(0.005 mole) of *p*-bromobenzyl bromede 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. Acid | Obs., m. p., °C. Ester | Halogen, % Calcd. Ester | Halogen, % Found Ester |
|---|---|---|---|---|
| Benzoic | 122 | 45 | 27.47 | 27.54 |
| *o*-Hydroxybenzoic | 159 | 71 | 26.04 | 26.20 |
| *m*-Hydroxybenzoic | 201 | 97[a] | 26.04 | 26.10 |
| *p*-Hydroxybenzoic | 213 | 146 | 26.04 | 26.04 |
| *o*-Nitrobenzoic | 147 | 69 | 23.79 | 23.87 |
| *m*-Nitrobenzoic | 141 | 114 | 23.79 | 23.90 |
| *p*-Nitrobenzoic | 242 | 121 | 23.79 | 23.93 |
| Cinnamic | 133 | 79[b,d] | 25.21 | 25.29 |
| *o*-Nitrocinnamic | 240 | 98[c,d] | 22.08 | 22.19 |
| *p*-Nitrocinnamic | 286 | 136[d] | 22.08 | 22.24 |
| *o*-Toluic | 104 | 46 | 26.25 | 26.33 |
| *m*-Toluic | 109 | Oil | | |
| *p*-Toluic | 179 | 72[e] | 26.25 | 26.29 |
| *o*-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.

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

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## *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 Fuson[2] 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 spectra[3] 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 Fuson[2] and melting at 168° must have been an impure sample of the *trans* acid, the contaminant being presumably the *cis* isomer.

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(1) See Bergmann, THIS JOURNAL, **70**, 1612 (1948).

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

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

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

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## 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 Baud[2] showed that the activated magnesium–copper alloy[3] 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

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(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).