

General Procedure for the Thermal Rearrangement of α -Phenylethyl Aryl Ethers.—Twelve grams of the ether was placed in a modified Claisen flask, and immersed in an oil-bath at 200° for five hours. During this time, a small amount of styrene distilled from the flask (dibromide m.p. 73°). The reaction mixture was cooled, taken up in petroleum ether, and extracted with 10% aqueous sodium hydroxide until a small portion of the alkaline extract gave only a slight opalescence on acidification. The alkali insoluble material was dried over anhydrous sodium sulfate, the solvent removed, and the residue distilled. In each case, no ether was recovered, but an unidentified high-boiling (180–240° (10 mm.)) material was obtained (1–2 g.).

The alkaline extracts were combined, acidified with hydrochloric acid, and the resulting oil taken up in benzene, dried, solvent removed by distillation and the residue distilled under reduced pressure. In each case, some of the phenol from which the ether had been prepared, and some α -phenylethylated phenols were obtained. The yields of materials are summarized in Table VI. The stereochemical results of the thermal rearrangements were given in Table IV.

TABLE VI

THERMAL REARRANGEMENTS OF α -PHENYLETHYL ARYL ETHERS

Ar	Starting ether		Recovered ArOH		α -Phenylethylated ArOH	
	G.	Moles	G.	Moles	G.	Moles
C ₆ H ₅	12.0	0.060	1.5	0.016	4.0	0.020
<i>p</i> -CH ₃ -C ₆ H ₄	12.0	.056	2.0	.018	3.0	.014
2,6-(CH ₃) ₂ -C ₆ H ₃	12.0	.053	3.0	.025	2.7	.012

α -Phenylethyl Mesityl Ether and Phenol.—A mixture of 8 g. (0.033 mole) of α -phenylethyl mesityl ether ($\alpha_D +37.25^\circ$) and 14 g. (0.15 mole) of phenol was heated in an oil-bath at 200° for 7 hours. The reaction mixture was worked up as described in the general procedure for the thermal rearrangements. No alkali insoluble material was obtained. Distillation of the alkali-soluble fraction gave 12.0 g. of a mixture of phenol and mesitol, and 3.0 g. of α -phenylethylphenols (72% ortho), b.p. 160–170° (5 mm.), α_D 0.00 \pm 0.03°.

EAST LANSING, MICHIGAN

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

Dicyclic Hydrocarbons. VII. Synthesis and Physical Properties of Some 1,3-Diphenyl- and 1,3-Dicyclohexyl-2-alkylpropane Hydrocarbons¹

BY ROBERT M. CAVES, R. L. McLAUGHLIN AND P. H. WISE

RECEIVED JULY 13, 1953

The methyl, ethyl and propyl homologs of 1,3-diphenyl- and 1,3-dicyclohexyl-2-alkylpropane were synthesized from 1,3-diphenyl-2-alkyl-2-propanols, which were prepared by the reaction of benzylmagnesium chloride with acid halide or esters. Dehydration of the alcohols with subsequent hydrogenation of the olefins was the method used to obtain the ethyl and propyl aromatic hydrocarbons, whereas the methyl hydrocarbon was obtained by the direct hydrogenolysis of the alcohol. The dicyclohexyl hydrocarbons were obtained by complete hydrogenation of the aromatic olefins or hydrocarbons. The physical properties obtained were melting point, boiling point, density, refractive index, heat of combustion and kinematic viscosity. Two new compounds, 1,3-diphenyl- and 1,3-dicyclohexyl-2-propylpropane, are reported.

Introduction

The methyl, ethyl and propyl homologs of the 1,3-diphenyl- and 1,3-dicyclohexyl-2-alkylpropane series were among those hydrocarbons of interest at this Laboratory for an investigation of the effects of structure on combustion characteristics and physical properties.² Although the methyl and ethyl hydrocarbons of both series have previously been described,^{3,4} the absence of some physical properties and lack of agreement among some of the published properties necessitated the work described herein. (References 3 and 4 give with each physical constant listed comprehensive primary references which cover adequately the various methods of syntheses for these hydrocarbons.)

The general method used for obtaining the hydrocarbons started with the reaction of two moles of benzylmagnesium chloride with one mole of either an ester⁵ or a halide of an aliphatic acid to produce the 1,3-diphenyl-2-alkyl-2-propanols. The ethyl-

and propylcarbinols were dehydrated to the olefins from which the aromatic hydrocarbons were obtained by hydrogenation of the double bond. The methyl aromatic hydrocarbon on the other hand was obtained in good yield directly from the methylcarbinol by hydrogenolysis. However, when this reaction was tried with the ethyl- and propylcarbinols, it failed to give satisfactory products and yields. The 1,3-dicyclohexyl-2-alkylpropanes were obtained by complete hydrogenation of either the purified aromatic hydrocarbons or intermediate olefins.

The syntheses were carried out on a scale to provide 500 ml. of each hydrocarbon with an estimated purity of about 99 mole per cent. It was possible to calculate the purity from the time-temperature melting curve only in the case of 1,3-dicyclohexyl-2-methylpropane. The time-temperature melting curve obtained for 1,3-diphenyl-2-methylpropane was too short for a valid estimation of purity. Since none of the other four compounds could be induced to crystallize, it can only be stated that the purities of these five hydrocarbons are believed to be of the same order as that of 1,3-dicyclohexyl-2-methylpropane, inasmuch as all the compounds were prepared and purified by similar methods.

In Table I, the physical properties and carbon-hydrogen analyses of the six 1,3-diphenyl- and 1,3-dicyclohexyl-2-alkylpropanes are presented. The apparatus and procedure used in the determination

(1) Presented before the Organic Division of the American Chemical Society, Buffalo, N. Y., March 24, 1952.

(2) Previous papers of this series giving physical properties of hydrocarbons closely related to these hydrocarbons are: K. T. Serijan and P. H. Wise, *THIS JOURNAL*, **74**, 365 (1952); P. H. Wise, K. T. Serijan, and I. A. Goodman, National Advisory Committee Aeronautical Report 1003 (1951).

(3) G. Egloff, "Physical Constants of Hydrocarbons," Vol. II, Reinhold Publishing Corp., New York, N. Y., 1940, pp. 210–211.

(4) G. Egloff, *ibid.*, Vol. III, 1946, pp. 360 and 370.

(5) M. Tiffeneau and J. Levy, *Bull. Soc. Chim.*, **33**, 735 (1923)

TABLE I
PROPERTIES OF HYDROCARBONS

Hydrocarbons	M.p., °C.	B.p., ^a at 760 mm.	<i>n</i> ²⁰ _D	<i>d</i> ²⁰ g./ml.	Net heat of comb., ^b kcal./ mole at 25°	Kinematic viscosity, ^c centistokes				Carbon, %		Hydrogen, %	
						32° F.	100° F.	140° F.	210° F.	Calcd.	Found	Calcd.	Found
1,3-Diphenyl-2-methylpropane	-33.7 ^d	303.0	1.5519	0.96694	2045	31.8	5.44	3.03	1.51	91.37	91.38	8.63	8.60
1,3-Diphenyl-2-ethylpropane	Glass	314.6	1.5491	.96457	2190	50.3	6.44	3.40	1.62	91.01	91.01	8.99	9.00
1,3-Diphenyl-2-propylpropane	Glass	323.2	1.5424	.95352	2345	70.8	7.43	3.75	1.71	90.69	90.72	9.31	9.28
1,3-Dicyclohexyl-2-methylpropane	+0.57 ^e	295.2	1.4756	.87151	2300	35.8	7.12	4.02	1.99	86.40	86.40	13.60	13.56
1,3-Dicyclohexyl-2-ethylpropane	Glass	306.1	1.4773	.87491	2445	72.1	9.22	4.80	2.20	86.36	86.34	13.64	13.66
1,3-Dicyclohexyl-2-propylpropane	Glass	316.1	1.4764	.87191	2590	^f	12.6	5.82	2.44	86.31	86.25	13.69	13.72

^a With slight decomposition. ^b A.S.T.M. procedure D240-39. ^c Determined in viscosimeters calibrated with NBS standard viscosity samples and using A.S.T.M. procedure D445-46T. ^d Time-temperature melting curve was too short for valid estimation of purity. ^e Heat of fusion, 5.8 kcal./mole; estimated purity, 99.9 mole per cent. ^f Value obtained is omitted because it was at variance with the other values when plotted on A.S.T.M. standard viscosity-temperature chart. D341-chart E.

TABLE II

SYNTHESES OF 1,3-DIPHENYL-2-ALKYL-2-PROPANOLS AND OLEFINS

Homo- log	Grignard reactants		Ester or acid halide, moles	1,3-Diphenyl-2-alkyl-2-propanol			1,3-Diphenyl-2-alkylpropene			
	Benzyl chloride, moles (g.)	Mag- nesium turn- ings, g atoms (g.)		Yield, % (g.)	B.p., (uncor.) (mm.)	<i>n</i> ²⁰ _D	Dehydrating agent	Yield, %	B.p., (uncor.) (mm.)	<i>n</i> ²⁰ _D
Methyl	115 (14,558)	110 (2675)	50 Ethyl acetate	62 (7000)	145-155 (6)	1.5699-1.5750	Reflux with 20% H ₂ SO ₄	87	170-175 (10)	1.5797-1.5917
Ethyl	111 (14,053)	110 (2675)	50 Propionyl chloride	51 (6100)	177 ^a (7)	1.5661 ^a	Reflux with 20% H ₂ SO ₄	88	190-200 (27)	1.5762-1.5774
Propyl	110 (13,925)	104 (2530)	50 Ethyl butyrate	53 (6730)	182 ^a (7)	1.5585 ^a	Alumina, 200- 250°	82	122-132 (1)	1.5642-1.5712

^a Values from selected fractions.

of physical properties and the equipment used in the purification of the hydrocarbons have been previously described and referenced.⁶ The physical properties of two hydrocarbons, 1,3-diphenyl- and 1,3-dicyclohexyl-2-propylpropane, are reported for the first time.

The authors are indebted to the Physical Constants Group and Analytical Section of this Laboratory for the determination of physical constants and of heats of combustion and carbon-hydrogen analyses.

Experimental

The syntheses and purification of the carbinols and corresponding olefins, being essentially the same for each of the isomers, are described in a general procedure; and the specific details pertinent to each synthesis are presented in Table II. The syntheses of each of the final hydrocarbons, on the other hand, are described individually since each was prepared generally from a different intermediate compound. The final hydrocarbons were purified using a standard procedure which is given in detail for the 1,3-diphenyl- and 1,3-dicyclohexyl-2-methylpropanes. Prior to the determination of the physical properties listed in Table I, the hydrocarbons were percolated through silica gel to remove trace impurities, particularly oxygenated compounds.

Materials.—The benzyl chloride (Heyden Chemical Corp.) was purified by vacuum distillation. To prevent decomposition, the center-cut of the distillate was collected over calcium hydride; this procedure permitted the benzyl chloride to be stored at least one to two months in clear glass bottles without decomposing. The ethyl acetate (Eimer and Amend C.P. grade) and ethyl butyrate (Eastman Kodak Co. white label grade) were dried over calcium chloride and used without further purification. The propionyl chloride (Eastman Kodak, white label) was used as received.

1,3-Diphenyl-2-alkyl-2-propanol.—The Grignard reagent was prepared in a 30-gallon, glass-lined reactor by the reaction of 110-115 moles of benzyl chloride in 7 gal. of dry ether

with 104-110 g atoms of magnesium covered with about 3 gal. of dry ether. Condensation of the benzylmagnesium chloride was accomplished with 50 moles of the acid halide or ester, dissolved in 3 gal. of dry ether. The reaction mixture, which was stirred overnight, was hydrolyzed the following morning with a saturated solution of ammonium chloride. The ether layer, syphoned from the hydrolysis sludge, was washed with sodium bicarbonate solution and several times with water, and the ether was distilled at atmospheric pressure. Distillation of the 1,3-diphenyl-2-alkyl-2-propanol was accomplished under reduced pressure in 3-ft. X 25 mm. i.d. heated glass columns packed with 1/4-inch Berl saddles. Since some dehydration of the ethyl- and propylcarbinols occurred during distillation, only those values for boiling point and refractive index from selected fractions are used in Table II.

1,3-Diphenyl-2-alkylpropenes.—The methyl- and ethylcarbinols were dehydrated to the corresponding olefins by refluxing about 2 hours in the presence of 20% sulfuric acid and the resulting olefins were purified by fractional distillation at reduced pressure. The propylcarbinol was dehydrated by passing the material over alumina heated to 250-280°. Vacuum distillation of the product in a 6-ft. glass-helix-packed column gave 1,3-diphenyl-2-propylpropene as shown in Table II.

Characterization of Olefins.—The methyl and propyl olefins were converted to the ozonides⁷ and upon cleavage, fragments corresponding only to 1,3-diphenyl-2-alkylpropene were found. Fragments from the methyl olefin were benzaldehyde and phenylacetone which were identified by preparing 2,4-dinitrophenylhydrazones and comparing these with authentic samples. Similarly, the two fragments obtained from the propyl olefin were: benzaldehyde, which was identified by preparing the 2,4-dinitrophenylhydrazone and comparing it to an authentic sample, and 1-phenyl-2-pentanone, which was identified by its semicarbazone, the m.p. of which was 83-84° (literature 82°).

For the ethylcarbinol and olefin, a carbon-hydrogen analysis of the carbinol was obtained. Calcd. for C₁₇H₂₀O: C, 84.95; H, 8.39; O, 6.66. Found: C, 84.96; H, 8.44.

1,3-Diphenyl-2-methylpropane.—The hydrogenolysis of 5,668 g. (25.1 moles) of 1,3-diphenyl-2-methyl-2-propanol,

(7) A. L. Henne and W. L. Perilstein, *ibid.*, **65**, 2183 (1943).

(8) J. B. Senderens, *Ann. chim.*, **28**, 321 (1913).

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

mixed with 1250 ml. of halogen-free dioxane, was accomplished in a 20-l. autoclave at 220–240° and 2800 p.s.i. hydrogen pressure in the presence of copper chromite catalyst (10% by wt.). Vacuum distillation of the product in 3-ft. columns packed with Berl saddles gave 4070 g. (77% yield) of 1,3-diphenyl-2-methylpropane, b.p. 128–132° (5 mm.), n_{D}^{20} 1.5518–1.5567. The hydrocarbon was then fractionated in a 7-ft. glass-helix-packed column to obtain 1260 g. of distillate which had a constant n_{D}^{20} 1.5519. Upon re-fractionation of the distillate through a 6-ft. Podbielniak column, 500 ml. of 1,3-diphenyl-2-methylpropane was obtained which, when percolated through silica gel, had the properties listed in Table I.

The hydrogenolyses of the ethyl- and propylcarbinols under similar reaction conditions were relatively unsuccessful. The products were found to contain unconverted carbinol, low-index material indicative of ring attack, and relatively low yields of the respective hydrocarbons. Yields of the 1,3-diphenyl-2-alkylpropane were: ethyl-, 39%; propyl-, 22%.

1,3-Dicyclohexyl-2-methylpropane.—A quantity (1212 g., 5.8 moles) of 1,3-diphenyl-2-methylpropane, dissolved in an equal volume of methylcyclohexane was hydrogenated over U.O.P. nickel catalyst (20% by wt.) at 100–150° and 1800 p.s.i. hydrogen pressure. The product was fractionated *in vacuo* in a 7-ft. glass-helix-packed column and 1220 g. (95% yield) of 1,3-dicyclohexyl-2-methylpropane was obtained, b.p. 141–143° (9 mm.), n_{D}^{20} 1.4755–1.4756. This hydrocarbon was then fractionated in a 6-ft. Podbielniak column to give a quantity of 850 g. which had a constant n_{D}^{20} 1.4755. The 1,3-dicyclohexyl-2-methylpropane was percolated through silica gel and 500 ml. of the hydrocarbon, which had the physical properties listed in Table I, was obtained.

1,3-Diphenyl-2-ethylpropane.—The hydrogenation of 1,3-diphenyl-2-ethylpropane (1883 g., 8.5 moles) was carried out over copper chromite catalyst (10%) at 220–240° and at 2500 p.s.i. hydrogen pressure. Vacuum distillation of the product produced 1565 g. (82% yield) of 1,3-diphenyl-2-ethylpropane, b.p. 153–167° (11 mm.), n_{D}^{20} 1.5495–1.5520. Fractionation of the hydrocarbon in a 6-ft. Podbielniak-column gave 798 g. of the 1,3-diphenyl-2-ethylpropane which

had the physical properties listed in Table I. The infrared spectrum of the hydrocarbon showed no absorption characteristic of the parent carbinol.

1,3-Dicyclohexyl-2-ethylpropane.—Total reduction of 1,3-diphenyl-2-ethylpropane (1235 g., 5.5 moles) with hydrogen in the presence of U.O.P. nickel catalyst was carried out at 160–200° and 1750 p.s.i. Vacuum distillation of the product gave 1225 g. (94% yield) of 1,3-dicyclohexyl-2-ethylpropane, b.p. 122–126° (2 mm.), and constant n_{D}^{20} 1.4771. Refractionation of the saturated hydrocarbon in a 6-ft. Podbielniak column produced 943 g. of the compound which had a constant n_{D}^{20} 1.4772 and constant d_{4}^{20} 0.8749. Examination of the infrared spectrum of the dicyclohexyl hydrocarbon showed that the maximum concentration of the parent aromatic hydrocarbon that could be present was 0.1%.

1,3-Diphenyl-2-propylpropane.—A portion of the 1,3-diphenyl-2-propylpropane (1560 g., 6.6 moles) with 200 ml. of methylcyclohexane as solvent, was hydrogenated over copper chromite catalyst (15% wt.) at 210–250° and 2500 p.s.i. After the solvent was removed by distillation at atmospheric pressure the product was vacuum distilled to obtain 1150 g. (74% yield) of 1,3-diphenyl-2-propylpropane, b.p. 144–154° (2 mm.) and n_{D}^{20} 1.5406–1.5421. Refractionation of the 1,3-diphenyl-2-propylpropane in a 6-ft. Podbielniak column produced 870 g. of the hydrocarbon, which had constant n_{D}^{20} 1.5422 and d_{4}^{20} 0.9534–0.9535. The infrared spectrum indicated that the hydrocarbon was not contaminated by unreacted carbinol.

1,3-Dicyclohexyl-2-propylpropane.—Another portion of the 1,3-diphenyl-2-propylpropane (1400 g., 5.9 moles) was totally reduced by hydrogen in the presence of U.O.P. nickel (9% by wt.) at 125–200° and 2500 p.s.i. Vacuum distillation of the product gave 1400 g. (94% yield) of 1,3-dicyclohexyl-2-propylpropane, b.p. 150–152° (2 mm.) and n_{D}^{20} 1.4761–1.4762. The hydrocarbon was then fractionated in a 6-ft. Podbielniak column to obtain 1035 g. of 1,3-dicyclohexyl-2-propylpropane, n_{D}^{20} 1.4763 and d_{4}^{20} 0.8718. Examination of the infrared spectrum of the dicyclohexyl hydrocarbon showed that the concentration of the parent aromatic hydrocarbon could not exceed 0.1%.

CLEVELAND, OHIO

[CONTRIBUTION FROM THE FULMER CHEMICAL LABORATORY, THE STATE COLLEGE OF WASHINGTON]

Cortical Steroid Analogs. I. Acetylcarbinols Obtained by the Hydration of Ethynylcarbinols¹

BY GARDNER W. STACY AND RICHARD A. MIKULEC²

RECEIVED AUGUST 31, 1953

A convenient procedure has been developed for the hydration of 1-ethynylcyclopentanol and 1-ethynylcyclohexanol, respectively, to yield the corresponding acetylcarbinols (α -ketols) in about 70% yield. The products obtained were of a high degree of purity, being free of any perceptible amount of isomeric α -ketol formed by ring enlargement. This has been established by periodic acid oxidation of selected fractions of these products to give cyclopentanone and cyclohexanone, respectively, in excellent yield, isolated as their 2,4-dinitrophenylhydrazones derivatives. Further confirmation of structure was obtained by reduction of the α -ketols to glycols and subsequent cleavage with lead tetraacetate to form acetaldehyde and the corresponding alicyclic ketone. 1-Acetylcyclopentanol was also converted by means of the haloform reaction to 1-hydroxycyclohexanecarboxylic acid. In the course of these studies, a good method for the preparation of 1-ethynylcyclopentanol also has been developed.

An approach to the synthesis of cortical steroid analogs, involving elements of structure common to the D-ring of cortisone, previously has been reported.³ This method involves the conversion of an alicyclic ketone to an ethynylcarbinol followed by hydration in an acidic mercuric sulfate medium to yield an α -ketol.

(1) Presented in part before the Division of Organic Chemistry at the 123rd Meeting of the American Chemical Society, Los Angeles, Calif., March 16, 1953.

(2) In part abstracted from a thesis submitted by Richard A. Mikulec in partial fulfillment of the requirements for the Degree of Master of Science, State College of Washington, June, 1953.

(3) G. W. Stacy and C. A. Hainley, *THIS JOURNAL*, **73**, 5911 (1951).

In parallel work in the steroid series, it had been previously observed that compounds having ethynyl and hydroxyl groups in the 17-position suffer rearrangement on attempted hydration to give an unanticipated D-homosteroid.⁴ To obtain the un-rearranged, acetylcarbinol structure, it was necessary to resort to modified conditions⁵; however, the yields were not generally good unless the 17-hydroxyl group had been acetylated prior to hydra-

(4) (a) L. Ruzicka, *et al.*, *Helv. Chim. Acta*, **21**, 1760 (1938); **22**, 626 (1939); (b) H. E. Stavely, *THIS JOURNAL*, **61**, 79 (1939); (c) a more detailed summary of previous work relating to this subject has recently been presented by R. B. Turner, *ibid.*, **75**, 3484 (1953).

(5) H. E. Stavely, *ibid.*, **62**, 489 (1940).