To the ether solution containing the ester was added a trace of picric acid to prevent polymerization. It was then dried over magnesium sulfate, filtered and the ether removed. The residue was distilled through a six-inch helices-packed column. A 2-g. fraction boiling at 132° at 5 mm., n^{20}D 1.5285, and a 5-g. fraction boiling at 132° at 5 mm., n^{20}D 1.5310, were collected. At this point, extensive polymerization occurred and the column was filled with solid polymer. The 5-g. fraction was redistilled through a 15-cc. modified Claisen flask and 4 g. of product was obtained boiling at 110° at 1 to 2 mm., n^{20}D 1.5287. The yield of *d-s*-butyl *p*-vinylbenzoate was 8 g. (15%) $[\alpha]^{50}$D + 24.0° (α, +0.89°; 0.5568 g. in 15 cc. of benzene solution).

Anal.[3] Calcd. for $C_{12}H_{10}O_2$: C, 76.43; H, 7.89. Found: C, 76.33; H, 8.05.

Poly-*d-s*-butyl *p*-Vinylbenzoate.—In a Pyrex test-tube were placed 1 g. of pure *d-s*-butyl *p*-vinylbenzoate and a small crystal of benzoyl peroxide. After heating at 40° for three hours a hard clear transparent polymer had formed. The polymer was dissolved in 20 cc. of benzene and slowly dropped into 300 cc. of methanol with vigorous stirring. The polymer precipitated in sticky masses. These were redissolved in benzene and precipitated as before. The polymer was thus obtained as a fine powder. It was dried for three days in vacuum and then showed a softening point 155–190° in a melting point tube, $[\alpha]^{50}$D + 22.9° (α, + 0.31°; 0.1355 g. in 10 cc. of benzene), $[\eta]$ 2.88.

Anal. Calcd. for $(C_{12}H_{16}O_2)_x$: C, 76.43; H, 7.89. Found: C, 76.27; H, 7.71.

Poly-*p*-vinylbenzoic Acid.—A 0.5-g. sample of the polyester was refluxed with a solution of 4 g. of potassium hydroxide and 25 cc. of alcohol in 10 cc. of water overnight. Addition of 20 cc. of water brought the salt into the solution and then the solution was acidified with dilute hydrochloric acid. The white gelatinous precipitate which separated was filtered, washed three times with water and dried. The dry polymer was then extracted further with water to remove salts and excess mineral acid and again dried. The polyacid softened above 350°. It was insoluble in benzene, chloroform and nitromethane but did dissolve in dimethylformamide. The optical rotation of this solution was zero, thus showing that no asymmetric synthesis had occurred during the polymerization.

Anal. Calcd. for $(C_9H_8O_2)_x$: C, 72.97; H, 5.44. Found: C, 72.87; H, 5.80.

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ortho- and *para*-Diethylbenzenes

BY J. V. KARABINOS, K. T. SERIJAN AND L. C. GIBBONS

As part of a project involving the synthesis and purification of 26 aromatic hydrocarbons,[1] six-gallon quantities of *o*- and *p*-diethylbenzenes were produced by the condensation of the appropriate ethylphenylmagnesium bromide with diethyl sulfate. In exploratory work, both hydrocarbons were prepared by the Grignard reaction and also by the Wurtz–Fittig reaction between the appropriate chloroethylbenzenes and ethyl bromide. A comparison of the yields, as shown in Table I, indicated the desirability of using the Grignard reaction to produce the hydrocarbons. The products were purified by distillation through a 100-theoretical plate column.

The pure bromoethylbenzenes were obtained by careful distillation of a mixture of *o*- and *p*-bromoethylbenzenes ("Alkazene 40") through a 40-theoretical plate column. The chloroethyl-

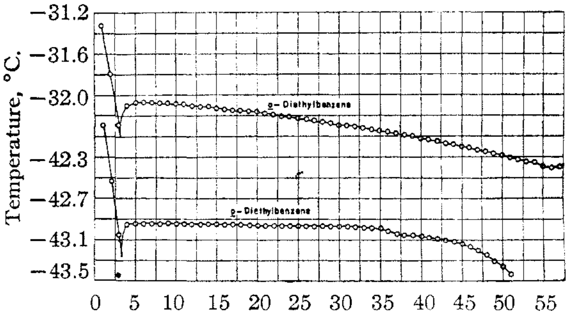

Fig. 1.—Time-temperature freezing curves of *o*- and *p*-diethylbenzene.

TABLE II

PHYSICAL PROPERTIES, YIELDS AND ANALYSES OF *o*- AND *p*-DIETHYLBENZENE

		o-Diethylbenzene	*p*-Diethylbenzene
F. p., °C.		−32.07	−42.95
B. p., °C. (760 mm.)		183.5	183.8
Density, g./ml., 20°		0.8790	0.8620
n^{20}D		1.5034	1.4950
Anal., % calcd.	Carbon	89.48	89.48
	Hydrogen	10.52	10.52
Anal., % found	Carbon	89.69	89.39
	Hydrogen	10.57	10.54
% Yields from bromoethylbenzenes[a]		49	58
% Yields from chloroethylbenzenes[b]		25	16

[a] Grignard reaction. [b] Wurtz–Fittig reaction.

TABLE I

PROPERTIES AND OXIDATION PRODUCTS OF THE ARYL HALIDES

-Ethylbenzene	F. p., °C.	B. p., °C.	Density, g./ml., 20°C.	n^{20}D	Permanganate oxidation product, benzoic acid	M. p., °C. Obs.	M. p., °C. Lit.[a]
o-Chloro-	−82.72	179		1.5219	*o*-Chloro-	139–140	140
p-Chloro-	−62.63	184.5	1.0454	1.5179	*p*-Chloro-	238–239	242
o-Bromo-	−67.46	199.5	1.3582	1.5492	*o*-Bromo-	148–149	150
p-Bromo-	−44.16	203.5	1.3422	1.5448	*p*-Bromo-	253–254	251

[a] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, pp. 183–184.

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(3) Microanalyses by Mr. H. S. Clark, Illinois State Geological Survey.

(1) Gibbons, *et al.*, THIS JOURNAL, **68**, 1130 (1946).

benzenes were obtained by a similar distillation of "Alkazene 21."

The physical constants and oxidation products of the aryl halides are given in Table I and the physical constants, yields and analyses of the diethylbenzenes are shown in Table II. The physical properties were determined by methods previously described.[1] The time–temperature freezing curves for *o*- and *p*-diethylbenzenes are shown in Fig. 1.

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The Hydrogenolysis of Ethyl β-Benzylaminopropionate[1]

BY ALBERT M. MATTOCKS[2] AND WALTER H. HARTUNG

During the course of investigations under way in these Laboratories, we had occasion to prepare ethyl β-benzylaminopropionate, a compound previously reported by Thayer and McElvain.[3] The prospect of converting it into ethyl β-aminopropionate by hydrogenolytic debenzylation offered another route to the synthesis of β-alanine. It was observed that if the N-benzyl intermediate is treated at 13 atm. of hydrogen with a catalyst made from charcoal on which has been deposited the palladium from 0.3 g. of palladium chloride and the platinum from 0.15 g. of platinum chloride, the benzyl group is removed as toluene, and the ester of β-alanine may be isolated in excellent yields.

Experimental

Ethyl β-bromopropionate was synthesized from hydracrylonitrile according to the method of Kendall and McKenzie.[4] This, on reaction with two equivalents of benzylamine in absolute ethanol, readily precipitated almost quantitatively benzylamine hydrobromide; removal of the crystals and addition of hydrogen chloride to the filtrate, led to the crystallization of the hydrochloride of ethyl β-benzylaminopropionate, melting 146–147°, the previously recorded value.[1]

Hydrogenation was carried out as already indicated, in ethanolic solution. Removal of the catalyst, concentration of the filtrate and addition of ether caused the precipitation in yields approaching quantitative of the hydrochloride of the amino ester. The melting point of the salt was 67°, which agrees with the previously reported value[5] for the hydrochloride of ethyl β-aminopropionate. *Anal.* Found: N (Kjeldahl), 9.29 and 9.35; calculated N for $C_5H_{11}O_2N \cdot HCl$, 9.12.

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[1] Paper no. 5 on synthesis of amino acids; for no. 4 see Mattocks and Hartung, *J. Biol. Chem.*, **165**, 501 (1946).

[2] Present address: Southern Research Institute, Birmingham, Ala.

[3] Thayer and McElvain, THIS JOURNAL, **49**, 2862 (1927).

[4] Kendall and McKenzie, "Organic Syntheses," Coll. Vol. I, p. 246.

[5] Hale and Honan, THIS JOURNAL, **41**, 770 (1919).

The Preparation of Phenylsuccinonitrile

BY DAVID T. MOWRY

The preparation of phenylsuccinonitrile reported by Cobb[1] and improved by Gitsels and Wibaut[2] involves the action of an aqueous alcoholic solution of potassium cyanide on ethyl phenylpropiolate. Attempts to improve the reported 20% yield have not been successful. Attempts made to cause hydrogen cyanide or sodium cyanide to react with cinnamonitrile to give the desired product were also unsuccessful. Its preparation by the action of potassium cyanide in an alcoholic solution on ethyl α-cyanocinnamate has now been worked out as follows.

Procedure.—A solution of 50 g. (0.25 mole) of ethyl α-cyanocinnamate and 29 g. (0.45 mole) potassium cyanide in 900 cc. of 90% ethanol was refluxed for two hours in the hood (some hydrogen cyanide is evolved along with the carbon dioxide). The alcohol was evaporated whereupon 30 g. of crude product (77% yield) crystallized from the residue. Two recrystallizations from dilute ethanol gave 25 g. (64% yield) of product, m. p. 68°. The melting point was not depressed by admixture with a sample prepared by the method of Gitsels and Wibaut.[2]

If the crude product did not crystallize readily from the reaction mixture after evaporation of the ethanol, the oil was dissolved in ether solution, washed with a little water and distilled. The colorless distillated boiled at 168–170° (3 mm.) and solidified in the receiver, m.p. 66–67°.

Ethyl α-cyanocinnamate is readily available in nearly quantitative yield from benzaldehyde and ethyl cyanoacetate. This new two-step synthesis, therefore, represents a decided improvement over the laborious four-step method, giving a 12% yield from the ethyl cinnamate through the intermediates ethyl α,β-dibromo-β-phenylpropionate,[3] phenylpropiolic acid[4] and ethyl phenyl-propiolate.

[1] Cobb, *Am. Chem. J.*, **45**, 604 (1911).

[2] Gitsels and Wibaut, *Rec. trav. chim.*, **59**, 1093–1103 (1940).

[3] Abbott and Althousen, "Organic Syntheses," Coll. Vol. II, 270 (1943).

[4] Abbott, *ibid.*, p. 515.

CENTRAL RESEARCH LABORATORIES
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The Purification of Hesperidin with Formamide

BY D. E. PRITCHETT[1] AND HAROLD E. MERCHANT[2]

The purification of hesperidin has been difficult because of its inadequate solubility in methanol and pyridine, the solvents most frequently selected for this purpose. This difficulty is reflected in the 15° range in the melting points which have been recorded.[3,4,5] It has now been found that the following procedure can be success-

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[1] Research Department, California Fruit Growers Exchange, Ontario, California.

[2] Chaffey College, Ontario, California.

[3] H. Scarborough, *Biochem. J.*, **39**, 271–278 (1945).

[4] A. Hilger, *Ber.*, **9**, 26 (1876).

[5] F. Tiemann and W. Will, *ibid.*, **14**, 946 (1881).