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

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

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Introduction

Previous reports have been made on the addition of chloroform and bromoform to *o*-chlorobenzaldehyde and *p*-chlorobenzaldehyde.[1,2]

In continuation of the study of these additions of chloroform and bromoform to substituted benzaldehydes, the present investigation was made with *m*-chlorobenzaldehyde and *p*-tolualdehyde.

Experimental Part

In general the same procedure was followed as in our previous reports. To a mixture of the aldehyde and chloroform or bromoform was added with constant stirring powdered potassium hydroxide over a one-hour period. After standing two more hours ether was added and the resultant mixture filtered. The ether and excess chloroform or bromoform was distilled off and the residue steam distilled to remove the excess aldehyde. The non-volatile portion was extracted with ether, 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.

The esters of these carbinols were prepared as follows: the acetate by heating with acetic anhydride at 150–160° for three hours; the propionate with propionyl chloride at 90–100° for three hours; and the butyrate with butyryl chloride at 110–120° for three hours. The usual procedure of the Schotten–Baumann reaction was followed in preparing the benzoate with benzoyl chloride.

Preparation of Trichloromethyl-*m*-chlorophenylcarbinol.—From a mixture of 46 g. of *m*-chlorobenzaldehyde, 60 g. of chloroform and 4 g. of powdered potassium hydroxide a yield of 18 g. of the carbinol of d^{20}_{20} 1.475 was obtained. It boiled at 182–183° at 24 mm. It is insoluble in water but readily soluble in ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform, carbon tetrachloride and carbon bisulfide.

Anal. Calcd. for $C_8H_6OCl_4$: Cl, 54.58. Found: Cl, 54.42.

ESTERS OF TRICHLOROMETHYL-*m*-CHLOROPHENYLCARBINOL

		Formula	Analyses for Cl, % Calcd.	Found
1	Acetate	$C_{10}H_8O_2Cl_4$	46.98	46.88
2	Propionate	$C_{11}H_{10}O_2Cl_4$	44.89	44.76
3	Butyrate	$C_{12}H_{12}O_2Cl_4$	42.99	43.03
4	Benzoate	$C_{15}H_{10}O_2Cl_4$	38.98	38.86

	B. p., °C.	Mm.	M. p., °C.	d^{20}_{20}
1			59–60	
2	172–3	12		1.413
3	183–4	10		1.494
4			92–93	

The acetate was recrystallized from 75% acetic acid and the benzoate from 95% alcohol. The acetate and benzoate were insoluble in water, sparingly soluble in methyl and ethyl alcohols, readily soluble in benzene, acetone, ether, chloroform, carbon tetrachloride and carbon bisulfide. The propionate and butyrate differed only in that they were also readily soluble in methyl and ethyl alcohols.

Preparation of Tribromomethyl-*m*-chlorophenylcarbinol.—From a mixture of 46 g. of *m*-chlorobenzaldehyde, 130 g. of bromoform and 4 g. of potassium hydroxide a yield of 40 g. of the carbinol was obtained. It boiled at 207–208° at 12 mm. It is a very viscous liquid of d^{20}_{20} 2.903. It is insoluble in water but readily soluble in ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform, carbon tetrachloride, and carbon disulfide.

Anal. Calcd. for $C_8H_6OClBr_3$: Cl, 9.01; Br, 60.96. Found: Cl, 9.03; Br, 60.82.

ESTERS OF TRIBROMOMETHYL-*m*-CHLOROPHENYLCARBINOL

		Formula	Chlorine, % Calcd.	Chlorine, % Found	Bromine, % Calcd.	Bromine, % Found
1	Acetate	$C_{10}H_8O_2ClBr_3$	8.14	8.24	55.08	55.18
2	Propionate	$C_{11}H_{10}O_2ClBr_3$	7.89	7.96	53.36	53.26
3	Butyrate	$C_{12}H_{12}O_2ClBr_3$	7.67	7.74	51.86	51.96
4	Benzoate	$C_{15}H_{10}O_2ClBr_3$	7.13	7.29	48.21	48.27

	B. p., °C.	Mm.	M. p., °C.	d^{20}_{20}
1			100–101	
2			61–62	
3	193	25		1.582
4			114–115	

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

The acetate, propionate and benzoate were insoluble in water, sparingly soluble in methyl and ethyl alcohols and readily soluble in benzene, acetone, ether, chloroform, carbon tetrachloride and carbon disulfide. The butyrate differed only in that it was readily soluble in methyl and ethyl alcohols.

Preparation of Trichloromethyl-*p*-tolylcarbinol.—From a mixture of 40 g. of *p*-tolualdehyde, 60 g. of chloroform and 4 g. of potassium hydroxide a yield of 20 g. of the carbinol was obtained. It boiled at 155–157° at 8 mm. It crystallized readily on standing and melted at 58–59°. It is insoluble in water but soluble in ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform, carbon tetrachloride and carbon disulfide.

Anal. Calcd. for $C_9H_9OCl_3$: Cl, 44.42. Found: Cl, 44.31.

ESTERS OF TRICHLOROMETHYL-*p*-TOLYLCARBINOL

		Formula	Analyses for Cl, % Calcd.	Found
1	Acetate	$C_{11}H_{11}O_2Cl_3$	37.79	37.65
2	Propionate	$C_{12}H_{13}O_2Cl_3$	36.01	35.98
3	Butyrate	$C_{13}H_{15}O_2Cl_3$	34.36	34.23
4	Benzoate	$C_{16}H_{13}O_2Cl_3$	30.79	30.71

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(1) Howard and Castles, THIS JOURNAL, **57**, 376 (1935).

(2) Howard, *ibid.*, **57**, 2317 (1935).

	B. p., °C.	Mm.	M. p., °C.	d^{20}_{20}
1			105–106	
2			59–60	
3	172–173	11		1.082
4			94–95	

The acetate and benzoate were recrystallized from 95% alcohol, the propionate from 60% alcohol.

The acetate, propionate, and benzoate were insoluble in water, sparingly soluble in methyl and ethyl alcohols and readily soluble in benzene, acetone, ether, chloroform, carbon tetrachloride and carbon disulfide. The butyrate differed in that it was also readily soluble in methyl and ethyl alcohols.

Preparation of Tribromomethyl-*p*-tolylcarbinol.—From a mixture of 40 g. of *p*-tolualdehyde, 130 g. of bromoform and 4 g. of potassium hydroxide a yield of 32 g. was obtained. It boiled at 183–186° at 4 mm. and was difficult to distill without undue decomposition. It crystallized on standing and on recrystallization from 6 *N* acetic acid melted at 61–62°.

It is insoluble in water but readily soluble in ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform, carbon tetrachloride and carbon disulfide.

Anal. Calcd. for $C_8H_9OBr_3$: Br, 64.31. Found: Br, 64.28.

ESTERS OF TRIBROMOMETHYL-*p*-TOLYLCARBINOL

		M. p., °C.	Formula	Analyses for Br, % Calcd.	Analyses for Br, % Found
1	Acetate	149–150	$C_{11}H_{11}O_2Br_3$	57.81	57.63
2	Propionate	170	$C_{12}H_{13}O_2Br_3$	55.90	55.83
3	Butyrate	63	$C_{13}H_{15}O_2Br_3$	54.14	53.98
4	Benzoate	126	$C_{16}H_{13}O_2Br_3$	50.28	50.11

These esters were all recrystallized from 95% alcohol. They are all insoluble in water, slightly soluble in ethyl and methyl alcohols and very soluble in benzene, acetone, ether, chloroform, carbon tetrachloride and carbon disulfide.

The average yield of all esters prepared was 85%.

Summary

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

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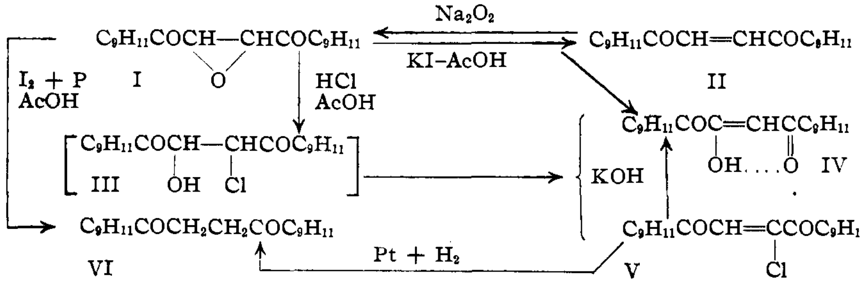
Reductions of Di-(trimethylbenzoyl)-ethylene Oxide

BY ROBERT E. LUTZ AND JOHN L. WOOD

This investigation was made because of interest in the effect of substitution of mesityl groups for phenyls on the reactivity of the unsaturated 1,4-diketones and related systems. As was anticipated, many reactions of di-(trimethylbenzoyl)-ethylene oxide are similar or parallel to those of the diphenyl analog which have been described in preceding papers.[1]

Di-(trimethylbenzoyl)-ethylene oxide (I) can be prepared easily in the usual way by the action of sodium peroxide on the unsaturated 1,4-diketone, II.



Attempts to convert the oxide into a chlorohydrin (as was done in the dibenzoyl series) were unsuccessful. Under the usual reaction conditions dimesitylbutanetrione enol IV was obtained, but there was produced in addition small amounts of di-(trimethylbenzoyl)-chloroethylene, V, the structure of which was shown by analysis, hydrolysis to the enol IV, and reduction to di-(trimethylbenzoyl)-ethane, VI. Undoubtedly the chlorohydrin III is formed in these reactions, but it is evidently less stable than the diphenyl analog and decomposes spontaneously in the two possible ways with loss of hydrogen chloride or water. In this connection it is significant that di-(trimethylbenzoyl)-chloroethane, VII, is distinctly less stable than the dibenzoyl analog and easily loses hydrogen chloride to give the unsaturated 1,4-diketone II.

Reduction of the oxide (I) with potassium io-

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(1) Lutz and Wilder, THIS JOURNAL, **56**, (a) 1987, (b) 2065 (1934).