which was induced to crystallize by trituration with 10 ml. of water containing six drops of 6 *N* hydrochloric acid. Recrystallization of the solid (0.50 g.) from carbon tetrachloride provided 0.380 g. (68%) of XVII, m.p. 137.4–138.4°.

In a similar experiment the oxazolidinedione IV was recovered unchanged after treatment with an equimolar amount of sodium hydride in dry dioxane.

Reaction of XX with Aqueous Sodium Hydroxide.—To a solution of 0.100 g. (0.261 millimole) of the diamide XX in 5 ml. of 95% ethanol and 1.5 ml. of dioxane at 0° was added 0.261 ml. of 1.00 *N* sodium hydroxide. After standing at 0° for five minutes, the solution was diluted with water and extracted with chloroform. The chloroform extract was filtered and evaporated under reduced pressure to a yellow oil which solidified upon trituration with petroleum ether. Further trituration of the solid with water–methanol yielded almost colorless benzyl phenaceturate (0.020 g., 27.1%), m.p. 94–95°.

Aminolysis of IV.—To a suspension of 0.350 g. (0.00104 mole) of the heterocycle in 10 ml. of dry benzene was added 0.242 g. (0.00208 mole) of benzylamine. Reaction took place immediately and after ten minutes the colorless solid which had precipitated was collected by filtration. The yield of N,N'-dibenzyloxamide, m.p. 220.5–222.0°, was 0.275 g. (98.5%). Evaporation of the filtrate and trituration of the residue with petroleum ether afforded benzyl phenaceturate as an almost colorless solid (0.200 g., 66%), m.p. 93–94°. Pure material, m.p. 93.6–95.0°, (0.156 g.) was obtained after one recrystallization from benzene-ligroin.

Treatment of IV with phenylhydrazine resulted in the formation of benzyl phenaceturate in 69% yield, while methylamine after a reaction time of twelve days yielded 53% of the theoretical benzyl phenaceturate along with only 71.5% of the theoretical N,N'-dimethyloxamide.

Aminolysis of III.—From 0.300 g. (0.931 millimole) of the anilide III suspended in 10 ml. of dry dioxane and 15 ml. of benzene there was obtained, after treatment with 1.99 g. (1.86 millimoles) of benzylamine for 12 hours, 96% of the theoretical N,N'-dibenzyloxamide, m.p. 220–222°, and 61% of the theoretical phenaceturic acid anilide, m.p. 158.0–162°, undepressed upon admixture with an authentic sample.

CAMBRIDGE 39, MASSACHUSETTS RECEIVED APRIL 17, 1951

[CONTRIBUTION FROM THE NACA LEWIS FLIGHT PROPULSION LABORATORY]

Dicyclic Hydrocarbons. V. Synthesis and Physical Properties of the Diphenyl- and Dicyclohexylbutanes

BY KASPER T. SERIJAN AND PAUL H. WISE

The synthesis and properties are described for fourteen hydrocarbons in the diphenyl- and dicyclohexylbutane series. In addition to the usual properties, heats of combustion and viscosities are presented for these compounds which were prepared in a high state of purity. The methods of preparation and properties for *dl*-2,3-dicyclohexylbutane, *meso*-2,3-dicyclohexylbutane, 1,3-dicyclohexylbutane, 2,2-diphenylbutane and 2,2-dicyclohexylbutane are reported for the first time.

As part of the program being conducted at this Laboratory involving the investigation of possible components of aviation fuel, the hydrocarbons that constitute the structures obtainable by substituting two phenyl or two cyclohexyl groups in the various combinations of positions on a *n*-butyl chain have been synthesized and purified. Since the *dl*- and *meso*-forms of 2,3-diphenylbutane and 2,3-dicyclohexylbutane were separated, a total of fourteen hydrocarbons are presented.

Previous papers of this series include the dicyclicalkanes through C_{15}[1] and also the α,α- and α,ω-diphenyl- and dicyclohexylpentanes and hexanes.[2]

The methods of preparation for 1,1-diphenyl-1-butanol and 1,2-diphenyl-2-butanol involved the condensation of phenylmagnesium bromide with ethyl *n*-butyrate[3] and of benzylmagnesium chloride with propiophenone.[4] The Grignard reagent of β-bromoethylbenzene was condensed with acetophenone to give the intermediate carbinol in the preparation of 1,3-diphenylbutane. The synthesis of 1,4-diphenylbutane involved the reaction of γ-phenylpropylmagnesium bromide with benzaldehyde[5] to give 1,4-diphenyl-1-butanol.

The general procedure, where a carbinol was an intermediate, consisted of dehydration, purification of the resulting olefins and hydrogenation to the aromatic hydrocarbon. The dicyclohexylbutanes were prepared by the hydrogenation of the purified aromatic hydrocarbons or by direct hydrogenation of the purified olefin intermediate.

Proof of structure was established by ozonolysis of the intermediate olefins and characterization of the fragments.

1,4-Diphenylbutane was also prepared by the Wurtz reaction using β-bromoethylbenzene and sodium.[4b] The isomers of 2,3-diphenylbutane were obtained from the condensation of α-bromoethylbenzene in the presence of sodium. The *dl*- and *meso*-forms of 2,3-diphenylbutane were also obtained in low yields as rearrangement products from the Friedel–Crafts synthesis of 2,2-diphenylbutane wherein 2-phenyl-2-butanol, benzene and aluminum chloride were used.

The identity of the *dl*- and *meso*-forms of 2,3-diphenylbutane was established by Ott[6] and confirmed by Wessely and Welleba.[7] The melting point reported for the *dl*-isomer as 8°[8] and also 12.5° when pure[7] was not in accord with the results obtained in the present work. Melting points ranging progressively from 10 to −25° were obtained for successive fractions in the initial fractional distillation. Upon further separation of small quantities of the *meso*-isomer by fractional crystallization and azeotropic distillation, the resulting liquid product could no longer be crystallized. This material is believed by the authors to be the *dl*-isomer in a higher state of purity. The saturated compounds obtained from the separate

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

[2] K. T. Serijan and P. H. Wise, *ibid.*, **73**, 5191 (1951).

[3] (a) H. Masson, *Compt. rend.*, **135**, 533 (1902); (b) F. Blicke and L. Powers, THIS JOURNAL, **51**, 3378 (1929).

[4] (a) P. Sabatier and M. Murat, *Compt. rend.*, **156**, 1430 (1913); (b) M. Tuot and M. Guyard, *Bull. soc. chim. France*, 1087 (1947).

[5] R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 123 (1928).

[6] E. Ott, *Ber.*, **61B**, 2124 (1928).

[7] F. Wessely and H. Welleba, *ibid.*, **74A**, 777 (1941).

[8] A. Lyepin, *C. A.*, **7**, 982 (1913).

hydrogenations of the purified *dl*- and *meso*-2,3-diphenylbutanes gave products which are presumed to be the corresponding configurations of 2,3-dicyclohexylbutane.

The scale of synthesis was planned to yield 500 ml. quantities of each hydrocarbon in maximum purity (99.0 mole % or better) for specific test purposes. Due to various experimental difficulties, however, the syntheses of the 2,2- and 2,3-diphenylbutanes and their corresponding saturated compounds were carried out on a considerably smaller scale.

The apparatus and procedure used in the determination of melting points, boiling points, refractive indices, densities, heats of fusion and combustion and kinematic viscosities as well as equipment used in purification of the compounds have been previously described.[9]

The properties of the fourteen diphenyl- and dicyclohexylbutanes are summarized in Table I. The purities of six of the compounds listed therein could not be evaluated since glasses were obtained on supercooling. The hydrocarbons described for the first time include *meso*- and *dl*-2,3-dicyclohexylbutanes, 1,3-dicyclohexylbutane and 2,2-dicyclohexylbutane. The only reference to 2,2-diphenylbutane in the literature is obviously erroneous as to the identity of the obtained hydrocarbon.[10]

Experimental

Preparation of Diphenylbutanes and Intermediates. 1,1-Diphenyl-1-butene.—A solution of 11,755 g. (75 moles) of bromobenzene in 7 l. of dry ether reacted with 1944 g. (80 g. atoms) of magnesium covered with 11 l. of dry ether in a 30-gal. glass-lined reactor. The Grignard reagent was condensed at reflux temperature with 2904 g. (25 moles) of ethyl *n*-butyrate (n^{20}D 1.3923) dissolved in 4 l. of dry benzene while cold water was circulated through the jacket of the reactor. After 40 hours of stirring, the reaction mixture was hydrolyzed by the addition of a saturated solution of ammonium chloride. The product was isolated and fractionally distilled *in vacuo* to give 674 g. of diphenyl and 4014 g. (77% yield) of 1,1-diphenyl-1-butene (n^{20}D 1.5896–1.5898), complete dehydration of the carbinol having occurred during the process. A selected sample had the following properties: m. p. −1.19°, b. p. 294.7° at 760 mm. and 156° at 12 mm., n^{20}D 1.5898 and d^{20} 0.99394 g./ml.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.21; H, 7.62.

Ozonization of 1,1-Diphenyl-1-butene.—A solution of the olefin in ethanol was converted to the ozonide using the apparatus and procedure described by Henne and Perilstein.[11] The degradation products were fractionated on a 2-ft. column to give a low and a high boiling fraction which were characterized through the 2,4-dinitrophenylhydrazones as propionaldehyde and benzophenone, respectively. No melting point depression was observed when samples of these derivatives were mixed with authentic samples. The structure of the olefin is thus established as 1,1-diphenyl-1-butene.

1,1-Diphenylbutane.—The olefin was hydrogenated to the aromatic hydrocarbon using an equal volume of ethanol and 10% (by wt.) of copper chromite catalyst. The reaction occurred at 110–130° at 1500 p.s.i. and the product was obtained in 91% yield following the initial fractional distillation. Unsatisfactory freezing and melting curve data led to attempts at further purification including refractionation, azeotropic distillation with triethylene glycol and percolation through silica gel. The redetermination

TABLE I

PROPERTIES OF DIPHENYL- AND DICYCLOHEXYLBUTANES

Butane 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.,[a] kcal./mole at 25°	Kinematic viscosity,[b] (centistokes) 32°F.	100°F.	140°F.	210°F.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
1,1-Diphenyl-	−25.2[c]	295.29	1.5568	0.97512	5.0	[d]	2035	24.78	4.71	2.71	1.38	91.37	91.34	8.63	8.56
1,2-Diphenyl-	Glass	292.52	1.5518	.96734	..	..	2030	28.83	5.04	2.83	1.43	91.37	91.31	8.63	8.63
1,3-Diphenyl-	Glass	302.5[e]	1.5523	.96982	..	..	2035	20.98	4.62	2.71	1.45	91.37	91.37	8.63	8.64
1,4-Diphenyl-	52.27	315.91	[f]	[f]	11.6	99.7	2035	[f]	[f]	2.80	1.49	91.37	91.35	8.63	8.56
meso-2,3-Diphenyl-	126.4–127.0[g]	290.91	[f]	[f]	[h]	..	2035	[f]	[f]	[f]	[f]	91.37	91.36	8.63	8.61
dl-2,3-Diphenyl-	Glass	304.0[e]	1.5547	.97229	..	..	2040	18.11	4.36	2.64	1.43	91.37	91.36	8.63	8.66
2,2-Diphenyl-	21.70	296.16	1.5673	.99446	4.7	99.1	2035	[f]	7.52	3.83	1.79	91.37	91.39	8.63	8.63
1,1-Dicyclohexyl-	−10.46	292.97	1.4843	.89021	4.9	99.6	2285	88.30	9.64	4.75	2.10	86.40	86.29	13.60	13.69
1,2-Dicyclohexyl-	Glass	295.90	1.4806	.88316	..	..	2295	48.31	7.83	4.20	2.00	86.40	86.38	13.60	13.59
1,3-Dicyclohexyl-	Glass	303.19	1.4797	.88012	..	..	2285	45.00	8.80	4.82	2.28	86.40	86.41	13.60	13.62
1,4-Dicyclohexyl-	11.62	309.0[e]	1.4751	.87027	7.6	99.2	2285	[f]	7.58	4.39	2.19	86.40	86.40	13.60	13.60
meso-2,3-Dicyclohexyl-	57.60	298.51	[f]	[f]	7.2	99.3	2295	[f]	[f]	5.85	2.61	86.40	86.29	13.60	13.69
dl-2,3-Dicyclohexyl-	Glass	300.85	1.4842	.89044	..	..	2285	48.91	9.01	4.90	2.34	86.40	86.39	13.60	13.63
2,2-Dicyclohexyl-	15.38	302.1[e]	1.4957	.91332	5.5	99.0	2290	[f]	13.72	6.47	2.74	86.40	86.41	13.60	13.60

[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 445-46 T. [c] A second crystalline modification melted at −28.4°. [d] Value obtained deemed invalid because of the short length of the equilibrium portion of the melting curve. [e] Some decomposition observed. [f] Solid at the indicated temperature. [g] Value obtained using a calibrated immersion thermometer with the substance in an attached capillary tube. [h] Melting point was beyond calibration limits of apparatus.

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

(10) W. Thörner and T. Zincke, *Ber.*, **11**, 1988 (1878), describe 2,2-diphenylbutane as having m.p. 127.5–128.5°. The hydrocarbon obtained in their work is probably meso-2,3-diphenylbutane.

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

of the melting curve indicated two crystalline modifications which are listed in Table I.

1,2-Diphenyl-2-butanol.—The carbinol was obtained in 94% yield by the condensation of 4800 g. (35.8 moles) of freshly-distilled propiophenone and an excess of benzylmagnesium chloride followed by hydrolysis with a saturated solution of ammonium chloride. The material distilling between 165–169° at 7 mm. was a viscous oil with a refractive index range between 1.5660–1.5682. The refractive index of the predominant fraction was $n^{20}\text{D}$ 1.5680.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.92; H, 8.01. Found: C, 84.87; H, 8.00.

1,2-Diphenylbutenes.—The dehydration of 2610 g. (11.5 moles) of 1,2-diphenyl-2-butanol was effected by passage through activated alumina heated to 275–325°. The fractional distillation of the dehydration product yielded no sharp separation of the possible isomeric olefins but gave 1956 g. (81%) of olefinic material which distilled between 130–148° at 5 mm. and had a refractive index range, $n^{20}\text{D}$, between 1.5828–1.6053.

A solid product amounting to 606 g. (31%) of the total olefin obtained crystallized out of the fractions having the higher refractive index. This olefin, which melted at 57.5–58.0° after recrystallization from ethanol, gave benzaldehyde and propiophenone upon ozonolysis. These fragments characterized through the 2,4-dinitrophenylhydrazones established the structure of the solid olefin as 1,2-diphenyl-1-butene.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.20; H, 7.80.

The portion of the distillate collected between 144–146° at 5 mm. ($n^{20}\text{D}$ 1.5947–1.5973) gave desoxybenzoin (m. p. 57–59°) and acetaldehyde as the fragments upon decomposition of the ozonide. The former gave no depression in the melting point when mixed with an authentic sample. The structure of this olefin fraction amounting to 587 g. (30% of the total olefin yield) is shown to be 1,2-diphenyl-2-butene.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.16; H, 7.79.

The remaining 39% of the total olefin yield was a mixture of the geometric isomers of 1,2-diphenyl-1-butene since only benzaldehyde and propiophenone could be obtained from the ozonolysis of several fractions.

1,2-Diphenylbutane.—Separate charges of the solid and liquid olefins shown to be stereoisomers of 1,2-diphenyl-1-butene as well as a charge of 1,2-diphenyl-2-butene were hydrogenated to the aromatic hydrocarbon using ethanol and copper chromite catalyst. The reaction occurred at 120–140° at 1500 p.s.i. in each case and hydrocarbons with nearly identical properties were obtained by fractional distillation. Despite repeated attempts to purify the hydrocarbon, it was not obtained in a crystalline form and no analysis of its purity could be made.

1,3-Diphenyl-2-butenes.—The Grignard reagent from 4995 g. (27 moles) of β-bromoethylbenzene was condensed with an equimolar quantity of freshly-distilled acetophenone using dry ether as the reaction solvent. The reaction product following hydrolysis with 10% sulfuric acid was processed to give 3953 g. of a mixture consisting of the carbinol and olefin. The dehydration was made complete by passing the material dissolved in toluene through a tube packed with activated alumina and maintained at 350–375°. Fractional distillation gave 3311 g. (59% over-all yield) of isomeric olefins with a refractive index range between, $n^{20}\text{D}$ 1.5723–1.5916.

The combined portion of the lower refractive index material upon refractionation gave several fractions at 138° (2 mm.) with a constant refractive index value ($n^{20}\text{D}$ 1.5735).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.11; H, 7.88.

Acetophenone, which was characterized through its 2,4-dinitrophenylhydrazone derivative was obtained from the decomposition of the ozonide. The other expected fragment, phenylacetaldehyde, could not be isolated.

The fractionation of the combined higher refractive index olefinic material gave a product distilling between 148–151° at 4 mm. and having refractive index values $n^{20}\text{D}$, between 1.5902–1.5924.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.21; H, 7.76.

The 2,4-dinitrophenylhydrazone derivative obtained from the degradation of the ozonide of this olefin was identical with the acetophenone derivative discussed above as indicated by mixed melting points and by comparison with an authentic sample. No trace of either formaldehyde or benzylacetophenone could be detected to indicate the presence of the expected position isomer 1,3-diphenyl-3-butene in the two fractions which were investigated. Thus both olefins have the same structure and are presumably the *cis*- and *trans*-isomers of 1,3-diphenyl-2-butene.

1,3-Diphenylbutane.—The geometric isomers of 1,3-diphenyl-2-butene and the combined intermediate fractions containing a mixture of the two forms and possibly some of the position isomer, 1,3-diphenyl-3-butene, were separately hydrogenated using ethanol and copper chromite catalyst. Hydrogenation occurred between 130–140° at 1600 p.s.i. Separate fractional distillations of the hydrogenation products yielded one hydrocarbon on the basis of boiling point and refractive index measurements. These products were combined and fractionated in a Podbielniak column to give 1,3-diphenylbutane which was not obtained in a crystalline form despite repeated attempts to crystallize the hydrocarbon. On the basis of constancy of refractive index and density, its purity was presumed to be of the same order as the other hydrocarbons described. This conclusion was supplemented by infrared analysis which demonstrated the absence of carbinol or olefin.

1,4-Diphenyl-1-butene.—An olefinic mixture was obtained in 75% yield from the distillation of the reaction product from γ-phenylpropylmagnesium bromide and benzaldehyde, nearly complete dehydration of the carbinol having occurred during solvent removal and distillation. A solid olefin, m. p. 39–40° after recrystallization from ethanol, was obtained from a portion of the olefin mixture by chilling in petroleum ether. 1,4-Diphenyl-1-butene is reported as a solid melting at 39°.[12]

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.29; H, 7.71.

1,4-Diphenylbutane.—The solid olefin was hydrogenated at 110° and 1800 p.s.i. using ethanol and copper chromite catalyst to give a quantitative yield of 1,4-diphenylbutane which was purified by fractional distillation and recrystallization from ethanol. The liquid olefin consisting of the mother liquor after removal of the crystalline isomer and presumedly a mixture of the geometric isomers of 1,4-diphenyl-1-butene, gave 1,4-diphenylbutane.

In an independent synthesis, 1,4-diphenylbutane was obtained in 18% yield by means of a Wurtz reaction similar to that described in the preparation of 2,3-diphenylbutane in which 4 moles of β-bromoethylbenzene was the starting material.

meso- **and** *dl*-**2,3-Diphenylbutanes.**—In a 5-l. flask equipped with a stirrer, condenser and dropping funnel, 161 g. (7 g. atoms) of sodium sand was prepared in 1500 ml. of purified toluene. The addition of 1295 g. (7 moles) of α-bromoethylbenzene (Columbia Organic Chemicals) was made over a period of six hours with the reaction flask maintained at 80–90°. Stirring was maintained for an additional 90 hours at the same temperature following which water was gradually added to the cooled reaction product. Fractionation of the washed and dried hydrocarbon layer gave a series of fractions between 120–127° at 1 mm. from which 80 g. (11% yield) of *meso*-2,3-diphenylbutane crystallized on standing. This was recrystallized from ethanol to a constant melting point. The mother liquor from the distillation amounting to 258 g. (35%) was essentially the *dl*-isomer. Refractionation of this material followed by an azeotropic distillation with triethylene glycol removed additional small amounts of the *meso*-isomer. The freezing point of successive fractions decreased from 10 to −25° after which a glass was obtained. The properties reported in Table I for the *dl*-form were obtained on the latter fractions after percolation through silica gel.

The solid and liquid isomers of 2,3-diphenylbutane were also obtained in low yields as rearrangement products in the Friedel–Crafts synthesis of 2,2-diphenylbutane described below.

2-Phenyl-2-butanol.—A procedure analogous to the Friedel–Crafts reaction used by the authors in the preparation of 2,2-diphenylpropane[1] was employed in the synthesis of 2,2-diphenylbutane. The carbinol used as a starting

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[12] M. Freund and P. Immerwahr, *Ber.*, **23**, 2845 (1890).

material was prepared in 78% yield from a 70-mole reaction involving the condensation of phenylmagnesium bromide with methyl ethyl ketone (n^{20}D 1.3788). The ether was removed by distillation after the mixture was hydrolyzed with a saturated solution of ammonium chloride. Careful fractionation *in vacuo* gave the carbinol with little or no dehydration. The properties of a selected sample were: b. p. 97° at 15 mm. and 107.5° at 20 mm., n^{20}D 1.5195 and d^{20} 0.97696 g./ml.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.93; H, 9.39.

2,2-Diphenylbutane. Rearrangement and Bimolecular Condensation Products from Friedel–Crafts Reaction.—In a typical synthesis 1202 g. (8 moles) of 2-phenyl-2-butanol, 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 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 addition of the carbinol-benzene mixture required three hours during which time the temperature of the reactants was kept below 20° by means of an ice-bath. Stirring was maintained for an additional 24 hours with the ice-bath removed and the reaction mixture was hydrolyzed by pouring the flask contents into dilute sulfuric acid and ice. The hydrocarbon layer was washed and dried and the benzene and low boiling impurities were removed by distillation. The remainder, after combination with similar material from a total of four identical runs (32 moles), was fractionally distilled *in vacuo* to give 750 g. (11%) of 2,2-diphenylbutane which was refractionated on a Podbielniak column.

The initial distillation also gave 40 g. of biphenyl and 240 g. (4%) of the solid and liquid isomers of 2,3-diphenylbutane. The identity of the isomeric rearrangement products was established by comparison of their physical properties and infrared spectra with those of *meso-* and *dl*-2,3-diphenylbutanes prepared from α-bromoethylbenzene.

The principal product from the Friedel–Crafts reaction was a viscous liquid which partially crystallized on standing. The solid, following recrystallization from ethanol, melted at 50.5–52° and is presumably 1-methyl-1,3-diethyl-3-phenylhydrindene formed by the bimolecular condensation of the reaction intermediate.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.85; H, 9.13.

The preparation of 1,1,3-trimethyl-3-phenylhydrindene (m. p. 51–52°) by an analogous procedure has been discussed in a previous paper of the series.[1] The mixing of the two solids for a mixed melting point determination gave a liquid at room temperature.

Preparation of Dicyclohexylbutanes. 1,4-Dicyclohexylbutane.—As previously stated, the saturated hydrocarbons were generally prepared by the total hydrogenation of the purified aromatic hydrocarbon. In a typical procedure, 1013 g. (4.8 moles) of 1,4-diphenylbutane dissolved in an equal volume of methylcyclohexane was hydrogenated in a rocker-type autoclave of 4$^1/_2$ l. capacity using 150 g. of U.O.P. nickel catalyst. Reaction occurred at 170–180° at 1700 p.s.i. and the temperature was maintained at a maximum of 200° until the theoretical amount of hydrogen was consumed. Following filtration of the catalyst, the solvent was removed by distillation. The remaining material was fractionally distilled *in vacuo* to give 967 g. (91%) of 1,4-dicyclohexylbutane. Selected fractions were refractionated on a Podbielniak column and the product was passed through silica gel prior to the determination of the physical properties.

CLEVELAND, OHIO RECEIVED JUNE 7, 1951

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

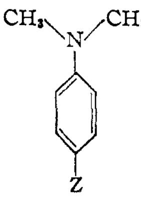
Steric Effect of Methylene Groups. VI

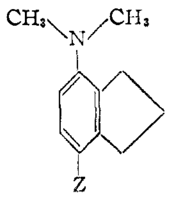
BY RICHARD T. ARNOLD, VINCENT J. WEBERS[1,2] AND R. M. DODSON

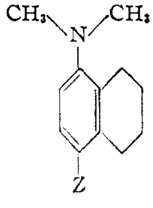
A number of *p*-substituted dimethylamino derivatives of the benzene, indan, tetralin and *o*-xylene series have been prepared. Comparison of their absorption spectra in the ultraviolet and near visible region has further demonstrated that the steric effect of an ortho methylene group in a six-membered ring is greater than that in a corresponding five-membered ring. New chemical data also supports this view.

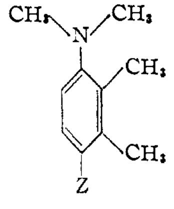
In several previous papers[3] considerable physical and chemical evidence has been presented which strongly indicates that the steric effect of a methylene group is not constant, and, in particular, that the ortho methylene groups in indan derivatives offer less steric hindrance to ring substituents than those in corresponding tetralin analogs.

During this study we prepared the sixteen compounds indicated below and examined their spectra in the ultraviolet and near visible region.









[Z = —CH=NOH, —C≡N, —N=N—C_6H_5, —N=N—C_6H_4—NO_2-*p*]

Table I gives the position and intensity of the major absorption band in the region studied. Two facts are immediately evident. In the first place, with some particular group "Z," the absorption intensity diminishes regularly through the benzene, indan and tetralin series. Secondly, both the position and the intensity of the absorption bands for the tetralin and *o*-xylene derivatives are remarkably similar.

With substituted aromatic amines, it has been reasonably well established[3,4] that the intensity of

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[1] Taken from the Ph.D. thesis of Vincent J. Webers, 1949.

[2] Allied Chemical and Dye Corporation fellow 1947–1948; du Pont fellow 1948–1949.

[3] Paper V of this series, R. T. Arnold and P. N. Craig, THIS JOURNAL, **72**, 2728 (1950).

[4] W. R. Remington, *ibid.*, **67**, 1838 (1945).