stant for the peroxybenzoic acid oxidation of *p,p'*-dichlorobenzyl sulfide in isopropyl alcohol was previously reported[3] to be 0.26 ± 0.01 l. mole^{-1} sec.$^{-1}$ at 35°. The corresponding rate constant for the hydrogen peroxide oxidation, as obtained by extrapolation of the data of Table I using the relation $\ln k = \ln A - E/RT$, was $1.45 \pm 0.03 \times 10^{-8}$ l. mole^{-1} sec.$^{-1}$ so that the rate of oxidation by peroxybenzoic acid is 7 powers of 10 faster than by hydrogen peroxide. However, at the same temperature the peroxybenzoic acid oxidation was only 3 powers of 10 faster than the sulfuric acid-catalyzed hydrogen peroxide oxidation, at 0.0245 *M* acid concentration. The activation entropies for the hydrogen peroxide and peroxybenzoic acid oxidations were found to be equal within experimental error while the experimental energies of activation were 17.2 ± 0.3 and 9.6 ± 0.5 kcal. mole^{-1}, respectively. Thus, the difference in oxidation rates between the uncatalyzed hydrogen peroxide and peroxybenzoic acid oxidations was almost entirely dependent on the difference in energies of activation of the two processes, whereas the spread in oxidation rates between the acid-catalyzed hydrogen peroxide and the peroxybenzoic acid oxidations was about 85% the result of the difference in activation entropies.

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

Synthesis and Physical Properties of Some C_{12} and C_{13} Phenylalkane and Cyclohexylalkane Hydrocarbons

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RECEIVED APRIL 18, 1953

The synthesis, purification and some of the physical properties, including heats of combustion and viscosities, of four phenylalkanes and three cyclohexylalkanes are reported. Melting points for 3-phenylhexane and 2,4-dimethyl-3-phenylpentane, which were prepared in a purity of 99 mole % or better, were determined. The synthesis and properties of 2-ethyl-1-cyclohexylbutane and 2,4-dimethyl-3-cyclohexylpentane are reported for the first time.

As part of a systematic study directed toward correlating hydrocarbon structure and physical properties, this Laboratory has synthesized and purified representative homologs in several series of dicyclic hydrocarbons: alkyldiphenylmethane,[1] 2-alkylbiphenyl,[2] 2-alkylbicyclohexyl,[3] and the diphenyl- and dicyclohexylalkane.[4] In order to make this evaluation of structural effects more comprehensive, several hydrocarbons have been synthesized which contain one phenyl or one cyclohexyl group attached to a side chain of six or more carbon atoms. The present paper describes the synthesis, characterization and purification of four aromatic hydrocarbons: 3-phenylhexane, 2-ethyl-1-phenylbutane, 2,4-dimethyl-3-phenylpentane and 2,4-dimethyl-1-phenylpentane; and three cyclohexyl compounds: 3-cyclohexylhexane, 2-ethyl-1-cyclohexylbutane and 2,4-dimethyl-3-cyclohexylpentane.

Although several of these hydrocarbons have been prepared previously, some of the physical properties desired for the correlation studies were not determined.[5] It was also desirable in synthesizing these compounds to choose methods that would lead to an unequivocal structure for each hydrocarbon. Of the aromatic hydrocarbons, 3-phenylhexane has been previously prepared by Levene and Marker.[6] The preparations of 2-ethyl-1-phenylbutane,[7] 2,4-dimethyl-3-phenylpentane[8] and 2,4-dimethyl-1-phenylpentane[9] have also been described. Of the cyclohexyl hydrocarbons reported in this paper, only the synthesis of 3-cyclohexylhexane[10] has been reported.

In the present investigation, the four aromatic hydrocarbons were synthesized by preparing phenyl-substituted alkylcarbinols by means of the Grignard reaction, dehydrating the carbinols over alumina to the corresponding olefins, then hydrogenating the olefins to the desired aromatic hydrocarbons. The three cyclohexyl compounds were prepared by either completely hydrogenating the olefins or saturating the aromatic ring of the purified aromatic hydrocarbons. The reactions were carried out on a scale sufficient to yield at least 500 ml. of the final hydrocarbons.

The phenylalkylcarbinols prepared in the present work were found to dehydrate when fractionated even at reduced pressure, so the crude Grignard reaction products were rapidly distilled at 20 mm. pressure to remove gross impurities. The carbinols were then dehydrated over alumina at temperatures between 220–260°, and the resulting olefins were hydrogenated to the desired phenyl or cyclohexyl hydrocarbons. The hydrocarbons were characterized by ozonolysis of the intermediate olefins.

The final hydrocarbon products were purified by fractional distillation in 6-ft. Podbielniak columns at 100 mm. pressure, followed by repeated percolation through silica gel; fractions that had constant indices of refraction and densities were combined for the determinations of physical properties. Examination of the infrared spectra of the phenylalkanes did not indicate the presence of any olefinic

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

[3] I. A. Goodman and P. H. Wise, *ibid.*, **73**, 850 (1951).

[4] (a) K. T. Serijan and P. H. Wise, *ibid.*, **73**, 4766 (1951); (b) **73**, 5191 (1951); (c) **74**, 365 (1952).

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[9] S. Tucker, M. Whalley and J. Forrest, *J. Chem. Soc.*, 3149 (1949).

[10] P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **97**, 563 (1932).

TABLE I

PREPARATION AND YIELDS OF THE INTERMEDIATE CARBINOLS

Phenylalkane	Halide	Carbonyl compound	Carbinol	Crude carbinol[a] yield, %
3-Phenylhexane	*n*-Propyl bromide (Eastman Kodak Co.; b.p. 70–71°)	Propiophenone (Eastman Kodak Co.; m.p. 16–18°)	3-Phenyl-3-hexanol	84
2-Ethyl-1-phenylbutane	Bromobenzene (Dow Chemical Co.; b.p. 156.9°)	2-Ethylbutyraldehyde (Eastman Kodak Co., tech. grade)	2-Ethyl-1-phenyl-1-butanol	72
2,4-Dimethyl-3-phenylpentane	Bromobenzene (Dow Chemical Co.; b.p. 156.9°)	Diisopropyl ketone (Du Pont de Nemours Co., tech. grade)	2,4-Dimethyl-3-phenyl-3-pentanol	73
2,4-Dimethyl-1-phenylpentane	Benzyl chloride (Heyden Chemical Co.; tech. grade)	Methyl isobutyl ketone (Carbide and Carbon Chem. Co., b.p. 115–116°)	2,4-Dimethyl-1-phenyl-2-pentanol	62

[a] The carbinols were found to dehydrate when fractionated and the yields are only approximate since the fractionated product undoubtedly contained some olefin. The yields are based on the quantity of carbonyl compound employed in the Grignard reaction.

TABLE II

BOILING POINTS, INDICES OF REFRACTION AND YIELDS OF INTERMEDIATE OLEFINS

Carbinol dehydrated	Olefin(s)	B.p., °C. (1 atm.)	$n^{20}D$	Olefinic mixture[a] yield, %
3-Phenyl-3-hexanol	3-Phenyl-2-hexene	218.0	1.5229–1.5233	85
	3-Phenyl-3-hexene	200.0	1.5117–1.5127	
2-Ethyl-1-phenyl-1-butanol	2-Ethyl-1-phenyl-1-butene	220.0–222.0	1.5213–1.5252	71
2,4-Dimethyl-3-phenyl-3-pentanol	2,4-Dimethyl-3-phenyl-3-pentene	210.0–213.0	1.5038–1.5073 (1.5066–1.5073)[b]	62
2,4-Dimethyl-1-phenyl-2-pentanol	2,4-Dimethyl-1-phenyl-2-pentene	222.5–224.5	1.4996–1.4998	42
	2,4-Dimethyl-1-phenyl-1-pentene	234.0–236.5	1.5192–1.5199	

[a] Based on the carbonyl compound used for the condensation with the Grignard reagent. [b] The range of the majority of the fractions of the distillate.

or carbinol impurities. Similarly, in the case of the cyclohexyl compounds, the infrared spectra did not indicate any aromatic impurities. Both 3-phenylhexane and 2,4-dimethyl-3-phenylpentane could be crystallized, and their purities were calculated to be better than 99 mole %. Although the other compounds could not be crystallized, it is believed that they were of comparable purity. The physical properties were determined according to methods referenced by Goodman and Wise.[2]

Experimental

The method of synthesis used in the preparation of each of the hydrocarbons reported in this paper is essentially one summarized by Boord and his co-workers[11]—preparation of the carbinol by means of the Grignard reaction, dehydration of the carbinol to the corresponding olefin, followed by hydrogenation of the olefin to the desired hydrocarbon. A general description is given for each of the operations used in preparing the phenyl- and cyclohexylalkanes.

Preparation of Carbinols.—The carbinols were obtained by the reaction of 50 moles of the appropriate carbonyl compounds with the Grignard reagents prepared from 53.5 moles of magnesium turnings and 50 moles of the appropriate halides. After the reaction mixtures were hydrolyzed with saturated aqueous ammonium chloride solution, the solvent, diethyl ether, was removed from the amber-colored oily layer by distillation at atmospheric pressure. Since dehydration of the carbinols occurred to some extent during distillations, the reaction products were rapidly distilled through a 30-mm. by 3-ft. glass column packed with $^1/_4$-in. glass helices, at reduced pressures. The reactants, products and yields of the distilled products are given in Table I.

Preparation of the Olefins.—The olefins were prepared by passing the distilled carbinols through a 1-inch by 3-ft. quartz column, which was packed with 8 to 14 mesh alumina and heated to 220–250°. The dehydration products were fractionated at atmospheric or 100 mm. pressures through 6-ft. glass columns (22-mm. i.d.) packed with $^3/_{16}$-inch glass helices. Except for 2-ethyl-1-phenyl-1-butanol and 2,4-dimethyl-3-phenyl-3-pentanol, each of which gave only one olefin whose double bond is conjugated with the aromatic ring, the carbinols dehydrated to give mixtures of isomeric olefins. The isomers were not separated rigorously by the fractional distillation, so some of the olefin mixtures subsequently hydrogenated boiled over a temperature range of as much as 2°. The predominant olefinic products, however, are listed in Table II along with the total yields of olefins from the dehydration reactions, and properties of the portions used in the hydrogenation reactions.

Characterizations of Olefins.—The olefins were characterized by ozonizing 0.1 to 0.2 mole of olefin, dissolved in 100 ml. of ethanol, according to the procedure of Henne and Perilstein.[12] The mixtures of ozonolysis fragments were fractionated through a $^1/_2$-inch by 2-ft. glass column, packed with $^3/_{16}$-inch glass helices. The 2,4-dinitrophenylhydrazone or the semicarbazone derivatives[13] of the fractions were then prepared, and were identified from their melting points and their mixed melting points with known derivatives. The fragments obtained upon ozonolysis, the melting points of their derivatives, and boiling points and indices of refraction of the olefins used in the ozonolysis experiments are given in Table III.

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[11] C. E. Boord, *et al.*, *Ind. Eng. Chem.*, **41**, 609 (1949).

[12] A. L. Henne and W. L. Perilstein, THIS JOURNAL, **65**, 2183 (1943).

[13] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., pp. 142–143.

TABLE III

CHARACTERIZATION OF THE INTERMEDIATE OLEFINS

Olefin	B.p., ° C. (1 atm.)	$n^{20}D$	Cpd. obtained upon ozonization	M.p. of the 2,4-dinitrophenylhydrazone derivative, °C.	
				Experimental	Literature[a]
3-Phenyl-2-hexene	218.0	1.5225	Acetaldehyde	146.0–147.5	148.0
			Butyrophenone	[b]	
3-Phenyl-3-hexene	200.0	1.5118	Propionaldehyde	150.0–151.0	156.0
			Propiophenone	172.5–173.0[c]	174.0[c]
2-Ethyl-1-phenyl-1-butene	220.0	1.5223	Benzaldehyde	239.5–240.5	237.0
			Diethyl ketone	156.0–156.5	156.0
2,4-Dimethyl-3-phenyl-2-pentene	211.0	1.5073	Isopropyl phenyl ketone	163.0–163.5	163.0
			Acetone	129.0–129.5	128.0
2,4-Dimethyl-1-phenyl-1-pentene	235.8	1.5201	Isobutyl methyl ketone	91.5–92.0	95.0
			Benzaldehyde	237.0–239.0	237.0
2,4-Dimethyl-1-phenyl-2-pentene	222.0	1.4997	Isobutyraldehyde	183.7–184.7	187.0
			Benzyl methyl ketone	186.0–187.0[c]	187.0–190.0[c]

[a] E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941. [b] Derivative was not isolated. [c] The m.p. of the semicarbazone, which was prepared instead of the 2,4-dinitrophenylhydrazone derivative, is given.

TABLE IV

PHYSICAL PROPERTIES OF THE HYDROCARBONS

Hydrocarbon	M.p., °C.	B.p., °C., at 760 mm.	$n^{20}D$	d^{20}, g./ml.	Net heat of combustion, kcal./mole	Kinematic viscosity, centistokes				Analyses, %			
										Carbon		Hydrogen	
						32°F.	100°F.	140°F.	210°F.	Calcd.	Found	Calcd.	Found
3-Phenylhexane[a]	−55.37	208.25	1.4867	0.85955	1615	2.86	1.33	0.98	0.65[b]	88.82	88.72	11.18	11.16
2-Ethyl-1-phenylbutane	Glass	216.66	1.4916	.86816	1620	3.09	1.40	1.03	.67[b]	88.82	88.96	11.18	11.30
2,4-Dimethyl-3-phenylpentane[c]	−24.45	219.01	1.4922	.87077	1760	4.99	1.99	1.39	.87	88.56	88.64	11.44	11.47
2,4-Dimethyl-1-phenylpentane	Glass	225.02	1.4872	.85659	1755	3.96	1.70	1.22	.80	88.56	88.70	11.44	11.35
3-Cyclohexylhexane	Glass	216.62	1.4525	.82334	1740	3.74	1.70	1.24	.81	85.63	85.60	14.37	14.50
2-Ethyl-1-cyclohexylbutane	Glass	214.52	1.4498	.81736	1740	3.91	1.77	1.28	.84	85.63	85.62	14.37	14.30
2,4-Dimethyl-3-cyclohexylpentane	Glass	214.84	1.4550	.82836	1890	3.86	1.79	1.30	.85	85.63	85.57	14.37	14.29

[a] Heat of fusion, 3.7 kcal./mole; estimated purity, *99.5 mole %. [b] Extrapolated value. [c] Heat of fusion, 4.1 kcal./mole; estimated purity, *99.6%. * Calculated by method of W. J. Taylor and F. D. Rossini, *J. Research Natl. Bur. Standards*, **32**, 197 (1944).

Preparation of the Phenylalkanes.—The olefins were hydrogenated to the aromatic hydrocarbons in a 4.5-liter rocking autoclave at 150–180° and 2500–2800 p.s.i., in the presence of 10% by weight of copper chromite catalyst. The yields were practically quantitative.

Preparation of the Cyclohexylalkanes.—The aromatic compounds were hydrogenated to the corresponding cyclocompounds at 170–180° and 2500 p.s.i., in the presence of 10% by weight of U.O.P. nickel catalyst. Additional quantities of the cyclohexyl hydrocarbon were also obtained by directly hydrogenating the olefins at 170–180° and 2500 p.s.i., in the presence of 10% by weight of U.O.P. nickel catalyst. The yields in both cases were practically quantitative.

Purification of the Hydrocarbons.—The phenylalkanes as well as the cyclohexylalkanes were purified by fractional distillations at reduced pressures in 6-ft. Podbielniak columns and subsequent percolation through silica gel. These processes were repeated until the various fractions had constant indices of refraction and constant densities. The physical properties of the purified hydrocarbons are listed in Table IV.

Acknowledgment.—The authors wish to thank Mrs. V. O. Fenn and Mr. F. P. Horacek as well as the members of the Analytical Section of this Laboratory for the determinations of physical properties, viscosities, heats of combustion and carbon–hydrogen analyses.

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