

Chlorobenzene (22.5 g., 0.20 mole) was introduced, and this was followed by a liquid ammonia solution of 0.20 mole of potassium amide, siphoned over from another flask^{8b} with good stirring. In one-half hour, 10 g. of ammonium bromide was added to stop further reaction, and the ammonia allowed to evaporate. Water (150 ml.) was introduced, and the oily mixture acidified with hydrochloric acid and extracted with ether. The ethereal solution was washed with a little dilute sodium bicarbonate to remove acid, dried over anhydrous sodium sulfate, and distilled, to obtain ether, a small amount of chlorobenzene (at 760 mm.) and then phenylacetonitrile, *b. p.* 90–95° (7 mm.) (3.62 g., 31%) and diphenylacetonitrile, *b. p.* 175–183° (7 mm.) (2.7 g., 28%). After several crystallizations from ligroin and from methanol, the latter melted at 73.5–74.5°, and at the same temperature when mixed with diphenylacetonitrile prepared by the method of Anschütz and Römig.⁸

Anal. Calcd. for C₁₄H₁₁N: C, 87.01; H, 5.74; N, 7.24. Found: C, 86.76; H, 5.89; N, 7.23.

Phenylation of Propionitrile.—In the same manner as above and with fifth molar quantities there was obtained 11.2 g. (43%) of an oil boiling at 105–112° (8 mm.); presumably this is α -phenylpropionitrile (hydratropionitrile),

(8) Anschütz and Römig, *Ann.*, **233**, 349 (1886).

but it was not further identified. The boiling point given by Janssen⁹ is 230–232° at about 760 mm.

Summary

1. Acetonitrile reacts with sodium amide in liquid ammonia to form a salt, NaCH₂CN·xNH₃ or (CH₂CN)⁻Na⁺·xNH₃, which can be alkylated to mono, di and trisubstituted acetonitriles, by reaction with an alkyl halide or an alkyl *p*-toluenesulfonate. Under the experimental conditions, very little if any sodium acetamidine can be formed.

2. Potassium acetonitrile can be catalytically phenylated in liquid ammonia to give phenylacetonitrile and diphenylacetonitrile.

3. Ethyl benzoate reacts with sodium acetonitrile to form sodium benzoate and sodium benzoylacetonitrile.

(9) Janssen, *ibid.*, **250**, 137 (1889).

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Some Analogs of Benzyl Benzoate¹

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A survey of the chemical literature revealed the fact, to the best of our findings, that nothing is known about benzyl benzoate derivatives possessing either chlorine or methyl groups in the aromatic nuclei. Recent developments in this Laboratory necessitated the synthesis of several of these esters.

Gomberg and Buchler,⁵ as well as the present authors,⁶ have investigated the reaction between benzyl chloride and aqueous sodium benzoate to form benzyl benzoate. Yields of 70–78% of the ester are readily obtainable when this reaction is conducted in an excess of sodium benzoate.

All of the new esters listed in Table I were synthesized after the method of Gomberg and Buchler by refluxing the appropriate benzyl chloride derivative with an aqueous solution of an excess of the suitably substituted sodium benzoate.

Experimental⁷

Materials.—The toluic acids, xylenes and *p*-chlorotoluene were obtained from the Eastman Kodak Company (white label), while the benzoic acid (reagent grade) was obtained from the Mallinckrodt Chemical Works.

The methylbenzenes were chlorinated to the corresponding benzyl chlorides according to the method of Kharasch

and Brown.⁸ Using 2 moles of the corresponding methylbenzenes, 1 mole of sulfuryl chloride, 0.005 mole of benzoyl peroxide and 0.7 mole of carbon tetrachloride, *p*-chlorotoluene gave an 81% yield of *p*-chlorobenzene, *m. p.* 26–27°, and of 95.9 purity, as shown by analysis for chlorine. In addition, 18.8 g. of *p*-xylene dichloride, *m. p.* 99.5–100°, was formed; ClCH₂C₆H₄CH₂Cl: Cl, calcd. 40.5; found 40.2. The *p*-, *m*- and *o*-xylenes gave yields of 79, 72 and 73%, with a purity of 92.4, 98.4 and 96.0% and a refractive index *n*^{20D} of 1.5321, 1.5340 and 1.5403, respectively. The chlorides were used in the ester reaction without further purification.

Using the procedure of v. Braun and Nelles⁹ 2,5-dimethylbenzyl chloride was made in 69.9% yield. It boiled at 74–76° (2–3 mm.); *n*^{20D} 1.5398.

Anal. Calcd. for C₉H₁₁Cl: Cl, 22.92. Found: Cl, 22.89.

A fraction of benzyl chloride (*n*^{20D} 1.5388), made by chloromethylating benzene,¹⁰ was used.

Anal. Calcd. for C₇H₇Cl: Cl, 28.01. Found: Cl, 28.01, 27.98.

The *p*-chlorobenzoic acid was prepared in 80.9% yield by the oxidation of *p*-chlorotoluene with alkaline potassium permanganate. It melted in a sealed capillary at 242°.

Anal. Calcd. for C₇H₅O₂Cl: Cl, 22.65. Found: Cl, 22.31.

Preparation of Esters.—One mole of sodium hydroxide in the form of a 16.7% aqueous solution by weight and one mole of the benzoic acid were placed in a 3-necked round-bottom flask equipped with a mercury-seal stirrer, a thermometer and a water-cooled reflux condenser. The reaction flask, immersed in an oil-bath, was brought with stirring to reflux temperature (105–110° bulk temperature) and an amount of the desired benzyl chloride, ranging from 0.25 to 0.5 mole per mole of acid, was added through

(8) Kharasch and Brown, *This Journal*, **61**, 2142 (1939).

(9) v. Braun and Nelles, *Ber.*, **67**, 1094 (1934).

(10) Lock, *ibid.*, **74**, 1568 (1941).

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(5) Gomberg and Buchler, *This Journal*, **42**, 2061 (1920).

(6) Rueggeberg, Ginsburg and Frantz, report on file at Edgewood Arsenal.

(7) Chlorine analyses were by the Parr bomb method.

TABLE I
 BENZYL BENZOATE ANALOGS

Benzoate formed	Molar ratio of sodium benzoate to chloride ^a	Boiling point		Yield, g.	n_D^{20}	d_4^{25}	Formula	Carbon, %		Hydrogen, %	
		°C.	Mm.					Calcd.	Found	Calcd.	Found
<i>p</i> -Chlorobenzyl	2.5	153	1/2-1	43.0 ^b	C ₁₄ H ₁₁ O ₂ Cl ^f	68.16	68.5-68.9	4.49	4.73-4.53
Benzyl <i>p</i> -chloro	2.0	155-160	1/2-1	42.8 ^c	1.5792	...	C ₁₄ H ₁₁ O ₂ Cl ^g	68.16	68.0-68.2	4.49	4.58-4.60
<i>o</i> -Methylbenzyl	2.0	155	1/2-1	67.9	1.5680	1.102	C ₁₄ H ₁₄ O ₂	79.62	79.4-79.6	6.24	6.42-6.56
<i>m</i> -Methylbenzyl	4.0	159-160	2	35.2	1.5632	1.092	C ₁₄ H ₁₄ O ₂	79.62	79.4-79.7	6.24	6.31-6.33
<i>p</i> -Methylbenzyl	4.0	133-135	1/4-1/2	25.8	1.5618	1.085	C ₁₄ H ₁₄ O ₂	79.62	79.7-79.9	6.24	6.57-6.65
Benzyl <i>o</i> -methyl	2.0	128	1/4-1/2	65.4	1.5662	1.102	C ₁₄ H ₁₄ O ₂	79.62	79.6-79.7	6.24	6.40
Benzyl <i>m</i> -methyl	2.0	125-127	1/2	79.0	1.5652	1.096	C ₁₄ H ₁₄ O ₂	79.62	79.60	6.24	6.21-6.35
Benzyl <i>p</i> -methyl	2.0	124-126	1/4-1/2	80.9 ^d	C ₁₄ H ₁₄ O ₂	79.62	79.6-79.7	6.24	6.23-6.31
2,5-Dimethyl-benzyl	2.0	160-161	1/2-1	60.1	1.5618	1.087	C ₁₄ H ₁₆ O ₂	79.92	79.7-79.9	6.71	6.90-7.00
<i>p</i> -Chlorobenzyl- <i>p</i> -chloro	2.7	165-166	1/2-1	56.6 ^e	C ₁₄ H ₁₀ O ₂ Cl ₂ ^h	59.81	59.8-60.0	3.59	3.71-3.75

^a One mole of sodium benzoate was used throughout, except in the preparation of benzyl *p*-chlorobenzoate, where 0.72 mole of sodium *p*-chlorobenzoate was used. ^b M. p. 58.0-58.5°. ^c M. p. 26-27°. ^d M. p. 45-47°. ^e M. p. 71.5-72.0°. ^f %Cl calcd. 14.37; found 14.43. ^g %Cl calcd. 14.37; found 13.98. ^h %Cl calcd. 25.22; found 25.08.

the reflux condenser. The reaction mixture was allowed to stir at reflux temperature (about 110°) for approximately four hours.

At the end of the reaction period, the product was transferred to a separatory funnel and the aqueous layer removed. The organic layer was washed with several portions of 5% aqueous sodium hydroxide. Usually, for runs where 1 mole of acid was used, three washings of 200 ml. each sufficed to extract the unused organic acid from the reaction product. The basic washes were followed by two water washes of about 200 ml. each. The initial water layer, the aqueous caustic extracts and the water washings were combined and extracted once with 50 ml. of carbon tetrachloride. The carbon tetrachloride extract was added to the washed organic product layer. Addition of concentrated hydrochloric acid to the combined aqueous extracts resulted in the recovery of unused benzoic acid.

The organic products were stripped free of carbon tetrachloride at about 200 mm. pressure, after which the pressure was reduced rapidly to about 0.25 to 1.0 mm. There was always encountered a small fraction of a benzyl alcohol (obtained through hydrolysis of the chloride) just prior to the distillation of the ester. All distillations of the products were carried out in a still having approximately a six-inch unpacked column of one inch diameter.

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Summary

The following benzoates have been prepared by refluxing aqueous sodium benzoate, or a nuclearly substituted derivative thereof, with benzyl chloride or some of its nuclear substitution analogs: *p*-chlorobenzyl, benzyl *p*-chloro-, *p*-chlorobenzyl *p*-chloro-, *o*-methylbenzyl-, *m*-methylbenzyl-, *p*-methylbenzyl-, benzyl *o*-methyl-, benzyl *m*-methyl-, benzyl *p*-methyl- and 2,5-dimethylbenzyl.

The substituted benzyl chlorides necessary for the syntheses of the esters were prepared by the action of sulfonyl chloride on the corresponding methylbenzenes in the presence of benzoyl peroxide as catalyst.

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2-Tolylpyrrolines and the Rearrangement and Hydrolysis of Aryl Cyclopropyl Ketimines

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The present paper is an extension of earlier work on (1) the synthesis of pyrrolines by the γ -chlorobutyronitrile-Grignard reaction,⁴ (2) the preparation of aryl cyclopropyl ketimines (VII) and their hydrochlorides (VII·HCl), (3) the rearrangement of (VII) and (VII·HCl) to the isomeric pyrrolines (XII) and pyrrolinium chlorides (XII·HCl) and (4) the rates of reaction of (VII·HCl) with water.⁵

(1) Most of the data on the ortho and meta compounds have been taken from a manuscript written by L. H. Baer in 1927-1928. Present address: U. S. Patent Office.

(2) From a thesis for the degree of Chemical Engineer, R. P. I. (1928). Present address: The B. F. Goodrich Co., Akron, Ohio.

(3) From a thesis for the degree of Ch.E. in 1931. Present address: U. S. Navy.

(4) Cloke, *THIS JOURNAL*, **51**, 1174 (1929).

(5) Cloke, *ibid.*, **62**, 117 (1940).

Experimental

I. The γ -Chlorobutyronitrile-Grignard Reaction.—The initial reaction of a Grignard reagent with γ -chlorobutyronitrile (III) follows two main paths as shown in the flow sheet. Of primary importance is the formation of the halogenomagnesium derivative of a γ -chloropropyl ketimine (VIII),⁴ which may give a pyrroline (XII) by three paths. (1) The hydrolysis of (VIII) gives the unstable ketimine⁴ (IX), which by rapid extraction, to avoid further saponification to the ketone (X), and gentle warming gives the pyrrolinium salt (XIII) and thence the pyrroline (XII) which compounds may be tautomeric. The hydrolysis procedure may give some of the ketone related to (V). (2) The pyrolysis of (VIII) gives (XII) directly,^{2,6} and therefore (VIII) and (XII) may be found together following the interaction of RMgX and (III). (3) The am-

(6) Craig, Bulbrook and Hixon, *ibid.*, **53**, 1831 (1931); Starr, Bulbrook and Hixon, *ibid.*, **54**, 3971 (1932).