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RESEARCH AND DEVELOPMENT DIVISION]

Polymerization of Thiophene and Alkylthiophenes

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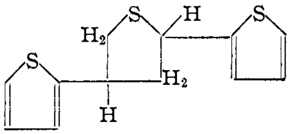
There are numerous references in the literature which state that thiophene can be polymerized by acidic materials.[1] However, in each case only amorphous, highly insoluble products were obtained. In contrast, it has now been found that 100% orthophosphoric acid, activated montmorillonite clays, such as Super-Filtrol, and synthetic silica-alumina catalysts, such as bead catalyst, will produce liquid polymers of thiophene and alkylthiophenes. These polymers are predominantly trimers with smaller amounts of pentamers and a trace of dimeric material. Materials which have been polymerized are thiophene, 2- and 3-methylthiophene and *t*-butylthiophene.

Discussion

A structure study has indicated that the trimeric material from thiophene is 2,4-di-(2-thienyl)-thiolane (I).



I

The infrared absorption spectrum of I indicated both the presence of a thiolane ring and a thiophene ring.[2] Molecular weight determinations on I were consistent with the trimer.

I yields a mixture of C_{12}-hydrocarbons, II, when destructively hydrogenated with cobalt-molybdate catalyst under pressure. II was shown to contain at least 20% of 5-methylundecane. This was proved by comparing the infrared absorption spectrum of this material with that of authentic 5-methylundecane.[2a] Further comparison with *n*-dodecane and multiple branched chain hydrocarbons ruled out the possibility of the remainder of II being *n*-dodecane or a highly branched chain C_{12}-hydrocarbon. The absence of olefinic linkages was also shown. Investigation of II in the mass spectrograph indicated the presence of about 20–25% of a $C_{12}H_{26}$ hydrocarbon (mass 170), about 50% of a $C_{12}H_{24}$ hydrocarbon (mass 168), and about 20–25% of $C_{12}H_{22}$ hydrocarbon (mass 166). Infrared spectrography gave no indications of the $>C{=}C<$ unit (which is easily detected if present) in these materials; further, no material was removed by concd. sulfuric acid. Therefore, it is concluded that the $C_{12}H_{24}$ and $C_{12}H_{22}$ contained in II are cyclic in nature rather than olefinic. Attempts to determine the nature of the cyclic material were unsuccessful but comparisons of the infrared spectrum of II with the spectra of a number of cyclobutane derivatives, while inconclusive, indicated the possibility of a cyclobutane ring.

The following mechanism is postulated to account for the formation of I in the presence of an acidic catalyst.

The first step involves the addition of a proton at the 2-position of thiophene. This leads to the three resonance forms, A, B and C, of which only A and B can react further. In A there is an electron-deficient carbon at the 3-position which can attack the electron-rich 2-position of thiophene with expulsion of a proton to yield IV (step 2a). Step 3a involves the addition of a proton to a sulfur-olefin system. This is analogous to the addition which takes place with vinyl ethers and should occur much more readily than the addition of a proton to a thiophene ring. Step 4a, which yields I, is similar to step 2a. Step 2b is the same as step 2a. In step 3b we have the possibility of adding a proton to either the 3- or 4-position of the thiolene ring system. If the proton were to add to the 3-position, steric hindrance would tend to prevent the thiophene from adding to the 4-position. However, the initial addition of a proton to the 4-position would lead to the unhindered attack of the thiophene at the 3-position. The final product in this case is again 2,4-di-(2-thienyl)-thiolane. Although it is believed that no 5-ethyldecane, the hydrogenated material which would occur from a reverse addition in step 3b, is present, its absence could not be determined with certainty.

The polymerization of thiophene has a distinct relation to the alkylation of thiophene since the polymerization reaction may be considered as an alkylation of thiophene with thiophene. The alkylation of thiophene with isobutylene and propylene in the presence of a variety of catalysts has recently been shown to give almost equimolar amounts of 2- and 3-isomers.[3,4,5] In this respect,

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(1) (a) V. Meyer, *Ber.*, **16**, 1468 (1883); (b) Klages and Liecke, *J. prakt. Chem.*, [2] **61**, 328 (1900); (c) Nellensteyn, *Chem. Weekblad*, **24**, 102 (1927); (d) Klatt, *Z. anorg. allgem. Chem.*, **232**, 393 (1937); (e) Bruce, Challenger, Gibson and Allenby, *J. Inst. Pet. Tech.*, **34**, 226 (1948); (f) Fredenhagen, *Z. physik. Chem.*, **A-164**, 176 (1933); (g) Kutz and Corson, THIS JOURNAL, **68**, 1477 (1946); (h) Hartough and Kosak, *ibid.*, **69**, 3093 (1947); (i) Caesar and Sachanen, *Ind. Eng. Chem.*, **40**, 922 (1948).

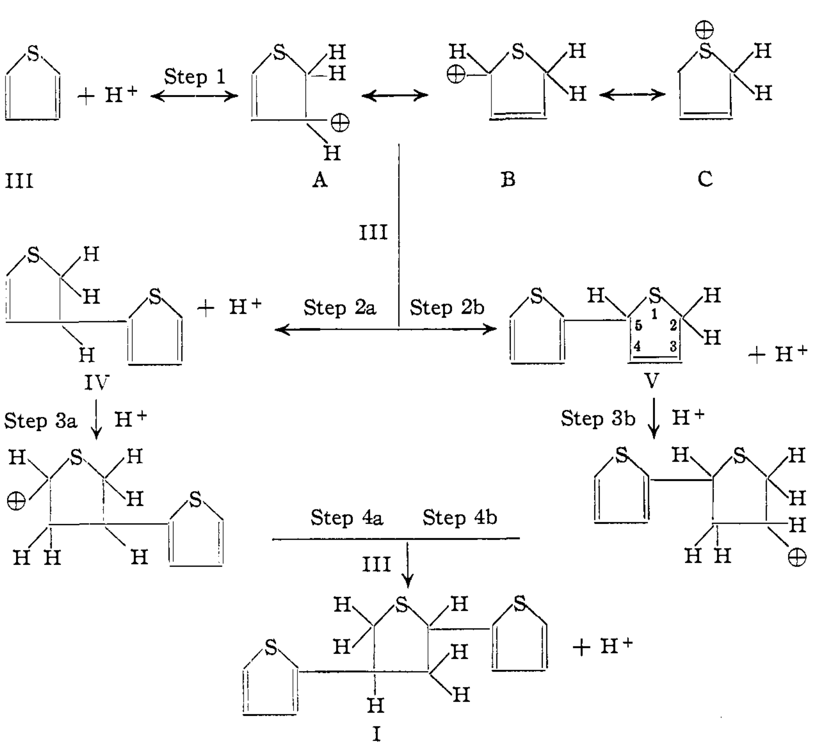
(2) The thiolane ring, in the absence of paraffins, is indicated by the strong absorption band characteristics of the CH_2 group at 3.4 to 3.5 μ and the thiophene ring by the strong absorption bands at 7.95 to 8.15 μ and at 14.0 to 14.5 μ. The spectrum of this compound will be discussed further in a subsequent publication from these laboratories. For further discussion see Hartough, "Thiophene and Related Compounds," Interscience Publishers, Inc., New York, Chapter III by F. P. Hochgesang, in press.

(2a) The authentic 5-methylundecane was supplied by Dr. R. L. Letsinger of Northwestern University.

(3) Kutz and Corson, THIS JOURNAL, **68**, 1477 (1946); **71**, 1503 (1949).

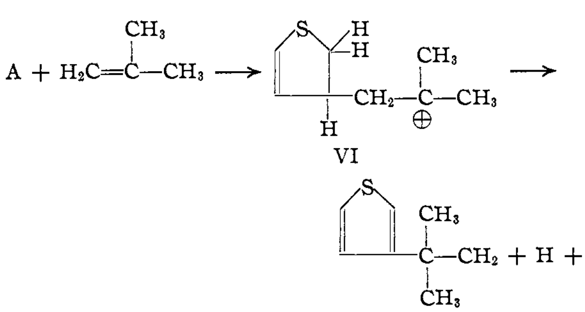
(4) Appleby, Sartor, Lee and Kapranos, *ibid.*, **70**, 1552 (1948).

(5) Caesar, *ibid.*, **70**, 3623 (1948).



alkylation is singular in yielding substantial amounts of 3-substitution. Nitration yields about 3% of 3-nitrothiophene,[6] sulfonation, a minor amount of 3-isomer,[6] and chlorination only about 0.3% of 3-isomer.[7] Acylation of thiophene, which may be carried out with catalysts[8] that will effect alkylation of thiophene, yields no detectable amount of 3-acetylthiophene when catalyzed by orthophosphoric acid.[9] Fractionation in a 60-plate fractionating column of a four-liter sample of crude acetylated thiophene obtained by acylation of thiophene with acetic anhydride in the presence of orthophosphoric acid (see ref. 8b) gave no detectable amount of 3-acetylthiophene.

These reactions involve the attack of the thiophene by a carbonium ion. Under alkylation conditions, it is possible to add a proton to the thiophene ring as demonstrated in step 1a above. It is suggested that the 3-isomers previously observed in the alkylation of thiophene[3-5] result from the addition of a proton to thiophene to form A which can then add to the isobutylene. Rearrangement of the first-formed carbonium ion, VI, and elimination of the proton are steps in this proposed mechanism. Although it is generally believed that 2-alkylthiophenes might arise from addition of the proton to the olefin followed by the usual attack of the thiophene nucleus, it is suggested that they may also arise from addition of the olefin to the resonance structure B, with subsequent rearrangement and expulsion of the proton as shown above.



The high yields of meta-isomer obtained from the alkylation of toluene and cumene[10] can be accounted for on the basis of a proton adding first to the benzene nucleus at the ortho or para positions.[10a] This can then add to the olefin to form a meta intermediate similar to VI which can then rearrange to form the meta-isomer.

Experimental[11]

Polymerization of Thiophene with Phosphoric Acid.—To 252 g. (3.0 moles) of thiophene were added 10 g. of phosphorus pentoxide and 25 g. of 85% orthophosphoric acid (approximately 0.35 mole of 100% phosphoric acid). The mixture was stirred and heated to reflux. During the course of six hours the temperature rose from 84 to 96°. A small amount of hydrogen sulfide was evolved throughout the reaction.

After cooling, 150 ml. of water was added to the reaction mixture and 60 g. of unreacted thiophene was steam distilled.[12] The viscous residue was diluted with 250 ml. of ether and filtered with suction to remove a small amount of high molecular weight, ether-insoluble material. The water layer was separated and extracted with ether which was added to the original filtrate. The ether-filtrate was washed twice with 10% sodium hydroxide and once with water. The ether layer was dried over Drierite and, finally, the ether was removed by distillation. About 150 g. of a light-orange oil was obtained. This represents a 60% conversion of thiophene to polymer. The bulk of the material, 116 g., distilled as a light-yellow oil at 167–170° at 1.0 mm., n^{20}_{D} 1.6450.[13]

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[6] Steinkopf and Hopner, *Ann.*, **501**, 174 (1933)

[7] Coonradt, Hartough and Johnson, THIS JOURNAL, **70**, 2564 (1948).

[8] (a) Hartough and Kosak, *ibid.*, **69**, 1012 (1947); (b) *ibid.*, **69**, 3093 (1947); (c) *ibid.*, **70**, 876 (1948); (d) Hartough, Kosak and Sardella, *ibid.*, **69**, 1014 (1947); (e) Hartough and Conley, *ibid.*, **69**, 3096 (1947).

[9] H. D. Hartough, unpublished work.

[10] Condon, THIS JOURNAL, **70**, 2265 (1948).

[10a] Since this paper has been submitted Brown, *et al.*, have presented a paper at the 116th Meeting, A. C. S., Atlantic City, Sept. 1949, postulating a similar type complex from the reaction of toluene, hydrogen chloride and aluminum chloride.

[11] The boiling points listed below are uncorrected.

[12] The steam distillation may be omitted if the recovery of starting material is not desired.

[13] A foreshot of 4 g., 127–167° at 1.0 mm., n^{20}_{D} 1.6246, may have been largely thiophene dimer.

This material analyzed as a thiophene trimer.

Anal. Calcd. for $(C_4H_4S)_3$: S, 38.1; mol. wt., 252. Found: S, 37.4; mol. wt., 247.

The residue, 20 g., analyzed as the thiophene pentamer.

Anal. Calcd. for $(C_4H_4S)_5$: S, 38.1; mol. wt., 420. Found: S, 35.4; mol. wt., 398.

Analyses of the residues of numerous experiments approximated that of the pentamer. The low sulfur content of the residue could be predicted since hydrogen sulfide was evolved during the reaction.

Polymerization of 2-Methylthiophene with Phosphoric Acid.—2-Methylthiophene was polymerized by the above procedure employing the same molar proportions. A 32% conversion to polymer was obtained (unreacted 2-methylthiophene was recovered). The trimeric material boils at 190–193° at 0.8 mm., $n^{20}\text{D}$ 1.6104.

Anal. Calcd. for $(C_5H_6S)_3$: S, 32.6; mol. wt., 294. Found: S, 31.4; mol. wt., 298.

Polymerization of 3-Methylthiophene with Phosphoric Acid.—3-Methylthiophene was polymerized by the above procedure employing the same molar proportions. A 51% conversion to polymer was obtained (unreacted 3-methylthiophene was recovered). The trimeric material boils at 174–176° at 0.3 mm., $n^{20}\text{D}$ 1.6170.

Anal. Calcd. for $(C_5H_6S)_3$: S, 32.6; mol wt., 294. Found: S, 31.6; mol. wt., 295.

Polymerization of Alkylthiophenes with Activated Clay.—Approximately 100 g. of *t*-butylthiophene[14] and 81 g. of Super Filtrol,[15] an activated montmorillonite clay, were mixed to make a thin paste. The mixture was heated to 75–80° for six days. At the end of this time the mixture was cooled to 30° and enough petroleum ether added to make a slurry. The solid clay was removed by filtration and the filtrate was distilled until a pot temperature of 240° was reached. About 55 g. of a clear, pale yellow, liquid was recovered as a residue. Upon standing the material solidified and was recrystallized from a water–alcohol mixture forming white crystals, m. p. 105°. The material analyzed as the trimer.

Anal. Calcd. for $(C_8H_{12}S)_3$: S, 22.9; mol. wt., 420. Found: S, 22.3; mol. wt., 395.

When the above reaction was carried out at 150–170° using a catalyst–reactant ratio of 1:2, a 69% yield of polymer could be obtained with a reaction time of fourteen hours.

A 93% yield of 2-methylthiophene polymer was obtained when the reaction was carried out at 80° for three days with a 1:1 catalyst–reactant ratio. 3-Methylthiophene yielded 81% polymer when the reaction was carried out as above for a period of five days. With thiophene, using a catalyst–reactant ratio of 0.8, a 30% yield was obtained with a reaction time of three days at 80°.

Synthetic silica–alumina compositions containing about 10% alumina also are effective and the yields are comparable.

Hydrogenation of Thiophene Trimer.—A mixture of 100 g. of distilled thiophene trimer obtained by the action of 100% orthophosphoric acid on thiophene (see above), 500 ml. of *n*-heptane and 75 g. of cobalt–molybdate catalyst on activated alumina[16] was placed in a shaker bomb and pressured with 1600 p. s. i. of hydrogen. Hydrogen absorption began at about 290°. The reaction temperature was maintained at 360 to 370°. After the pressure remained constant for two hours at this temperature heating was discontinued and the bomb allowed to cool. The pressure at room temperature was 900 p. s. i. A considerable portion of this pressure was due to hydrogen sulfide.

The catalyst was removed by filtration and the *n*-heptane distilled. A residue of 37 g. remained which was distilled *in vacuo*. A cut of 14 g., b. p. 85–88° at 10 mm., $n^{20}\text{D}$ 1.4376, was then dissolved in 30 ml. of *n*-heptane and treated with 25 ml. of concentrated sulfuric acid. The mixture was stirred vigorously for two hours. A slight coloration developed in the sulfuric acid layer. The sulfuric acid was separated and this acid treat was repeated twice more. The last time no color developed in the sulfuric acid layer. The sulfuric acid was separated from the hydrocarbons and the *n*-heptane distilled. A little potassium carbonate was added to remove the last traces of acid and the residue, 8 g., was distilled *in vacuo*, b. p. 71° at 6 mm., $n^{20}\text{D}$ 1.4336.

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Summary

Methods have been developed to successfully control the polymerization of thiophene and alkylthiophenes to obtain trimeric and pentameric derivatives. The structure of the thiophene trimer has been shown to be 2,4-di-(2-thienyl)-thiolane. The mechanisms of the polymerization of thiophene and the alkylation of thiophene are discussed and correlated.

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[14] Product was a mixture of 40% 3-*t*-butylthiophene and 60% 2-*t*-butylthiophene.

[15] Purchased from the Filtrol Corp.

[16] Obtained from Harshaw Chemical Company.