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).

The average yield of all of these esters was 85%.

ESTERS OF TRICHLOROMETHYL-*p*-CHLOROPHENYLCARBINOL

		M. p., °C.	Formula	Analyses for Cl, % Calcd.	Analyses for Cl, % Found
1	Acetate	120–121	$C_{10}H_8O_2Cl_4$	46.98	47.18
2	Propionate	71–72	$C_{11}H_{10}O_2Cl_4$	44.89	45.17
3	Benzoate	128–129	$C_{15}H_{10}O_2Cl_4$	38.98	38.87

The butyrate boils at 172–173° at 6 mm., d^{20}_{20} 1.331. The butyrate is insoluble in water but readily soluble in ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform, carbon tetrachloride and carbon bisulfide. The other esters differ from this in that they are only sparingly soluble in ethyl and methyl alcohols.

A number of attempts were made to make these same esters of tribromomethyl-*p*-chlorophenylcarbinol using the same reagents and experimental conditions but the carbinol always came through unchanged. Attempts were also made to prepare the acetate by heating with acetyl chloride at 60–70° for three hours and the benzoate by heating with benzoic anhydride at 180–190° for five hours. The results here were also negative.

Summary

Trichloromethyl-*p*-chlorophenylcarbinol and its acetic, propionic, butyric and benzoic esters have been prepared and studied. The corresponding tribromo carbinol was prepared but it does not form these esters under the same experimental conditions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Natural and Synthetic Rubber. XV. Oxygen in Rubber

BY THOMAS MIDGLEY, JR., A. L. HENNE, A. F. SHEPARD AND MARY W. RENOLL

The harmful effects of oxygen on rubber have long been known, and the formation of peroxides during milling has been qualitatively demonstrated.[1] However, quantitative measurements of the oxygen have never been made, and the nature of the oxygen compounds has not been investigated.

Rubber frequently has been analyzed by combustion and the ratio of the carbon percentage to the hydrogen percentage has invariably been found to correspond closely to a $(C_5H_8)_n$ formula. However, it does not follow that such is the formula of rubber. In every instance, the total of the carbon and the hydrogen content has fallen short of 100%. The deficiency is very small, especially in the case of pure rubber, but it invariably exists. The best analyses available, those of the Bureau of Standards,[2] done on highly purified, and on recrystallized rubber, show a deficiency of 0.3%. This cannot be accounted for entirely by contamination of the samples, nor can the combustion be assumed to be that inaccurate. It is logical to regard this deficiency as the oxygen and nitrogen content of the sample.

In the present work, the quantity of oxygen present in rubber samples has been measured by means of the combustion method described by the Bureau of Standards; an effort has been made to determine the type of oxygen present and to study the progressive oxidation of rubber. The technique of the Bureau has been altered in only two details: (1) a Jena combustion tube was substituted for the Pyrex tube, to prevent sintering at the high temperature used to burn out the last traces of carbon; (2) weighings were improved to ±0.00002 g.

Procedure

Sol rubber was prepared and purified by fractional precipitation[3] until it contained only 0.007 ± 0.0003% of nitrogen by Nessler titration. A sample of this rubber was analyzed by combustion to determine the H/C ratio and the oxygen and nitrogen content by deficiency. Another sample of the same specimen was treated with methylmagnesium iodide and the resulting methane measured to determine the amount of active hydrogen. The amount of carboxylic or ketonic groups present was investigated by treating a third sample with thionylmagnesium iodide, purifying the reaction product and analyzing it for sulfur.[4] The data are listed in Tables I and II together with the results of the same methods used on purified sodium rubber and on the degraded products of both.

Discussion of the Results

The striking fact shown by the tables is that pure synthetic rubber is oxygen free, while natu-

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[1] Busse, *Ind. Eng. Chem.*, **24**, 140 (1932).

[2] Smith, Saylor and Wing, *Bur. Standards J. Research*, **10**, 479–92 (1933).

[3] Midgley, Henne and Renoll, THIS JOURNAL, **53**, 2733 (1931).

[4] Midgley, Henne, Shepard and Renoll, *ibid.*, **56**, 1325 (1934).