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Dicyclic Hydrocarbons. X. Synthesis and Physical Properties of Some Propyl- and Butyldiphenylmethanes and 4-Isopropyldicyclohexylmethane

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Methods of synthesis and purification are described for the 4-propyl-, 4-isopropyl-, 2- and 4-butyl- and 2- and 4-*s*-butyldiphenylmethanes and 4-isopropyldicyclohexylmethane. 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. Except for the 4-propyl- and 4-isopropyldiphenylmethanes all of these hydrocarbons are being reported for the first time and new or improved values of the properties of the 4-propyl- and 4-isopropyldiphenylmethanes are presented.

This paper describes the synthesis, purification and properties of six diphenylmethane hydrocarbons (4-propyl-, 4-isopropyl-, 2-butyl-, 4-butyl-, 2-*s*-butyl- and 4-*s*-butyldiphenylmethane) and of 4-isopropyldicyclohexylmethane. These hydrocarbons were required in approximately 500-ml. quantities of 99 mole % purity for a systematic investigation of the effect of changes in structure on the physical properties of dicyclic hydrocarbons. A previous paper of this series describes the methyldiphenylmethanes and methyldicyclohexylmethanes.[1]

The only references in the literature to the work of other investigators on the hydrocarbons discussed in this paper were for the 4-propyldiphenylmethane[2] and the 4-isopropyldiphenylmethane,[3] and in these references very few properties were reported on the small impure samples available.

Two general methods of synthesis were employed for the diphenylmethane hydrocarbons. The 4-isopropyl-, 2-*s*-butyl- and 4-*s*-butyldiphenylmethanes were synthesized by hydrogenolysis of the corresponding alkylbenzhydrols which were prepared by treating the appropriate Grignard reagent with benzaldehyde. This method was chosen because several previously known alkylbenzhydrols were solids which could be highly purified by crystallization. In the present work the 4-isopropyl- and 4-*s*-butylbenzhydrols crystallized readily, but the 2-*s*-butylbenzhydrol could not be crystallized.

In order to expedite the syntheses, the 4-propyl-, 2-butyl- and 4-butyldiphenylmethanes were prepared by a one-step Grignard synthesis involving the condensation of benzyl chloride with the appropriate Grignard reagent. This direct synthesis was employed successfully here, whereas in previous work at this Laboratory with the lower members of the series (methyl and ethyl) the products obtained could not be completely separated by fractionation from the Grignard coupling products (dialkylbiphenyls). All of the alkyldiphenylmethanes reported herein crystallized very readily on cooling and estimates of purity, based on time–temperature melting curves, indicated values over 99.7 mole %. 4-Butyldiphenylmethane exists in two crystalline modifications and time–temperature melting curves were obtained for each form. On initial cooling it crystallizes in the lower-melting modification which on several hours standing changes to the more stable and higher-melting form.

The 4-isopropyldicyclohexylmethane was prepared by the hydrogenation of the purified 4-isopropyldiphenylmethane. The geometrical 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. The products isolated are therefore referred to simply as the low- and high-boiling isomers. The efficiency of separation was not high because of the proximity of the boiling points; the portion of distillate which consisted of mixtures of the two isomers amounted to 37% of the total. Neither isomer could be crystallized and fractions were combined on the basis of constant refractive index and density values. An evaluation of purity could not be made for these isomers, but the distinct plateaus of refractive index and density values determined on fractions from the distillation indicated that each isomer was in a high state of purity.

The physical properties and analyses of the eight hydrocarbons are listed in Table I. References to the methods of purification and of determination of physical properties have been previously cited,[4] and the estimated mole % purities were determined according to the method of Glasgow, Streiff and Rossini.[5]

Experimental

4-Isopropylbenzhydrol.—In a 10-gal. water-cooled, glass-lined reactor, the Grignard reagent from 40 moles of *p*-bromoisopropylbenzene[6] was condensed with 32 moles (80% of the theoretical amount) of freshly distilled technical grade benzaldehyde. The reaction mixture was hydrolyzed by adding it 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 water in a 30-gal. reactor. (Reference 1 contains a discussion of the reasons for (1) using the hydrolysis procedure mentioned in this report and (2) using less than the theoretical amount of benzaldehyde.) After the ether solution was separated and washed with water and dilute sodium bicarbonate solution, the ether was removed by heating the reactor with steam.

The 4-isopropylbenzhydrol solution from the reactor was distilled and the fraction boiling from 155–165° at 1.5 mm. was collected. This fraction, which solidified on cooling, amounted to 6239 g. The solid was crystallized twice from hot (65°) commercial isoöctane by dissolving 250-g. quantities in 1.7 l. of solvent and allowing the solution to cool slowly to room temperature. The yield of white, cottony needles of 4-isopropylbenzhydrol from the first

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[1] J. H. Lamneck, Jr., and P. H. Wise, THIS JOURNAL, **76**, 1104 (1954).

[2] R. C. Fuson, THIS JOURNAL, **48**, 2937 (1926).

[3] A. Klages and P. Allendorff, *Ber.*, **31**, 998 (1898).

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

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

[6] J. H. Lamneck, Jr., THIS JOURNAL, **76**, 1106 (1954).

TABLE I

PHYSICAL PROPERTIES AND ANALYSES OF SOME ALKYLDIPHENYLMETHANES AND 4-ISOPROPYLDICYCLOHEXYLMETHANE

Methane derivative	M.p., °C.	B.p., °C. at 760 mm.	$n^{20}D$	d^{20}, g./ml.	Heat of fusion, kcal./mole	Estimated purity, mole, %	Net heat of combn., kcal./mole	Kinematic viscosity,[a] cs. 32° F.	100° F.	140° F.	210° F.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
4-Propyldiphenyl-	−22.48	311.12	1.5556	0.96618	5.8	99.8	2025	9.01	3.27	2.18	1.29	91.37	91.38	8.63	8.69
4-Isopropyldiphenyl-	−13.36	305.60	1.5554	.96634	5.2	99.9	2045	8.46	3.11	2.08	1.25	91.37	91.48	8.63	8.59
2-Butyldiphenyl-	−16.56	315.18	1.5536	.96677	7.0	99.9	2170	20.17	4.78	2.83	1.50	91.01	91.04	8.99	8.98
4-Butyldiphenyl-	−34.95[b]	326.41	1.5492	.95696	6.0	99.9	2175	10.48	3.68	2.43	1.43	91.01	90.95	8.99	9.13
2-*s*-Butyldiphenyl-	−27.52	305.63	1.5545	.96926	4.5	99.9	2170	30.91	5.53	3.10	1.56	91.01	90.90	8.99	9.06
4-*s*-Butyldiphenyl-	−20.86	318.59	1.5500	.95907	5.6	99.7	2165	12.79	3.95	2.53	1.44	91.01	90.95	8.99	9.07
4-Isopropyldicyclohexyl-[c]	Glass	300.22	1.4780	.87839	..	..	2280	40.04	8.04	4.47	2.18	86.40	86.45	13.60	13.54
4-Isopropyldicyclohexyl-[d]	Glass	301.81	1.4752	.87082	..	..	2275	37.98	7.47	4.17	2.04	86.40	86.33	13.60	13.66

[a] Determined in viscosimeters calibrated with N.B.S. standard viscosity samples and using A.S.T.M. procedure D445-46T. [b] A second modification was found to melt at −40.62°. [c] Low-boiling isomer, 63% of hydrogenation product. [d] High-boiling isomer, 37% of hydrogenation product.

crystallization was 5100 g. and from the second crystallization was 4500 g. (62.2%, based on 32 moles of benzaldehyde). The m.p. was 60.5°.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.93; H, 8.07.

2-*s*-Butylbenzhydrol.—Freshly distilled technical grade benzaldehyde (2.8 moles, 80% of the theoretical amount) was added to the Grignard reagent from *o*-bromo-*s*-butylbenzene[6] (3.5 moles) in a 3-l. flask. Before the Grignard complex precipitated, hydrolysis was accomplished by pouring the reaction mixture into a solution of cracked ice, 285 ml. of concd. hydrochloric acid (3.5 moles HCl), and water. After the ether solution was separated and washed with water and dilute sodium bicarbonate solution, the ether was removed by evaporation.

The impure 2-*s*-butylbenzhydrol from four Grignard preparations was distilled twice rapidly and *in vacuo* to avoid decomposition. The material boiling between 142–148° at 4 mm. ($n^{20}D$ 1.5668–1.5671) was collected, but could not be crystallized. The yield of clear oily 2-*s*-butylbenzhydrol amounted to 1985 g. (73.8%, based on 11.2 moles of benzaldehyde).

Anal. Calcd. for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.86; H, 8.42.

4-*s*-Butylbenzhydrol.—The Grignard reagent from *p*-bromo-*s*-butylbenzene[6] (6 moles) was condensed with freshly distilled technical grade benzaldehyde (4.8 moles, 80% of the theoretical amount) in a 5-l. flask. The reaction mixture was hydrolyzed by pouring it into a mixture of cracked ice, 485 ml. of concd. hydrochloric acid (6 moles HCl) and water. This was done soon after the last of the benzaldehyde was added in order to keep the contents of the flask from solidifying. The resulting ether solution was washed with water and dilute sodium bicarbonate solution and the ether was removed by evaporation. The residual yellow oil amounted to 1305 g.

The impure 4-*s*-butylbenzhydrol was distilled and the fraction boiling at 175–185° at 5 mm. (888 g.) was collected. This yellow oil was dissolved in 2.6 l. of commercial isoöctane. The solution was cooled to about 5° and maintained at this temperature until crystallization was complete (several days). The solid (524 g.) on recrystallization from 2 l. of isoöctane yielded 398 g. (34.5%, based on 4.8 moles of benzaldehyde) of white, cottony needles of 4-*s*-butylbenzhydrol with a m.p. of 36–37°.

Anal. Calcd. for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.88; H, 8.42.

4-Isopropyl-, 2-*s*-Butyl- and 4-*s*-Butyldiphenylmethane.—A solution of 1000 g. of 4-isopropyl-, 2-*s*-butyl- or 4-*s*-butylbenzhydrol in 500 ml. of absolute alcohol was mixed with 100 g. of copper chromite catalyst in a 4.5-l. rocking autoclave and hydrogenated for 20 hours at 225° 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 distilled *in vacuo* through a 3-ft. glass column (22-mm. diam.), packed with 3/16-inch glass helices, to give about a 90% yield of alkyldiphenylmethane. Material from two hydrogenations of the same alkylbenzhydrol was further purified by fractional distillation at reduced pressure (2 to 3 mm.) through a 6-ft. Podbielniak column (22-mm. diam.). After approximately 40 ml. was removed, the subsequent fractions had essentially constant refractive indices and constant densities. The maximum difference in m.p. values for these constant refractive index and density fractions was 0.1° for the 4-isopropyldiphenylmethane, 0.4° for the 2-*s*-butyldiphenylmethane and 1° for the 4-*s*-butyldiphenylmethane. Several of the purest fractions (highest m.p.) of each compound, sufficient to yield the desired 500-ml. quantities, were combined and percolated through silica gel prior to the determination of the final physical properties.

4-Propyl-, 2-Butyl- and 4-Butyldiphenylmethane.—The Grignard reagent from 3.5 moles of the appropriate aryl halide (*p*-bromopropylbenzene, *o*-bromobutylbenzene or *p*-bromobutylbenzene)[6] was prepared in a 3-l. flask and condensed with freshly distilled technical grade benzyl chloride (4 moles). The reaction mixture was hydrolyzed by adding it to cold water while stirring. After the ether layer was separated and washed with water, the ether was evaporated.

The combined products from five preparations (17.5 moles) of the same hydrocarbon were distilled *in vacuo* through a 3-ft. glass column (22-mm. diam.) packed with 3/16-inch glass helices. The fractions boiling between 150–170° at 6 mm. were combined and fractionally distilled *in vacuo* (3–4 mm.) through a 6-ft. (22-mm. diam) Podbielniak column. Fractions having constant refractive index and constant density values represented over-all yields of 25% for the 4-propyldiphenylmethane, 28% for the 2-butyldiphenylmethane and 23% for the 4-butyldiphenylmethane. The maximum difference in m.p. values for the constant refractive index and constant density fractions of each compound in the same order as above was 0.14°, 0.08° and 0.01°. Several of the purest fractions (highest m.p.) of each compound, sufficient to yield the desired 500-ml. quantities, were combined and percolated through silica gel prior to the determination of the final physical properties.

4-Isopropyldicyclohexylmethane.—A solution of 4000 g. of distilled 4-isopropyldiphenylmethane in an equal volume of methylcyclohexane was mixed with 400 g. 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 (97% yield, $n^{20}D$ 1.4770) was fractionally distilled *in vacuo* (3 mm.) through a 6-ft. (22 mm. diam.) Podbielniak column. Fractions with constant refractive index and constant density values were combined to obtain the desired 500-ml. quantities of each isomer. The samples were percolated through silica gel prior to the determination of the final physical properties.

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