a hot water bath, the brown residue (7535 g.) solidified. This solid was ground and washed with petroleum ether (b.p. 30–60°). The light yellow solid (6740 g.) was distilled and the clear, colorless fraction, boiling at 143–144° at 1.5 mm., was collected. Crystallization was accomplished by saturating hot (55°) petroleum ether (b.p. 60–90°) with the 2-methylbenzhydrol and allowing the solution to cool slowly to room temperature. The solid precipitated out of the solution as thick colorless prisms (5320 g.), which were recrystallized as before to yield 4900 g. (61.8%, based on 40 moles of benzaldehyde) of purified 2-methylbenzhydrol with a m.p. of 90.0°.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.68; H, 7.07.

3-Methylbenzhydrol.—The solution of the 3-methylbenzhydrol was heated at reduced pressure with hot water to evaporate the rest of the ether. The ether-free material was distilled and the fraction boiling at a temperature of 150–160° at 2 mm. was collected. This fraction amounted to 4360 g. of clear yellow liquid that solidified on cooling. Quantities of 250 g. each were dissolved in 1.6 l. of heated petroleum ether (b.p. 30–60°) and allowed to cool slowly to room temperature. The yellow liquid was decanted and the white solid collected on a filter. The total recovery from the first crystallization was 3710 g. A second crystallization yielded 3440 g. and a third, 3310 g. (55.7%, based on 30 moles of benzaldehyde) of white cottony needles of purified 3-methylbenzhydrol with a m.p. of 52.8°.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.93; H, 7.18.

4-Methylbenzhydrol.—The ether remaining in the solution was removed by heating at reduced pressure with hot water. The residual yellow oil solidified on standing. This material was distilled and the fraction boiling at 165–170° at 3 mm. was collected. This fraction, amounting to 4048 g., solidified on standing. Quantities of 500 g. each of melted solid were mixed in 2-l. erlenmeyer flasks with 1500 ml. of commercial isoöctane at about 55°. The 4-methylbenzhydrol crystallized slowly on cooling to room temperature. An additional small amount of solid precipitated when the supernatant liquid was decanted from the solid cake and cooled to about 5°. A second crystallization was carried out in an identical manner as the first except that 1200-ml. quantities of isoöctane were used as solvent. The precipitates from the second crystallization were hard, solid cakes which could not be easily removed from the flasks. Each cake was therefore dissolved in 900 ml. of isoöctane, transferred to a 4-l. stainless steel beaker and cooled in an ice-water bath while stirring. The 4-methylbenzhydrol precipitated as a fine, granular solid which was easily filtered on a buchner funnel. The yield of recrystallized 4-methylbenzhydrol was 3188 g. (53.7%, based on 30 moles of benzaldehyde). The solid had a melting point of 53.6°.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 85.03; H, 7.22.

Preparation of Methyldiphenylmethanes.—A solution of 2500 g. of methylbenzhydrol in 1.5 l. of absolute alcohol was mixed with 250 g. of copper chromite catalyst in a 20-l. rocking autoclave and hydrogenated for 20 hours at 225° and an initial pressure of 1500 p.s.i. After the solution was filtered from the catalyst and the solvent removed by distillation, the hydrocarbon was distilled to give a 92 to 95% yield of methyldiphenylmethane. This material was further purified by fractional distillation at reduced pressure (3 to 18 mm.) through a 6-ft. (30 mm. diam.) glass column packed with $^3/_{16}$-inch glass helices. After approximately 200 ml., consisting of 3 or 4 fractions, was removed, the subsequent individual fractions were of constant refractive index and varied in melting point less than 0.1°. A number of the purest fractions (highest m.p.) sufficient to yield the desired 500-ml. quantity were combined and percolated through silica gel prior to the determination of the physical properties.

Preparation of Methyldicyclohexylmethanes.—A solution of 4000 to 5000 g. of distilled methyldiphenylmethane in an equal volume of methylcyclohexane was mixed with 400 to 500 g. (10% by wt. of methyldiphenylmethane) of U.O.P. nickel catalyst in a 20-l. rocking autoclave and hydrogenated for 12 hours at 200° and an initial pressure of 1200 p.s.i. After the solution was filtered from the catalyst and the solvent removed by distillation, the hydrocarbon was fractionally distilled *in vacuo* (2–20 mm.) through a 6-ft. (22-mm. diam.) Podbielniak column. Fractions for combination as purest samples of each isomer were chosen on the basis of highest melting point values and passed through silica gel prior to the determination of the physical properties. In the case of the high-boiling isomer of 3-methyldicyclohexylmethane, however, constant refractive index and constant density values were employed as criteria for the selection of fractions since this compound could not be crystallized.

CLEVELAND, OHIO

[CONTRIBUTION FROM THE LEWIS FLIGHT PROPULSION LABORATORY OF THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

Bromination of the Two Propylbenzenes and Three Butylbenzenes

BY JOHN H. LAMNECK, JR.

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The ortho- and para-monobromo derivatives of propyl-, isopropyl-, butyl-, isobutyl- and *s*-butylbenzenes were prepared by direct bromination and purified to a state of purity of over 99 mole %. The ortho–para percentage ratios were found to be 31/69 for bromopropylbenzene, 23/77 for bromoisopropylbenzene, 37/63 for bromobutylbenzene, 25/75 for bromoisobutylbenzene and 21/79 for bromo-*s*-butylbenzene. The physical properties presented include melting point, boiling point, refractive index, density and heat of fusion. Except for the *o*- and *p*-bromoisopropylbenzenes, the physical constants are reported more completely and on more highly purified samples than in previous chemical literature.

In connection with the syntheses of several diphenylmethane hydrocarbons, the ortho- and para-monobromo derivatives of propyl-, isopropyl-, butyl-, isobutyl- and *s*-butylbenzenes were prepared in 1- to 2-liter quantities. The mixtures of isomers were separated to determine the relative percentages of bromine substitution in the ortho and para positions. Each isomer was further purified to isolate samples on which to determine physical properties. Except for the *o*- and *p*-bromoisopropylbenzenes[1] the physical constants of these bromides either are not reported in the literature or have been determined on samples which were not adequately purified.

The method of preparation employed was the direct bromination of an excess of aromatic hydrocarbon dissolved in glacial acetic acid. The reaction was conducted in the dark with iodine and reduced iron powder as catalysts. The experimental conditions were chosen to keep undesirable side-chain bromination products at a minimum, but it was nevertheless necessary to eliminate those which did form. The time-consuming procedure of decomposing side-chain halogen-containing

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(1) R. R. Dreisbach and R. A. Martin, *Ind. Eng. Chem.*, **41**, 2875 (1949).

TABLE I

PHYSICAL PROPERTIES AND YIELDS OF BROMOALKYLBENZENES

Bromide	M.p., °C.	B.p., °C. at 1 atm.	n^{20}_D	d^{20}, g./ml.	Heat of fusion, kcal./mole	Estimated purity, mole %	Yield of mixed bromides, %	Wt. % of isomer in mixture	M.p. of bromobenzoic acid,[a] °C.	Mol. wt.[b,c]	Br,[d] %
o-Bromopropylbenzene	−46.38	217.20	1.5395	1.2992	4.0	99.9	59.6	30.9	147–148.5	197.1	40.0
p-Bromopropylbenzene	−41.53	225.07	1.5367	1.2858	2.9	99.9		69.1	257–258	195.1	40.0
o-Bromoisopropylbenzene	−58.90	210.32	1.5412	1.3035	2.9	99.9	62.3	22.9	145.5–146.5	193.5	39.6
p-Bromoisopropylbenzene	−22.46	218.77	1.5359	1.2856	2.1	99.9		77.1	253–254	194.8	39.7
o-Bromobutylbenzene	−44.89	237.02	1.5328	1.2542	3.9	99.9	61.1	37.1	147.5–149.5	209.3	37.1
p-Bromobutylbenzene	−25.65	245.55	1.5305	1.2429	3.0	99.9		62.9	255–256	207.2	37.1
o-Bromoisobutylbenzene	−47.30	227.24	1.5304	1.2476	3.1	99.7	58.4	25.3	148–149.5	209.1	37.7
p-Bromoisobutylbenzene	−49.68	236.10	1.5282	1.2354	3.1	99.9		74.7	255–256	207.4	37.1
o-Bromo-*s*-butylbenzene	Glass	226.78	1.5353	1.2610	...	..	49.7	21.2	146.0–147.5	206.1	37.1
p-Bromo-*s*-butylbenzene	−41.35	236.87	1.5318	1.2468	3.1	99.9		78.8	255–256	206.9	37.4

[a] Literatue values, ortho 146–147°; para 244–248° (L. A. Bigelow, THIS JOURNAL, **44**, 2010 (1922). [b] 5.07 used as cryoscopic constant of benzene. [c] Calculated values, propyls 199.1; butyls 213.1. [d] Calculated values, propyls 40.1; butyls 37.5.

groups with alcoholic caustic was adequately replaced by refluxing the impure product at atmospheric pressure followed by distillation *in vacuo*.

The ortho and para isomers were separated in a helix-packed glass column *in vacuo* and each was further purified in a Podbielniak column *in vacuo*. The percentages of ortho and para substitution were calculated and agree with those that would be expected from an analysis of nitration and other substitution data. The ortho–para ratio is 1/1.70 for bromobutylbenzene, 1/2.24 for bromopropylbenzene, 1/2.95 for bromoisobutylbenzene, 1/3.37 for bromoisopropylbenzene and 1/3.72 for bromo-*s*-butylbenzene.

Molecular weights were determined for identification purposes. A sample of each bromoalkylbenzene was oxidized to the corresponding bromo benzoic acid on which a melting point was determined in order to establish the ortho or para relationship.

The data in Table I include, in addition to those previously mentioned, percentage yields of mixed bromides based on the amount of bromine used, melting points, boiling points, densities, indices of refraction and heats of fusion. The last five properties were determined by procedures referenced in a previous paper from this Laboratory.[2] The estimated mole % purities determined according to methods described by Glasgow, Streiff and Rossini[3] are also included.

Experimental

Sources of Alkylbenzenes.—Isopropylbenzene and *s*-butylbenzene were obtained commercially and purified by distillation through 30-foot columns.[4] Propylbenzene, butylbenzene[5] and isobutylbenzene[6] were synthesized by hydrogenation of the corresponding purified olefins obtained from Grignard reactions utilizing, respectively, as halides and condensing agents, bromobenzene and allyl chloride, benzyl chloride and allyl chloride, and bromobenzene and methallyl chloride.

Bromination of Alkylbenzenes.—The bromination apparatus consisted of a 5-l. flask equipped with a glass stirrer, thermometer, long-stemmed addition funnel, and reflux condenser with an attached gas scrubber. The flask was enclosed in a metal container through which cold water could be circulated and which was provided with a cover to exclude light.

The initial charge to the flask consisted of 10 moles of alkylbenzene, 500 ml. of glacial acetic acid, 2.5 g. of reduced iron powder and 2.5 g. of iodine crystals. The contents of the flask were cooled to 10–20° while stirring. A solution of 8 moles (80% of theoretical) of technical bromine in 1 l. of glacial acetic acid was added from the addition funnel to the reaction flask over a period of 5 to 6 hours. The reaction mixture was stirred for several days at 10–25°.

The contents of the 5-l. flask were transferred to a 6-l. separatory funnel. The upper layer, containing the bulk of the bromoalkylbenzene and unreacted hydrocarbon together with some acetic acid, was separated from the lower layer of unreacted bromine, iodine and iron salts in acetic acid. By diluting this lower layer with a large volume of water, an additional small quantity of impure bromoalkylbenzene was obtained. The bromoalkylbenzene was washed twice with cold water, once with dilute sodium bisulfite solution, and once with dilute sodium bicarbonate solution, dried over anhydrous sodium sulfate, filtered and distilled rapidly *in vacuo* (10–25 mm.). Most of the unreacted alkylbenzene was separated at this stage.

Purification of Bromoalkylbenzenes.—Material from several bromination runs was combined in a 5-l. flask attached to a 3-foot helix-packed glass column (22-mm. diam.). Additional unreacted alkylbenzene was distilled off *in vacuo* (10–25 mm.) and the residue in the flask was refluxed at atmospheric pressure for 6 to 7 hours to decompose the side-chain bromination products. The remaining contents of the flask were distilled *in vacuo* (20–25 mm.) through the 3-foot helix-packed column.

The ortho and para isomers were separated by fractional distillation at 20 mm. through a 7-foot glass column (22-mm. inside diam.) packed with $^3/_{16}$-inch glass helices. Each isomer was purified further by fractional distillation at 20 mm. through a 3-foot Podbielniak column (22-mm. inside diam.). The samples for physical constants were obtained by selection of the fractions with the highest melting point values, and percolation of these fractions through silica gel. In the case of *o*-bromo-*s*-butylbenzene, however, constant refractive index and constant density values were employed as criteria for the selection of fractions since this compound could not be crystallized.

Structure of Bromoalkylbenzenes.—Each bromoalkylbenzene was analyzed for percentage of bromine by decomposing a 0.5-g. sample with 10 g. of sodium in 100 ml. of alcohol and titrating according to the Volhard method. The oxidations to the bromobenzoic acid derivatives were accomplished by refluxing 5-ml. samples with solutions of 100 ml. of concentrated nitric acid in 200 ml. of water. Molecular weights were determined by the freezing point depression method using benzene as the solvent.

CLEVELAND, OHIO

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[2] I. A. Goodman and P. H. Wise, THIS JOURNAL, **72**, 3076 (1950).

[3] A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

[4] T. W. Reynolds and G. H. Sugimura, *Natl. Advisory Comm. Aeronaut.* Tech. Note 2342 (April, 1951).

[5] J. V. Karabinos and J. M. Lamberti, *ibid.*, Tech. Note 1019 (January, 1946).

[6] C. M. Buess, J. V. Karabinos, P. V. Kunz and L. C. Gibbons, *ibid.*, Tech. Note 1021 (June, 1946).