bath for 5 minutes. The derivative was recovered unchanged after this treatment, which has been shown in other cases to isomerize β,γ- to α,β-unsaturated dinitrophenylhydrazones.[5,10]

A solution of 0.322 g. of the partially hydrogenated acetal described above in 10 ml. of methanol was reduced in the presence of 0.05 g. of 10% palladium-on-Norit; hydrogen absorption amounted to 90% of one molar equivalent and was complete in 1 hour. Treatment of the reduction product (not isolated) with 2,4-dinitrophenylhydrazine hydrochloride in ethanol gave 0.541 g. (93%) of cycloheptanecarboxaldehyde 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. with an authentic sample 133–134.5°.

Reaction of Cycloöctatetraene Dichloride with Sodium Methoxide in Methanol.—Cycloöctatetraene dichloride[2,12] (42.5 g.) was added with stirring at 0° to a solution of sodium methoxide prepared from 12.0 g. of sodium and 200 ml. of dry methanol. The mixture was stirred at 0° for 2 hours, at room temperature for 1.5 hours, and then was heated under reflux for 3 hours (a mildly exothermic reaction occurred on heating to the reflux temperature). The mixture was allowed to stand at room temperature overnight, filtered to remove sodium chloride and the filtrate was concentrated to a volume of 100 ml. under reduced pressure. The concentrate was diluted with 100 ml. of water and extracted with ether. The extracts were washed with water, dried over sodium sulfate and concentrated. Fractionation of the residue through a semi-micro column separated 0.51 g. of a yellow forerun, b.p. 83–88° (11 mm.), $n^{25}\text{D}$ 1.5388, from 27.7 g. (69%) of crude V as a colorless liquid, b.p. 93–95° (11 mm.), $n^{25}\text{D}$ 1.5064–1.5087. The infrared spectrum of a fraction with $n^{25}\text{D}$ 1.5067 was practically identical with the spectrum of pure V, except for the presence of additional weak bands at 1640 and 780 cm.$^{-1}$ which probably indicate the presence of a small amount of a styrene derivative as an impurity. Observation of stronger absorption in the ultraviolet spectrum ($\lambda_{\max}$ 261 mμ, ϵ 5010 in cyclohexane) for III from this source than for pure III also could be explained by the presence of such an impurity. A fraction was converted into 2,4,6-cycloheptatriene-1-carboxaldehyde 2,4-dinitrophenylhydrazone in 84% yield by the method described above for preparation of this derivative from pure V, and identified by m.p. and mixed m.p. with the analytical sample of the 2,4-dinitrophenylhydrazone prepared from pure V described above.

Hydrogenation of 6.46 g. of V prepared from cycloöctatetraene dichloride under the conditions described above for reduction of pure V resulted in absorption of 94% of three molar equivalents of hydrogen in 1.7 hours. Fractionation of the product separated 0.93 g. of a forerun, b.p. 78–90° (12 mm.), $n^{25}\text{D}$ 1.4577–1.4699, from 4.74 g. (71%) of VI, b.p. 90–91° (12 mm.), $n^{25}\text{D}$ 1.4500–1.4530, identified by its infrared spectrum and by conversion in 77% yield into the 2,4-dinitrophenylhydrazone of VI (m.p. and mixed m.p. with an authentic sample after recrystallization from benzene–ethanol, 134.5–135.5°).

CAMBRIDGE, MASSACHUSETTS

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

Dicyclic Hydrocarbons. IX. Synthesis and Physical Properties of the Monomethyldiphenylmethanes and Monomethyldicyclohexylmethanes

BY JOHN H. LAMNECK, JR., AND PAUL H. WISE

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Methods of synthesis and purification are described for the 2-, 3- and 4-methyldiphenylmethanes and for both geometrical isomers of the corresponding methyldicyclohexylmethanes. Each of these hydrocarbons has been prepared in a state of purity of 99 mole %, or better. The physical properties presented include melting point, boiling point, refractive index, density, heat of fusion, net heat of combustion and kinematic viscosities at four different temperatures. The methyldicyclohexylmethanes are being reported for the first time and the physical constants for the methyldiphenylmethanes have been improved and extended.

As part of a study of the effect of structure on the properties of dicyclic hydrocarbons the 2-, 3- and 4-methyldiphenylmethanes and corresponding dicyclohexylmethanes were synthesized and purified. The scale of the synthesis was planned so that approximately 500-ml. quantities of each hydrocarbon would be made available in 99 mole % purity for specific test purposes.

None of the methyldicyclohexylmethanes has been mentioned in the literature and the preparation and physical properties of these hydrocarbons are thus described for the first time. The methyldiphenylmethanes have been prepared previously, but only boiling points, indices of refraction and densities are reported and the data from the various sources are not in agreement.

A general method of synthesis was employed for the preparation of the methyldiphenylmethanes and corresponding methyldicyclohexylmethanes. The first step was the preparation of the solid methylbenzhydrol by the Grignard reaction utilizing an appropriate aryl halide and benzaldehyde. The Grignard complex was hydrolyzed by pouring it into an ice-cold acid solution. This hydrolysis procedure, in which the reactants are kept ice-cold, is necessary if good yields are to be obtained. Otherwise intermolecular dehydration probably occurs with the formation of an ether in the same manner as dibenzhydryl ether is formed from benzhydrol by heating with dilute hydrochloric acid at 120–130°.[1] The yield of methylbenzhydrol was improved if less than the theoretical amount (75 to 80%) of benzaldehyde was used for the condensation. This minimized the possibility of oxidation of the reaction product by excess benzaldehyde.[2] Because of differences in solubility and crystal structure, it was necessary to employ various solvents and crystallization techniques for the purification of each methylbenzhydrol.

The methyldiphenylmethanes were prepared by hydrogenolysis of the purified solid methylbenzhydrols. These methyldiphenylmethanes crystallized very readily on cooling and estimates of purity, based on time–temperature melting curves, indicated values over 99.9 mole %. 3-Methyldiphenylmethane exists in two crystalline modifications and time–temperature melting curves were obtained for each form.

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(1) H. Wieland, C. Schopf and W. Hermsen, *Ann.*, **444**, 40 (1925).

(2) J. Marshall, *J. Chem. Soc.*, **107**, 509 (1915).

The methyldicyclohexylmethanes were prepared by hydrogenation of the purified methyldiphenylmethanes. Each methyldicyclohexylmethane consisted of a pair of geometrical isomers. These isomers were separated by fractional distillation in high efficiency columns, but in the absence of the necessary thermodynamic data no specific assignment of *cis* and *trans* configurations can be made, and the products isolated are referred to simply as the low- and high-boiling isomers. The efficiency of separation of the three pairs of isomers varied as the proximity of the boiling points; the portion of distillate which consisted of mixtures of the low- and high-boiling isomers was 5% for the 2-methyldicyclohexylmethane, 23% for the 3-methyldicyclohexylmethane and 20% for the 4-methyldicyclohexylmethane. Much of this intermediate material could be resolved into the pure isomers on repeated fractionation.

All of the methyldicyclohexylmethane hydrocarbons, except the high-boiling isomer of 3-methyl dicyclohexylmethane, were successfully crystallized. However, because of their very slow rate of crystal formation and high viscosity at the crystallization point, the time–temperature melting curves and heats of fusion were difficult to obtain. Melting points to only a tenth of a degree and no heats of fusion are recorded herein for the high-boiling isomer of 2-methyldicyclohexylmethane and the low-boiling isomer of 3-methyldicyclohexylmethane. It is not possible, therefore, to estimate the purity of these last two named hydrocarbons or of the uncrystallized high-boiling isomer of 3-methyldicyclohexylmethane. However, the distinct plateaus of refractive index and density values determined on fractions from the distillations indicate purities of the same order of magnitude as those recorded for the other dicyclohexylmethanes.

The physical properties, yields and analyses of the nine hydrocarbons are listed in Table I. The apparatus and procedures used for the purification of the hydrocarbons, as well as references to the methods used for the determination of the physical properties, have been described previously.[3] The estimated mole % purities were determined according to the method of Glasgow, Streiff and Rossini.[4]

TABLE I

PHYSICAL PROPERTIES AND ANALYSES OF METHYLDIPHENYLMETHANES AND METHYLDICYCLOHEXYLMETHANES

Methane derivative	M.p., °C.	B.p., °C. at 1 atm.	n^{20}_D	d^{20}, g./ml.	Heat of fusion, kcal./mole	Estimated purity, mole %	Net heat of combustion, kcal./mole	Relative yeld, %	Kinematic viscosity,[a] (centistokes) 32°F.	100°F.	140°F.	210°F.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
2-Methyldiphenyl-	6.61	280.50	1.5763	1.00198	5.0	99.9	1735	..	10.81[b]	3.26	2.08	1.18	92.26	92.24	7.74	7.67
3-Methyldiphenyl-	−27.83[c]	279.24	1.5712	0.99135	4.7	99.9	1750	..	6.84	2.58	1.76	1.07	92.26	92.35	7.74	7.76
4-Methyldiphenyl-	4.58	281.96	1.5692	.98739	4.9	99.9	1745	..	5.62[b]	2.30	1.61	1.01	92.26	92.24	7.74	7.73
2-Methyldicyclohexyl-[d]	−28.06	264.61	1.4760	.87458	4.8	99.8	1975	48	13.11	3.99	2.55	1.42	86.51	86.57	13.49	13.46
2-Methyldicyclohexyl-[e]	−32.5[f]	267.94	1.4799	.88495	[g]	..	1985	52	21.39	5.36	3.20	1.68	86.51	86.52	13.49	13.50
3-Methyldicyclohexyl-[d]	−38.4[f]	263.25	1.4727	.86713	[g]	..	1985	82	13.99	3.99	2.49	1.38	86.51	86.48	13.49	13.54
3-Methyldicyclohexyl-[e]	Glass	264.32	1.4756	.87571	[g]	..	1990	18	17.00	4.63	2.84	1.53	86.51	86.45	13.49	13.57
4-Methyldicyclohexyl-[d]	−25.53	265.07	1.4710	.86410	4.5	99.4	2000	55	14.11	4.16	2.60	1.43	86.51	86.42	13.49	13.52
4-Methyldicyclohexyl-[e]	−28.49	266.84	1.4760	.87603	4.8	99.2	1990	45	18.07	4.96	3.02	1.62	86.51	86.52	13.49	13.54

[a] Determined in viscosimeters calibrated with N.B.S. standard viscosity samples and using A.S.T.M. procedure D445-46T. [b] Supercooled liquid. [c] A second modification was found to melt at −34.46°. [d] Low-boiling isomer. [e] High-boiling isomer. [f] Equilibrium portion of melting curve was very short. [g] Failed to crystallize in apparatus.

Experimental

Preparation of Methylbenzhydrols.—In a 10-gal. glass-lined reactor, 973 g. (40 moles) of magnesium turnings in 16 l. of dry ether reacted with 40 moles of aryl halide (*o*-bromotoluene, *m*-iodotoluene, or *p*-bromotoluene) which was obtained from commercial sources and purified by distillation. To the cooled solution of the arylmagnesium halide was added gradually 9 l. of an ether solution of 30 to 40 moles of freshly distilled technical-grade benzaldehyde. The mixture was hydrolyzed by adding it rapidly to a mixture of 100 lb. of cracked ice, 3.25 l. of concd. hydrochloric acid (40 moles HCl), and 3 to 5 gal. of cold water in a 30-gal. reactor. After hydrolysis was complete, the acid-water layer was separated and the ether solution washed successively with cold water, with dilute sodium bicarbonate solution, and again with cold water. The main bulk of the ether was removed by heating with steam, after which the reddish-amber methylbenzhydrol solution was removed from the reactor.

2-Methylbenzhydrol.—After the remaining ether in the 2-methylbenzhydrol was evaporated at reduced pressure in

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

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

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).