to 1000 p.s.i. was maintained. Shaking of the autoclave was commenced and the reaction mixture was heated to 100–115° for 5 hours. The crude reaction product was washed with excess 5% NaOH solution, extracted with isopropyl ether, water-washed and dried over anhydrous magnesium sulfate. The solvent was removed and the product fractionated *in vacuo*. Yields and physical constants are recorded in the table.

Hydrolysis of O,O-Di-(*n*-propyl)-S-(2-octyl) Thionophosphate (V).—A mixture of 126 g. (0.38 mole) of triester, 240 ml. of water and 86.5 g. (2.16 moles) of sodium hydroxide was heated to reflux with stirring for 20 hours. The mixture was then added to 500 ml. of water and the organic layer was extracted with ether. The extract was washed with water and dried over anhydrous $MgSO_4$. The ether was removed and the residue fractionated *in vacuo* yielding 16.2 g. (29%) of 2-octyl mercaptan, b. p. 82° (24 mm.); $n^{20}\text{D}$ 1.4497. This material was identified through its 2,4-dinitrophenylthio ether, m. p. 47.5°, prepared by the method of Bost, Turner and Norton.[8]

Anal. Calcd. for $C_{14}H_{20}N_2O_4S$: S, 10.26. Found: S, 10.16.

Hydrolysis of O,O-Di-(*n*-propyl)-S-(α-phenethyl) Thionophosphate (XVI).—A 29% yield of α-phenethyl mercaptan, b. p. 80–81.5° (16 mm.), $n^{20}\text{D}$ 1.5580, was obtained on hydrolysis of this triester by the procedure described above. The 2,4-dinitrophenylthio ether was prepared for characterization purposes, m. p. 110.5–111.5°.[9]

Anal. Calcd. for $C_{14}H_{12}N_2O_4S$: S, 10.53. Found: S, 10.65.

Alkoxide Cleavage of O,O-Diethyl-S-(2-octyl) Thionophosphate (I).—Sodium ethoxide was prepared by dissolving 23 g. (1 mole) of sodium in 300 ml. of absolute ethanol. The resulting solution was heated to reflux and 149 g. (0.5 mole) of triester was added dropwise over a period of one-half hour. After the addition was complete the solution was refluxed for six hours. The cooled solution was then blown with carbon dioxide to precipitate unreacted caustic as sodium carbonate. The latter was removed by filtration and the filtrate was diluted with 500 ml. of water. The organic layer was extracted with ether and the extract dried over anhydrous $MgSO_4$. The ether was removed and the residue fractionated *in vacuo*, yielding 54 g. (62%) of 2-octyl ethyl sulfide, b. p. 92.7–94° (10 mm.), $n^{20}\text{D}$ 1.4563.

Anal. Calcd. for $C_{10}H_{22}S$: S, 18.4. Found: S, 18.47.

The extracted aqueous solution obtained above was evaporated to dryness on a steam-bath. The salt obtained was dried by refluxing in benzene until no further water was trapped. The benzene was then removed under vacuum. The crystalline product was then dissolved in 150 ml. of cold ethyl acetate and the solution filtered to remove a small amount of Na_2CO_3. This solution was then diluted with 1500 ml. of petroleum ether (80–110°). On standing the hygroscopic product, sodium diethyl thionophosphate, crystallized as fine white needles, m.p. 204–204.5°; yield 47 g. (49%). Recrystallization did not raise the melting point.

Anal. Calcd. for $C_4H_{10}O_3PSNa$: Na, 12.0; P, 16.14; S, 16.66. Found: Na, 11.9; P, 15.95; S, 16.7.

2-Octyl Ethyl Sulfide.—Sodium ethyl mercaptide was prepared by adding ethyl mercaptan (37.2 g., 0.6 mole) to a mixture of 12.7 g. (0.55 mole) of sodium ribbon in 300 ml. of anhydrous dioxane. The mixture was heated to reflux under a Dry Ice–acetone condenser for four hours, until no trace of unreacted sodium remained. 2-Octyl bromide (96.5 g., 0.5 mole) was then added dropwise to the mixture over a one-half hour period. After refluxing for an additional eight hours the mixture was poured into one liter of water. The aqueous layer was saturated with NaCl and the organic layer was extracted with ether. The extract was washed with water and dried over anhydrous $MgSO_4$. The ether was removed and the residue fractionated *in vacuo* yielding 48 g. (55%) of 2-octyl ethyl sulfide, b.p. 87–88° (8 mm.), $n^{20}\text{D}$ 1.4564.

Acknowledgment.—The authors wish to thank Mr. Harry Ferber, who carried out the phosphorus and sulfur determinations.

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[8] R. W. Bost, J. O. Turner and R. D. Norton, THIS JOURNAL, **54**, 1985 (1932).

[9] Previously reported as melting at 109° by M. S. Kharasch, E. M. May and F. R. Mayo, *J. Org. Chem.*, **3**, 175 (1938).

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

The Chlorination of Thiophene. III. Influence of Catalysts in the Exhaustive Chlorination of Thiophene

BY HARRY L. COONRADT, HOWARD D. HARTOUGH AND HENRY D. NORRIS

Exhaustive chlorination of thiophene in the presence of catalytic amounts of iodine yields a compound to which the structure 2,2,3,4,5,5-hexachloro-3-thiolene has been assigned. In contrast, non-catalytic chlorination and chlorination in the presence of other chlorination catalysts yields tetrachlorothiophene, 2,2,3,4,5,5-hexachlorothiolane or resinous products. Physical constants, proof of structure, and some of the reactions of 2,2,3,4,5,5-hexachloro-3-thiolene are reported.

Prior communications[1,2] in this series have discussed the chlorine addition products and the substitution products of thiophene. In the absence of catalysts exhaustive chlorination of thiophene could be directed to produce either 2,2,3,4,5,5-hexachlorothiolane (I)[1] or tetrachlorothiophene (II).[2]

An investigation of the exhaustive chlorination of thiophene in the presence of catalysts has now been made. A catalytic amount of iodine brings about formation of a compound, C_4Cl_6S, to which the structure 2,2,3,4,5,5-hexachloro-3-thiolene (III)[3] has been assigned.

Bromine has no such catalytic influence and instead 2,2,3,4,5,5-hexachlorothiolane (I) is formed. Phosphorus trichloride also yields compound I. Iron gives low yields of compound I and decomposition products, and antimony trichloride gives only resinous decomposition products. Thus, the formation of III is peculiar to the catalytic influence of iodine.

The course of the reaction leading from thiophene to III is not clear. However, there is evidence that it differs substantially from the course of the non-catalytic reaction and is not merely catalytic chlorination of one of the exhaustive chlorination products I or II formed by a non-catalytic mechanism.[2] Firstly, I, hexachlorothiolane, is recovered unchanged when treated further with chlorine in the presence of iodine. Secondly, as already described,[2] II is formed from thiophene

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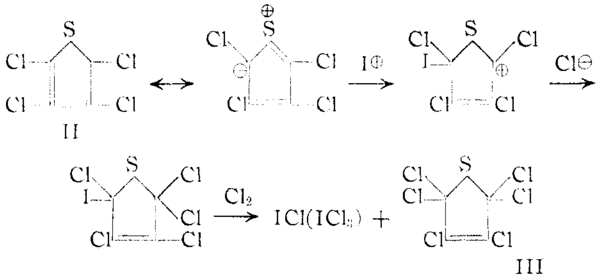
[1] H. L. Coonradt and H. D. Hartough, THIS JOURNAL, **70**, 1158 (1948).

[2] H. L. Coonradt, H. D. Hartough and G. C. Johnson, *ibid.*, **70**, 2564 (1948).

[3] This nomenclature was first described in ref. 1. Alternate nomenclature is 2,2,3,4,5,5-hexachlorothiacyclopent-3-ene and 2,2,3,4,5,5-hexachloro-2,5-dihydrothiophene.

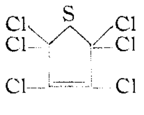
in the absence of catalysts only when high temperatures and/or dehydrochlorination agents are employed. Therefore, if II is an intermediate, it is formed by a different mechanism than in the absence of a catalyst; and, as already noted, its formation cannot occur through dehydrochlorination of I. II actually does react with chlorine in the presence of iodine to give theoretical amounts of III and may be an intermediate. The possible course of the reaction is outlined below

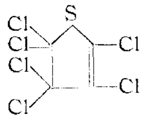


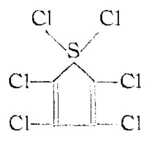
2,2,3,4,5,5-Hexachloro-3-thiolene (III) is a colorless, lachrymatory, low melting, crystalline material readily soluble in most organic solvents. It can be crystallized from petroleum ether. Fumes from III show mild vesicant action on the eyelids and between the fingers. Like I, it has little or no insecticidal activity when tested against the common house fly in the Peet–Grady test chamber.

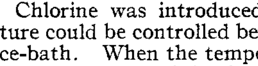
Compound III is stable under normal storage conditions in a clear glass bottle over a period of several years. At temperatures above 180°, it evolves chlorine to yield 2,3,4,5-tetrachlorothiophene (II). III can be steam distilled without appreciable decomposition. When it is warmed to 90° with an excess of aqueous potassium iodide, chlorine is evolved rapidly and iodine is liberated. Fuming nitric acid converts III to dichloromaleic acid. III reacts with an excess of sodium methoxide to form a tetramethoxy ether, IV, $C_8H_{12}Cl_2O_4S$.

The structure 2,2,3,4,5,5-hexachloro-3-thiolene (III), was assigned from a study of reaction products, infrared spectrogram, and synthesis from and degradation to 2,3,4,5-tetrachlorothiophene (II). There are three possible chemical isomers of the empirical formula, C_4Cl_6S, containing the designated heterocyclic ring. Structure IIIb was discarded after consideration of the chemical properties and the infrared spectrogram. This spectrogram showed no evidence of a conjugated diene system nor a resonating thiophene system.[4] It did, however, show strong absorption in the region indicative of a single olefinic double bond. IIIb contains the linkage R–SCl$_2$–R which is notoriously unstable. Dibenzothiophene is known to form a 5,5-dichloro derivative but it is unstable and is decomposed to the sulfoxide[5] by water at 0°. The subject composition C_4Cl_6S is quite stable toward water and aqueous solutions of sodium carbonate and sodium thiosulfate. In addition to these considerations, structure IIIb could scarcely be expected to yield a tetramethoxy derivative with sodium methoxide. Differentiation between structures III and IIIa was possible by degradation of the thiophene ring with fuming nitric acid whereby dichloromaleic acid was obtained. Structure IIIa would not be expected to yield this acid. Compound IV, $C_8H_{12}Cl_2O_4S$, then has the probable structure 3,4-dichloro-2,2,5,5-tetramethoxy-3-thiolene. Further, the composition C_4Cl_6S has the structure III, 2,2,3,4,5,5-hexachloro-3-thiolene.


III


IIIa


IIIb


IV

Experimental

All melting points are corrected; boiling points are uncorrected. The purity of the thiophene used in this work was greater than 99.5%.

2,2,3,4,5,5-Hexachloro-3-thiolene (III).—Thiophene (210 g.) and iodine (10 g.) were placed in a 1-liter flask equipped with stirrer, a spiral-type condenser, thermometer and chlorine inlet tube. Chlorine was introduced at such a rate that the temperature could be controlled between 40 and 60° by means of an ice-bath. When the temperature fell below 40°, the ice-bath was removed. A further decrease in temperature indicated that the reaction was complete. The chlorine addition was discontinued and the product was dissolved in about two volumes of ether, washed twice with water, twice with 5% potassium carbonate solution, twice with 5% sodium thiosulfate solution, and, finally, twice with water. The ethereal solution was dried over sodium sulfate, the ether was evaporated, and the product, III, was distilled in a fractionating column of ten theoretical plates, b.p. 90.5–91.5° at 2 mm. The yield was essentially quantitative. Upon cooling, the liquid crystallized, and after recrystallization from petroleum ether melted at 40.5–41.0°. When mixed with crystals of 2,2,3,4,5,5-hexachlorothiolane, I, m.p. 45–46°, the mixture became liquid at ambient temperatures. The following physical properties were determined: n^{20}_{D} 1.5878,[6] n^{47}_{D} 1.5774, n^{50}_{D} 1.5757, $\Delta n_D/\Delta t = -0.0005$, $d^{26.5}_{4}$ 1.753,[6] dispersion (Abbe number calcd. at 50°) 35.10.

Anal. Calcd. for C_4Cl_6S: C, 16.40; H, 0.00; Cl, 72.7; S, 10.9. Found: C, 16.49; H, 0.05; Cl, 72.9; S, 10.9.

This compound, III, liberated iodine from hot (90°) aqueous potassium iodide. Alcoholic silver nitrate gave an immediate precipitate of silver chloride. III was relatively stable at the boiling point of water and 92% of the original material was recovered after steam distillation.

Pyrolysis of 2,2,3,4,5,5-Hexachloro-3-thiolene (III).—Sixty-seven grams of crystalline III was gently heated under reflux for 72 hours. A slow stream of nitrogen was introduced throughout the pyrolysis. The yellow effluent gas was bubbled into a potassium iodide solution and an immediate test for free iodine was observed indicating evolution of molecular chlorine. At the end of the prescribed heating period, the condenser was inverted and the material was distilled; 54 g. of 2,3,4,5-tetrachlorothiophene, m.p. and mixed m.p. 29–30°, was obtained.

Oxidation of 2,2,3,4,5,5-Hexachloro-3-thiolene (III).—A variation of the method of Angeli and Ciamician[7] for the oxi-

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[4] This spectrogram will be published elsewhere. See H. D. Hartough, "Compounds Containing Thiophene Rings," Interscience Publishers, Inc., New York, N. Y., 1951, Chapter IV (by F. P. Hochgesang), p. 124.

[5] R. K. Brown, R. G. Christiansen and R. B. Sandin, THIS JOURNAL, **70**, 1748 (1948).

[6] Determined on the super-cooled liquid.

[7] A. Angeli and G. Ciamician, *Ber.*, **24**, 74 (1891).

dation of tetrachlorothiophene to dichloromaleic acid was used. To 5 g. of III, cooled to −10°, was added 15 ml. of fuming nitric acid (density 1.52). At −10° the oxidation did not proceed and the mixture was slowly allowed to warm to 10° where an uncontrollable exothermic reaction set in. After the reaction subsided, the oily layer was decanted and discarded. The acid layer was diluted with an equal volume of water and then the *p*H was adjusted to about 6.0 by solid potassium carbonate. Five grams of sodium bisulfate was then added, and the *p*H adjusted to about 1 with 85% orthophosphoric acid. Enough water was added to dissolve the insoluble salts and the mixture was extracted three times with 50 ml. of ether. Evaporation of the ether gave a crystalline acid which melted at 103–105° after recrystallizing twice from a mixture of benzene and ASTM naphtha.[8] The dianiline salt of this acid was prepared and recrystallized three times from alcohol. This material darkened at 125° and melted at 153–154° with decomposition.[9]

Anal. Calcd. for $C_{16}H_{16}Cl_2N_2O_4$: N, 7.5. Found: N, 7.0.

Preparation of 2,2,5,5-Tetramethoxy-3,4-dichloro-3-thiolene (IV).—Commercial sodium methylate powder, 100 g. (1.85 moles), was added slowly into one liter of absolute methanol with cooling to about 45°. To this solution was added 100 g. (0.34 mole) of molten hexachloro-3-thiolene (III) over a period of one hour; the temperature of the reaction mixture meanwhile rose from 45° to 55°. After boiling for six hours, the mixture was cooled, decanted from the salt, and about 75% of the methanol distilled off. The residue of the distillation was combined with salt from the decantation and enough water was added to give a saturated salt solution. This was then extracted three times with ether. After drying the ether extract over potassium carbonate, the ether was removed by distillation, and the 59 g. of crude product was fractionated *in vacuo* to give 18 g. of 2,3,4,5-tetrachlorothiophene (II), b.p. 102–107° at 11 mm., m.p. 29–30°, and 37 g. (40%) of IV, b.p. 135° at 11 mm., n^{20}_{D} 1.5120.

Anal. Calcd. for $C_8H_{12}Cl_2O_4S$, IV: C, 34.91; H, 4.36; S, 11.7. Found: C, 33.93; H, 4.15; S, 11.6.

Attempted Chlorination of 2,2,3,4,5,5-Hexachlorothiolane (I).—A solution of chloroform (200 ml.) containing 29.5 g. (0.1 mole) of 2,2,3,4,5,5-hexachlorothiolane and 25.4 g. (0.2 gram atom) of iodine was treated with 55 g. (0.8 mole) of chlorine at about 10° over a period of 65 minutes. This solution was then washed in turn with 10% sodium carbonate, 10% sodium thiosulfate, water, 10% sodium carbonate and finally with water. After drying over sodium sulfate, the chloroform was distilled and the residue distilled *in vacuo*. I was recovered almost quantitatively, b.p. 87° at 0.1 mm.

Chlorination of 2,3,4,5-Tetrachlorothiophene, II. A. Non-catalytic.—To 100 g. (0.45 mole) of 2,3,4,5-tetrachlorothiophene (II) was added 4.9 moles of chlorine at 30° over a period of two hours. The reaction mixture was washed in turn with water, 5% sodium carbonate and water and finally it was fractionated under reduced pressure. Eighty-seven grams of II was recovered, b.p. 85–87° at 4 mm. There was 4 g. of residue.

B. **In the Presence of Iodine.**—2,3,4,5-Tetrachlorothiophene (II) 100 g. (0.45 mole) was dissolved in 200 ml. of carbon tetrachloride and 3 g. (0.024 gram atom) of iodine was added. Chlorine (0.9 mole) was added to this solution at 25–50° over a 30-minute period. The product was washed in turn with aqueous solutions of sodium carbonate, sodium thiosulfate, sodium carbonate and finally with water. The organic solution was dried over sodium sulfate, the solvent was removed by distillation and the residue was fractionated under reduced pressure. No unreacted II could be recovered. One hundred and fourteen grams (87%) of 2,2,3,4,5,5-hexachloro-3-thiolene (III) was obtained; b.p. 120–125° at 6–7 mm., m.p. 37.5–40°. A mixture with an authentic sample of III melted at 38.5–40°.

Exhaustive Chlorination of Thiophene in the Presence of Chlorination Catalysts. A. Bromine.—Thiophene (170 g.) and bromine (20 g.) were mixed and exhaustively chlorinated between 40 and 60° as described above under the preparation of III. Distillation yielded about 20 g. of 2,3,4,5-tetrachlorothiophene, and 486 g. of 2,2,3,4,5,5-hexachlorothiolane (I),[10] b.p. 94–95° (2 mm.), n^{20}_{D} 1.5778. The material crystallized upon standing; melting point and mixed melting point with an authentic sample,[1] 45–46°.

B. **Phosphorus Trichloride.**—Thiophene (170 g.) was exhaustively chlorinated in the presence of phosphorus trichloride (20 g.) in the manner described above. The only product that could be identified was 2,2,3,4,5,5-hexachlorothiolane (I) (475 g.).

C. **Iron Powder.**—Thiophene (170 g.) was exhaustively chlorinated in the presence of 20 g. of iron powder in the manner described above. The dark, viscous reaction product was dissolved in chloroform and washed with 5% hydrochloric acid to remove iron salts and then with 5% sodium carbonate to remove hydrochloric acid. After drying, filtering, and removal of the chloroform 400 g. of a black viscous liquid was obtained. Distillation *in vacuo* gave only 147 g. of distillable material, b.p. 80–100° (2 mm.). Fractionation of this material through a 12-plate column indicated that it was a complex mixture from which 26 g. of 2,2,3,4,5,5-hexachlorothiolane (I) was obtained.

D. **Antimony Trichloride.**—Thiophene (170 g.), when exhaustively chlorinated in the presence of 20 g. of antimony trichloride under the conditions described above, gave a black tacky solid insoluble in chloroform from which no distillable material was obtained.

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(8) There are several different melting points of this acid given in the literature ranging from 116 to 120° all of which are within the range of the melting point of the anhydride of dichloromaleic acid and no clear distinction can be made as to whether these are melting points of the anhydride or the acid.

(9) A. Salmony and H. Simonis, *Ber.*, **38**, 2591 (1905), reported that the dianiline salt of dichloromaleic acid darkened at 125° and melted at 155° with decomposition.

(10) In this group of experiments entrainment losses of thiophene were high and quantitative assessment of yields can not be made.