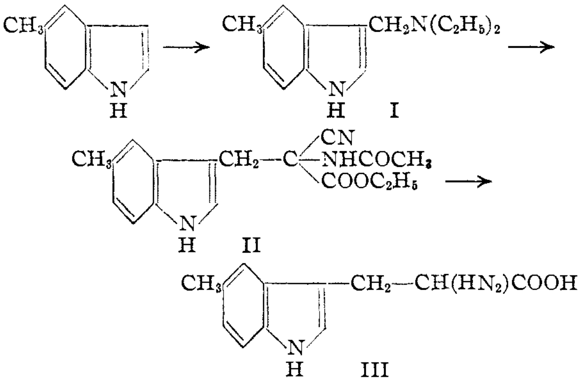
this compound but the yields in several of the steps were so low that the procedure proved to be unsatisfactory for our purpose. It was found that syntheses recently developed for the parent substance, tryptophan, could be applied here successfully.[2] The required 5-methylindole was prepared essentially by Robson's method.[1] It was converted to 3-diethylaminomethyl-5-methylindole (I) in 86% yield by treatment with formalin and diethylamine in acetic acid solution. The Mannich base condensed readily with ethyl acetamidocyanoacetate[3] to give II in 86% yield. Hydrolysis to 5-methyltryptophan (III) was effected in 55% of the theoretical yield by refluxing with dilute sodium hydroxide. Robson[1] stated that the amino acid, III, melted at 259–264° and was soluble in water. Our compound was found to melt at 284–288° and could be precipitated from an aqueous solution of its sodium salt by acidification with acetic acid. The analytical data agreed quite well with the theoretical values.



Experimental

5-Methylindole.—The method of Robson[1] was followed except that *p*-tolylhydrazine was prepared by the method described in "Organic Syntheses" for phenylhydrazine.[4]

3-Diethylaminomethyl-5-methylindole (I).—Thirty-five milliliters of a 40% formalin solution and a solution of 73 g. (1 mole) of anhydrous diethylamine in 66.5 ml. of acetic acid were added dropwise and simultaneously to 65.3 g. of 5-methylindole. The flask was swirled during the addition. After standing overnight (all the indole had dissolved), the dark reaction mixture was poured into water and filtered to remove a small amount of insoluble material. The filtrate was made basic with 10% sodium hydroxide solution and the gum that separated soon solidified. It was collected on a filter, washed with water and dried; the yield was 97.7 g. or 86% of the theoretical. It was sufficiently pure for the next step. On crystallization from dilute ethanol it melted at 89–92°.

Anal. Calcd. for $C_{14}H_{20}N_2$: N, 12.95. Found: N, 12.90.

Ethyl α-Acetamido-α-cyano-(5-methylindole)-propionate (II).—To a solution of 10.35 g. of sodium in 800 ml. of dry ethanol there was added 97.7 g. of 3-diethylaminomethyl-5-methylindole and 76.0 g. of ethyl acetamidocyanoacetate. When all the solids had dissolved, 94.6 g. of methyl sulfate was added dropwise to the stirred solution. The reaction mixture was cooled occasionally to prevent the temperature from rising above 40°. After standing overnight the mixture was poured into water with stirring and the solid that separated was collected and thoroughly washed with water. After air drying, the substance weighed 123 g. (87%). A sample crystallized from dilute ethanol with the aid of charcoal melted at 197–198°.

Anal. Calcd. for $C_{17}H_{19}N_3O_3$: N, 13.41. Found: N, 13.41.

5-Methyltryptophan (III).—A mixture of 123 g. of II and 123 g. of sodium hydroxide in 1110 ml. of water was refluxed for fifteen hours and cooled. The solution was carefully acidified to about *p*H 5 and the precipitate filtered. The amino acid was recrystallized from acetic acid containing a small amount of water. The crystals were filtered off and dissolved in dilute sodium hydroxide. The solution was decolorized with Darco G-60, filtered and acidified with acetic acid. The substance that separated was washed with water, ethanol and finally ether. After drying for twenty four hours at 50° it weighed 47 g. (55%), and melted at 284–288°. It was insoluble in water, ethanol and cold acetic acid, soluble in sodium hydroxide solution, hydrochloric acid and hot acetic acid. The purity as determined by a perchloric acid titration[5] was 100.1%.

Anal. Calcd. for $C_{12}H_{14}N_2O_2$: N, 12.84. Found: N, 12.80.

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(2) Snyder and Smith, THIS JOURNAL, **66**, 350 (1944); Albertson, Archer and Suter, *ibid.*, **66**, 500 (1944); **67**, 36 (1945); Howe, Zambito, Snyder and Tishler, *ibid.*, **67**, 38 (1945); Albertson and Tullar, *ibid.*, **67**, 502 (1945).

(3) Tullar, U. S. Patent 2,393,723 (1946).

(4) "Organic Syntheses," Coll. Vol. I, 442 (1941).

(5) Toennies and Callan, *J. Biol. Chem.*, **125**, 259 (1938).

CONTRIBUTION FROM THE
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Polymerization of *d-s*-Butyl *p*-Vinylbenzoate[1]

BY C. S. MARVEL AND C. G. OVERBERGER

d-s-Butyl *p*-vinylbenzoate has been prepared and polymerized in bulk. The change in rotation as the monomer is polymerized is too small to make this monomer of use in kinetic studies of polymerization. It is of some interest to note that saponification of the optically active polyester gives an inactive polyacid, hence no asymmetric synthesis occurred during polymerization.

Experimental

***d-s*-Butyl *p*-Vinylbenzoate.**—In a 300-cc. Erlenmeyer flask were placed 100 g. (1.35 moles) of *d-s*-butyl alcohol and 38 g. (0.28 moles) of *p*-vinylbenzoic acid.[2] To this was added 10 g. of dry hydrogen chloride at room temperature and the slurry was allowed to shake for four hours and then to stand overnight. About 600 cc. of dry benzene, containing 0.01 g. of picric acid and 1.0 g. of *p-t*-butylcatechol was added and the solution was transferred to a 1-liter, round-bottomed flask equipped with a distilling column with a variable take-off. The water and benzene were removed slowly at a reflux ratio of 15 to 1. After four hours the theoretical amount of water had been collected and the remainder of the benzene was then distilled. The residue was dissolved in 300 cc. of ether, the ether solution was washed twice with 100-cc. portions of water, twice with 100-cc. portions of 10% sodium bicarbonate solution and three times with 100-cc. portions of water. On acidification of the sodium bicarbonate solution with dilute hydrochloric acid, 8 g. of impure *p*-vinylbenzoic acid was recovered. The first water extracts were combined and saturated with powdered sodium carbonate. Thirty grams of impure *d-s*-butyl alcohol separated from the water layer and was recovered.

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(1) The work described in this note was done under sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(2) Marvel and Overberger, THIS JOURNAL, **67**, 2250 (1945).

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

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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-

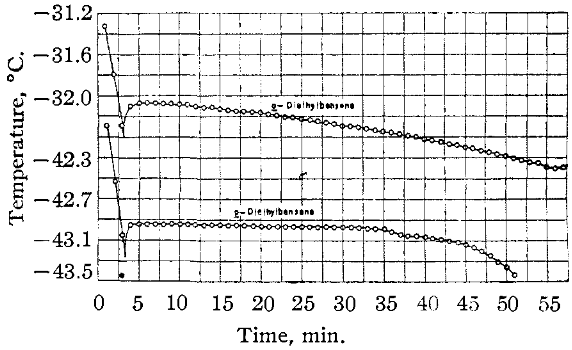

Fig. 1.—Time-temperature freezing curves of *o*- and *p*-diethylbenzene.

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