TABLE VIII

CONSTANTS OF THE 1,2-DIHYDROBENZOFURANS

No.	1,2-Dihydrobenzofuran	Method of prepn.	B. p., °C.	B. p., Mm.	d^{20}_{20}	n^{20}_D	Formula	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % Found H
1	1,1-Dimethyl	1, 2, 3	62	7	0.996	1.5190	$C_{10}H_{12}O$	81.08	8.17	80.08	8.37
2	1,1,6-Trimethyl	1, 3, 4	74	8	.983	1.5150	$C_{11}H_{14}O$	81.43	8.70	81.56	8.70
3	1,1,5-Trimethyl	1, 2, 3, 4	87	11	.978	1.5167	$C_{11}H_{14}O$	81.43	8.70	81.50	8.73
4	1,1,4-Trimethyl	1, 3, 4	88	10	.978	1.5151	$C_{11}H_{14}O$	81.43	8.70	81.53	8.70
5	1,1-Dimethyl-4-chloro	1	96	5	1.135	1.5300	$C_{10}H_{11}OCl$	65.93	6.06	65.52	6.24

TABLE IX

CONSTANTS OF THE MERCURATED 1-METHYL-1,2-DIHYDROBENZOFURANS

No.	1,2-Dihydrobenzofuran	M. p., °C.	Formula	Mercury analyses, % Calcd.	Mercury analyses, % Found
1	1-Chloromercurimethyl-1-methyl	81	$C_{10}H_{11}OClHg$	52.35	51.90
2	1-Chloromercurimethyl-1,6-dimethyl	72.5	$C_{11}H_{13}OClHg$	50.53	50.32
3	1-Chloromercurimethyl-1,4-dimethyl	102.4	$C_{11}H_{13}OClHg$	50.53	50.60
4	1-Iodomercurimethyl-1,4-dimethyl	73	$C_{11}H_{13}OIHg$	40.98	40.78
5	1-Bromomercurimethyl-1,4-dimethyl	93–94	$C_{11}H_{13}OBrHg$	45.48	45.05

Summary

1. Methylallyl phenyl ethers rearrange upon heating to give *o*-methylallylphenols.

2. *o*-Methylallylphenols (a) on heating or (b) by treatment with pyridine hydrochloride, give dimethyldihydrobenzofurans, (c) by catalytic reduction give isobutylphenols, (d) by action of sodium hydroxide give isobutenylphenols, (e) by addition of mercuric salts give mercurated dimethyldihydrobenzofurans.

3. The isobutyl group does not enhance the antiseptic action of the phenols as much as the *n*-butyl or higher molecular weight alkyl groups.

URBANA, ILLINOIS RECEIVED DECEMBER 5, 1934

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

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

BY JOSEPH W. HOWARD AND IRWIN CASTLES

Introduction

Previous work has shown that benzaldehyde is one of the few aldehydes to which chloroform and bromoform will add forming the corresponding trichloromethyl and tribromomethyl carbinols.[1,2,3]

The present work was undertaken in order to ascertain whether or not chloroform and bromoform would add in a similar manner to *o*-chlorobenzaldehyde. It was found that such a reaction did take place. In addition the acetates, propionates, butyrates, and benzoates of the resulting carbinols have been prepared and studied.

Experimental Part

Preparation of Trichloromethyl-*o*-chlorophenylcarbinol.—To a mixture of 46 g. of freshly distilled *o*-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 three hours, ether was added, and the resultant mixture filtered. The filtrate was distilled until the temperature of 130° at 6 mm. was reached. The residue was then steam distilled to remove the last traces of *o*-chlorobenzaldehyde and *o*-chlorobenzoic acid. It was washed with dilute sodium carbonate solution, extracted with ether, dried over sodium sulfate and the ether distilled off. The carbinol was then removed by distillation, coming over at 170–171° at 6–7 mm. The yield was 20 g. of d^{20}_{20} 1.580.

Anal. Calcd. for $C_8H_6OCl_4$: Cl, 54.58. Found: Cl, 54.61.

Preparation of Tribromomethyl-*o*-chlorophenylcarbinol.—The above procedure was followed with the substitution of 130 g. of bromoform for 60 g. of chloroform. This compound boils at 195–196° at 8 mm. The yield was 29 g. of d^{20}_{20} 2.117.

Anal. Calcd. for $C_8H_6OClBr_3$: Cl, 9.01; Br, 60.96. Found: Cl, 9.04; Br, 60.80.

Both of these carbinols are insoluble in water but readily soluble in carbon bisulfide, ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform and carbon tetrachloride.

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(1) Jocicz, *Chem. Centr.*, **68**, I, 1013 (1897).

(2) Siegfried, *ibid.*, I, 606 (1899).

(3) Howard, THIS JOURNAL, **47**, **455** (1925); **52**, 5059 (1930).

Preparation of the Esters

The acetates were prepared by heating the carbinols with acetic anhydride at 160–170° for three hours, the propionates with propionic anhydride at 180–190° for three hours. The butyrates were prepared by heating with butyryl chloride at 120–130° for three hours.

The usual procedure of the Schotten–Baumann reaction was used in preparing the benzoates with benzoyl chloride. The benzoate of trichloromethyl-*o*-phenylcarbinol was also prepared by heating with benzoic anhydride at 230–235° for three hours, but this resulted in excessive decomposition in the case of the tribromo compound.

ESTERS OF TRICHLOROMETHYL-*o*-CHLOROPHENYLCARBINOL

		Formula	Analyses for Cl, % Calcd.	Analyses for Cl, % Found
1	Acetate	$C_{10}H_8O_2Cl_4$	46.98	47.04
2	Propionate	$C_{11}H_{10}O_2Cl_4$	44.89	44.74
3	Butyrate	$C_{12}H_{12}O_2Cl_4$	42.99	43.13
4	Benzoate	$C_{15}H_{10}O_2Cl_4$	38.98	39.20

	B. p., °C.	Mm.	M. p., °C.	d^{20}_{20}
1	162–163	4	86	...
2	175	4	38	...
3	201	15	..	1.363
4	.....	..	81	...

The acetate and propionate crystallize slowly on standing at room temperature for several weeks. The benzoate was recrystallized from 95% alcohol.

ESTERS OF TRIBROMOMETHYL-*o*-CHLOROPHENYLCARBINOL

		Formula	Chlorine, % Calcd.	Chlorine, % Found	Bromine, % Calcd.	Bromine, % Found
1	Acetate	$C_{10}H_8O_2ClBr_3$	8.14	8.28	55.08	55.19
2	Propionate	$C_{11}H_{10}O_2ClBr_3$	7.89	7.97	53.36	53.19
3	Butyrate	$C_{12}H_{12}O_2ClBr_3$	7.67	7.76	51.86	51.97
4	Benzoate	$C_{15}H_{10}O_2ClBr_3$	7.13	7.39	48.21	48.37

	B. p., °C.	Mm.	M. p., °C.	d^{20}_{20}
1	.....	...	102–103	...
2	.....	...	78	...
3	208–210	4	.....	1.803
4	.....	...	91	...

The acetate was recrystallized from 75% acetic acid, the propionate and benzoate from 95% alcohol.

The average yield of all these esters was 85%.

All of the esters are insoluble in water and readily soluble in carbon bisulfide, benzene, acetone, ether, chloroform and carbon tetrachloride.

The butyrates are readily soluble in 95% ethyl alcohol and methyl alcohol, while the acetates, propionates and benzoates are only sparingly soluble in these solvents.

Summary

Trichloromethyl-*o*-chlorophenylcarbinol and tribromomethyl-*o*-chlorophenylcarbinol as well as their acetic, propionic, butyric and benzoic esters have been prepared and studied.

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[CONTRIBUTION NO. 116 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A Total Asymmetric Synthesis by Addition of Bromine to an Ethylenic Linkage

BY TENNEY L. DAVIS AND ROBERT HEGGIE

Partial asymmetric syntheses, in which a molecule containing an asymmetric atom is taken at the beginning and additional asymmetry is found in the product, have now been reported in considerable number.[1] Asymmetric decompositions have been reported by Kuhn and Braun,[2] Kuhn and Knopf,[3] and Mitchell.[4] Souty[5] has recently found that the rate of mutarotation of certain sugars is different in right and in left circularly polarized light of wave length 5461 Å. but not different in right and in left circularly polarized light of wave length 5890 Å. A number of unsuccessful attempts to add bromine asymmetrically to the ethylenic linkage have been recorded.[6] So far as we are aware, the only total asymmetric synthesis, starting from optically inert materials, which has been reported heretofore is that of Karagunis and Drikes,[7] who procured optically active products by the addition of chlorine to triarylmethyl radicals in circularly polarized light of wave lengths 4300 and 5890 Å.

We now wish to report the production of optically active trinitrostilbene dibromide by the addition of bromine to 2,4,6-trinitrostilbene in circularly polarized light of wave length 3600–4500 Å. This reaction has seemed to us to be particularly well suited to the purpose of asymmetric synthesis in visible light, for the reasons that the

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[1] Ritchie, "Asymmetric Synthesis and Asymmetric Induction," Oxford, 1933, Part I, Chapters II and III.

[2] Kuhn and Braun, *Naturwissenschaften*, **17**, 227–228 (1929).

[3] Kuhn and Knopf, *ibid.*, **18**, 183 (1930); *Z. physik. Chem.*, **7B**, 292–310 (1930).

[4] Mitchell, *J. Chem. Soc.*, 1829–1834 (1930).

[5] Souty, *Compt. rend.*, **199**, 198–199 (1934).

[6] Ritchie, *loc. cit.*, Part I, Chapter IV; *cf.* Mitchell, "The Cotton Effect and Related Phenomena," London, 1933.

[7] Karagunis and Drikes, *Naturwissenschaften*, **21**, 697 (1933); *Nature*, **132**, 354 (1933).