Anal. Calcd. for $(C_7H_{12}SO_2)_n$: C, 52.5; H, 7.50; S, 20.00. Found: C, 52.38, 52.32; H, 7.55, 7.62; S, 19.5, 19.4.

Summary

1. Methylpropene, 1-pentene, 2-pentene, 1-nonene, 3-cyclohexylpropene and 3-methylcyclohexene give polysulfones by the addition of sulfur dioxide. These polysulfones are all neutral products and the first five of them have alcohol groups at the ends of the chains. Evidence has been obtained to indicate that 1-pentenepolysulfone is degraded with alkali in a manner which is like that reported for propylenepolysulfone, whereas the methylpropene and 2-pentene derivatives are degraded more nearly after the manner of the cyclohexene derivative. The molecular weights of these polysulfones are in the range of 100,000 to 200,000.

2. Highly substituted olefins do not add sulfur dioxide under the experimental conditions used in our work.

3. Polysulfones have been obtained from 1-heptyne and from undecylenyl alcohol. No evidence of addition of sulfur dioxide to typical olefins containing chloro, cyano, phenolic hydroxyl, aldehydo, carboethoxy, carboxyl or salt of carboxyl groups could be obtained.

URBANA, ILLINOIS RECEIVED AUGUST 16, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF NEBRASKA]

Arsenicals Containing the Furan Nucleus. II. Action of Chlorine. Some Substituted Furan Arsenicals

BY WESLEY G. LOWE[1] AND CLIFF S. HAMILTON

The action of chlorine on furyldichloroarsine, difurylchloroarsine and trifurylarsine in chloroform or carbon tetrachloride solution leads in every instance to the formation of 2-chlorofuran tetrachloride. This reaction can be carried out at room temperature or by introducing dry chlorine gas into a chloroform solution of the arsenical at −78° followed by evaporation of the solvent at room temperature. 2-Chlorofuran, prepared from Hill's 5-chloropyromucic acid[2] by decarboxylation in aqueous mercuric chloride,[3] adds four atoms of chlorine under the same conditions and the 2-chlorofuran tetrachloride thus obtained is identical with that prepared from the furan arsenicals.

In agreement with the observation made by Hill and Hartshorn[4] that 2,5-dibromofuran tetrabromide in alcoholic potassium hydroxide solution loses two molecules of hydrogen bromide to yield tetrabromofuran, we have found that from a similar solution of 2-chlorofuran tetrachloride 40% of the total chlorine can be precipitated with silver nitrate, indicating the loss of two molecules of hydrogen chloride and the formation of a trichlorofuran. The action of aqueous silver nitrate on an alcoholic solution of 2-chlorofuran tetrachloride is complex, varying conditions of temperature and acidity leading to a precipitation of 60, 70 and 75% of the total chlorine as silver chloride. Hydrolysis of the symmetrical molecule, 2,5-dibromofuran tetrabromide, involves a loss of five-sixths of the total bromine yielding bromomaleic acid as a final product.[4] This stepwise loss of chlorine is the same for chlorofuran tetrachloride prepared by either of the methods mentioned and is further proof of identity of structure.

Efforts to isolate a second product from the chlorination of furyldichloroarsine were unsuccessful. However, in each of six chlorinations of difurylchloroarsine it was possible to isolate a white solid which on exposure to air gave off hydrogen chloride gas. This compound was not identified as such, but on hydrolysis with cold water it yielded difurylarsinic acid which was purified by crystallization from hot water. Although it is not necessary to fractionate difurylchloroarsine to purity before chlorination in order to obtain this acid, efforts to prepare it from the mixture of arsenicals before distillation were unsuccessful. The acid, when pure, is stable to air and light, but it is more sensitive to sulfuric acid than is furoic acid and can be detected in very dilute solution by the formation of a dark ring at the water–sulfuric acid interface.

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[1] Parke, Davis and Company Fellow.

[2] Hill and Jackson, *Proc. Am. Acad. Arts Sci.*, **24**, 320 (1889).

[3] Gilman and Wright, THIS JOURNAL, **55**, 3302 (1933).

[4] Hill. *Ber.*, **16**, 1132 (1883); Hill and Hartshorn, *ibid.*, **18**, 449 (1885).

Trifurylarsine dichloride was prepared in small yields by slow evaporation of a chloroform or ether solution of chlorinated trifurylarsine. It was obtained as large diamond-shaped transparent crystals, stable in air, but readily hydrolyzed in a water–alcohol solution. Neither trifurylarsine dichloride nor difurylarsinic acid reacted with mercuric chloride in alcoholic solution to form 2-chloromercurifuran as does trifurylarsine.[5] This fact, in view of the results that have been obtained on mercuration of benzene arsenicals,[6] makes it appear that the substitution of arsenic by mercury on aromatic nuclei is a property of trivalent but not of pentavalent arsenic.

In the chlorination of furan arsenicals, three separate reactions are involved: (1) the oxidation of trivalent arsenic, (2) the saturation of the furan nucleus and (3) the scission of the carbon–arsenic bond. Since these could occur in any order, there are six possible courses for the total reaction. The isolation of difurylarsinic acid and trifurylarsine dichloride eliminates two of these since scission of the carbon–arsenic bond cannot, therefore, occur first. Against the probability of scission occurring at the second step, it has been noted that the removal of arsenic from an aromatic nucleus by means of chlorination is not accomplished at the temperature here employed,[7] and that removal of arsenic from an aliphatic radical by this means occurs only after the arsenic has been oxidized. Consequently it is most probable that scission of the carbon–arsenic bond occurs only after the nucleus has been saturated and the arsenic oxidized. Von Baeyer[8] has shown that loss of arsenic from methyltetrachloroarsine occurs at −10°. However, the results of these chlorinations are best explained by assuming that both of the reactions involving scission of the carbon–arsenic bond as the final step occur simultaneously. In other words, the oxidation of the furan nucleus and trivalent arsenic are essentially competitive in nature. Consequently it has not been found possible by means of controlled chlorination of difurylchloroarsine to preclude the formation of either 2-chlorofuran tetrachloride or difurylarsinic acid; both products always appear together. In view of these circumstances the usefulness of chlorination as a general method for preparing various furylarsonic and difurylarsinic acids is limited by the ease of chlorination of substituted furan nuclei. In addition to its failure to produce furylarsonic acid from furyldichloroarsine, repeated applications of the method to di-5-chlorofurylchloroarsine failed to lead to the synthesis of di-5-chlorofurylarsinic acid. This latter result is in accord with our observation that under similar conditions 2-chlorofuran adds chlorine more readily than does furan itself.

Tri-5-chlorofurylarsine and tri-5-bromofurylarsine were prepared by arsenation of 5-chloro-2-chloromercurifuran and 5-bromo-2-chloromercurifuran in benzene solution. The former arsenical was separated by fractional distillation and the latter by fractional crystallization. Both of these compounds are crystalline solids. An attempt was made to prepare tri-5-iodofurylarsine from 5-iodo-2-chloromercurifuran. The arsenation proceeded with great ease, but the resulting mixture of arsenicals was so unstable to the action of air that separation of its components was abandoned.

A study of the action of alcoholic mercuric chloride on these substituted trifurylarsines was made. It was found that although the arsenic can be replaced by mercury to yield the original mercurical, the action is less complete than was observed in the case of trifurylarsine itself.[5] The order of ease of substitution of arsenic by mercury in these arsenicals is: trifurylarsine, tri-5-chlorofurylarsine, tri-5-bromofurylarsine. Since this reaction is characteristic of aromatic nuclei, the aromaticity of furan is lessened by the presence of halogen in the α-position.

Experimental

2-Chlorofuran Tetrachloride.—*Method 1.*—Two grams of furyldichloroarsine, difurylchloroarsine, trifurylarsine or a mixture of these arsenicals was dissolved in 10 cc. of chloroform, the solution chilled by immersing in a bath of solid carbon dioxide and ether and chlorine passed in slowly. Chlorination was continued until on allowing a sample of the solution to warm to room temperature bubbles of chlorine gas were observed to form. The solution was then placed in an evaporating dish and allowed to stand in the open until the chloroform had evaporated. The viscous oil remaining was steam distilled until no more droplets passed over, collected with a small pipet, and dried by allowing to stand in a desiccator; yield 20%.

Method 2.—Six grams of 2-chlorofuran was dissolved in 20 cc. of chloroform, chilled and chlorinated as described above, the chloroform removed by evaporation and the product steam distilled; yield 3 g. The low yields result from the hydrolysis of the oil during steam distillation.

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[5] Lowe and Hamilton, THIS JOURNAL, **57**, 1081 (1935).

[6] German Patent 272,289; *Chem. Zentr.*, I, 1469 (1914).

[7] Michaelis, *Ber.*, **10**, 622 (1887).

[8] Von Baeyer, *Ann.*, **107**, 274 (1858).

2-Chlorofuran tetrachloride is slightly yellow and has a pungent, penetrating odor, d^{25}_4 1.620.

Anal. Calcd. for $C_4H_3OCl_5$: Cl, 72.57. Found: Cl, 72.48, 72.06.

Reactions of 2-Chlorofuran Tetrachloride.—1. To 20 cc. of saturated alcoholic solution of potassium hydroxide was added approximately 60 mg. of 2-chlorofuran tetrachloride. A bright orange coloration appeared which faded while a precipitate of potassium chloride separated. After fifteen minutes the solution was diluted with water, made acid with nitric acid and silver nitrate added. The precipitated silver chloride was dried at 135° and weighed.

Anal. Calcd. for 40% of 72.57: Cl, 29.03. Found: Cl, 29.51, 29.40.

2. Approximately 50 mg. of 2-chlorofuran tetrachloride was placed in 15 cc. of alcohol and made slightly acid with nitric acid. Aqueous silver nitrate was added and a precipitate was observed to form gradually. The precipitation was complete at the end of twelve hours.

Anal. Calcd. for 60% of 72.57: 43.54. Found: (average of four determinations) Cl, 42.98.

3. Approximately 50 mg. of 2-chlorofuran tetrachloride was placed in 15 cc. of alcohol, made slightly acid with nitric acid and heated to boiling. When the precipitate had coagulated, it was filtered, dried and weighed.

Anal. Calcd. for 70% of 72.57: 50.80. Found: Cl, 50.75, 51.05.

4. The filtrate from the above determination was made strongly acid with nitric acid and boiled until brown fumes appeared. The coagulated precipitate was dried and weighed, the weight of this precipitate added to that found in the previous determination and per cent. of chlorine determined on the basis of this sum.

Anal. Calcd. for 75% of 72.57: 54.52. Found: Cl, 53.87, 53.87.

Difurylarsinic Acid.—Thirty-eight grams of 2-chloromercurifuran, 12 g. of arsenic trichloride, and 50 cc. of benzene was refluxed for three hours. The fraction containing difurylchloroarsine was obtained as described in a previous paper,[5] no attempt being made to purify it by further fractionation. This fraction was dissolved in 20 cc. of chloroform, the solution chilled in a bath of solid carbon dioxide and ether, and chlorine introduced slowly. From time to time a sample was removed and allowed to evaporate. When the amount of white solid formed on evaporation was a maximum, the chlorination was stopped and the entire solution evaporated by allowing to stand at room temperature in an evaporating dish. The crystals were washed three times with dry ether to remove the arsenic trichloride and 2-chlorofuran tetrachloride present and allowed to stand overnight in water. The crystals were washed with cold water, dried at room temperature and analyzed. Further purification can be effected by recrystallization from hot water. The acid is soluble in alcohol and glycol; yield, 1.1 g. or 8% of the total furan present in the mercurial; m. p. 138°.

Anal. Calcd. for $(C_4H_3O)_2AsO_2H$: As, 31.00; neut. equiv., 242. Found: As, 31.10, 31.00; neut. equiv., 228.

Trifurylarsine Dichloride.—The ether washings from the above preparation were placed in a beaker and allowed to stand overnight. A heavy oil remained in which transparent, diamond-shaped crystals were present. These were picked out and washed with ligroin, yield 0.25 g. In alcoholic solution the chlorine present in this compound was precipitable with silver nitrate; m. p. 132°.

Anal. Calcd. for $(C_4H_3O)_3AsCl_2$: As, 21.60; Cl, 20.44. Found: As, 21.47; Cl, 20.29.

5-Chloro-2-chloromercurifuran.—This compound was prepared from 5-chloropyromucic acid[2] by boiling a solution of its sodium salt with an equivalent amount of mercuric chloride, using the directions given by Gilman for the preparation of substituted 2-chloromercurifurans.[3] The mercurial was obtained in 65% yield and no other product was formed. It was purified by recrystallization from hot alcohol, m. p. 181°.

Anal. Calcd. for $C_4H_2OHgCl_2$: Hg, 59.42; Cl, 21.03. Found: Hg, 59.02; Cl, 21.13.

Tri-5-chlorofurylarsine.—Forty-three grams of 5-chloro-2-chloromercurifuran, 16 g. of arsenic trichloride and 100 cc. of benzene was refluxed for thirty minutes. The precipitated mercuric chloride was filtered off and the benzene removed from the filtrate by distillation. When the temperature of the distilling vapors reached 85° distillation was continued using a water pump until the excess arsenic trichloride was removed. The arsenicals were then twice distilled at 1 mm., the distillate being separated into two equal fractions in the second distillation. Decomposition during distillation was slight as compared with that observed in the distillation of unsubstituted arsenicals. An analysis for arsenic and chlorine indicated that the first fraction contained impure di-5-chlorofurylchloroarsine, a slightly green liquid. The second fraction on standing solidified to a white solid; total yield of arsenicals, 6 g., or 20–25%.

The trichlorofurylarsine was obtained from the second fraction by fractional crystallization from ether in the form of fine white needles, m. p. 63°.

Anal. Calcd. for $(ClC_4H_2O)_3As$: As, 19.74. Found: As, 19.54, 19.60.

No attempt was made to purify the first fraction. Chlorination failed to form di-5-chlorofuryl arsinic acid but yielded an arsenic-free highly chlorinated oil so readily decomposed during steam distillation that no analysis was attempted. Its odor, ease of hydrolysis and loss of chlorine in the presence of silver nitrate, indicated that it was probably 2,5-dichlorofuran tetrachloride.

Tri-5-bromofurylarsine.—Forty-two grams of 5-bromo-2-chloromercurifuran, 10 g. of arsenic trichloride and 100 cc. of benzene was refluxed for thirty minutes and the mercuric chloride, benzene and arsenic trichloride removed from the arsenicals as described above. After removal of the arsenic trichloride, the mixture on cooling set to a black mass in which crystals were plainly visible. On dissolving in ether and allowing to evaporate the oily constituents formed a ring at the edge of the dish and were absorbed in filter paper. By repeating this treatment four times the tri-5-bromofurylarsine was obtained as white, beautifully formed needle-shaped crystals; yield 8 g., 40%, m. p. 106°.

Anal. Calcd. for $(BrC_4H_2O)_3As$: As, 14.60; Br, 46.76. Found: As, 14.76; Br, 46.64.

Mercuration of Tri-5-chlorofurylarsine.—One-half gram of tri-5-chlorofurylarsine, 1.1 g. of mercuric chloride and 10 cc. of alcohol were heated to boiling and set aside for fifteen minutes. On the addition of water a white precipitate formed which contained 13% arsenic. Repeated crystallization from hot alcohol gave a 15% yield of 5-chloro-2-chloromercurifuran, m. p. 179–180°.

Mercuration of Tri-5-bromofurylarsine.—Mercuration of this material was attempted by the method above, the same ratio of molecular concentrations of reactants being employed. On addition of water tri-5-bromofurylarsine was precipitated almost unchanged. The experiment was repeated, water being added to the alcohol to the point where precipitation was just avoided. Boiling was continued for fifteen minutes. On cooling and adding water a precipitate was obtained which on recrystallization from water–alcohol gave a 7% yield of 5-bromo-2-chloromercurifuran, m. p. 178°.

Summary

Chlorination of furyldichloroarsine, difurylchloroarsine and trifurylarsine yields 2-chlorofuran tetrachloride in all cases. Stepwise loss of chlorine from this compound has been described. Difurylarsinic acid has been prepared by hydrolysis of a chlorination product of difurylchloroarsine and trifurylarsine dichloride has been isolated. Chlorination of furyldichloroarsine and di-5-chlorofurylchloroarsine in an effort to form furylarsonic acid and di-5-chlorofurylarsinic acid has given negative results. The chlorination of furan arsenicals is regarded as competitive oxidation of arsenic and the furan nucleus.

The preparation of some substituted furan arsenicals has been described, and a study of the action of mercuric chloride on tri-5-chlorofurylarsine and tri-5-bromofurylarsine indicates that the aromaticity of the furan nucleus is less in these compounds than in trifurylarsine itself.

LINCOLN, NEBRASKA RECEIVED JULY 29, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE UNIVERSITY OF MONTANA]

The Addition of Chloroform and Bromoform to *p*-Chlorobenzaldehyde

BY JOSEPH W. HOWARD

Introduction

The fact that benzaldehyde is one of the few aldehydes to which chloroform and bromoform will add forming the corresponding trichloromethyl and tribromomethyl carbinols,[1] has led the author to undertake a study of these additions with substituted benzaldehydes.

A study of this reaction with *o*-chlorobenzaldehyde has been recently reported.[2] The present investigation was made with *p*-chlorobenzaldehyde.

Experimental Part

Preparation of Trichloromethyl-*p*-chlorophenylcarbinol.—To a mixture of 46 g. of freshly distilled *p*-chlorobenzaldehyde and 60 g. of dry chloroform was added with constant stirring 4 g. of powdered potassium hydroxide over a one-hour period. The mixture was allowed to stand for at least three hours, ether was added and the resultant mixture filtered. The ether and excess chloroform were distilled off. The residue was steam distilled to remove *p*-chlorobenzaldehyde and *p*-chlorobenzoic acid. The non-volatile portion was extracted with ether, the ether extract washed with 2% sodium hydroxide solution and dried over sodium sulfate. The ether was distilled off and the carbinol removed by distillation under diminished pressure. It came over at 187–188° at 26 mm. The yield was 20 g. of d^{20}_{20} 1.523.

Anal. Calcd. for $C_8H_6OCl_4$: Cl, 54.58. Found: Cl, 54.64.

This carbinol is insoluble in water but readily soluble in ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform, carbon tetrachloride and carbon bisulfide.

Preparation of Tribromomethyl-*p*-chlorophenylcarbinol.—The above procedure was followed with the substitution of 130 g. of bromoform for 60 g. of chloroform. This compound boils at 198–200° at 19 mm. It solidified readily on cooling and was recrystallized from 95% ethyl alcohol. The yield was 25 g.; m. p. 90–91°.

Anal. Calcd. for $C_8H_6OClBr_3$: Cl, 9.01; Br, 60.96. Found: Cl, 9.05; Br, 60.86.

This carbinol differs in solubility from the trichloromethyl-*p*-chlorophenylcarbinol in that it is only very sparingly soluble in ethyl and methyl alcohols.

Preparation of the Esters

The esters of trichloromethyl-*p*-chlorophenylcarbinol were prepared as follows: the acetate by heating with acetic anhydride at 150–160° for three hours, the propionate with propionic anhydride at 170–180° for three hours and the butyrate with butyryl chloride at 120–130° for three hours. The usual procedure of the Schotten–Baumann reaction was used in preparing the benzoate with benzoyl chloride. The acetate was recrystallized from 75% acetic acid, the propionate and benzoate from 95% ethyl alcohol. The butyrate remained a viscous oil even after long standing.

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(1) Jocicz. *Chem. Centr.*, **68**, I, 1013 (1897); Siegfried, *ibid.*, **70**, I, 606 (1899); Howard, THIS JOURNAL, **47**, 455 (1925); **52**, 5059 (1930).

(2) Howard and Castles, *ibid.*, **57**, 376 (1935).