p-aminobenzenesulfonyl urea. The therapeutic properties of this compound and some of its salts are under investigation.

*p*-Acetaminobenzenesulfonyl Ethyl-isourea.—In a fiveliter flask provided with a mechanical stirrer was placed 600 g. of anhydrous potassium carbonate, 2 liters of acetone and 100 cc. of water. The suspension of carbonate-acetone-water was stirred and cooled in an ice-bath. To this suspension 272 g. (2.2 moles) of ethyl-isourea hydrochloride was added gradually over a period of one-half hour. With each addition some water was added until the total amount was 400 cc. The ice-bath was removed after the addition and the reaction mixture stirred at room temperature for four hours.

The reaction material was then poured into five liters of water, and the crude product filtered and washed. The weight of the crude dried product was 458 g. (87% yield). It crystallized from 50% acetic acid as white needles and melted at  $223-224^{\circ}$ .

Anal. Calcd. for  $C_{11}H_{15}O_4N_8S$ : N, 14.71. Found: N, 14.76, 14.79.

p-Aminobenzenesulfonyl Urea.—One mole (285 g.) of p-acetaminobenzenesulfonyl ethyl-isourea (crystallized once from dilute acetic acid) was placed in a two liter flask and covered with 700 cc. of concentrated hydrochloric acid. The isourea first dissolved and then reprecipitated as the hydrochloride. The flask was immersed in a boiling waterbath and the reaction mixture stirred until solution took place (fifteen to twenty minutes). Decolorizing charcoal was added while still hot and the solution was filtered. After the addition of an equal volume of alcohol the filtrate was set aside to crystallize. The dried crystalline product weighed 200 g. (80% yield). White needles were produced when the product was recrystallized from dilute acetic acid. The compound melted with gas formation (ammonia) at 140–146°.<sup>2,3</sup>

Anal. Calcd. for  $C_7H_9O_8N_8S$ : N, 19.54. Found: N, 19.53, 19.59.

Salts of p-Aminobenzenesulfonyl Urea.—The ammonium, potassium and sodium salts were prepared by treating slightly more than one equivalent of the p-aminobenzenesulfonyl urea with one equivalent of the metallic carbonate in 50% alcohol. After the addition of the carbonate, ether was added to produce the maximum yield of the salt.

Ammonium Salt. Anal. Calcd. for  $C_7H_{12}O_3N_4S$ : N, 24.12. Found: N, 24.09, 24.19.

**Potassium Salt.** Anal. Calcd. for C<sub>7</sub>H<sub>8</sub>O<sub>3</sub>N<sub>8</sub>SK: N, 16.59. Found: N, 16.54, 16.56.

Sodium Salt. Anal. Caled. for C<sub>7</sub>H<sub>8</sub>O<sub>3</sub>N<sub>8</sub>SNa: N, 17.71. Found: N, 17.59, 17.64.

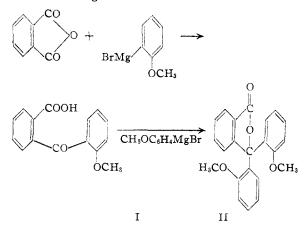
Acknowledgment.—The author thanks the Monsanto Chemical Company for a generous supply of *p*-acetoaminobenzenesulfonyl chloride.

DEPARTMENT OF CHEMISTRY SWARTHMORE COLLEGE SWARTHMORE, PA. RECEIVED JUNE 16, 1942

## A Synthesis of 2-(2'-Methoxybenzoyl)-benzoic Acid

#### BY BRADFORD P. GEYER<sup>1</sup>

In the course of a projected synthesis of 1-hydroxyfluorenone it became necessary to prepare a quantity of 2-(2'-methoxybenzoyl)-benzoic acid (I). This keto acid was prepared previously by Sieglitz<sup>2</sup> by methylation of 2-salicylylbenzoic acid. The synthesis of I has now been accomplished, using phthalic anhydride and *o*-bromoanisole as starting materials.



A by-product formed in the Grignard reaction of *o*-anisylmagnesium bromide with phthalic anhydride is 2,2-di-*o*-anisylphthalide (II), reported earlier by Ferrario<sup>3</sup> and by Blicke and Weinkauff.<sup>4</sup>

# Experimental

Before preparing the Grignard reagent, o-anisylmagnesium bromide, the flask containing 9.6 g. (0.4 mole) of magnesium was heated with a low, free flame to expel traces of moisture. A 20-ml. portion of anhydrous diethyl ether, freshly distilled from an ethereal ethylmagnesium bromide solution and containing 10 drops of ethyl bromide, was placed in the flask with the magnesium. To this mixture, agitated by means of a mercury-seal stirrer, 63 g. (0.34 mole) of o-bromoanisole in 100 ml. of diethyl ether, the latter likewise freshly distilled from the same ethylmagnesium bromide solution, was added dropwise. After complete addition of the o-bromoanisole, the solution of the arylmagnesium halide was heated under reflux for one-half hour. This Grignard reagent was then introduced slowly, dropwise, to a vigorously stirred, hot solution of 37 g. (0.25 mole) of phthalic anhydride in 600 ml. of thiophene-free benzene, ether being removed simultaneously by distillation. Pale yellowish-white solid formed immediately. After the addition of all of the re-

<sup>(2)</sup> The properties of this compound as given by Geigy, British Patent 538,884, are not in agreement with those recorded here.

<sup>(3)</sup> Since the completion of this work, *p*-aminobenzenesulfonyl urea has been reported by Roblin and his co-workers, THIS JOURNAL. 64, 1683 (1942).

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<sup>(2)</sup> Sieglitz. Ber., 57, 316 (1924).

<sup>(3)</sup> Ferrario. Gazz. chim. ital., 41, I. 1 (1911).

<sup>(4)</sup> Blicke and Weinkauff, THIS JOURNAL, 54, 1452 (1932).

agent, the resulting mixture was stirred for several minutes longer, heated under reflux for two hours and then allowed to cool and stand overnight at room temperature. The reaction flask was cooled in an ice-waterbath and the pale yellow product decomposed with dilute hydrochloric acid. A 300-ml. quantity of diethyl ether was added to dilute the benzene solution of 2-(2'-methoxybenzoyl)-benzoic acid and 2,2-di-o-anisylphthalide. The ether-benzene layer was extracted with potassium carbonate solution, and the carbonate extract then run dropwise into vigorously stirred, ice-cold hydrochloric acid. In this way the keto acid first separated as a pasty mass which soon became solid. This pale fawn-colored, granular solid was filtered off and washed with cold diethyl ether. Upon drying, 34.5 g. (54%) of crude acid was obtained. After four recrystallizations from glacial acetic acid, 2-(2'-methoxybenzoyl)-benzoic acid was secured in the form of short, colorless, small prisms; m. p. 143-143.5°; yield 30 g. (47%), based on phthalic anhydride). Sieglitz<sup>2</sup> reported 144-145° as the m. p. of this acid.

Anal. Neutralization equivalent, calcd. for  $C_{18}H_{12}O_4$ : 256.2. Found: 257.9.

From the above-mentioned benzene-ether layer, after the potassium carbonate extraction and concentration of the solution to a small volume, a colorless powder was obtained. This material, 2,2-di-o-anisylphthalide, when recrystallized three times from glacial acetic acid, formed small, colorless crystals, m. p. 148-149°; yield 10.5 g. (18%, based on o-bromoanisole). The phthalide was found to be soluble in concentrated sulfuric acid with a very deep violet color which gradually changed to ruby-red and finally to orange.

DEPARTMENT OF CHEMISTRY UNIVERSITY OF WASHINGTON SEATTLE, WASHINGTON RECEIVED JUNE 24, 1942

## The Dissociation of Hexaarylethanes. XIV.<sup>1</sup> Ethanes Derived from Mixtures of Triaryl Halides

By C. S. MARVEL AND CHESTER M. HIMEL

Since symmetry seemed to be important in connection with the influence of substituents on the degree of dissociation of triarylmethyls, it occurred to us that treating an equimolecular mixture of two triarylmethyl halides with silver might produce a truly unsymmetrical ethane rather than a mixture of ethanes. Table I contains a list of some mixtures of chlorides which were thus treated and the degree of dissociation calculated from magnetic susceptibility measurements on the assumption that a mixed ethane was formed. In one case (the first in the table) the mixed ethane was prepared by mixing preformed solutions of the individual ethanes rather than by action of silver on the mixed halides.

(1) For the thirteenth communication see J. Org. Chem., 7, July (1942).

TABLE I								
DISSOCIATION	of	Some	MIXED	HEXAARYLETHANES				

Chlorides used	- x×	α at 0.1 M, %	α of corre- sponding ethane at 0.1 M, %	Ref.
o-Chlorophenyldiphenyl- methyl o-Bromophenyldiphenyl- methyl	0.6620	<b>14</b> ≠ 2	$\begin{cases} 12 \neq 1 \\ 17 \neq 1 \end{cases}$	1 1
o-Tolyldiphenylmethyl α-Naphthyldiphenylmethyl	. 6320	26 <b>±</b> 2	$\begin{cases} 25 \ \pm 1 \\ 27 \ \pm 2 \end{cases}$	2 3
o-Tolyldiphenylmethyl Di-o-tolylphenylmethyl	.6282	27 <b>±</b> 2	$\begin{cases} 25 \neq 1 \\ 82 \neq 2 \end{cases}$	2 4
Tri- <b>p</b> -diphenylmethyl ) Tri-β-naphthylmethyl )	.6765	25 <b>±</b> 3ª	$\begin{cases} 25 \neq 5 \\ 25 \neq 5 \end{cases}$	3 3
p-t-Amylphenyldiphenyl- methyl Phenyl-di-p-t-amylphenyl- methyl	.6985	3.5 <b>±</b> 1	$\begin{cases} 8.0 \neq 1 \\ 9.0 \neq 1 \end{cases}$	4 4
Tri-p-t-butylphenylmethyl p-t-Butylphenyldiphenyl- methyl	. 6997	3.5 = 1	$\begin{cases} 20 \neq 4 \\ 7.5 \neq 1 \end{cases}$	4 4

<sup>a</sup> The actual measurement was made at 0.025 M and the dissociation at this concentration was  $43 \pm 4\%$ . The value in the table was calculated by means of the mass law.

The method and apparatus have been described in previous papers in this series. It can be seen readily that the observed degrees of dissociation are not the average of the two simple ethanes, but in general are lower than this value. There are several equilibria possible in this complicated system and a complete appraisal of the significance of these experimental results will not be possible until these equilibria are more thoroughly studied. Since it seems unlikely that this can be done soon, these results are recorded.

(2) Marvel, Mueller, Himel and Kaplan. This Journal, 61, 2771 (1939).

Marvel, Shackleton, Himel and Whitson. *ibid.*, **64**, 1824 (1942).
Marvel, Kaplan and Himel, *ibid.*, **63**, 1892 (1941).

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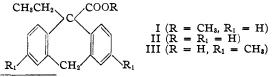
URBANA, ILLINOIS

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### The Reaction of Furoic Acid with Aromatic Compounds. III

By Charles C. Price, E. C. Chapin and Martin Rieger

The isolation of methyl 9-ethyl-9,10-dihydro-9anthroate (I) from the aluminum chloride catalyzed reaction of methyl furoate with benzene<sup>1</sup> suggests the presence of the corresponding acid (II) in the mixture obtained from a similar re-



(1) Price and Huber. THIS JOURNAL. 64, 2136 (1942).