N 15.7; S 18.0%. The mother liquor was vacuum-evaporated, and the residue (9.3 g of a viscous oil) was vacuum-distilled to give 5.77 g (41%) of Schiff base XI as a thick, viscous oil with bp 195-197° (0.32 mm). Found: C 59.1; H 5.5; N 10.8; S 24.5%. $\text{C}_{19}\text{H}_{14}\text{N}_2\text{S}_2$. Calculated: C 59.5; H 5.4; N 10.7; S 24.4%.

N-(2-Methylmercapto-5-ethyl-3-thienylidene)- α -aminopyridine (IX). A 1-g sample of azomethine XI was heated for several minutes with 3 ml of methyl iodide, and the solution was allowed to stand overnight. The precipitated orange crystals were removed by filtration and dried to give 1.76 g of a solid product from

*Here and in the other cases described below, the alkylmercapto formylthiophene obtained by hydrolysis was identified as the 2,4-DNP and by comparison with an authentic sample of aldehyde VI by gas-liquid chromatography.

which, after two recrystallizations from alcohol, 0.5 g of methiodide IX with mp 226–228° was isolated. Found: C 41.7; H 4.5%. $C_{14}H_{17}IN_2S_2$. Calculated: C 41.6; H 4.2%. The mother liquor was evaporated to give a residue consisting of a mixture of light-yellow and orange crystals. The light-colored crystals were separated, squeezed out on a porous plate, and recrystallized from alcohol containing ethyl acetate to give 0.4 g of α -aminopyridine methiodide with mp 146–148° (mp 149–150° [20]). This product did not depress the melting point of a genuine sample of α -aminopyridine methiodide.

Hydrolysis of Methiodide IX. A 0.25-g sample of methiodide IX was refluxed with 3 ml of distilled water until all of it had dissolved. The resulting oil was extracted with ether, and the ether solution was washed with water and dried with $MgSO_4$. The ether was removed by distillation to give 0.08 g of an oil, which, judging from the GLC data and the composition of the 2,4-DNP was aldehyde VI. The aqueous solution was filtered, and the filtrate was evaporated in a dish to give 0.12 g of yellow crystals of α -aminopyridine methiodide with mp 149–150° (from alcohol). This product did not depress the melting point of a known sample of α -aminopyridine methiodide.

Action of Methyl Iodide on N-(2-Mercapto-5-ethyl-3-thienylidene)- α -aminopyridine (I). A solution of 0.5 g of I in excess CH_3I was heated for several minutes and allowed to stand overnight. The resulting precipitate was removed by filtration, washed with absolute alcohol, and dried to give 0.2 g of orange crystals of methiodide IX with mp 226–228° (from absolute alcohol). This product did not depress the melting point of methiodide IX previously obtained. The mother liquor was treated with alcohol and allowed to stand to give 0.1 g of a light-yellow substance corresponding in composition to N,N-bis(5-ethyl-3-thiono-3-thienylidenemethyl)- α -aminopyridine (X) with mp 181–182° (from ethyl acetate). Found: C 57.1; H 4.6; S 31.2%. $C_{19}H_{18}N_2S_4$. Calculated: C 56.7; H 4.5; S 31.9%.

Action of Methyl Iodide on N-(2-Mercapto-5-ethyl-3-thienylidene)cyclohexylamine (XIII). A 0.5-g sample of N-(2-mercapto-5-ethyl-3-thienylidene)cyclohexylamine [2] was dissolved by heating in 3 ml of CH_3I , and the solution was allowed to stand overnight. The CH_3I was evaporated, and the residue was treated with ether. The ether extract was washed with water and dried, and the ether was removed by distillation to give 0.15 g of a red oil, from which 0.26 g of the 2,4-DNP of aldehyde VI with mp 203–204° (from ethyl acetate) was obtained. The ether-insoluble portion of the reaction product was reprecipitated twice from chloroform solution by the addition of heptane to give 0.3 g (65%) of colorless crystals of cyclohexylamine hydriodide (XV) with mp 188–190°. This product did not depress the melting point of cyclohexylamine hydriodide (mp 192–194°) obtained by heating cyclohexylamine with HI. Found: C 31.8; H 6.4; I 55.5%. $C_6H_{13}N \cdot HI$. Calculated: C 31.8; H 6.2; I 55.9%.

Action of Methyl Iodide on the Zinc Chelate of N-(2-Mercapto-5-ethyl-3-thienylidene)cyclohexylamine (XIV). A 0.5-g sample of zinc chelate XIV was dissolved by heating in excess CH_3I , and the solution was allowed to stand overnight. The CH_3I was removed by distillation, and the residue – a viscous dark oil – was treated with water and ether. The ether solution was washed with water and dried, and the ether was removed by distillation to give 0.15 g of an oil, from which the 2,4-DNP of aldehyde VI with mp 202–203° was obtained. The aqueous layer was allowed to stand and gradually evaporate to give colorless crystals of the complex of N-methylcyclohexylamine hydriodide and zinc iodide (XVI) with mp 159.5–160.5° (after two recrystallizations from alcohol–ethyl acetate). Found: C 21.5; H 4.2; I 63.3; Zn 8.2%. $2C_7H_{15}N \cdot 2HI \cdot ZnI_2$. Calculated: C 21.0; H 4.0; I 63.3; Zn 8.0%.

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