hart.[8] Smith[9] has recently proposed an extension of Urquhart's treatment, and applied it to cellulose, nylon and wool. However, our absorption and desorption data do not give the linear extrapolation characteristic of the approximate method of Smith. The excellent data of Wiegerink[10] on the sorption of wool give a curve of similar shape to that obtained from our data when plotted according to Smith; and it is quite possible that the protein gels require a more complicated swelling function than the simple weight function used by Smith. Moreover, several observations have been made which seem to indicate that the structure of casein is fairly open and most of the groups should be freely available to water vapor without swelling. The first of these is that even though the large benzoyl group has been introduced to modify the amino group there is apparently little disruption of the remainder of the molecule, as shown by the strict linearity of the absorption *versus* amino-content plots of the earlier paper.[3] This situation does not prevail in the cellulose–cellulose acetate system, where opening of the structure by intermediate degrees of acetylation is clearly demonstrable.[11] Secondly the lack of hysteresis in the absorption of the amino group indicates that no new amino groups are made available by swelling.

Summary

Desorption isotherms have been obtained for a number of benzoylated casein samples with various amounts of free amino groups.

A definite hysteresis in the sorption phenomena of about one-half the absorption value at 6% R.H. and about one-fifth at 50% R.H. was observed.

The hysteresis was independent of the content of free amino groups in the samples, although the amino group is responsible for one-fourth the water absorption in casein.

The hysteresis appears to be of two types: a constant hysteresis independent of the humidity from which desorption was started, and a hysteresis proportional to the amount absorbed and due only to absorption above the upper break in the absorption curve. This appears to be the first demonstration of the two-fold nature of the hysteresis phenomena.

[8] Urquhart, *J. Textile Inst.*, **20**, 125T (1929).

[9] Smith, THIS JOURNAL, **69**, 646 (1947).

[10] Wiegerink, *Textile Research*, **10**, 357 (1940).

[11] Hoover and Mellon, *Textile Research J.*, **17**, 714 (1947).

PHILADELPHIA 18, PA. RECEIVED SEPTEMBER 27, 1947

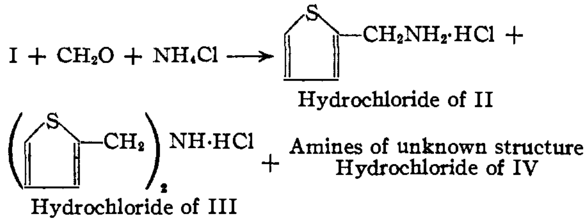
[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES, A DIVISION OF SOCONY-VACUUM OIL CO., INC., RESEARCH AND DEVELOPMENT DEPARTMENT]

Aminomethylation of Thiophene. I. The Reaction of Thiophene with Formaldehyde and Ammonium Salts

BY HOWARD D. HARTOUGH, SIGMUND J. LUKASIEWICZ AND EVERETT H. MURRAY, JR.[1]

Recently the authors reported that thiophene possessed alpha hydrogens of sufficient reactivity to undergo a type of Mannich reaction.[2] At the same time Holdren and Hixon reported that the Mannich reaction had been extended to 2-methylfuran.[3] They also reported that only resinous products were obtained from the use of ammonium chloride with formaldehyde. Bachman and Heisey reported that pyrroles, azoles and their benzalogs which contain the —NH— group in the heterocyclic ring will undergo the Mannich reaction.[4]

The reaction of thiophene, I, with ammonium chloride and formaldehyde has been investigated and found to give a variety of products. Besides the formation of complex amines of unknown structure, IV, 2-thenylamine (2-aminomethylthiophene), II, and di-(2-thenyl)-amine, III, have been isolated.



The yields of II and III leave much to be desired and many unsuccessful attempts were made to improve the yields over those previously reported.[2] Lower yields were obtained when the reaction quantities were increased five-fold. Yields obtained from various molar ratios of reactants are listed in Table I.

TABLE I

EFFECT OF MOLAR CONCENTRATION ON YIELDS OF AMINES II, III AND IV

Moles of reactants				Weight % of total product		
C_4H_4S	CH_2O (Aqueous)	NH_4Cl	Mole ratio	II	III	IV
5	10	5	1:2:1	17.6	5.3	77
2	2	2	1:1:1	15.6	3.1	80
4	2	2	2:1:1	17.7	20.3	62
5	4	4	1.25:1:1	22.2		77
1	1	3	1:1:3	36.8	15.2	48

Hexamethylenetetramine in the presence of concentrated hydrochloric acid was found to react

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[1] Present address: Owens-Illinois Glass Co., Glassboro, N. J.

[2] Hartough, *et al.*, THIS JOURNAL, **68**, 1389 (1946).

[3] Holdren and Hixon, *ibid.*, **68**, 1198 (1946).

[4] Bachman and Heisey, *ibid.*, **68**, 2496 (1946).

with thiophene in the same manner as ammonium chloride and formaldehyde.

In an effort to determine the molar ratios involved in the basic reaction, excess amounts of both ammonium chloride and thiophene were used with trioxymethylene and the unreacted portions recovered. Within reasonable limits the basic reaction was found to involve one mole of thiophene, one mole of ammonium chloride and two moles of formaldehyde. These observations are summarized in Table II.

TABLE II

DETERMINATION OF MOLAR RATIOS IN BASIC REACTION

Reactants used, moles			Reactants recov., moles			Mole ratio of basic reaction		
I	CH_2O	NH_4Cl	I	CH_2O	NH_4Cl	I	CH_2O	NH_4Cl
4	2	1	2.9	0	0	1.1	2	1
5	10	5	1.0	0	1.0	1	2.5	1
2	2	2	1.0	0	0.95	1	2	1
4	2	2	3.0	0	1.13	1	2	0.9

No successful degradation of polymeric amine IV types could be carried out by oxidation similar to the oxidation of polymers obtained from hydroxylamine, thiophene and formaldehyde.[5]

It is probable, however, that the polymeric linking takes place through the 2- and 5-positions. The structure of these polymeric materials will be discussed in later publications. The position of the $—CH_2NH_2$ group in the thenylamine was proven by oxidation of the 2-thenylamine to 2-thiophenecarboxylic acid.

No tri-(2-thenyl)-amine has been isolated. The failure to isolate this amine may be due to the fact that sub-resinous polymeric amines (IV) decompose to hard resinous masses at 180–210°. This is below the calculated boiling point of the tertiary amine under the reduced pressures used.

Blocking one of the reactive 2,5-positions in the thiophene nucleus leads to a somewhat less complicated reaction. 2-Methylthiophene reacts similarly to I in that the primary amine, 5-methyl-2-thenylamine (VI) as the hydrochloride, the secondary amine, di-(5-methyl-2-thenyl)-amine (VII) as the hydrochloride, are formed, along with a smaller amount of amines of unknown structure (X) as the hydrochloride. However, at 88° there were obtained appreciable amounts of the tertiary amine, tri-(5-methyl-2-thenyl)-amine (VIII) as the hydrochloride, and di-(5-methyl-2-thienyl)-methane (IX).

Not all the factors influencing this reaction are understood since it has been found that if the reaction is controlled at a lower temperature, 60–70°, less X is formed and VIII could not be isolated.

2-Chlorothiophene failed to react with aqueous formaldehyde and ammonium chloride but reacted with trioxymethylene and ammonium chloride to give di-(5-chloro-2-thenyl)-amine, XI. No other simple amine could be isolated and the reaction was complicated with amines of type IV.

A reaction with 2-*t*-butylthiophene, formaldehyde and ammonium chloride gave tri-(5-*t*-butyl-2-thenyl)-amine hydrochloride, XII. None of the secondary amine was isolated but a small amount of an unidentified product believed to be of type IV was obtained.

3-Methylthiophene was not investigated other than to determine that it reacted similarly to thiophene giving a series of amines including the sub-resinous type IV.

The alkylamine hydrochlorides have not been investigated to any great extent but in general they cause condensation of thiophene with aqueous formaldehyde. 2-Methylthiophene reacted with formaldehyde in the presence of dimethylamine hydrochloride to give a 45% yield of di-(5-methyl-2-thienyl)-methane, IX, along with higher polymers and a small amount of an unidentified amine containing sulfur. Similar reactions with thiophene gave high yields of polymers. Caesar and Sachanen reported that salts of weak bases and strong acids caused condensation of formaldehyde with thiophene thereby producing polymers.[6] No study has been made with polymeric formaldehyde and the alkylamine hydrochlorides and this may give the desired products rather than direct condensation of the formaldehyde and thiophene.

Superficially, at least, this reaction can be classified as a modified Mannich reaction. Although this reaction proceeds very readily with ammonium chloride to give the products listed above when alkylamine hydrochlorides are used it proceeds with reluctance and further investigation is needed to completely typify it.

Resins were obtained from the condensation of thiophene and formaldehyde with urea, ethylenediamine, and aniline (low yields) and with ammonium chloride. Morpholine hydrochloride caused no condensation with thiophene. A reaction occurred with thiourea but the oils obtained were so unstable and possessed such a stench that identification work was abandoned.

In general, when ammonium chloride is used, II, III, and IV are always obtained if the formaldehyde is used in amounts of two moles or less per mole of thiophene and ammonium chloride. Paraformaldehyde gave comparable results. For example, 11% II, 11% III, and 78% sub-resinous IV were obtained from a reaction involving 18 moles of thiophene, 18 moles of paraformaldehyde and 15 moles of ammonium chloride. II and III are not obtained when more than two moles of paraformaldehyde per mole of thiophene is used.

Ammonium chloride, ammonium bromide and, presumably, ammonium iodide undergo this reaction but other ammonium salts such as the acetate, phosphate, diacid phosphate, sulfate and acid sulfate do not react.

Experimental

Reaction of Thiophene, Aqueous Formaldehyde and Ammonium Chloride.—To a well-stirred mixture of 84

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[5] Hartough, THIS JOURNAL, 69, 1355 (1947).

[6] Caesar and Sachanen, Paper presented at 110th Meeting of the American Chemical Society, Chicago, September 9, 1946.

g. (1 mole) of thiophene and 162 g. (3 moles) of ammonium chloride was added 81 g. (1 mole) of 37% formaldehyde solution. After fifteen minutes heating at the reflux temperature, 72°, a yellow color appeared indicating the start of the reaction. The mixture was heated at reflux for one hour, cooled, the condenser inverted and the excess thiophene distilled off; 51 g. (0.63 mole) was recovered. The reaction mixture was then filtered to remove excess ammonium chloride, the filter washed with alcohol until colorless, the filtrate concentrated on the steam-bath to remove alcohol, cooled, made alkaline with 100 g. of 40% sodium hydroxide solution, and extracted three times with 50 ml. of benzene. The benzene was removed by distillation and the amines distilled *in vacuo;* 17.5 g. of 2-thenylamine, II, b. p. 82° at 17 mm.[7,8]; 7.0 g. di-(2-thenyl)-amine, III, b. p. 134–135° at 3 mm.; and 23 g. of sub-resinous amines, IV, were obtained. Refractionation of II and III through a 12-plate column to effect higher purity gave the following refractive indices; II, $n^{20}{}_D$ 1.5615; III, $n^{20}{}_D$ 1.6032. These products correspond to yields of 42% of II and 18.3% III based on the 0.37 mole of thiophene used in the reaction.

Anal. Calcd. for C_5H_7NS (II): N, 12.39. Found: N, 12.33. Calcd. for $C_{10}H_{11}NS_2$ (III): S, 30.62; N, 6.69. Found: S, 30.43; N, 6.65.

Analysis of typical samples of IV indicated that the nitrogen and sulfur ratios varied from 2:3 to 1:1.

II reacts rapidly with carbon dioxide in the air and a thin film on glass quickly forms a white solid, presumably the carbamate. II is soluble in water in all proportions but can be salted out conveniently with sodium chloride.

Oxidation of II with alkaline permanganate gave 2-thiophenecarboxylic acid, XIV, m. p. 129.5–130°. A mixed melting point with an authentic sample gave no depression.

The hydrochloride of II was prepared and crystallized from 20% hydrochloric acid solution by cooling in an ice-salt-bath; m. p. 188–189°.

Anal. Calcd. for C_5H_8ClNS: N, 9.30. Found: N, 9.30.

The hydrochloride of III was prepared and recrystallized from water; m. p. 252–253° with decomposition.

Anal. Calcd. for $C_{10}H_{12}ClNS_2$: S, 26.07; N, 5.66. Found: S, 25.59; N, 5.59.

The N-(2-thenyl)-N'-phenylthiourea, XV, was prepared by standard procedures from phenyl isothiocyanate and 2-thenylamine. After two recrystallizations from water and alcohol the product melted at 123.5–124°.[9]

Anal. Calcd. for $C_{12}H_{12}N_2S_2$: N, 11.28. Found: N, 11.36.

The di-(2-thenyl)-amine did not give a crystalline derivative with phenyl isothiocyanate.

The N-(2-thenyl)-benzamide, XVI, was prepared according to standard procedures, from II and benzoyl chloride; m. p. 121–122°.

Anal. Calcd. for $C_{12}H_{11}NOS$: N, 6.4. Found: N, 6.3.

The N-(2-thenyl)-stearamide, XVII, was prepared by refluxing 20 g. (0.177 mole) of 2-thenylamine and 50 g. (0.177 mole) of stearic acid in 200 ml. of xylene until 2.5 ml. (3.5 ml. calcd.) of water was collected in a water trap. After cooling, the white crystalline XVII was filtered off and recrystallized twice from benzene; 42 g. (67% yield), m. p. 92.5–93°.

Anal. Calcd. for $C_{23}H_{41}NOS$: N, 3.7. Found: N, 3.9.

Preparation of N-(2-Thenyl)-phthalimide, XVIII, and N,N'-Di-(2-thenyl)-phthalamide, XIX.—A mixture of 22 g. (0.2 mole) of 2-thenylamine and 14.8 g. (0.1 mole) of phthalic anhydride in 100 ml. of xylene was refluxed until 1.4 ml. (1.8 ml. calcd.) of water was collected in the water trap. Upon cooling 20 g. of XIX was filtered off, washed with cold benzene, and recrystallized twice from benzene, m. p. 169–169.5°. Removal of the xylene yielded 9 g. of XVIII, which after two recrystallizations from alcohol melted at 126–127°.

Anal. Calcd. for $C_{13}H_9NO_2S$ (XVIII): N, 5.76. Found: N, 5.65. Calcd. for $C_{18}H_{16}N_2O_2S_2$ (XIX): N, 7.81. Found: N, 7.86.

Preparation of N-(2-Thenyl)-urea, XX, and N,N'-Di-(2-thenyl)-urea, XXI.—A mixture of 20 g. (0.177 mole) of 2-thenylamine, 50 ml. of water, 17.6 g. of concentrated hydrochloric acid, and 12 g. (0.20 mole) of urea was heated at reflux for nine hours at the reflux temperature, 106°. The hot aqueous solution was decanted from the bottom organic layer (8 g., XXI), and 15 g. of XX was obtained by crystallization from the water solution. XX was purified by three treatments with decolorizing charcoal and recrystallization from hot water; m. p. 129.5–130.5°. XXI was purified by digesting once with water and three recrystallizations from hot alcohol; m. p. 164–165°.

Anal. Calcd. for $C_6H_8N_2OS$ (XX): N, 17.95; S, 20.51. Found: N, 17.45; S, 20.66. Calcd. for $C_{11}H_{12}N_2OS_2$ (XXI): N, 11.11; S, 25.39. Found: N, 11.01; S, 25.21.

The Reaction of Thiophene, Hexamethylenetetramine and Hydrochloric Acid.—To a well-stirred mixture of 168 g. (2 moles) of thiophene and 70 g. (0.5 mole) of hexamethylenetetramine was added 200 g. of hydrochloric acid (36%) over a period of forty minutes. After addition of the acid the mixture was maintained at a reflux temperature of 76–80° for one hour. The procedure from this point follows that previously described. Thirty-three grams of 2-thenylamine, II (identity established by mixed melting point of the N-(2-thenyl)-N'-phenylthiourea), 16 g. of di-(2-thenyl)-amine, III, and 100 g. of sub-resinous amine, IV, were obtained.

The Reaction of Thiophene, Formaldehyde and Ammonium Chloride.—To a mixture of 18 moles (1312 g.) of thiophene and 15 moles (803 g.) of ammonium chloride was added 18 moles (1460 g.) of 36% formaldehyde. The mixture was heated slowly over a two-hour period to 72° whereupon the reaction became vigorous and was controlled by means of an ice-bath. After twenty minutes the reaction was completed. The reaction mixture was cooled, 12 moles of sodium hydroxide as a 40% aqueous solution was added, the salt filtered off by suction, the oil layer decanted from the filtrate, the filter washed with thiophene (or benzene) and the filtrate extracted once with thiophene. The thiophene, I, was recovered by distillation and 123 g. of II, 97 g. of III, and 660 g. of IV were obtained.

Reaction of Thiophene, Urea and Hydrochloric Acid.—To a cooled mixture of 30 g. (0.5 mole) of urea, 42 g. (0.5 mole) of thiophene and 41 g. (0.5 mole) of formaldehyde (36%) was slowly added 50 g. of concentrated hydrochloric acid. A white solid material began to form immediately. The reaction mixture was heated to reflux for six hours, cooled, the resin washed with water, dilute sodium hydroxide, and then digested with hot water. The resin, 93 g., analyzed as follows: S, 14.2; N, 20.6.

Reaction of Thiophene, Formaldehyde and Ethylenediamine Dihydrochloride.—To 30 g. (0.5 mole) of ethylenediamine, cooled in an ice-bath, was added 100 g. of concentrated hydrochloric acid. To this dihydrochloride of ethylenediamine was added 84 g. (1 mole) of thiophene and 83 g. (1 mole) of formaldehyde (36%) and the mixture was refluxed for two hours at 75°. After cooling, the resinous material was washed with hot water several times, dried in an oven and analyzed (S, 19.0; N, 5.98).

Reaction of 2-Methylthiophene, Formaldehyde and Ammonium Chloride. Procedure A.—To a well-stirred mixture of 196 g. (2 moles) of 2-methylthiophene and 161 g. (3 moles) of ammonium chloride was added 162 g.

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(7) Blicke and Burckhalter, THIS JOURNAL, **64**, 478 (1942).

(8) Putokhin and Egorova, *J. Chem. Soc.* (*U.S.S.R.*), **10**, 1873 (1940); *C. A.*, **35**, 4377 (1941), gave b. p. of 88° at 26 mm., 77° at 16 mm.; $n^{15}{}_D$ 1.5678; $d^{15}{}_4$ 1.1370.

(9) v. Braun, Fussgänger and Kühn, *Ann.*, **445**, 218 (1925), prepared this compound from the reaction of 2-thenyl isothiocyanate with aniline, m. p. 123°.

(2 moles) of formaldehyde (36%). The mixture was warmed to 40° where the reaction started and the temperature rose to 87° without further heating. When the rate of reaction decreased sufficiently the mixture was heated at the reflux temperature (85°) an additional thirty minutes, cooled, 200 ml. of benzene added, and the reaction mixture neutralized with 40% sodium hydroxide solution. After three more extractions with 100 ml. of benzene, the benzene was removed by distillation and the products fractionated under reduced pressure to yield 21 g. of 5-methyl-2-thenylamine, VI, b. p. 68–69° at 4 mm., $n^{20}\mathrm{D}$ 1.5518; 21 g. of di-(5-methyl-2-thienyl)-methane, IX, b. p. 135–136° at 4 mm.; 39 g. of di-(5-methyl-2-thenyl)-amine, VII, b. p. 161–162° at 4 mm., $n^{20}\mathrm{D}$ 1.5832; 32 g. of tri-(5-methyl-2-thenyl)-amine, VIII, b. p. 207–214° at 3 mm., m. p. 81–81.5°; and 83 g. of residue X. Extraction of the residue with boiling alcohol yielded an additional 10 g. of VIII.

Anal. Calcd. for $C_{12}H_{15}NS_2$, VII: S, 27.00; N, 5.91. Found: S, 27.03; N, 5.98.

Anal. Calcd. for $C_{18}H_{21}NS_3$, VIII: S, 27.68; N, 4.01. Found: S, 27.73; N, 4.04.

Anal. Calcd. for $C_{11}H_{12}S_2$, IX: S, 30.7. Found: S, 30.4.

The N-(5-methyl-2-thenyl)-N′-phenylthiourea, XXII, was prepared in order to properly identify VI since it picked up carbon dioxide from the air too rapidly to obtain good analyses. XXII melted at 133–134°.

Anal. Calcd. for $C_{13}H_{14}N_2S_2$, XXII: N, 10.69. Found: N, 10.45.

While VII appeared to form a thiourea derivative with phenyl isothiocyanate, no crystalline product could be obtained.

Procedure B.—To a well-stirred mixture of 490 g. (5 moles) of 2-methylthiophene and 535 g. (5 moles) of ammonium chloride was added 425 g. (5 moles) of 36% formaldehyde. The mixture was warmed to 40°, the heat was discontinued and the temperature controlled at 60–70° by means of an ice-bath. Crystals began to form and within a few minutes a slurry developed which became very hard to stir. After thirty minutes the ice-bath was no longer necessary and the reaction mixture was stirred an additional one and one-half hours. After cooling to 10° the mixture was filtered, the precipitate washed with benzene and recrystallized from six liters of water to yield 379 g. (56% yield) of di-(5-methyl-2-thenyl)-amine hydrochloride, XXIII, m. p. 216–217° with decomposition.

Anal. Calcd. for $C_{12}H_{16}ClNS_2$ (XXIII): S, 23.40; N, 5.12. Found: S, 23.54; N, 5.36.

The filtrate contained the benzene layer which upon evaporation yielded 82 g. of IX. A water and benzene insoluble oil, 66 g. XA, was not identified. It contained 16.3% S and 4.1% N, which cannot be reconciled with any simple structure. Neutralization of the water layer with sodium hydroxide followed by extraction of the products gave 15 g. of VI, and 109 g. of a light red viscous oil, XB (analysis showed S, 22.98; N, 7.87). Only a trace of VIII could be extracted from XB with hot alcohol.

Reaction of 2-Chlorothiophene, Paraformaldehyde and Ammonium Chloride.—To 119 g. (1 mole) of 2-chlorothiophene was added 30 g. (1 mole) of paraformaldehyde, 54 g. (1 mole) of ammonium chloride and 10 ml. of acetic acid. The mixture was heated with stirring at 85–90° for one and one-half hours, cooled, 50 ml. of water added and 34 g. of di-(5-chloro-2-thenyl)-amine hydrochloride, XI, was filtered off. After digesting twice in 700 ml. of hot water the product melted at 240–242° with decomposition.

Anal. Calcd. for $C_{10}H_{10}Cl_3NS_2$: S, 20.35; N, 4.45. Found: S, 20.30; N, 4.72.

The filtrate was neutralized with 40% sodium hydroxide solution, extracted three times with 50 ml. of benzene, the extracts combined, and upon evaporation of the solvent 19 g. of a viscous red oil was obtained (*Anal.* Found: S, 17.9; N, 5.04). This product reacted with phenyl isothiocyanate but no crystalline products could be obtained.

Reaction of 2-*t*-Butylthiophene, Formaldehyde and Ammonium Chloride.—To a mixture of 276 g. (2 moles) of 2-*t*-butylthiophene[10] and 161.5 g. (3 moles) of ammonium chloride heated to 75° was added 84 g. (1 mole) of formaldehyde (36%) over a period of thirty minutes. The mixture was heated at 85–90° for one hour, cooled and the organic layer separated. Upon dilution of the organic layer with petroleum ether 14 g. of XII separated out and was recrystallized from alcohol; m. p. 204–206° with decomposition. Recovery of 2-*t*-butylthiophene by distillation yielded an additional 44 g. of tri-(5-*t*-butyl-2-thenyl)-amine hydrochloride, XII, as a residue.

Anal. Calcd. for $C_{27}H_{40}ClNS_3$: S, 19.20; N, 2.81. Found: S, 18.94; N, 2.83.

Neutralization of the water layer with 40% sodium hydroxide solution followed by extraction with benzene yielded 4.5 g. of light yellow oil (*Anal.* Found: S, 15.9; N, 8.5).

Acknowledgments.—The authors wish to thank Dr. D. E. Badertscher for his advice and interest in this problem and Mrs. Josephine Sindoni Piel and Miss Loretta G. Conley for technical assistance.

Summary

Thiophene, formaldehyde and ammonium salts have been found to undergo a type of Mannich reaction to yield 2-thenylamine (2-aminomethylthiophene), di-(2-thenyl)-amine, and polymeric amines of unknown structure.

With 2-methylthiophene, formaldehyde, and ammonium chloride, 5-methyl-2-thenylamine, di-(5-methyl-2-thenyl)-amine, tri-(5-methyl-2-thenyl)-amine, two complex amines of unknown structure, and di-(5-methyl-2-thienyl)-methane have been isolated.

2-Chlorothiophene and 2-*t*-butylthiophene reacted to give both simple and complex amines.

The alkylamine hydrochlorides such as dimethylamine hydrochloride do not react in a similar manner to ammonium chloride. While unidentified amines were formed the major reaction is a coupling action of formaldehyde with thiophene forming polymers containing no nitrogen.

In addition to sixteen new aminomethyl derivatives of thiophene, N-thenylstearamide, -benzamide, -phthalamide, -phthalimide, N-(2-thenyl)-urea, di-N,N′-(2-thenyl)-urea, N-(2-thenyl)-N′-phenylthiourea and N-(5-methyl -2′-thenyl)-N′-phenylthiourea have been prepared and characterized.

PAULSBORO, NEW JERSEY RECEIVED SEPTEMBER 9, 1947

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[10] Sample received from P. D. Caesar of these laboratories; data will be published later.