were used for determination of infrared spectra which were obtained with a Perkin–Elmer infrared spectrometer, Model 12-C.

3α-Hydroxy-11,20-diketo-Δ^{16}-pregnene (II).—In a solution of 30 ml. of acetic acid and 10 ml. of water, 3.065 g. of 3α-hydroxy-21-acetoxy-11,20-diketo-12α-bromo-Δ^{16}-pregnene (I) was stirred for ten minutes at 15° with 6 g. of zinc dust. The suspended material was removed by filtration, washed with methanol and the combined filtrates were evaporated under reduced pressure nearly to dryness. Addition of water precipitated material which weighed 1.9 g. Crystallization four times from methanol–water gave material which melted at 220–222°, $[\alpha]^{24°}\mathrm{D}$ +91° ($CHCl_3$), $\lambda_{max.}$ 235 mμ, ϵ 7,400. Ninety-eight per cent. of the theoretical amount of bromide ion was present in the aqueous phase.

Anal. Calcd. for $C_{21}H_{30}O_3$: C, 76.34; H, 9.15. Found: C, 76.10; H, 9.07.

When treatment with zinc was carried out at 15° for three minutes a 71% yield of II was obtained, m.p. 208–212°, $[\alpha]^{24°}\mathrm{D}$ +87° ($CHCl_3$).

$3\alpha,20\alpha$-Dihydroxy-11-keto-Δ^{16}-pregnene (III).—The combined mother liquors from the preceding experiment (II from 3.065 g. of I) were concentrated under reduced pressure and yielded 800 mg. of crystalline solid. Recrystallization from ethyl acetate gave a product which melted at 183–185°, $[\alpha]^{24°}\mathrm{D}$ +61° ($CHCl_3$).

When treatment with zinc was extended to 130 minutes at 30–38°, the yield of crude material, m.p. 178–180°, $[\alpha]^{24}\mathrm{D}$ +60° ($CHCl_3$), was 43%. Recrystallization several times from ethyl acetate raised the melting point to 189–190°, $[\alpha]^{24}\mathrm{D}$ +57° ($CHCl_3$). This compound did not have an absorption maximum between 225 and 250 mμ and did not show an acetate band in the infrared spectrum. It gave a negative α-ketol test with alkaline 2,3,5-triphenyltetrazolium chloride reagent and a positive test for unsaturation with tetranitromethane.

Anal. Calcd. for $C_{21}H_{32}O_3$: C, 75.85; H, 9.70. Found: C, 75.72; H, 9.58.

3,11,20-Triketo-Δ^{16}-pregnene (IV).—To a solution of 990 mg. of 3α-hydroxy-11,20-diketo-Δ^{16}-pregnene in 4 ml. of chloroform and 1 ml. of acetic acid was added 0.33 ml. (130%) of 23.7 *N* aqueous chromic acid. After vigorous stirring for 15 minutes at 0°, 0.33 ml. of 18 *N* sulfuric acid was added and the mixture was stirred for one hour at 0°. Water and chloroform were added and the organic phase was washed with dilute hydrochloric acid, a 5% solution of sodium carbonate, and with water, dried and evaporated under reduced pressure. Crystallization from methanol afforded 446 mg. of product which melted at 196–198°. Addition of water to the methanol gave 306 mg. as a second crop, m.p. 180–185°. Recrystallization of the first crop from methanol raised the melting point to 205–210°, $[\alpha]^{24}\mathrm{D}$ +110° ($CHCl_3$); $\lambda_{max.}$ 235 mμ, ϵ 8,900.

Anal. Calcd. for $C_{21}H_{28}O_3$: C, 76.80; H, 8.59. Found: C, 76.97; H, 8.57.

3α-Hydroxy-11,20-diketopregnane (V).—Hydrogenation of 500 mg. of 3α-hydroxy-11,20-diketo-Δ^{16}-pregnene was carried out in 10 ml. of methanol with 1.5 g. of 2% palladium hydroxide on calcium carbonate at room temperature and atmospheric pressure. After 11 minutes the catalyst was filtered out, the solution was concentrated under reduced pressure, the product was precipitated with water and recrystallized from ethyl acetate. The crystals, 220 mg., melted at 175–177°, $[\alpha]^{24}\mathrm{D}$ +114° ($CHCl_3$). The reported melting point is 172–174°.[3] The melting point was not depressed by admixture with an authentic sample of V. The infrared spectrum of this product was identical with that of a sample of V previously prepared in this Laboratory.

$3\alpha,20\alpha$-Dihydroxy-11-ketopregnane (VI).—In a solution of 5.0 ml. of methanol 280 mg. of $3\alpha,20\alpha$-dihydroxy-11-keto-Δ^{16}-pregnene (III) was hydrogenated at room temperature and pressure in the presence of 506 mg. of 2% palladium hydroxide on calcium carbonate. After nine minutes the catalyst was filtered out, the filtrate was evaporated under reduced pressure, and the residue was crystallized from ether–petroleum ether. The compound [179 mg. (64%), m.p. 203–205°], after recrystallization from methanol–acetone, melted at 214–217°, $[\alpha]^{24}\mathrm{D}$ +63° (alcohol). The melting point of a mixture with an authentic sample of VI was 216–219°. The reported constants[5,6] are m.p. 217–219° and 219–221°, $[\alpha]^{27}\mathrm{D}$ +59° and $[\alpha]^{25}\mathrm{D}$ +61° (alcohol). The ether–petroleum ether filtrate yielded 61 mg. (22%) of needles melting at 171–172°. This material was not investigated further.

3,11,20-Triketopregnane (VII).—Hydrogenation of 100 mg. of 3,11,20-triketo-Δ^{16}-pregnene (IV) by the procedure given for the preparation of VI from III yielded 71 mg. of VII which was crystallized from ether–petroleum ether, m.p. 160–162°, $[\alpha]^{24}\mathrm{D}$ +113° (acetone). The reported[4] melting point is 154–156°, $[\alpha]^{20}\mathrm{D}$ +119° (acetone).

3,11,20-Triketopregnane (VII).—Oxidation of 100 mg. of $3\alpha,20\alpha$-dihydroxy-11-ketopregnane with 0.085 ml. of 23.7 *N* aqueous chromic acid and 0.07 ml. of 18 *N* sulfuric acid in chloroform–acetic acid yielded, after crystallization from ether, 67 mg. of VII, m.p. 160–161°, $[\alpha]^{24}\mathrm{D}$ +114° (acetone). The melting point was not depressed when this product was mixed with the sample of VII prepared from IV. The infrared spectra of the two preparations were identical.

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Dicyclic Hydrocarbons. III. Diphenyl- and Dicyclohexylalkanes through C_{15}

BY KASPER T. SERIJAN AND PAUL H. WISE

The synthesis and properties including heats of combustion and viscosities are described for a series of dicyclic alkanes prepared in a purity of 99 mole % or higher. The series, starting with diphenylmethane, extends through the diphenylpropanes and comprises a total of fourteen hydrocarbons including the corresponding dicyclohexylalkanes. Melting or freezing point values are reported for each member of the series, eight of these being indicated for the first time. Three new compounds, namely, 2-cyclohexyl-2-(cyclohexan-4-ol)-propane, 2-cyclohexyl-2-(cyclohexen-3-yl)-propane and 2-phenyl-2-cyclohexylpropane are also described.

Several classes of dicyclic hydrocarbons have been synthesized and purified at this Laboratory as part of a program concerned with investigating possible components of aviation fuel. The present paper describes all the diphenyl- and dicyclohexylalkanes from C_{13} through C_{15}; previously reported are some substituted alkylbiphenyls[1] and alkylbicyclohexyls.[2]

Although most of the hydrocarbons prepared in the present work are not new compounds, melting points and viscosities necessary for evaluating the usefulness of these materials as possible fuels, were generally not available. Also, lack of information concerning purity and the fact that the values of the boiling points, densities and refractive indices of many of these hydrocarbons were not in agreement[3,4] made it virtually impossible to distinguish

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

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

[3] G. Egloff, "Physical Constants of Hydrocarbons," Vol. II, Reinhold Publishing Corp., New York, N. Y., 1940.

[4] G. Egloff, *ibid.*, Vol. III, 1946.

those values most nearly correct. Because an objective of the hydrocarbon research program at this Laboratory is the correlation of molecular structure with physical constants,[5] the synthesis, purification, and determination of physical properties of these compounds were required.

The reactions by which each of the hydrocarbons was synthesized were selected so that the final product could be obtained in 500-ml. quantities with purities greater than 99 mole %. 1,1-Diphenylethane and 1,1-diphenylpropane were prepared by the reaction of benzophenone with methylmagnesium chloride[6] and ethylmagnesium bromide,[7,8] respectively, dehydration of the resultant carbinols, and hydrogenation of the olefins. 1,2-Diphenylpropane was obtained in a similar manner from benzylmagnesium chloride and acetophenone.[9,10] Hydrogenation of dibenzyl ketone to the corresponding carbinol, dehydration and subsequent hydrogenation yielded 1,3-diphenylpropane, and the Friedel–Crafts reaction of dimethylphenylcarbinol with benzene gave 2,2-diphenylpropane. Diphenylmethane was purified from commercial material and 1,2-diphenylethane (bibenzyl) was obtained as a by-product from various syntheses involving the use of benzylmagnesium chloride.

In those instances where the structures of the diphenylalkanes might be questioned, ozonolysis of intermediate olefins or alternate methods of synthesis were employed.

2-Phenyl-2-cyclohexylpropane was prepared from *p*-α-cumylphenol for the purpose of observing the effect of the hydrogenation of only one ring on the physical properties. This hydrocarbon and two intermediates in the synthesis, namely, 2-cyclohexyl-2-(cyclohexan-4-ol)-propane and 2-cyclohexyl-2-(cyclohexen-3-yl)-propane are described for the first time.

The dicyclohexylalkanes were prepared by the hydrogenation of the purified diphenyl hydrocarbons. 2,2-Dicyclohexylpropane was also prepared directly by the total hydrogenation of *p*-α-cumyl phenol.

Melting points, boiling points, refractive indices, densities, heats of fusion, heats of combustion and kinematic viscosities for the purified diphenyl and dicyclohexyl hydrocarbons are given in Table I. The apparatus and procedure used in the determination of these properties have been previously referenced.[1]

The estimated purity of these hydrocarbons was calculated from time–temperature melting or freezing curves following the procedure described by Glasgow and co-workers.[11]

Two crystalline modifications were observed for 1,1-dicyclohexylpropane, but the conditions for obtaining one or the other modification were not ascertained.

TABLE I: PHYSICAL PROPERTIES AND ANALYSES OF THE DIPHENYL- AND DICYCLOHEXYLALKANES THROUGH C_{15}

Hydrocarbon	M.p., (°C.)	B.p., (°C. at 760 mm.)	$n^{20}D$	d^{20} (g./ml.)	Heat of fusion (kcal./mole)	Estimated purity (mole per cent.)	Net heat of combn.^{a} (kcal./mole) at 25°	Viscosity, centistokes^{b}				Analyses, % Carbon		Hydrogen	
								32°F.	100°F.	140°F.	210°F.	Calcd.	Found	Calcd.	Found
Diphenylmethane	25.20^{c}	264.27	1.5776	1.00592	4.4^{d}	99.9	1595	^{e}	2.22	1.55	0.97	92.81	92.81	7.19	7.17
1,1-Diphenylethane	−18.01	272.63	1.5725	.99954	4.2	99.8	1735	8.93	2.90	1.89	1.11	92.26	92.19	7.74	7.81
1,2-Diphenylethane	51.16	280.5^{f}	^{e}	^{e}	7.3	99.9	1740	^{e}	...	1.96	1.14	92.26	92.20	7.74	7.76
1,1-Diphenylpropane	13.29	283.22	1.5643	.98663	4.0	99.0	1885	^{e}	3.72	2.25	1.23	91.78	91.80	8.22	8.20
1,2-Diphenylpropane	0.14	283.66	1.5585	.97739	5.4	99.6	1880	16.87	4.02	2.42	1.30	91.78	91.76	8.22	8.23
1,3-Diphenylpropane	−20.78	298.7^{f}	1.5594	.97996	4.4	99.9	1885	12.38	3.64	2.31	1.31	91.78	91.78	8.22	8.18
2,2-Diphenylpropane	29.12	281.19	1.5703	.99806	4.3	99.8	1895	^{e}	4.56	2.71	1.43	91.78	91.80	8.22	8.19
Dicyclohexylmethane	−18.70	252.8^{f}	1.4763	.87646	4.1	99.8	1845	12.96	4.10	2.60	1.43	86.58	86.56	13.42	13.42
1,1- Dicyclohexyl-	−20.87	271.17	1.4845	.89309	4.7	99.8	1995	21.33	5.59	3.37	1.76	86.51	86.49	13.49	13.49
1,2- ethane	11.45	274.38	1.4759	.87395	6.3	99.9	1995	^{e}	5.39	3.24	1.72	86.51	86.45	13.49	13.36
1,1- Dicyclohexyl-	−23.46^{g}	283.56	1.4848	.89299	^{i}	99.8^{h}	2140	32.93	6.42	3.66	1.83	86.45	86.43	13.54	13.43
1,2- propane	−21.46	284.5^{f}	1.4798	.88173	4.1	99.5	2165	28.33	6.44	3.74	1.88	86.45	86.44	13.54	13.47
1,3- Dicyclohexyl-	−14.82	291.69	1.4752	.87128	6.2	99.7	2155	24.87	6.40	3.82	1.96	86.45	86.40	13.54	13.56
2,2- propane	15.61	286.2^{f}	1.4918	.90677	^{j}	99.8^{h}	2150	^{e}	9.79	5.14	2.41	86.45	86.43	13.54	13.52

[a] A.S.T.M. procedure D240-39. [b] Determined in viscosimeters calibrated with N.B.S. standard viscosity samples and using A.S.T.M. procedure D445-46T. [c] Value obtained from the freezing curve. [d] Calculated value selected from H. Huffman, G. Parks and A. Daniels, THIS JOURNAL, 52, 1547 (1930). [e] Indeterminate at the indicated temperature. [f] Some decomposition observed. [g] A second crystalline modification had m.p. −28.21°. [h] A heat of fusion value of 4.0 kcal./mole was used in calculating this value. [i] Value affected by crystalline modifications. [j] Omitted because of inaccuracy due to calibration limitations of apparatus.

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

(6) A. Klages, *Ber.*, **35**, 2646 (1902).

(7) C. Hell and H. Bauer, *ibid.*, **37**, 230 (1904).

(8) A. Klages and S. Heilmann, *ibid.*, **37**, 1447 (1904).

(9) P. Sabatier and M. Murat, *Compt. rend.*, **155**, 385 (1912).

(10) M. Tuot and M. Guyard, *Bull. soc. chim. France*, 1087 (1947).

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

Experimental

Preparation of Diphenylalkanes and Intermediates. Purification.—The methods of purification generally used involved fractional distillation at reduced pressures (1–20 mm.) through 6-ft. columns packed with $^3/_{16}''$ glass helices. If this failed to produce the required purity, a second distillation was conducted using a 6-ft. Podbielniak column operated *in vacuo*. In a few instances, where specifically indicated, azeotropic distillation was also employed. Solid intermediates were similarly purified by distillation supplemented by fractional recrystallization from appropriate solvents.

Prior to the determination of physical properties, the diphenyl- and dicyclohexylalkanes were percolated through tubes packed with silica gel. This procedure, because of its high selectivity for slight traces of residual aromatics, is most effective in the purification of the dicyclohexylalkanes.

Diphenylmethane.—Maximum purity was obtained by a single fractionation of a commercial grade of diphenylmethane (Dow) since neither subsequent straight nor azeotropic distillation using tripropylene glycol showed any improvement over the initially distilled product.

1,1-Diphenylethane.—The procedure of Klages[6] modified by the use of methylmagnesium chloride gave 81–97% yields[12,13] of diphenylmethylcarbinol which after recrystallization from petroleum ether melted at 80–81°.[14] 1,1-Diphenylethene obtained by refluxing the carbinol with acetic anhydride had the following properties following fractional distillation on a column of 30-theoretical plates efficiency: m.p. 8.62°, b.p. 277.10° at 760 mm., $n^{20}\text{D}$ 1.6087 and d^{20} 1.0243 g./ml.

1,1-Diphenylethane was obtained by two procedures, namely, reduction of the olefin in a Parr hydrogenation apparatus using Adams catalyst and ethanol and also by hydrogenolysis of the carbinol at 170° and 1900 p.s.i. using copper–chromite catalyst (10% by wt.) and ethanol.

1,2-Diphenylethane (Bibenzyl).—A sufficient quantity of crude material was available as a by-product from various syntheses involving the use of benzylmagnesium chloride. After fractionation at reduced pressure, the material showed no change in the freezing point upon four successive recrystallizations.

1,1-Diphenyl-1-propene.—The previously reported procedures for the preparation of 1,1-diphenyl-1-propene[7,8] were modified by using ethyl bromide and by avoiding an excess of magnesium to minimize pinacol formation.[13] Distillation of the crude carbinol *in vacuo* gave a partially dehydrated product. Total conversion to the olefin was obtained by refluxing with a trace of iodine for 4 hours.[15] The product was washed, dried and distilled *in vacuo*. An olefinic solid crystallized on standing. A careful fractional distillation of the mother liquor gave additional olefin, b.p. 161–163° at 21 mm., and unreacted benzophenone in the labile form, m.p. 23.64°, $n^{20}\text{D}$ 1.6071 (identified by reduction to benzhydrol, m.p. 67°). The over-all yield of olefin was 46% (based on total benzophenone) which after recrystallization from ethanol melted at 48.5–49.0°.

The olefin was characterized by ozonolysis according to the procedure described by Henne and Perilstein.[16] Acetaldehyde and benzophenone were obtained as the fragments, and the 2,4-dinitrophenylhydrazone derivatives showed no depression in melting points when mixed with authentic samples.

1,1-Diphenyl-1-propene was reduced at room temperature in the low-pressure Parr apparatus using freshly-prepared Raney nickel catalyst and dioxane as solvent, 1,1-diphenylpropane being obtained essentially in quantitative yield.

1,2-Diphenyl-1- and 2-propene.—Acetophenone (30 moles) reacted in a 30-gal. glass-lined reactor with the Grignard reagent prepared from 30 moles of freshly-distilled benzyl chloride[9,10] and, after stirring for 15 hours, the mixture was hydrolyzed with saturated ammonium chloride solution. The ether solvent was removed from the reaction products by distillation which then gave a solid olefinic fraction and a liquid mixture. The latter was refluxed for 2 hours with acetic anhydride, washed, dried and fractionated to give some solid olefin which was identical to that originally isolated, 1390 g. of liquid olefin boiling from 161–164° at 18 mm. and 475 g. (9% yield) of dibenzyl.

The solid olefin totalling 1714 g. (28% yield) was recrystallized from ethanol to give a product melting at 80–81°.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. *Found:* C, 92.65; H, 7.25.

Ozonolysis of the solid olefin gave benzaldehyde and acetophenone which were identified by 2,4-dinitrophenylhydrazone derivatives melting at 234–236° and 247–249°, respectively. The benzaldehyde fragment was also oxidized to benzoic acid which showed no depression in melting point when mixed with an authentic sample. The solid olefin is thus proved to be 1,2-diphenyl-1-propene and not 1,2-diphenyl-2-propene as proposed by Tuot and Guyard.[10]

The liquid olefinic product upon refractionation gave a pure product with the following properties: m.p. 0.52°, b.p. 292.57° at 760 mm. (slight dec.), $n^{20}\text{D}$ 1.5914 and d^{20} 1.01284 g./ml.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.65; H, 7.30.

Ozonolysis of the liquid olefin gave desoxybenzoin as one of the fragments which upon recrystallization from petroleum ether melted at 56–57° and gave no depression in melting point when mixed with an authentic sample. The 2,4-dinitrophenylhydrazone derivative after two recrystallizations from ethanol melted at 203–204°. Accordingly, the structure of the liquid olefin is shown to be 1,2-diphenyl-2-propene.

1,2-Diphenylpropane.—The isomeric olefins were hydrogenated quantitatively to 1,2-diphenylpropane using copper–chromite catalyst (15% by weight) in ethanol solution, the reaction occurring at 130–150° at 1600 p.s.i. Final purity was achieved by two fractionations on the Podbielniak column.

1,3-Diphenyl-2-propanol.—A 7-mole charge of freshly-distilled dibenzyl ketone (Edcan Laboratories) was hydrogenated at 150–160° at 1700 p.s.i. using copper–chromite (10% by weight) as the catalyst. The fractional distillation of the crude product gave 1073 g. (72%) of a colorless viscous oil, b.p. 198° at 20 mm. and $n^{20}\text{D}$ 1.5725.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.86; H, 7.59. Found: C, 84.70; H, 7.55.

1,3-Diphenyl-1-propene.—The dehydration of 1,3-diphenyl-2-propanol was obtained by passing 989 g. (4.7 moles) dissolved in 1 l. of toluene through alumina at 360–375°. The theoretical amount of water was obtained and the crude product was fractionated after removal of the toluene by distillation. The product amounting to 600 g. (67%) consisted of a mixture of stereoisomers distilling at 170–180° at 20 mm. and having a refractive index range between 1.5940–1.6011. A selected fraction representing the predominant product had the following properties: m.p. 11.8°, b.p. 313° (approx.) at 760 mm., $n^{20}\text{D}$ 1.6000 and d^{20} 1.0061 g./ml.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.73; H, 7.27. Found: C, 92.64; H, 7.29.

1,3-Diphenylpropane.—The mixture of stereoisomers in an equal volume of ethanol was reduced at 140–150° at 1600 p.s.i. using 15% by weight of copper–chromite catalyst. The reported purity was obtained after three careful fractionations including an azeotropic distillation with triethylene glycol.

A second method of preparation involving the condensation of benzaldehyde with the Grignard reagent of β-phenylethyl bromide, dehydration of the carbinol and reduction of the olefin yielded the identical hydrocarbon.

2,2-Diphenylpropane and Bimolecular Condensation Product from Friedel–Crafts Reaction.—In a typical synthesis, 1088 g. (8 moles) of dimethylphenylcarbinol (m.p. 30–31°), prepared from phenylmagnesium bromide and acetone 1875 g. (24 moles) of benzene and 536 g. (4 moles) of aluminum chloride reacted in a 5-l. flask equipped with a stirrer, dropping funnel and a condenser. One-third of the benzene was used as solvent for the carbinol and the remainder was added to the reaction flask containing the aluminum chloride. The flask was cooled by an ice-bath and the carbinol–benzene solution was added over a period of three hours. The temperature was kept between 3–10° during the addition following which stirring was maintained for an additional 18 hours at room temperature. A 10% solution of hydrochloric acid in ice was used in the hydroly-

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(12) F. F. Blicke and L. D. Powers, THIS JOURNAL, **51**, 3378 (1929).

(13) H. Gilman and R. E. Fothergill, *ibid.*, **51**, 3149 (1929).

(14) M. S. Kharasch and F. L. Lambert, *ibid.*, **63**, 2315 (1941).

(15) M. S. Kharasch and D. C. Sayles, *ibid.*, **64**, 2972 (1942).

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

sis and the hydrocarbon layer, after separation, was washed with a solution of sodium carbonate and dried over anhydrous sodium sulfate. It was distilled to remove the benzene and other readily removable impurities. The remainder, after combination with similar batches from other runs, was fractionally distilled to give 2,2-diphenylpropane (28% yield) in excellent purity as shown in Table I. A small amount of biphenyl was obtained in addition to the substituted hydrindene compound described below.

The principal product obtained in the Friedel–Crafts synthesis just described was a solid which melted at 51–52° after recrystallization from ethanol. This product, probably formed by the bimolecular condensation of the reaction intermediate in a yield of 38%, is apparently identical with the material obtained from the reaction involving 2-chloro-2-phenylpropane, benzene and stannic chloride described by Schoepfle and Ryan as 1,1,3-trimethyl-3-phenylhydrindene.[17] The analysis confirmed this empirical formula but the possibility of a substituted dihydroanthracene structure is also present.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.22; H, 8.47.

Several attempts made to obtain 2,2-diphenylpropane by means of the analogous reaction using 2-phenyl-1-propene (n^{20}D 1.5384) instead of the carbinol were unsuccessful, a resinous product being obtained in each case.

The structure for 2,2-diphenylpropane was determined by means of an independent synthesis of the corresponding saturated compound, 2,2-dicyclohexylpropane, and is described more fully under the preparation of the saturated compound.

Preparation of Dicyclohexylalkanes. Dicyclohexylmethane.—The general procedure for the preparation of the saturated compounds is illustrated by the preparation of dicyclohexylmethane. A mixture containing 1009 g. (6 moles) of purified diphenylmethane, 1 l. of methylcyclohexane and 150 g. of U.O.P. nickel catalyst was hydrogenated in a rocker-type autoclave of 4.5 l. capacity. Reaction occurred at 160° at 1500 p.s.i. and the temperature was maintained at a maximum of 200° until the theoretical amount of hydrogen was consumed. After cooling, the filtered solution was made solvent-free by rapid distillation and the remaining material was fractionated *in vacuo* to give 962 g. (90% yield) of product. After combining the fractions on the basis of constant boiling point and refractive index, the several portions were separately passed through silica gel. The data in Table I represent the physical properties of the hydrocarbon in maximum purity.

2-Cyclohexyl-2-(cyclohexan-4-ol)-propane.—*p*-α-Cumyl phenol (Dow, m.p. 70°) was hydrogenated using 673 g. (3 moles) dissolved in 1 l. of warmed methylcyclohexane. The reaction occurred between 170–180° using U.O.P. nickel catalyst and the heat of reaction raised the temperature to a maximum of 210°. The product was made solvent-free by distillation after filtration from the catalyst. An extremely viscous oil was obtained upon fractionation amounting to 478 g. (67%) having the following properties: b.p. 143° at 22 mm. and n^{20}D 1.5064.

Anal. Calcd. for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.33; H, 12.58.

Upon prolonged standing, partial crystallization occurred and the solid isolated from the mother liquor amounted to 90 g. after two recrystallizations from petroleum ether. It melted over a wide range at 80–90°, and is presumably one of the geometric isomers since analysis of a sample of the crystals showed the same carbon–hydrogen content as the original oil. The mother liquor resisted all further efforts toward crystallization.

2-Cyclohexyl-2-(cyclohexen-3-yl)-propane.—The dehydration of the above described carbinol (mixture of geometric isomers) was effected by passing 1795 g. (8 moles) in 2500-ml. of toluene over a period of four hours through a 2.5 × 120 cm. quartz tube packed with alumina and maintained at 350–375°. The theoretical amount of water was obtained and the material recovered after solvent removal and fractionation *in vacuo* amounted to 1085 g. (66%) of product. A selected fraction had the following properties: b.p. 124° at 5 mm., 152° at 20 mm. and 290° (approximately) at 760 mm., n^{20}D 1.5022 and d^{20} 0.92342 g./ml.

Anal. Calcd. for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.29; H, 12.70.

2,2-Dicyclohexylpropane.—The hydrogenation of 1282 g. (6.2 moles) of 2-cyclohexyl-2-(cyclohexen-3-yl)-propane using 80 g. of Raney nickel catalyst and 500-ml. of methylcyclohexane as solvent occurred between 140–160° at 1500 p.s.i. A preliminary distillation gave a product in 83% yield with a refractive index identical with that of the hydrocarbon obtained by the hydrogenation of 2,2-diphenylpropane prepared by means of the Friedel–Crafts synthesis.

The subsequent fractional distillation of the material prepared from the olefin gave a product of approximately 97–98% purity and neither azeotropic distillation nor silica gel absorption gave further improvement.

The hydrocarbon was also obtained directly as previously stated, by the simultaneous ring reduction and hydrogenolysis of *p*-α-cumylphenol using U.O.P. nickel and methylcyclohexane at 250° and 2000 p.s.i. This product similarly could not be purified satisfactorily.

The data for the hydrocarbon listed in Table I were taken on the material prepared by the hydrogenation of 2,2-diphenylpropane using U.O.P. nickel and methylcyclohexane. The reaction occurred at 160° at 1800 p.s.i. and the yield was essentially quantitative.

2-Phenyl-2-cyclohexylpropane.—A solution of 1236 g. (6 moles) of 2-cyclohexyl-2-(cyclohexen-3-yl)-propane in an equal volume of toluene was passed through a quartz tube packed with chromia–alumina catalyst and maintained at 390–420°. The initial fractional distillation of the crude material gave 870 g. (72%) of a product with a rather wide refractive index range (1.5163–1.5308). This material upon refractionation followed by percolation through silica gel several times gave a 24% over-all yield of 2-phenyl-2-cyclohexylpropane which had a constant boiling point and refractive index. Since subsequent processing through silica gel showed no change in the refractive index, the possibility of an aromatic-naphthenic physical mixture was minimized. This conclusion was further supported by infrared analysis of the product and its probable contaminants, namely, 2,2-diphenylpropane and 2,2-dicyclohexylpropane. 2-Phenyl-2-cyclohexylpropane had the following properties: b.p. 281.98° at 760 mm., n^{20}D 1.5259 and d^{20} 0.94644 g./ml.

Anal. Calcd. for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 89.02; H, 11.05.

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[17] C. S. Schoepfle and J. D. Ryan, THIS JOURNAL, **52**, 4021 (1930).