

was added. With styrene the thermal polymerization proceeded at a convenient rate, while methyl acrylate and methacrylate apparently contained enough adventitious catalyst to effect reaction. Vinyl acetate samples were polymerized by irradiating with a mercury vapor lamp. Samples and heating times were chosen to yield 100–300 mg. of polymer. Methyl methacrylate and acrylate polymers were worked up by precipitating three times from ethyl acetate with petroleum ether in a 50-ml. centrifuge tube. The polymers were then redissolved in approximately 5 cc. of ethyl acetate and transferred in portions to tared aluminum dishes 26 mm. in diameter and 3 mm. deep and the solvent evaporated under an infrared lamp. The centrifuge tubes were washed with additional benzene and the dishes dried under the lamp overnight (approx. 8 in. from a 250-watt bulb was found to yield a smooth bubble-free film). Blank experiments showed that this treatment was adequate to remove all solvent, and yields were determined by weighing the dishes. Relative polymer activities were then measured by placing the dishes covered by a mask with a hole approximately 20 mm. in diameter under the thin mica window of a Radiation Counter Laboratories Mark I Model 2 Geiger-Mueller counter attached to an Instrument Development Laboratories Scaling Circuit. For the styrene and vinyl acetate experiments, the polymer isolation procedure was modified in that the partially polymerized samples were transferred to a large side-arm test-tube and unreacted monomer distilled off *in vacuo* at room temperature. The polymer was redissolved (in chlorobenzene or toluene, respectively) and the solvent again distilled off. This procedure was repeated twice more and the residual polymer transferred to an aluminum dish for counting.

Actually, for the determination of the relative activity, R , theoretical activities of completely polymerized samples were calculated from a completely polymerized polystyrene sample, correcting for differences in mercaptan

concentration in the reaction mixtures and polymer densities. Thus the measured activity of the styrene sample was multiplied by 1.06/1.19 for comparison with methacrylate since, because polymethacrylate has a greater density, the measured β -radiation is coming from a thinner layer of the polymer surface. Counts of relative activities were always extended to several thousand impulses to avoid significant random variations and comparisons of any set of polymers with the standard were always carried out consecutively since background count and sensitivity of the instruments varied from day to day.

Acknowledgment.—The writer wishes to thank Dr. Herbert N. Campbell for aid in operating the electronic apparatus.

Summary

1. A convenient method for the synthesis of radioactive mercaptans from zinc sulfide containing S^{35} has been worked out.

2. The transfer constants of *n*-butyl mercaptan with styrene, methyl methacrylate, methyl acrylate and vinyl acetate have been measured using radioactive mercaptan, and the advantages of tracer methods in polymer chemistry are discussed.

3. The results are shown to indicate that ionic forms in the transition state, similar to those involved in radical addition reactions, may be important in determining reactivity in radical displacement reactions as well.

PASSAIC, NEW JERSEY

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The Chlorination of Thiophene. II. Substitution Products; Physical Properties of the Chlorothiophenes; the Mechanism of the Reaction

BY HARRY L. COONRADT, HOWARD D. HARTOUGH AND GEORGE C. JOHNSON

The preceding paper¹ in this series reported the isolation and identification of chlorine addition products formed by the chlorination of thiophene. This paper describes the chlorine substitution products, reports their physical properties, and presents a mechanism for the reaction.

The substitution products formed by the chlorination of thiophene have been reported to be 2-chloro-,^{2,3} 2,5-dichloro-,^{2,3} 2,3,5-trichloro-,² and 2,3,4,5-tetrachlorothiophene.² In contrast with these results we have isolated and identified eight chlorine substitution products. The ninth and remaining possible substitution product, 3-chlorothiophene, was identified by infrared absorption spectrograms as present in small amounts.

The pure substitution products were separated by fractionation after the chlorine addition products had been removed. This prior removal or destruction of addition products generally was neces-

sary because they decomposed into chlorothiophenes and hydrogen chloride during the course of the distillation and interfered with the fractionation. The method previously used^{2,3,4} to destroy the addition products consisted of prolonged heating of the chlorination products with alcoholic potassium hydroxide. The preceding paper¹ described how addition products could be isolated from the reaction mixture. This had a pronounced effect on the ratio of the different substitution products.

The chlorine addition products were destroyed when chlorinated thiophene, like brominated thiophene,⁵ was heated with solid sodium hydroxide or with potassium hydroxide. Calcium oxide was not effective. Other satisfactory procedures were prolonged pyrolysis or steam distillation of the reaction mixture from aqueous alkali or from a suspension of zinc or iron powder in water. Different

(1) Coonradt and Hartough, *THIS JOURNAL*, **70**, 1158 (1948).

(2) Steinkopf and Köhler, *Ann.*, **532**, 250 (1937).

(3) Weitz, *Ber.*, **17**, 792 (1884).

(4) Steinkopf, "Die Chemie des Thiophens," Theodor Steinkopff, Dresden, 1941, p. 35.

(5) Blicke and Burckhalter, *THIS JOURNAL*, **64**, 477 (1942).

yields and ratios of substitution products resulted when different methods of converting the addition products were used.

The monochlorosubstitution product produced by the chlorination of thiophene (I) at 50° was 99.7% 2-chlorothiophene (II) and 0.3% 3-chlorothiophene (III). The latter was indicated to be present in the higher boiling monochlorothiophene fractions by infrared absorption at wave lengths characteristic of *beta*-substituted thiophenes. Chlorination of II gave a dichlorothiophene fraction of 99% 2,5-dichlorothiophene (IV) and 1% 2,3-dichlorothiophene (V). The far faster rate of substitution of α -hydrogen as contrasted with β -hydrogen was indicated by these two reactions. Substitution reactions occur less readily after both α -hydrogens have been replaced.

While the only dichlorothiophene previously reported from chlorinated thiophene was 2,5-dichlorothiophene (IV), fractionation of the reaction mixture revealed the other three possible dichlorothiophenes: 2,3-dichlorothiophene (V), 2,4-dichlorothiophene (VI), and 3,4-dichlorothiophene (VII). Direct and random substitution of thiophene cannot be the source of all of these isomers in view of the strong directive influence of the sulfur atom shown above. Further, if direct substitution were the only source of VII the yield would be limited by the intermediate III; but a much higher proportion of VII than of III was obtained.

The origin of these isomers was clarified by the study of the dehydrohalogenation of the chlorine addition products.¹ Pyrolysis of the α -isomer of 2,3,4,5-tetrachlorothiophene (XI) gave a dichlorothiophene fraction composed of about 50% V, 50% VI with a trace of IV and no VII. The same compound with ethanolic potassium hydroxide formed a dichlorothiophene fraction composed of approximately 54% VII, 44% VI, 2% IV and no V. Since XI consisted of at least two geometrical isomers, the composition of XI would also influence the ratio of isomeric dichlorothiophenes. *The principal source of V, VI and VII is, therefore, the dehydrohalogenation of tetrachlorothiophene.*

The structure of 2,5-dichlorothiophene (IV) has been established.⁴ The general method of preparation of 2,3-dichlorothiophene reported² in the literature was used to prepare the compound for comparison with V. The structure of VII was established when further chlorination yielded a trichlorothiophene fraction consisting of 2,3,4-trichlorothiophene (VIII), rather than 2,3,5-trichlorothiophene (IX) which would be the expected isomer from the other dichlorothiophenes. The properties of VII also were in satisfactory agreement with those previously reported for 3,4-dichlorothiophene prepared by a different procedure.² VI, by elimination, must be 2,4-dichlorothiophene.

The proof of structure of the two isomeric trichlorothiophenes, VIII and IX, was necessary

since their properties differed from those previously reported. Steinkopf and Köhler stated² that two substances which they believed to be 2,3,4-trichlorothiophene and 2,3,5-trichlorothiophene possessed amazingly similar physical properties, formed numerous derivatives with similar melting points, and gave no depression of the melting point when corresponding derivatives of the two compounds were mixed. Our results indicate that the two materials they studied were probably samples of the same isomer, VIII, of slightly different degree of purity. The structure of the two isomers obtained in the present study was indicated when chlorination of IV yielded a trichlorothiophene fraction composed solely of IX, thus indicating IX was 2,3,5-trichlorothiophene and VIII, by elimination, was 2,3,4-trichlorothiophene. Further evidence was that VIII reacted and IX did not react with mercuric chloride. This reaction is characteristic of thiophene compounds with an α -hydrogen atom.^{4,6}

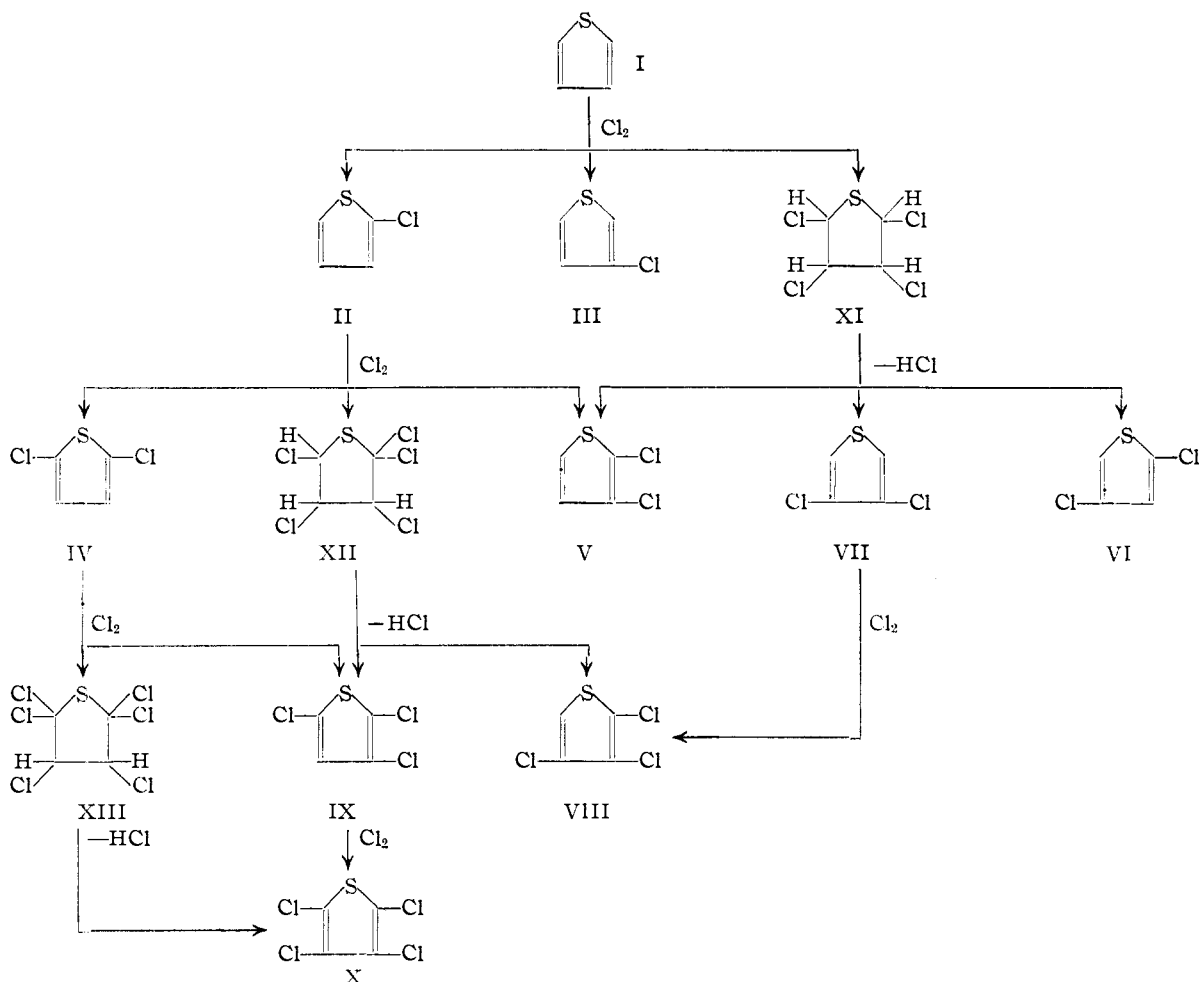
Since the principal dichlorothiophene formed in the reaction of thiophene with chlorine was 2,5-dichlorothiophene, it might be expected that the principal trichlorothiophene formed would be 2,3,5-trichlorothiophene. However, when the chlorination was conducted near room temperature and the product treated with solid alkali, the trichlorothiophene fraction was 98% 2,3,4-trichlorothiophene and 2% IX. The principal source of VIII cannot be a substitution reaction because the direct formation of its intermediate, VII, under these conditions is indicated to be small. In view of the dehydrohalogenation of 2,2,3,4,5-pentachlorothiophene (XII) to 65% VIII and 35% IX with ethanolic potassium hydroxide and the effect of the method of dehydrohalogenation upon the ratio of isomers,¹ *the mechanism accounting for the formation of most of VIII is the conversion of the reaction intermediate II to XII and subsequent alkaline dehydrohalogenation of the latter.*

When chlorination at or near reflux temperatures and subsequent or concomitant pyrolysis was employed, however, the principal isomer obtained was IX, not VIII. This is in accord with the observation that pyrolysis of XII gave 92% IX and only 8% VIII. It was also found that the reaction intermediate IV could be converted to IX, preferably at elevated temperatures. *The source of IX in the chlorination of thiophene is thus both the dehydrohalogenation of XII and the direct substitution of IV.* Both of these reactions are favored by elevated temperatures.

The statement has been made^{2,4} that trichlorothiophene was the most difficult of the substitution products to prepare since it was readily chlorinated further to 2,3,4,5-tetrachlorothiophene (X). However, it was found that IX was substituted by chlorine only with difficulty. For example, after a ten mole excess of chlorine was passed through

(6) Volhard, *Ann.*, **267**, 172 (1892).

TABLE I
ESTABLISHED CHLORINATION REACTIONS OF THIOPHENE



IX at 180°, 42% of IX was recovered unchanged. Furthermore, the other trichlorothiophene, VIII, arises mainly in the alkaline dehydrohalogenation reaction and forms only in minor amounts in the chlorination reaction itself.

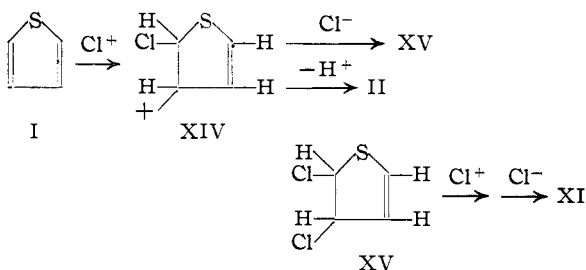
The yield and ratio of tetrachlorothiophene (X) and 2,2,3,4,5,5-hexachlorothiophene (XIII) is dependent upon the extent of chlorination and dehydrohalogenation. Extensive chlorination with concomitant pyrolysis gave a product containing 80% X and 14% IX. Extensive chlorination at lower temperatures, however, yielded primarily XIII. In the latter case substitution of IV was negligible and addition of chlorine to form XIII occurred. Dehydrohalogenation of XIII by pyrolysis or alkali yielded X.

A compound isolated in small yields from the still residues of products obtained by the action of excess chlorine on thiophene at elevated temperatures was identified as hexachlorodithienyl.⁷

(7) Eberhard, *Ber.*, **28**, 2385, 3302 (1895), reported the action of sulfuryl chloride on 2,2'-dithienyl gave 3,4,5,3',4',5'-hexachloro-2,2'-dithienyl, orange crystals, m. p. 189.5-190° (cor.).

Table I outlines the established parts of the course of the reaction of chlorine with thiophene in the absence of a catalyst.

Mechanisms have been postulated for the chlorination, alkaline dehydrohalogenation and pyrolysis. I adds first a positive chlorine ion to form a positive chlorothiolenium ion (XIV) which either loses a positive hydrogen ion to give II or adds a negative chlorine ion to give a dichlorothiolenium ion (XV) which then adds chlorine to form XI.



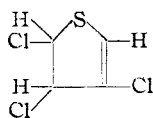
Similar ionic reactions account for the conversion of II to both IV and XII, and the conversion of

TABLE II
 THE PHYSICAL PROPERTIES OF EIGHT CHLOROTHIOPHENES

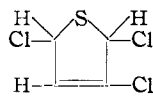
Cpd.	Chloro- thio- phenes	B. p., °C.	F. p., °C.	n_{20}^D	n_{20}^o	n_{20}^g	n_{20}^D	d_{20}^4	d_{20}^4	Vis- cos- ity, c. p. 30°	Surf. tens., dynes/ cm., 30°	R_{20}^D	R_{20}^D	Mol. vol., ml. at 20°	Mol. vol., ml. at 30°
II	2- ^a	128.32	-71.91	1.5487	1.5530	1.5726	1.5430	1.2863	1.2737	0.803	34	29.32	29.34	92.19	93.10
IV	2,5- ^a	162.08	-40.46 ^b	1.5626	1.5672	1.5880	1.5572	1.4422	1.4288	0.997	35.5	34.44	34.49	106.11	107.14
VI	2,4- ^c	167.58	-37.2	1.5660	1.4553	1.091	..	34.30	...	105.15
V	2,3- ^a	172.70	-37.3	1.5651	1.4605	34.14	...	104.78
VII	3,4- ^a	182.01	-0.54	1.5762	1.4867	1.465	..	34.07	...	102.93
IX	2,3,5- ^d	198.66	-16.06	1.5791	1.5837	1.6046	1.5741	1.5856	1.5724	1.464	38	39.30	39.35	118.24	119.23
VIII	2,3,4- ^a	209.60	-2.76	1.5861	1.6125	2.181	..	39.02	...	116.27
X	2,3,4,5- ^{a,e}	233.39	+29.09 ^f	1.5915	1.7036	3.318	40	...	44.05	130.27

^a Infrared analysis did not disclose the presence of any impurities in the specimen. ^b A second form freezes at -50.92°. ^c The properties are for a material containing 96 mole % 2,4-dichlorothiophene, 3% 2,5-dichlorothiophene and 1% 3,4-dichlorothiophene. ^d Infrared analysis showed a trace of 3,4-dichlorothiophene as impurity. *Anal.* Calcd. for C₄HCl₃S: Cl, 56.8; S, 17.0. Found: Cl, 57.0; S, 17.3. ^e *Anal.* Calcd. for C₄Cl₄S: Cl, 63.9; S, 14.5. Found: Cl, 64.2; S, 14.8. ^f Refs. 2 and 3 list m. p. 36°; ref. 14 lists 38°. These products were obtained by chlorination of 2,5-dibromothiophene. Repetition of this method using a large excess of chlorine gave a product, m. p. 51-52.5°, containing Br, 39.7%, Cl, 30.6%. The X froze sharply with a time-temperature cooling curve typical of highly purified materials.

IV to both IX and XIII. Ethanolic potassium hydroxide acts on the α -isomer of XI to effect the initial preferential elimination of the more negative α -chlorine ion and a β -hydrogen ion. This leads to the intermediate 3,4,5-trichloro-2-thiolene (XVI). XVI then loses α -chlorine and β -



XVI



XVII

hydrogen to give VII, or now since the chlorine on carbon atom four is allylic and more easily expelled, XVI also dehydrohalogenates in a different manner to give the other principal product VI. The mechanism of the pyrolytic dehydrohalogenation of the α -isomer of XI must differ from that of the ethanolic potassium hydroxide dehydrohalogenation in view of the greatly different products. The formation of the two isomers is consistent with the formation of 2,3,5-trichloro-3-thiolene (XVII) as an intermediate which dehydrohalogenates to V and VI.

Physical Properties.—The physical property data which have been obtained are collected in Table II. The methods used for the measurements of the physical properties have been described previously.⁸ Some of the densities were determined with a 2-ml. pycnometer of the type described by Lipkin and co-workers⁹ rather than by the suspended sinker method used before. The boiling points determined by measurements made relative to the freezing point of water and to the freezing point of tin were extensively checked by direct intercomparisons.

The chlorothiophenes dissolved at 25° in equal volume mixtures with *n*-heptane, diisobutene, cyclohexane, decalin, tetralin, benzene, thiophene, acetic acid, nitromethane, carbon tetrachloride, carbon disulfide, acetone, ethyl acetate, dioxane

and *n*-propanol. The chlorothiophenes were not miscible with water, ethylene glycol or propylene glycol at 25°. The critical solubility temperatures of the chlorothiophenes lay close to 25° and varied from compound to compound in glycerol- α -mono-chlorohydrin, diethylene glycol, triethylene glycol, methanol and ethanol.

The chlorothiophenes changed from colorless to light yellow when stored for several months in partially filled bottles in diffuse light at room temperature. On boiling in air for a few hours a similar color change was noted. In both cases the change in refractive index did not exceed 0.0001.

Calculations from Table II show that substitution of a chlorine atom for a hydrogen atom at an α -position increases the molecular volume more than substitution at a β -position. This observation, together with arithmetic estimations, indicated that the molecular volume of 3-chlorothiophene at 20° is 91.73 ml. and d_{20}^4 1.292. Interpolations of the present data indicate that the previously reported values² are substantially correct for the b.p., 136-137°, and for the refractive index, n_{20}^D 1.5543 (calcd. from 22°).

It is believed that the values determined in this study supersede previously published determinations.^{2,3,10-14} Most of the earlier preparations were made with very small quantities of materials with attendant difficulty.

Experimental

Chlorinations.—The conditions and results of nine chlorinations are given in Table III. Identification of products was made by the boiling points and by infrared absorption spectra.

Specimens for Physical Property Measurements.—The 2-chlorothiophene and 2,5-dichlorothiophene were first redistilled in a 10-theoretical plate column and then in a 90-95 theoretical plate column at a reflux ratio above 120:1. The 2,3-dichlorothiophene was made by chlorin-

(10) Rosenberg, *Ber.*, **19**, 630 (1886).(11) Steinkopf and Otto, *Ann.*, **424**, 61 (1921).(12) Auwers and Kohlhaas, *J. prakt. Chem.*, [2] **108**, 321 (1924).(13) Bonino and Manzoni-Ansidei, *Z. physik. Chem.*, **B25**, 327 (1934).(14) Perkin and Haddock, *J. Chem. Soc.*, 541 (1938).(8) Johnson, *This Journal*, **69**, 150 (1947).(9) Lipkin, Davison, Harvey and Kurtz, *Ind. Eng. Chem., Anal. Ed.*, **16**, 56 (1944).

TABLE III
 CHLORINATION OF THIOPHENE AND CHLOROTHIOPHENES

Reactant	Chlorination		Time, hr.	Dehydrohalogenation		Time, hr.	Composition of product, g.
	Moles Cl ₂ : moles reactant	Temp., °C.		Method	Temp., °C.		
I	25:25	50	3	KOH, NaOH	80-100	36	II, 1088 ^a ; IV, 519; V, 63; VI, 64; VII, 113; trichlorothiophene, ^b 123
I	3.2:3.2	25-35	4	10% Na ₂ CO ₃ ^c	100	..	I, 52; II, 181; IV, 64; residue, 19
I	3.2:3.2	25-35	4	Zn ^d	100	..	I, 62; II, 182; IV, 66; residue, 10
II ^e	6.8:6.8	50	1.5	KOH, NaOH	125	22	II, 201; IV, 507; V, 5; VIII, 116; IX, 65
I	140:35	45-190 ^f	14.5	Pyrolysis	190	2.5	IV, 1227; other dichlorothiophenes, 316; VIII, 496; IX, 2283; X, 1503; residue, 88
I	75:10	40-205 ^f	5.5	10% Na ₂ CO ₃ ^h	120	3	IX, 275; b. p. 95-118° (26 mm.), 11; X, 1548; b. p. 125-135° (26 mm.), 79; residue, ^f 32
IV ^e	1:1	150	2	KOH, NaOH	125	24	IV, 55; VIII, 0; IX, 8; X, 43
VII	0.1:0.15	90-100	3	KOH, NaOH	125	24	VII, 64%; VIII, 27%; X, 9%
IX	5.3:0.53	180	2	Pyrolysis	180	2	IX, 42; X, 47; residue, 8

^a Contained 99.7% II, 0.3% III concentrated in higher boiling monochlorothiophene fractions in 90-95 theoretical plate distillation. ^b VIII, 98%; IX, 2%. ^c 28 g. of solid α -XI first separated by cooling in Dry Ice-acetone bath and was filtered off. ^d 0.4 g. lead sulfide was formed in a lead acetate trap. ^e Purified by fractionation in a 90-95 theoretical plate column. ^f Residue washed with petroleum ether, recrystallized several times from chloroform, to give yellow-white hexachlorodithienyl, m. p. 188.5-90°. *Anal.* Calcd. for C₈Cl₆S₂: Cl, 57.0; S, 17.2; mol. wt., 372.9. Found: Cl, 56.9; S, 17.3; mol. wt. 350 (ebullioscopic method). ^g Mixture kept below reflux temperature until about one-third of chlorine added, then kept at reflux temperature. ^h Pyrolysis occurs at chlorination temperature; 300 ml. of sodium carbonate was used.

ating 2-thiophenecarboxylic acid to 4,5-dichloro-2-thiophenecarboxylic acid and then decarboxylating the latter by the method of Steinkopf and Köhler.² The crude product, containing ether, acetic acid and 2,3-dichlorothiophene was distilled in a 28-theoretical plate column. The 2,3-dichlorothiophene fraction was shaken with sodium hydroxide solution to remove possible traces of acetic acid. The 2,4-dichlorothiophene and 3,4-dichlorothiophene were prepared from *alpha*-2,3,4,5-tetrachlorothiophene by dehydrohalogenation with ethanolic potassium hydroxide. After a preliminary fractionation in a 28-theoretical plate column at a 30-35:1 reflux ratio, each was redistilled in the same column. The 2,3,4-trichlorothiophene was redistilled in a 28-theoretical plate column. The 2,3,5-trichlorothiophene and 2,3,4,5-tetrachlorothiophene were each redistilled in a 25-theoretical plate column.

Acknowledgment.—The authors are grateful to Dr. D. E. Badertscher and Dr. C. C. Price for their advice and interest in this problem, to Mr. J. G. Ehlers for infrared absorption spectra analyses, and to Miss Emily Burns for assistance in the laboratory work.

Summary

The substitution products formed by the reaction of chlorine with thiophene were investigated. Eight of the nine possible isomers were isolated. The remaining isomer, 3-chlorothiophene, was identified by infrared absorption spectrograms as present in small amounts.

Pronounced orientation during substitution in

the thiophene nucleus was indicated by a monochlorothiophene fraction consisting of 99.7% 2-chlorothiophene and 0.3% 3-chlorothiophene. Similarly, chlorination of 2-chlorothiophene yielded a dichlorothiophene fraction composed of 99% 2,5-dichlorothiophene, 1% 2,3-dichlorothiophene and no 2,4-dichlorothiophene.

2,3-, 2,4- and 3,4-dichlorothiophenes were formed largely by the dehydrohalogenation of 2,3,4,5-tetrachlorothiophene and not by substitution. 2,5-Dichlorothiophene was formed by substitution.

2,3,4-Trichlorothiophene was prepared by low temperature chlorination and was formed largely after the chlorination by the action of alkali on 2,2,3,4,5-pentachlorothiophene. 2,3,5-Trichlorothiophene was prepared by high temperature chlorination and was formed both by the substitution of 2,5-dichlorothiophene and by the pyrolysis of pentachlorothiophene.

Tetrachlorothiophene was formed both by substitution of 2,3,5-trichlorothiophene and by pyrolytic or alkaline dehydrohalogenation of 2,2,3,4,5,5-hexachlorothiophene.

Physical properties were determined on eight chlorothiophenes.

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