CHLOROMETHYLATION OF SUBSTITUTED DI(2-THIENYL)METHANES AND THE REDUCTIVE DESULFURATION OF SOME DIAMINES OF THE THIOPHENE SERIES

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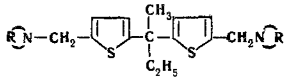
The action of chloromethyl ether on di(2-thienyl)methane, 1,1-di-(2-thienyl)ethane, 2,2-di(2-thienyl)propane, 2,5-bis(dimethyl-2-thienylmethyl)thiophene, and 1,1,1-tri(2-thienyl)ethane has given, respectively: 5-chloromethyl-2-thienylthiophene, 1,1-bis(5-chloromethyl-2-thienyl)ethane, 2,2-bis(5-chloromethyl-2-thienyl)propane, 2,5-bis(dimethyl-5-chloromethyl-2-thienylmethyl)thiophene, 1-(2-thienyl)-1,1-bis(5-chloromethyl-2-thienyl)-ethane, and the corresponding amines: 5-diethylaminomethyl-2-thienylthiophene, 1,1-bis(5-diethylaminomethyl-2-thienyl)ethane, 2,2-bis(5-aminomethyl-2-thienyl)propane, 2,2-bis(5-methylaminomethyl-2-thienyl)propane, 2,5-bis(dimethyl-5-dimethylaminomethyl-2-thienylmethyl)thiophene, and 2,8,8,14,20,20-hexamethyl-2,14-diaza-3,2,3,2-α-cyclotetrathiene. The reductive desulfonation over Raney nickel of the diacetyl derivatives of 2,2-bis(5-aminomethyl-2-thienyl)propane and 2,2-bis(5-methylaminomethyl-2-thienyl)propane has given the diacetyl derivatives of aliphatic amines.

Together with Santalova, [1] we have previously shown that by the action of Raney cobalt on ditertiary amines of types I and Ia

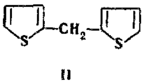

I, Ia

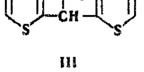
I $R = -(CH_2)_5-$
Ia $R = -(CH_2)_2-O-(CH_2)_2-$

it is possible to obtain higher alkylenediamines with comparatively long carbon atom chains.

It appeared of interest to extend the method of reductive desulfonation to other amines of the thiophene series and also to study the conditions of synthesizing chloromethyl derivatives of di(2-thienyl)ethane, which we subsequently used to obtain thiophene bases.

The following compounds, which have been described in the literature [2–4], were used as starting materials for our work: di(2-thienyl)methane (II), 1,1-di(2-thienyl)ethane (III), 2,2-di(2-thienylpropane)(IV), 2,5-bis(dimethyl-2-thienylmethyl)thiophene (V), and 1,1,1-tri(2-thienyl)ethane (VI):


II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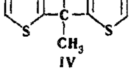
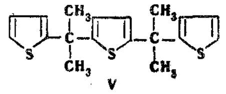
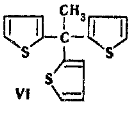
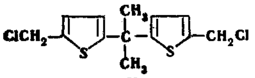
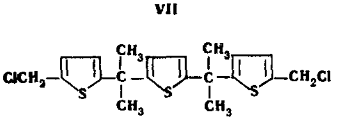

IV

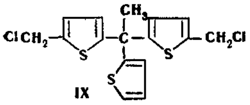

V


VI

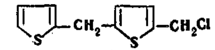
Under the conditions described in the experimental part, chloromethylation with chloromethyl ether, taken in an amount of 2.5 mole per mole of initial compound, took place smoothly in the case of IV and V. The reaction products were, respectively, 2,2-bis(5-chloromethyl-2-thienyl)propane (VII) and 2,5-bis-(dimethyl-5-chloromethyl-2-thienylmethyl)thiophene (VIII), which were isolated with yields reaching 50–60%. Under similar conditions, 1,1,1-tri(2-thienyl)ethane gave 1-(2-thienyl)-1,1-bis(5-chloromethyl-2-thienyl)ethane (IX), but its yield was low.


VII


VIII

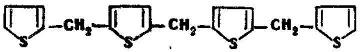

IX

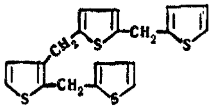
Compounds II and III, in the aliphatic bridge of which there are unsubstituted hydrogen atoms, react so readily that the process goes too far and leads to their complete resinification. Chloromethylation under milder conditions (room temperature, equimolar amount of chloromethyl ether) avoids the resinification of II and III, but the reaction takes place differently in the two cases. Thus, the chloromethylation of II gave 5-chloromethyl-2-thenylthiophene (X)


X

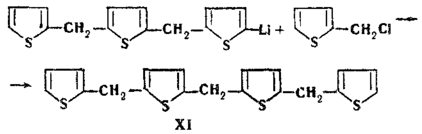
which, however, could not be freed from impurities by vacuum distillation. Consequently, after preliminary distillation, compound X was treated with diethylamine and converted into the corresponding amine. The base obtained in this way was purified through the picrate.

In addition to compound X, our experiments also yielded a mixture of high-boiling reaction products from which a substance with the composition $C_{19}H_{16}S_4$ (mp 78.5–79.5° C) was isolated. Since the chloromethylation of thiophene may be accompanied by side reactions with the formation of 2- and 2,5-substituted thiophenes [2], this compound could be assigned the structure XI, although a priori it was impossible to exclude other possible structures such as XII.


XI


XII

Starting from 2,5-bis(2-thenyl)thiophene, the structure of which has been demonstrated previously [2] and 2-chloromethylthiophene, we obtained **XI** by the following method:



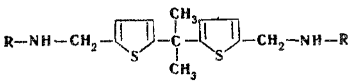
XI

A mixture of the compound with the composition $C_{19}H_{16}S_4$ isolated from the chloromethylation of di(2-thienyl)methane with **XI** gave no depression of the melting point. In the light of the results obtained and the observations made previously [1], it can be stated that under the conditions that we selected the chloromethylation of substituted di(2-thienyl)methanes and 2,5-di(2-thenyl)thiophenes takes place without appreciable resinification if the hydrogen atoms in the methylene bridge are completely replaced by alkyl radicals. In other cases, polycondensation products are formed in addition to mono- and bischloromethyl derivatives.

For the preparation of the amines, the chloromethyl derivatives were used both in the pure form and without preliminary isolation in the form of washed and dried benzene solutions.

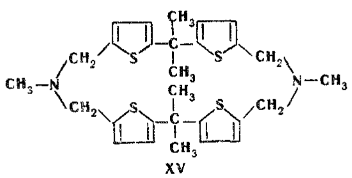
The action on freshly distilled **VII** of hexamethylenetetramine gave the corresponding salt and from it, by the usual method, 2,2-bis(5-aminomethyl-2-thienyl)propane (**XIII**) was obtained. When a benzene solution of unpurified **VII** was saturated with an excess of methylamine, 2,2-bis(5-methylaminomethyl-2-thienyl)propane (**XIV**) was formed.

Under very mild conditions (in benzene at 40° C), the amine **XIV** reacts with **VII**, forming a compound which, judging from its molecular weight and the results of elementary analysis, must be assigned the structure **XV** given below. Although the yield of the macrocyclic diamine **XV** in this case was very low, we have grounds for assuming that it can be raised by certain changes in the experimental conditions.



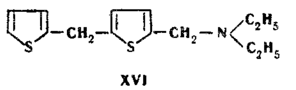
XIII, XIV

XIII R=H
XIV R=CH3

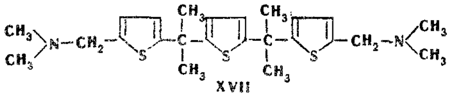


XV

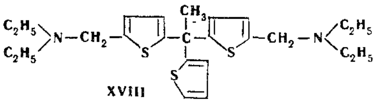
Under similar conditions, the action of dimethyl- and diethylamines on the chloromethyl derivatives **X**, **VIII**, and **IX** gave, respectively, the monoamine **XVI** and the diamines **XVII** and **XVIII**:



XVI



XVII

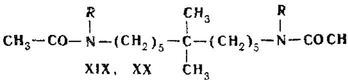


XVIII

For the reductive desulfonation of the compounds mentioned with an amine function, we decided to use Raney nickel, although its use in hydrogenolysis reactions is not infrequently accompanied by the formation of undesirable by-products. Thus, for example, its action on aliphatic-aromatic amines with the amino group in the side chain leads to deamination with the formation of the corresponding hydrocarbons, and the hydrogenation of primary arylamines in the presence of Raney nickel leads to a mixture of primary and secondary amines [5]. To prevent the formation of a secondary amine the addition to the reaction mixture of a substance binding the primary amine formed (glacial acetic acid, acetic anhydride, etc.) is recommended [6].

In the reductive desulfonation of amino acids by one of us and others [7] it was possible to prevent the formation of by-products by the preliminary acetylation of the amino group.

It was possible to become convinced that such protection plays a positive role in this case also. In actual fact, by the action of W-5 Raney nickel [8] on the acetylated amines **XIII** and **XIV** in boiling methanol we succeeded in obtaining the diacetylamines **XIX** and **XX** with yields of the order of 35–40%.



$$CH_3{-}CO{-}\underset{}{\overset{R}{\overset{|}{N}}}{-}(CH_2)_5{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}(CH_2)_5{-}\overset{R}{\overset{|}{N}}{-}COCH_3$$

XIX, XX

XIX R = H
XX R = CH3

EXPERIMENTAL

5-Chloromethyl-2-thenylthiophene (X). With stirring at a temperature of 20–25° C, 24.2 g (0.3 mole) of chloromethyl ether in 30 ml of glacial acetic acid was added over 3 hr to a solution of 54 g (0.3 mole) of di(2-thienylmethane) in 60 ml of glacial acetic acid. The contents of the flask were poured into 300 ml of ice water and extracted with benzene. The benzene layer was washed successively with ice water, bicarbonate solution, and water again. After drying over calcium chloride, the chloromethylation product was used in the following experiment.

5-Diethylaminomethyl-2-thenylthiophene (XVI). With stirring at 60° C, 58.5 g (0.8 mole) of diethylamine was added over 1 hour to the benzene solution from the preceding experiment. The mixture was left for 16 hr. The crystals of diethylamine hydrochloride that deposited were filtered off. The benzene was driven off from the filtrate and the residue was distilled in vacuum (2 mm). The following fractions were obtained: 1) bp 100–120° C, 18.2 g (unchanged di(2-thienyl)methane); 2) bp 120–170° C, 23.6 g; 3) bp 175–220° C, 9.5 g.

On standing, the last fraction crystallized. Two redistillations of the second fraction gave 18.9 g of a faintly yellowish liquid with bp 130–136° C (1.5 mm), which was purified via the picrate to give 6.5 g (12.5% on the **II** that had reacted) of **XVI** in the form of a faintly reddish liquid with bp 136–137° C (5 mm); n_D^{20} 1.5658; d_4^{20} 1.088. The constants found for compound **XVI** were in good agreement with those reported in the literature [9]. Found, %: C 63.35, 63.23; H 7.20, 7.21; S 24.10, 24.19. Calculated for $C_{14}H_{19}NS_2$., %: C 63.33; H 7.21; S 24.16. After two recrystallizations for ethanol, the picrate melted at 89–90° C. Found, %: N 11.47, 11.49. Calculated for $C_{14}H_{19}NS_2 \cdot C_6H_3N_3O_7$. %: N 11.33. **Methiodide,** mp 150.5–151.5° C (from absolute ethanol). Found, %: C 44.26, 44.01; H 5.49, 5.42. Calculated for $C_{15}H_{22}INS_2$, %: C 44.22; H 5.43.

After three recrystallizations from pentane, the third fraction gave 2.31 g of **XI**, mp 78.5–79.5° C. Found, %: C 61.33, 61.50; H 4.38, 4.29; S 34.19, 34.43. Calculated for $C_{19}H_{16}S_4$, %: C 61.25; H 4.33; S 34.43.

2, 2-Bis[5-(2-thenyl)-2-thienyl]methane (XI). This experiment was carried out in an atmosphere of nitrogen. With stirring at −3 to 0° C, over a period of 30 min 2.25 g (0.035 mole) of an ethereal solution of butyllithium was added to a solution of 6.2 g (0.023 mole) of 2, 5-bis(2-thenyl)thiophene in 30 ml of absolute ether protected from atmospheric moisture. The contents of the flask were stirred for another 20 minutes and then 4.65 g (0.035) of thenyl chloride in 25 ml of dry ether was added to the mixture at 0° C. The resulting mixture was kept at room temperature for 16 hr, boiled in the water bath under reflux for 5 hr, and treated with ice water. The ethereal layer was separated off, washed with water, and dried over calcium chloride. The residue after the elimination of the ether was distilled in vacuum (5 mm); fractions with bp 220–250° C, 3.10 g, and with bp 250–275° C, 1.63 g, were collected, the latter solidifying on standing to form a faintly colored substance with mp 59–63° C. After purification with activated carbon and three recrystallizations from heptane, mp 78.5–79.5° C. A mixture of **XI** with the substance of composition $C_{19}H_{16}S_4$ obtained in the chloromethylation of di(2-thienyl)methane melted without depression (mp 78.5–79.5° C).

2, 2-Bis(5-chloromethyl-2-thienyl)propane (VII). A mixture of 20.8 g (0.1 mole) of freshly distilled di(2-thienyl)propane, 35 ml of glacial acetic acid, and 23.3 g (0.29 mole) of chloromethyl ether was left at 20° C for 16 hr and was then heated with stirring in the water bath at 40° C for 2 hr, after which it was poured into 150 ml of ice water and extracted with benzene. The benzene extract was washed with ice water, sodium hydrogen carbonate solution, and water again, and was dried with calcium chloride. After the solvent had been evaporated off, the residue was twice distilled in vacuum. This gave 16.9 g (55%) of a faintly yellowish liquid with bp 182–185° C (2 mm); n_D^{20} 1.6081; d_4^{20} 1.2910. Found, %: C 51.00, 51.36; H 4.68, 4.61; S 20.87, 20.87. Calculated for $C_{13}H_{14}Cl_2S_2$, %: C 51.14; H 4.65; S 21.01.

2, 2-Bis(5-aminomethyl-2-thienyl)propane (XIII). The salt of VII with hexamethylenetetramine, obtained from 10.6 g (0.039 mole) of distilled **VII** and 12.2 g (0.09 mole) of hexamethylenetetramine in 140 ml of dry chloroform, was heated in the water bath with 25 ml of concentrated hydrochloric acid in 200 ml of ethanol for 2 hr. The crystalline hydrochloride of **XIII** that separated out when the solvent was evaporated off was treated with 40% NaOH solution until the reaction was alkaline. The mixture was extracted with benzene and the extract was dried over barium oxide. After elimination of the solvent, the residue was distilled twice in vacuum. This gave 4.55 g (48%) of **XIII**, bp 165–168° C (2 mm); n_D^{20} 1.6072; d_4^{20} 1.1884. Found, %: C 58.41, 58.70; H 6.67, 6.75; S 23.91, 24.01; MR_D 77.76. Calculated for $C_{13}H_{18}N_2S_2$, %: C 58.56; H 6.81; S 24.07; MR_D 77.33. **Picrate,** mp 154–155° C (from ethanol). Found, %: N 15.40. Calculated for $C_{13}H_{18}N_2S_2 \cdot 2C_6H_3N_3O_7$, %: N 15.47.

2, 2-Bis(5-methylaminomethyl-2-thienyl)propane (XIV). A benzene solution of crude **VII** prepared from 31.3 g (0.15 mole) of di(2-thienyl)-propane and 34.06 g (0.42 mole) of chloromethyl ether was diluted with dry benzene to a volume of 1200 ml and, with stirring and cooling to −10° C, it was saturated with dry ethylamine until the increase in weight was 46 g (1.5 mole). The mixture was kept at 5–10° C for 48 hr. The crystals of methylamine hydrochloride that separated out were filtered off. The filtrate was washed with 10% caustic soda solution and with water and was dried over barium oxide. After the benzene had been distilled off, the residue was twice distilled in vacuum, giving 13.1 g (30%, calculated on the **IV** of a colorless viscous reaction product, bp 210–213° C (3 mm); n_D^{20} 1.5789; d_4^{20} 1.1225. Found, %: C 60.88, 61.07; H 7.37, 7.47; S 21.98, 21.89; MR_D 87.15. Calculated for $C_{15}H_{22}N_2S_2$, %: C 61.16; H 7.53; S 21.78; MR_D 86.92. The picrate, recrystallized twice from ethanol, had mp 155.5–157° C. Found, %: N 14.93, 15.14. Calculated for $C_{15}H_{22}N_2S_2 \cdot 2C_6H_3N_3O_7$, %: N 14.89.

2, 5-Bis(dimethyl-5-chloromethyl-2-thienylmethyl)thiophene (VIII). This was obtained similarly to **VII** from 31 g (0.093 mole) of **V**, 22.3 g (0.28 mole) of chloromethylether, and 35 ml of glacial acetic acid. The chloromethylation product was twice distilled in vacuum to give 16.1 g (40%) of a yellowish viscous liquid with bp 240–242° C (1 mm); n_D^{20} 1.6145. Found, %: C 56.00, 55.86; H 5.26, 5.22; Cl 16.51, 16.51; S 22.31, 22.27. Calculated for $C_{20}H_{22}Cl_2S_3$, %: C 55.93; H 5.16; Cl 16.51; S 22.40.

2, 5-Bis(dimethyl-5-dimethylaminomethyl-2-thienylmethyl)thiophene (XVII). At a temperature of 15–18° C, dimethylamine was passed into a solution of crude **VIII** and 1200 ml of dry benzene prepared from 31 g (0.093 mole) of 2, 5-bis(dimethyl-2-thienylmethyl)-thiophene and 22.3 g (0.29 mole) of chloromethyl ether, until the increase in weight was 49 g (1.1 mole). After a treatment similar to that described in the preceding experiment, the reaction product was twice distilled in vacuum. This gave 22.6 g (55%) of **XVII** in the form of a viscous liquid [bp 230–235° C (2 mm)] which solidified on standing. After two recrystallizations from aqueous ethanol, mp 48.5–49° C. Found, %: C 64.57, 64.21; H 7.63, 7.55; S 21.56, 21.45. Calculated for $C_{24}H_{34}N_2S_3$, %: C 64.57; H 7.67; S 21.71. After two recrystallizations from methanol, the dimethiodide melted at 210–213° C (decomp; in a sealed capillary). Found, %: C 42.83, 42.60; H 5.53, 5.36. Calculated for $C_{26}H_{40}I_2N_2S_3$, %: C 42.74; H 5.52. **Picrate,** mp 139–140° C (from ethanol). Found, %: N 12.14, 12.17. Calculated for $C_{24}H_{34}N_2S_3 \cdot 2C_6H_3N_3O_7$, %: N 12.38.

1, 1-Bis(5-diethylaminomethyl-2-thienyl)ethane (XVIII). To a solution of 29.4 g (0.147 mole) of 1, 1-di(2-thienyl)ethane in 105 ml of glacial acetic acid was added 28 g (0.35 mole) of chloromethyl ether in an equal volume of glacial acetic acid. The mixture was stirred at room temperature for 5 hr and then at 35° C for 1.5 hr. After a treatment similar to that described in the first experiment, 44 g (0.60 mole) of diethylamine was added to the washed and dried benzene solution. The mixture was left for 16 hr and was then boiled under reflux for 1.5 hr. The precipitate of hydroxylamine hydrochloride was filtered off from the mixture cooled to room temperature. The filtrate was washed with 10% alkali solution and with water and was dried with calcined potassium carbonate. The benzene was distilled off and the residue in the flask was twice distilled in vacuum in a current of nitrogen to give 18 g of reaction product with bp 215–218° C (8 mm). Purification via the picrate furnished 3.6 g of a liquid with bp 179–181° C (0.55 mm); n_D^{20} 1.5419; d_4^{20} 1.0378. Found, %: C 65.87; H 8.99; S 17.45. Calculated for $C_{20}H_{32}N_2S_2$, %: C 65.86; H 8.82; S 17.59. The picrate after three recrystallizations from ethanol, melted at 145–146° C. Found, %: N 13.78, 13.65. Calculated for $C_{20}H_{32}N_2S_2 \cdot 2C_6H_3N_3O_7$, %: N 13.62.

1, 1-Bis(5-chloromethyl-2-thienyl)-1-(2-thienyl)ethane (IX). A solution of 14.49 g (0.18 mole) of chloromethyl ether in 20 ml of glacial acetic acid was added in drops to 14.5 g (0.05 mole of 1, 1, 1-tri(2-thienyl)ethane (VI) in 150 ml of glacial acetic acid. The mixture was kept at 35° C for 4 hr. After the usual working up, the reaction product was used for amination.

1, 1-Bis(5-dimethylaminomethyl-2-thienyl)-1-(2-thienyl)ethane (XVIII). Diethylamine (29.24 g; 0.4 mole) was added to 300 ml of the washed and dried benzene extract from the preceding experiment. After being boiled for 1 hr, the mixture was left for 15 hr. Then it was filtered and the benzene was evaporated off, and the residue was twice distilled in vacuum. This gave 1.3 g (5.8%, calculated on the VI taking part in the reaction) of **XVIII** in the form of a very viscous liquid with bp 152–157° C (5 mm); n_D^{20} 1.5772. Found, %: C 64.57, 64.38; H 7.81, 7.73; S 21.27, 21.26. Calculated for $C_{24}H_{34}N_2S_3$, %: C 64.52; H 7.67; S 21.57.

2, 8, 8, 14, 20, 20-Hexamethyl-2, 14-diaza-3, 2, 3, 2-α-cyclotetrathiene* (XV). A flask fitted with a mechanical stirrer, a thermometer, two dropping funnels, and a calcium chloride tube was charged with 1500 ml of absolute benzene. The contents of the flask were heated to 40° C, after which, at this temperature, with effective stirring, a solution of 19.25 g (0.063 mole) of **XIV** of 500 ml of absolute benzene and a solution of 9.2 g (0.032 mole) of **VII** in 500 ml of absolute benzene were added simultaneously over 10 hr. The mixture was left at 5–10° C for 16 hr. The colorless precipitate of the hydrochloride of **XIV** that deposited was filtered off. After this, 2200 ml of benzene was distilled off and the contents of the flask were kept in the refrigera-

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*For the nomenclature of compound **XV**, see [10].

tor at 5° C for 10 hr. The precipitate of the hydrochloride of **XIV** was again filtered off, and the remaining benzene was distilled off from the filtrate. The reaction product—a thick viscous liquid—was extracted four times with 450 ml of dry ether. The extract was concentrated to a volume of 90–100 ml and was left in the refrigerator for three days. The crystals that deposited were filtered off, forming 1.15 g of **XV** with mp 164–167° C. After purification with activated carbon and recrystallization from ether, mp 168.5–170° C. Found, %: C 63.80, 63.93; H 6.61, 6.65; S 23.80, 24.04; mol. wt. 496.6. Calculated for $C_{28}H_{34}N_2S_4$, %: C 63.83; H 6.50; S 24.35; mol. wt. 526.8. After two recrystallizations from a mixture of methanol and acetone, the picrate of **XV** melted at 155.5–157° C (decomp.). Found, %: N 11.91, 11.03. Calculated for $C_{28}H_{34}N_2S_4 \cdot 2C_6H_3N_3O_7$, %: N 11.2.

1, 11-Di(acetylamino)-6, 6-dimethylundecane (XIX). A mixture of 8.2 g (0.03 mole) of **XII** and 37 g (0.37 mole) of acetic anhydride was left to stand for several hours. The acetic acid and the excess of acetic anhydride were distilled off in vacuum. The residue in the flask consisted of a colorless substance (11.75 g), mp 146.5–147° C (from ethanol).

A solution of 10.25 g (0.029 mole) of 2, 2-bis(5-acetylaminomethyl-2-thienyl)propane in 500 ml of methanol was boiled with 80 g of Raney nickel with stirring for 8 hr (until the test for sulfur was negative). The nickel was filtered off and washed with hot methanol. After the methanol had been distilled off, the residue was poured into water, extracted with ether, and dried over barium oxide. The ether was evaporated off and the residue was distilled twice in vacuum, giving 3.3 g (40%) of a viscous liquid with bp 232–236° C (0.5 mm); n_D^{20} 1.4812. Found, %: C 68.69, 68.68; H 11.57, 11.65. Calculated for $C_{17}H_{34}N_2O_2$, %: C 68.41; H 11.48.

1, 11-Bis(acetylmethylamino)-6, 6-dimethylundecane (XX). A mixture of 9.8 g (0.033 mole) of **XIV** and 23 g (0.23 mole) of acetic anhydride yielded 11.9 g of 2, 2-bis(5-acetylaminomethyl-2-thienyl)propane. A solution of the latter in 800 ml of methanol was boiled with 84 g of Raney nickel, with stirring. After 6 hr, the test for sulfur was negative. Two distillations of the hydrogenolysis product in vacuum gave 3.3 g (33%) of a colorless viscous liquid with bp 202–204° C (0.15 mm); n_D^{20} 1.4808; d_4^{20} 0.954. Found, %: C 69.97, 69.83; H 11.74, 11.79. Calculated for $C_{19}H_{38}N_2O_2$, %: C 69.88; H 11.73.

REFERENCES

1. T. I. Santalova, P. A. Konstantinov, and Ya. L. Gol'dfarb, DAN, **131**, 1102, 1960.
2. Ya. L. Gol'dfarb and Ya. L. Danyushevskii, Izv. AN SSSR, OKhN, 1361, 1956.
3. J. W. Schick and D. J. Growley, J. Am. Chem. Soc., **73**, 1377, 1951.
4. W. Steinkopf, Die Chemie des Thiophens, 138, 1941.
5. B. M. Bogoslovskii and Z. S. Kazakova, Skeletal Catalysts, Their Properties and Applications in Organic Chemistry [in Russian], GNTI khim. lit., Moscow, p. 78, 1957.
6. K. Kindler, W. Peschke, and E. Brandt, Ber., **68**, 2241, 1935.
7. Ya. L. Gol'dfarb, E. A. Krasnyanskaya, and B. P. Fabrichnyi, Izv. AN SSSR, OKhN, 1825, 1962.
8. H. Adkins and H. R. Billika, J. Am. Chem. Soc., **70**, 695, 1948.
9. Ya. L. Gol'dfarb and M. B. Ibrazimova, DAN, **113**, 594, 1957.
10. L. Ya. Gol'dfarb, Z. S. Taits, and L. I. Belen'kii, ZhOKh, **29**, 3564, 1959.

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