

Acknowledgment.—The authors are pleased to acknowledge their indebtedness to Dr. M. J. Shear, Dr. Jonathan L. Hartwell, and Dr. Albert J. Dalton for valuable suggestions and encouragement, to Merck and Company for the supply of 4-methyl-2-hydroxyethylthiazole, and to the National Cancer Institute for a grant-in-aid in support of this work.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY OF
CARSON-NEWMAN COLLEGE

JEFFERSON CITY, TENN. RECEIVED DECEMBER 3, 1947

Density Data for Two Methylchlorosilanes

By E. W. BALIS, W. F. GILLIAM, E. M. HADSELL, H. A. LIEBHAFSKY AND E. H. WINSLOW

Density data for dimethyldichlorosilane (DDS) and for methyltrichlorosilane (MTS), which were used several years ago to lay the foundation for a successful routine method to aid in controlling chlorosilane distillation, are given below. There appear to be no comparable earlier published data.

Pure Compounds.—As a by-product of painstaking distillation work done in 1943, the details of which are to be published later, the following densities (g./ml. at 25°) were obtained on chlorosilanes among the purest ever prepared here: for DDS, 1.0663; for MTS, 1.2691. The corresponding weight percentages of chlorine by hydrolysis were: DDS, 54.93 vs. 54.95 (theor.); MTS, 71.19 vs. 71.17 (theor.), the deviations from the theoretical being comparable with the possible uncertainty in the atomic weight of silicon.¹

Temperature Coefficients.—For the interval 25–30°, dilatometric measurements on the best materials available from the pilot plant in 1944² yielded the following values for the change in density with temperature (g./ml./°C.): DDS, 0.00145; MTS, 0.00173. These precise results are in good agreement with older data (0.0015 and 0.0018, respectively) obtained on a Westphal balance.

The 50-ml. dilatometer was designed and manipulated to give a precision better than 0.005% in a density determination. Special techniques were required to mitigate the difficulty of handling the methylchlorosilanes, and the dilatometer itself did not change weight by more than a few tenths milligram—if at all—during the measurements.

Volume Additivity.—In order to establish whether any volume change on mixing DDS

and MTS is negligible for purposes of routine control, the routine density-balance (to be described elsewhere) was used on DDS² and MTS², and on six solutions carefully prepared by weight therefrom. The measured densities are given in Table I alongside densities calculated for the solutions on the assumption of volume additivity.

TABLE I
VOLUME ADDITIVITY OF DDS AND MTS AT 27°

Weight fraction DDS	Measured densities, g./ml.	Calculated densities, g./ml.
MTS	1.2593
DDS	1.0618
0.81450	1.0939	1.0936
.66014	1.1217	1.1216
.42930	1.1665	1.1662
.42930	1.1659	1.1662
.29397	1.1940	1.1940
.14036	1.2275	1.2273

The measured densities tend to exceed those calculated by an amount comparable with the experimental error; consequently, volume additivity could permissibly be assumed in the control work. The data in Table I indicate that this pair of methylchlorosilanes belongs among those for which volume additivity comes closest to being realized, which suggests that a thorough investigation of these and other chlorosilanes along lines laid down by Young³ would be welcome.

(3) Young, "Distillation Principles and Processes," Macmillan and Co., Limited, London, England, 1922, pp. 31 *et seq.*

RESEARCH LABORATORY

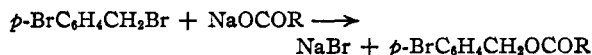
GENERAL ELECTRIC COMPANY

SCHENECTADY, NEW YORK RECEIVED DECEMBER 17, 1947

p-Bromobenzyl Bromide in the Identification of Some Aromatic Carboxylic Acids

By B. A. FIEKERS AND E. M. DI GERONIMO

As part of a study of suitable derivatives for the identification of organic acids, *p*-bromobenzyl esters of benzoic acid, some of its derivatives and similar acids have been prepared and characterized in this Laboratory. The general preparation of these esters is given by the equation.



Experimental

***p*-Bromobenzyl Bromide.**—This was prepared from *p*-bromotoluene by bromination of the side-chain, using ultraviolet light, quartzware and heat.¹ The solid product was purified by recrystallization from alcohol until a constant melting point (61.5°) was obtained.

Preparation of the Esters.—The sodium salt of the acid was formed by dissolving a slight excess of the acid in 5 ml. of 0.5 *M* sodium carbonate solution. The mixture was refluxed on a steam-bath and water was added sparingly, when necessary, until solution was complete. 1.25 g.

(1) Weizmann and Patai, *THIS JOURNAL*, **68**, 150 (1946).

(1) Baxter, Guichard and Whytlaw-Gray, *THIS JOURNAL*, **69**, 731 (1947). The chlorine titrations were not of atomic weight precision. Correction of the final average chlorine contents for all conceivable sources of error would lower the percentages by 0.02; taking 28.10 as the atomic weight of silicon would produce the same change in the theoretical values. The density data have been corrected for all conceivable sources of error.

(2) The methylchlorosilanes used in the work on temperature coefficients and volume additivity were sufficiently pure for these purposes as the following data show. DDS, density at 25°, 1.065 g./ml.; wt. % Cl by hydrolysis, 54.72, 54.64. MTS, density at 25°, 1.263 g./ml.; wt. % Cl by hydrolysis, 70.64, 70.89.

(0.005 mole) of *p*-bromobenzyl bromide and 10 ml. of 95% ethyl alcohol were then added and the mixture was refluxed. The refluxing was continued for an hour after the solution had again cleared. When necessary, more alcohol was added in order to bring the reagent into solution. The solution was then cooled rapidly in a stream of cold water and finally in an ice mixture. The esters were filtered and recrystallized from alcohol until constant melting points were obtained. Departures from this general procedure are noted in Table I. All given temperatures are uncorrected.

Analysis.—The Parr bomb was used in conjunction with the Volhard titration method.

TABLE I

p-BROMOBENZYL ESTERS OF SOME AROMATIC CARBOXYLIC ACIDS

Acid	Obs., m. p., °C.		Halogen, %	
	Acid	Ester	Calcd. Ester	Found Ester
Benzoic	122	45	27.47	27.54
<i>o</i> -Hydroxybenzoic	159	71	26.04	26.20
<i>m</i> -Hydroxybenzoic	201	97 ^a	26.04	26.10
<i>p</i> -Hydroxybenzoic	213	146	26.04	26.04
<i>o</i> -Nitrobenzoic	147	69	23.79	23.87
<i>m</i> -Nitrobenzoic	141	114	23.79	23.90
<i>p</i> -Nitrobenzoic	242	121	23.79	23.93
Cinnamic	133	79 ^{b,d}	25.21	25.29
<i>o</i> -Nitrocinnamic	240	98 ^{e,d}	22.08	22.19
<i>p</i> -Nitrocinnamic	286	136 ^d	22.08	22.24
<i>o</i> -Toluic	104	46	26.25	26.33
<i>m</i> -Toluic	109	Oil		
<i>p</i> -Toluic	179	72 ^e	26.25	26.29
<i>o</i> -Chlorobenzoic	142	57	35.47	35.59
Anisic	184	95	24.89	25.01

^a Crystallized with partial evaporation. ^b 5 ml. excess of water required to dissolve the salt. ^c Potassium salt of the acid was prepared from potassium carbonate.

^d Acetone replaced alcohol as solvent for this reaction.

^e Slightly more than 5 ml. excess of water required to dissolve the salt.

Acknowledgment.—The authors are pleased to acknowledge an experimental survey of this problem done by J. Benotti under the direction of T. L. Kelly.

DEPARTMENT OF CHEMISTRY
COLLEGE OF THE HOLY CROSS
WORCESTER 3, MASS.

RECEIVED DECEMBER 19, 1947

cis and *trans* Forms of β -(*p*-Chlorophenyl)-cinnamic Acid

BY REYNOLD C. FUSON AND HAROLD L. JACKSON

In view of results communicated to us privately by Dr. F. Bergmann,¹ we have modified the procedure of Alexander, Jacoby and Fuson² for the preparation of β -(*p*-chlorophenyl)-cinnamic acid by the Reformatsky method and have been able to isolate the acid in *cis* and *trans* modifications.

In the revised procedure 5 g. of crude ethyl β -phenyl- β -(*p*-chlorophenyl)- β -hydroxypropionate, made by the method of Alexander, Jacoby and Fuson,² was heated under reflux for two hours with 50 ml. of glacial acetic acid and 25 ml. of acetic anhydride. The acetic acid and acetic

anhydride were removed by distillation at the aspirator. The residue was distilled under 1–2 mm. pressure, and the product that distilled between 65 and 69° was collected.

This distillate was treated with 10 g. of sodium hydroxide dissolved in 20 ml. of water and 10 ml. of ethanol. The alkaline hydrolysis mixture was heated under reflux for twenty hours. When the cooled solution was poured into 100 ml. of cold water, a white crystalline solid precipitated. The mixture was made acid with dilute hydrochloric acid. The product melted over a range of 140 to 157°; yield, 3.4 g. Fractional crystallization of this product from dilute ethanol yielded two isomers; one melted at 164.8–165.7° and the other at 173.0–173.8°. Mixed melting point determinations with samples, kindly supplied by Dr. Bergmann, showed these acids to be identical with his low-melting and high melting compounds.

Infrared absorption spectra³ indicated that the two forms were *cis* and *trans* isomers. The presumption that the low-melting isomer was the *cis* modification was supported by the observation that it was more soluble in diethyl ether than the high-melting isomer.

From these results it appears that the compound described by Alexander, Jacoby and Fuson² and melting at 168° must have been an impure sample of the *trans* acid, the contaminant being presumably the *cis* isomer.

(3) Infrared absorption spectra were determined by Mrs. J. L. Johnson.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

RECEIVED FEBRUARY 16, 1948

2-Benzofuryllithium and 3-Benzofuryllithium

BY HENRY GILMAN AND DONALD S. MELSTROM

2-Bromobenzofuran does not react with magnesium, under conventional conditions, to give a Grignard reagent.¹ However, Reichstein and Baud² showed that the activated magnesium-copper alloy³ react with 3-bromobenzofuran to give, subsequent to carbonation, about 1% of 3-benzofurancarboxylic acid in addition to 28% of *o*-hydroxyphenylacetylene.

By means of the recently developed halogen-metal interconversion reaction, we have shown that 2-bromobenzofuran reacts with *n*-butyllithium to give, on carbonation, a 62% yield of pure 2-benzofurancarboxylic acid.

The yield of 3-benzofurancarboxylic acid, from 3-bromobenzofuran and *n*-butyllithium, was 12%. However, this reaction was particularly interesting because of the formation of appreciable quantities of the isomeric 2-benzofurancarboxylic acid. It is probable that the 2-acid was formed from the 3-bromo compound in essential accordance with

(1) E. W. Smith, unpublished studies.

(2) Reichstein and Baud, *Helv. Chim. Acta*, **20**, 892 (1937).

(3) Gilman, Peterson and Schulze, *Rec. trav. chim.*, **47**, 19 (1928).

(1) See Bergmann, *This Journal*, **70**, 1612 (1948).

(2) Alexander, Jacoby and Fuson, *ibid.*, **57**, 2208 (1935).