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Dicyclic Hydrocarbons. IV. Synthesis and Physical Properties of α,α - and α,ω -Diphenyl- and Dicyclohexyl- Pentanes and Hexanes¹

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Data are presented for the synthesis, purification and physical properties of eight dicyclic hydrocarbons, consisting of the α,α - and α,ω -diphenylpentanes and diphenylhexanes and the corresponding dicyclohexylalkanes. Melting point values are given for each of these hydrocarbons, all of which have been prepared in a state of purity of 99 mole %, or better. The kinematic viscosity at four temperatures and the heat of combustion are included in the physical properties presented. The physical properties of 1,1-dicyclohexylpentane and 1,1-dicyclohexylhexane are reported for the first time. Some properties and yields of various synthesis intermediates are briefly discussed.

The program of the systematic development of the diphenyl- and dicyclohexylalkane series as one of several classes of dicyclic hydrocarbons being currently investigated at this Laboratory has been extended to include the α,α - and α,ω -diphenyl- and dicyclohexyl- pentanes and hexanes.

The synthesis, purification and physical properties of the fourteen hydrocarbons comprising this series through C₁₅ have been recently published,² and correlations between molecular structure and physical properties for some of these compounds have also been reported.³ The desirability for additional data with respect to certain molecular configurations involved in the correlations led to the preparation of this group of eight hydrocarbons reported in the present paper.

This paper describes the synthesis, purification and physical properties of 1,1- and 1,5-diphenylpentane, 1,1- and 1,6-diphenylhexane as well as the corresponding dicyclohexyl compounds. The 1,1-diphenylalkane hydrocarbons were obtained through the Grignard synthesis involving the condensation of ethyl *n*-valerate and ethyl *n*-caproate with phenylmagnesium bromide, followed by dehydration of the carbinol and reduction of the resulting olefin. The α,ω -diphenylalkane hydrocarbons were prepared by a similar procedure involving the condensation of hydrocinnamaldehyde with β -phenylethylmagnesium bromide and γ -phenylpropylmagnesium bromide. The dicyclohexylalkane hydrocarbons were prepared by the complete hydrogenation of the purified aromatic hydrocarbons or intermediate olefins.

As in the previous preparations, the scale of synthesis was planned so that approximately 500-ml. quantities of each hydrocarbon would be made available in maximum purity for specific test purposes.

Proof of structure was effected by the ozonolysis of the intermediate olefins and also by an independent synthesis in the case of 1,6-diphenylhexane.

The physical properties for the eight hydrocarbons listed in Table I, including viscosities at four selected temperatures, heats of combustion and heats of fusion, in addition to the usual properties, were determined by procedures previously described.⁴ Values of purity were determined by the

method of Glasgow and co-workers⁵ and are shown in Table I to be a minimum of 99 mole %. Melting points for most of these hydrocarbons are being reported for the first time.

Evidence of two crystalline modifications for 1,1-dicyclohexylhexane was obtained by the appearance of two distinct plateaus during the heat of fusion determination. The melting point of the higher-melting modification could not be accurately measured by the usual time-temperature procedure, since crystals of only the lower-melting form could be obtained despite numerous attempts.

A search of the literature indicated no references pertinent to 1,1-dicyclohexylpentane and 1,1-dicyclohexylhexane. The preparation and the physical properties of these hydrocarbons are thus described for the first time.

Experimental

1,1-Diphenyl-1-pentene.—A synthesis similar to the procedure used by Lagrave⁶ was employed in the preparation of 1,1-diphenyl-1-pentene. Ethyl *n*-valerate (Eastman Kodak Co.) was purified by fractional distillation before use and had the following properties: b.p. 144.95° at 760 mm., n_{20}^D 1.4007 and d_{20}^{20} 0.87433 g./ml.

The reaction, carried out in a 30-gal. glass-lined reactor, involved the use of 9420 g. (60 moles) of freshly-distilled bromobenzene and 1550 g. (63.8 g. atoms) of magnesium covered with 10 l. of dry ether. The preparation of the Grignard reagent required 3 hours for completion and 2 hours were required for the addition of 3500 g. (26.9 moles) of the ester dissolved in 3 l. of dry ether. The reaction mixture was stirred for 48 hours and hydrolyzed by the addition of a saturated solution of ammonium chloride. The ether layer was siphoned off and the residual solid was decomposed with 15% hydrochloric acid and worked up separately. Each portion was neutralized and the ether was removed by distillation. This procedure resulted in complete dehydration of the carbinol. The dried products from the two batches were combined since the boiling points and refractive indices were identical. Fractional distillation gave a total of 5081 g. (85% yield) of an olefinic product. A selected fraction had the following properties: b.p. 125–126° at 1 mm., and 308.76° at 760 mm., n_{20}^D 1.5811 and d_{20}^{20} 0.98137 g./ml.

Anal. Calcd. for C₁₇H₁₈: C, 91.84; H, 8.16. Found: C, 91.81; H, 8.12.

The structure of the olefin was established by ozonolysis⁷ to be 1,1-diphenyl-1-pentene since the degradation products were identified as butyraldehyde and benzophenone by means of their 2,4-dinitrophenylhydrazones.

1,1-Diphenylpentane.—The hydrogenation of 1,1-diphenyl-1-pentene occurred at 140–150° at 1900 p.s.i. using copper chromite catalyst (15% by wt.), but fractional dis-

(1) Presented before the Organic Division of the American Chemical Society, Cleveland, Ohio, April, 1951.

(2) K. T. Serijan and P. H. Wise, *THIS JOURNAL*, **73**, 4766 (1951).

(3) P. H. Wise, K. T. Serijan and I. A. Goodman, *Natl. Advisory Comm. Aeronaut. Report* 1003 (1951).

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

(5) A. R. Glasgow, A. J. Streif and F. D. Rossini, *J. Research Natl. Bur. Standards*, **55**, 355 (1945).

(6) R. Lagrave, *Ann. chim.*, [10] **8**, 363 (1927).

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

TABLE I
 PHYSICAL PROPERTIES OF α,α - AND α,ω -DIPHENYL- AND DICYCLOHEXYL- PENTANES AND HEXANES

Hydrocarbon	M.p., °C.	B.p., °C. at 760 mm.	n_D^{20}	d_4^{20} , g./ml.	Heat of fusion, kcal./ mole	Esti- mated purity, mole %	Net heat of comb., ^a kcal./ mole, at 25°	Kinematic viscosity, ^b (centistokes)				Analyses, %			
								32° F.	100° F.	140° F.	210° F.	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
1,1-Diphenylpentane	-12.06	307.89	1.5511	0.96594	6.4	99.8	2190	41.50	6.36	3.38	1.62	91.01	91.01	8.99	8.97
1,5-Diphenylpentane	-7.95	330.62	1.5463	.96083	6.2	99.8	2180	19.48	5.02	3.05	1.64	91.01	91.01	8.99	8.96
1,1-Diphenylhexane	-11.76	321.03	1.5450	.95639	6.3	99.0	2330	46.51	7.19	3.78	1.78	90.69	90.69	9.31	9.26
1,6-Diphenylhexane	-11.99	345.67	1.5409	.95237	7.0	99.7	2330	22.28	5.72	3.33	1.81	90.69	90.68	9.31	9.30
1,1-Dicyclohexyl- pentane	15.29	308 ^c	1.4838	.88788	9.1	99.5	2445	...	13.90	6.16	2.47	86.36	86.33	13.64	13.64
1,5-Dicyclohexyl- pentane	-13.61	325.15	1.4751	.86872	7.8	99.2	2445	38.79	8.86	5.01	2.46	86.36	86.35	13.64	13.67
1,1-Dicyclohexyl- hexane	3.39 ^d	316. ^e	1.4827	.88478	7.8	99.2	2585	...	16.44	7.16	2.77	86.32	86.43	13.68	13.65
1,6-Dicyclohexyl- hexane	10.21	340.5 ^e	1.4750	.86775	8.2	99.9	2585	...	10.46	5.75	2.75	86.32	86.32	13.68	13.72

^a A.S.T.M. procedure D 240-39. ^b Determined in viscosimeters calibrated with N.B.S. standard viscosity samples and using A.S.T.M. procedure D 445-46T. ^c Some decomposition observed. ^d A second crystalline modification as indicated by the heat of fusion data melted at 8.7° (approx.).

tillation of the product showed slight traces of olefinic contaminations. A second hydrogenation involving the use of ethanol as a solvent gave complete reduction of the olefin. Purification of the product was effected by fractionation *in vacuo* on a 6-ft. Podbielniak column. The properties listed in Table I were taken on a freshly-distilled sample since an aldehyde odor indicated that oxidation occurs when the hydrocarbon stands for a few days in contact with air.

1,1-Dicyclohexylpentane.—A charge consisting of 975 g. (4.4 moles) of purified 1,1-diphenylpentane, an equal volume of methylcyclohexane, and 146 g. (15% by wt.) of U.O.P. nickel catalyst was hydrogenated in a 3-l. rocker-type autoclave. Reduction occurred at 170–180° at 1900 p.s.i., and 879 g. (85% yield) of 1,1-dicyclohexylpentane with constant refractive index and boiling point was obtained by fractional distillation of the reaction product. Selected fractions from the distillation were percolated through silica gel prior to the determination of the physical properties.

1,5-Diphenyl-3-pentanol.—A solution of 5550 g. (30 moles) of freshly-distilled β -phenylethyl bromide (n_D^{20} 1.5560) in 4 l. of dry ether was added to 765 g. (31.5 g. atoms) of magnesium covered with 8 l. of dry ether. The Grignard reagent was condensed with a solution of 4024 g. (30 moles) of freshly-distilled hydrocinnamaldehyde (b.p. 100° at 10 mm. and n_D^{20} 1.5215) in 4 l. of ether and the reaction mixture was stirred for 12 hours. Hydrolysis with 10% hydrochloric acid was followed by distillation of the neutralized and dried crude product. After removal of the ether, the distillation pressure was reduced and 5570 g. (77% yield) of the desired carbinol was obtained as a liquid which solidified on standing. The carbinol, recrystallized from petroleum ether, melted at 48.5–49.4° which is in agreement with the value reported for the same compound prepared by the reduction of dibenzylacetone.⁶

Anal. Calcd. for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.78; H, 8.38.

1,5-Diphenyl-2-pentene.—A solution of 5450 g. (22.7 moles) of the carbinol in 3 l. of toluene was dehydrated by passage over alumina heated to 350–400°. A yield of 3300 g. (65%) was obtained upon the fractional distillation of the 1,5-diphenyl-2-pentene, a sample of which had the following properties: b.p. 330° (dec.) at 755 mm. and 158° at 3 mm., n_D^{20} 1.5618 and d_4^{20} 0.97681 g./ml. The *cis* and *trans* isomers could not be readily separated.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.74; H, 8.16.

The ozonide of 1,5-diphenyl-2-pentene gave fragments whose 2,4-dinitrophenylhydrazone derivatives after recrystallizations from ethanol melted at 120–121° and 148–152°. These values correspond with the literature with respect to phenylacetaldehyde and hydrocinnamaldehyde. The recrystallized derivative obtained from a known sample of hydrocinnamaldehyde melted at 153–156° and the mixed melting point was 150.5–154°.

1,5-Diphenylpentane.—The hydrogenation of 1,5-diphenyl-2-pentene with copper-chromite catalyst occurred at 130° at 1800 p.s.i. However, an olefinic impurity was detected in the distilled hydrogenation product. Another hydrogenation involving the use of ethanol as solvent gave complete conversion to 1,5-diphenylpentane. A very pure product was obtained by a single fractionation through a Podbielniak column operated at reduced pressure.

1,5-Dicyclohexylpentane.—A second portion of 1,5-diphenyl-2-pentene was hydrogenated directly to the saturated compound using an equal volume of methylcyclohexane as the solvent and 10% by wt. of U. O. P. nickel catalyst. The olefinic bond was reduced at 120° at 1700 p.s.i. and ring saturation occurred at 170–180° at 1500 p.s.i. The solvent was removed by distillation and the product was purified by fractional distillation *in vacuo*. The distilled 1,5-dicyclohexylpentane was passed through silica gel prior to the determination of the physical properties.

1,1-Diphenyl-1-hexanol.—In a Grignard synthesis 14,067 g. (89.6 moles) of freshly-distilled bromobenzene in 6 l. of dry ether reacted with 2286 g. (94.1 g. atoms) of magnesium covered with 12 l. of dry ether. Four hours were required for the preparation of the Grignard reagent, following which 6460 g. (44.8 moles) of purified ethyl *n*-caproate (m.p. -67.64°, b.p. 166.91° at 760 mm., n_D^{20} 1.4073 and d_4^{20} 0.87129 g./ml.) dissolved in 6 l. of dry ether was added. The addition was completed in 2 hours during which period cold water was circulated through the jacket of the reactor. The reaction mixture was hydrolyzed with a saturated solution of ammonium chloride; the product layer was siphoned off, washed and dried and made essentially solvent-free by evaporation of the ether. The carbinol could not be purified by distillation because of dehydration upon moderate heating. A portion of the oil was chilled in petroleum ether to give the crystalline carbinol, m.p. 46.5–47.5°, which agrees with the value reported by Masson.⁹

Anal. Calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.78; H, 8.75.

1,1-Diphenyl-1-hexene.—The distillation *in vacuo* of the principal portion of the crude carbinol gave complete dehydration. The 1,1-diphenyl-1-hexene was fractionally distilled to give 8915 g. (84% over-all yield) of product, a selected sample of which had the following properties: b.p. 321.80° at 760 mm., n_D^{20} 1.5725 and d_4^{20} 0.97113 g./ml.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.48; H, 8.51.

The 2,4-dinitrophenylhydrazone derivatives of the fragments obtained by the reduction of the ozonide of 1,1-diphenyl-1-hexene melted at 106.5–107.5° and 240–242° following recrystallization from ethanol. The same derivatives from known samples of valeraldehyde and benzophenone gave no depression on mixed melting points.

1,1-Diphenylhexane.—1,1-Diphenyl-1-hexene dissolved in ethanol was reduced at 130–140° and 1800 p.s.i. with 10% by wt. of copper-chromite catalyst. Fractional distillation

(8) W. Borsche and J. Wollemani, *Ber.*, **45**, 3713 (1912).

(9) H. Masson, *Compt. rend.*, **135**, 533 (1902).

in vacuo yielded a constant refractive index plateau product which had a purity of 99 mole %. No improvement in purity was shown when the material was hydrogenated once more and was purified by distillation and percolation through silica gel.

1,1-Dicyclohexylhexane.—Another portion of the olefin was hydrogenated to the saturated compound directly by using an equal volume of methylcyclohexane and 15% by wt. of U.O.P. nickel catalyst. Reduction of the double bond and of the aromatic nuclei occurred at 130° and at 170–180° at 1500 p.s.i., respectively. Purification consisted of a single fractionation in a Podbielniak column followed by percolation through silica gel.

1,6-Diphenyl-3-hexanol.—A solution of 6,580 g. (33 moles) of γ -phenylpropyl bromide (b.p. 122° at 10 mm.) in 6 l. of dry ether reacted with 710 g. (29.4 g. atoms) of magnesium covered with 8 l. of dry ether in a 30-gal. reactor. A solution of 3676 g. (27.4 moles) of freshly-distilled hydrocinnamaldehyde in 4 l. of dry ether condensed with the Grignard reagent and the reaction mixture was stirred for 12 hours. An emulsion formed during hydrolysis with 10% hydrochloric acid was broken by adding acid of increased concentration (15%). The product layer was worked up in the usual manner and the yield of 1,6-diphenyl-3-hexanol obtained after distillation was 5720 g. (82%); b.p. 196–199° at 3 mm. and n_D^{20} 1.5547. When the oil was dissolved in petroleum ether and chilled, a solid was obtained which melted at 35–35.5°.

Anal. Calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.96; H, 8.70.

1,6-Diphenyl-3-hexene.—A solution of 5610 g. (22.1 moles) of the carbinol dissolved in 3 l. of benzene was passed through a tube packed with alumina and maintained at 350–375°. The theoretical amount of water was obtained and the olefinic product recovered from the distillation was 4980 g. (95% yield). A subsequent fractional distillation gave an olefin with the following properties: m.p. –8.41°, b.p. 340° (dec.) at 760 mm. and 167° at 3.5 mm., n_D^{20} 1.5551 and d_4^{20} 0.96766 g./ml.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.36; H, 8.59.

The reduction of the ozonide prepared from a sample of the 1,6-diphenyl-3-hexene gave hydrocinnamaldehyde which was characterized as the 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 152.5–156°. This identified the olefin as 1,6-diphenyl-3-hexene. No evidence was found to indicate the presence of the isomeric 1,6-diphenyl-2-hexene which would also be expected as a product of this dehydration reaction.

1,6-Diphenylhexane.—An ethanol solution of 1,6-diphenyl-3-hexene was hydrogenated in a Parr apparatus at room temperature by the use of Adams catalyst. The yield was quantitative and the product was obtained in satisfactory purity by a single fractionation.

The Wurtz reaction involving the coupling of γ -phenylpropyl bromide in the presence of sodium was used as an independent synthesis. Finely divided sodium was obtained by heating 200 g. (8.7 g. atoms) in 1 l. of toluene while maintaining vigorous stirring. After cooling to room temperature, 1701 g. (8.5 moles) of γ -phenylpropyl bromide was added over a period of 6 hours, the reaction flask being intermittently cooled to keep the temperature below 25°. After the addition was completed, the temperature was kept at 50–70° while stirring was maintained for 48 hours. Water was added gradually to the cooled reaction mixture to consume the unreacted sodium. The hydrocarbon layer, after removal, was washed, dried and distilled. Since it gave a positive test for unsaturation, the material was reduced following the same procedure used for 1,6-diphenyl-3-hexene. Subsequent fractionation gave 429 g. (42% over-all yield) of 1,6-diphenylhexane in a state of purity comparable to that of the product obtained from the Grignard synthesis.

1,6-Dicyclohexylhexane.—A charge consisting of 908 g. (3.8 moles) of 1,6-diphenylhexane in an equal volume of methylcyclohexane with 100 g. of U. O. P. nickel catalyst was reduced at 180–190° at a pressure of 1700 p.s.i. in a 3-l. bomb. The catalyst was filtered out and the solvent was distilled from the product. The fractional distillation of the remaining material gave 892 g. (94%) of 1,6-dicyclohexylhexane which was percolated through silica gel prior to the determination of the physical properties.

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Synthesis of Alkoxy Silanols and Siloxanes¹

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The alkoxy silanol, -disiloxanol and -trisiloxanol derivatives of methylisobutylcarbinol have been prepared and isolated in good yields. The silanol and disiloxanol have been employed in the stepwise synthesis of linear alkoxytrisiloxanes, and linear and branched alkoxytetrasiloxanes. Attempted preparations of a linear and branched pentasiloxane were unsuccessful, as was the isolation of the alkoxy silanol derivative of 2-ethylhexanol.

In an examination of the effects of siloxane chain structure upon the liquid properties of alkoxy siloxanes it was desired to synthesize certain tri-, tetra- and pentasiloxanes by routes which avoid the inherent difficulties of chlorosiloxanes² or orthosilicate esters³ as starting materials. A stepwise synthesis has been examined, based upon single condensation reactions of alkoxy silanol and alkoxy chlorosilane derivatives of methylisobutylcarbinol and 2-ethylhexanol. Because of the somewhat general instability of alkoxy silanols but two references have been made to their isolation and these are limited to derivatives of *t*-butyl alcohol,^{4,5}

where steric factors appear to favor stability. No stepwise condensations of the materials were reported, but Backer⁴ has described the hexaalkoxydisiloxane as a very high melting solid. Our desire to study liquid alkoxy siloxanes ruled out further investigation of systems derived from *t*-butyl alcohol.

Of the two alcohols selected only methylisobutylcarbinol gave a trialkoxy silanol (IV) of sufficient stability for isolation. This product as well as the corresponding di-(IX) and trisiloxanol (XI) derivatives were prepared in good yields. Figure 1 illustrates the preparation of these materials and the utilization of IV and IX in the syntheses of the disiloxane (V), linear trisiloxane (VI) and the branched and linear tetrasiloxanes (VII and X). Repeated attempts to prepare the linear pentasiloxane by reaction between the trisiloxanol (XI) and the chlorodisiloxane (VIII) were not successful. Also, the branched

(1) This paper is taken from a portion of the research sponsored by the Hodges Research and Development Company, Redwood City, California. Further work on this subject is being conducted by the Oronite Chemical Company, San Francisco, California.

(2) W. C. Schumb and D. Holloway, *THIS JOURNAL*, **63**, 2753 (1941).

(3) E. Kourad, O. Bachle and R. Signer, *Ann.*, **474**, 276 (1929).

(4) H. J. Backer and H. A. Klasens, *Rec. trav. chim.*, **61**, 500 (1942).

(5) C. S. Miner, *et al.*, *Ind. Eng. Chem.*, **39**, 1368 (1947).