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

Dicyclic Hydrocarbons. XI. Synthesis and Physical Properties of the Monoethyldiphenylmethanes and Monoethyldicyclohexylmethanes

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Methods of synthesis and purification are described for the 2-, 3- and 4-ethyldiphenylmethanes and for the geometrical isomers of the corresponding ethyldicyclohexylmethanes. Each of these hydrocarbons, with the exception of the lower-boiling isomer of 3-ethyldicyclohexylmethane, has been prepared in a state of purity of 99 mole %, or better. The physical properties presented include melting point, boiling point, refractive index, density, heat of fusion, net heat of combustion and kinematic viscosities at four different temperatures. The 2- and 3-ethyldiphenylmethanes and the five ethyldicyclohexylmethanes are being reported for the first time.

The 2-, 3- and 4-ethyldiphenylmethanes and the corresponding ethyldicyclohexylmethanes were prepared as part of an investigation of the effect of small changes in structure upon the physical properties of dicyclic hydrocarbons. The scale of the syntheses was planned so that approximately 500-ml. quantities of each hydrocarbon would be made available in 99 mole % purity for specific test purposes.

The preparation and physical properties of 2- and 3-ethyldiphenylmethane and the ethyldicyclohexylmethanes are described for the first time. The 4-ethyldiphenylmethane has been prepared previously, but only a boiling point and density were reported.[1]

Previous papers of this series include the methyldiphenyl- and methyldicyclohexylmethanes[2] and some propyl- and butyldiphenyl- and dicyclohexylmethanes.[3]

The 2- and 4-ethyldiphenylmethanes were prepared by hydrogenolysis of the corresponding benzhydrols, which had been highly purified by crystallization. The benzhydrols were synthesized by reaction of the appropriate Grignard reagent with benzaldehyde. The steps employed for the synthesis of 3-ethyldiphenylmethane consisted of hydrogenation of *m*-ethylphenol to 3-ethylcyclohexanol, oxidation of 3-ethylcyclohexanol to 3-ethylcyclohexanone, condensation of 3-ethylcyclohexanone with benzylmagnesium chloride, dehydration and dehydrogenation.

All the ethyldiphenylmethanes reported herein crystallized very readily on cooling; and, based on time–temperature melting curves, the purities of the hydrocarbons were estimated to be over 99.9 mole %.

The 2- and 4-ethyldicyclohexylmethanes were prepared by the hydrogenation of the purified 2- and 4-ethyldiphenylmethanes. The 3-ethyldicyclohexylmethane was prepared by hydrogenation of the olefin mixture obtained by dehydration of the product from the Grignard reaction of 3-ethylcyclohexanone with benzylmagnesium chloride.

Each ethyldicyclohexylmethane consisted of a pair of geometrical isomers. With the exception of the isomeric 3-ethyldicyclohexylmethanes, these isomers were separated by fractional distillation in high-efficiency columns; but in the absence of the necessary thermodynamic data no specific assignment of *cis* and *trans* configurations can be made, and the products isolated are referred to simply as the low and high boiling isomers.

The percentage of each isomer in its original mixture of two is reported in Table I. These values were estimated from fractionation data and do not represent the amounts of the isolated pure compounds, which are much smaller.

The low boiling isomer of 3-ethyldicyclohexylmethane could not be purified by repeated fractionation in a 6-ft. Podbielniak column. The distillation fractions had neither constant density nor constant refractive index values. This purification failure probably occurred because of the low relative yield (estimated at 20% or less) of this isomer compared with the high boiling isomer and the close proximity of the boiling points of the two.

The only ethyldicyclohexylmethanes that could be crystallized were the high boiling isomer of 2-ethyldicyclohexylmethane and the low boiling isomer of 4-ethyldicyclohexylmethane. The heat of fusion of the high boiling isomer of 2-ethyldicyclohexylmethane was not obtained, as the crystals could not be induced to grow in the apparatus employed. Estimates of purity were possible only for the low boiling isomer of 4-ethyldicyclohexylmethane. However, from the methods of purification employed and the analysis of the fractionation data, it is believed that purities of the order of magnitude of 99 mole % or better have been obtained.

The physical properties and analyses of the eight hydrocarbons are listed in Table I. The apparatus and procedures for the purification of the hydrocarbons, as well as references to the methods used for the determination of the physical properties, have been previously described.[4] The estimated mole % purities were determined according to the method of Glasgow, Streiff and Rossini.[5]

Experimental

2-Ethylbenzhydrol.—In a 30-gal. water-cooled, glass-lined reactor, the Grignard reagent from 40 moles of *o*-bromoethylbenzene ($n^{20}\text{D}$ 1.5489, m.p. −67.3°) was condensed with 38 moles (95% of the theoretical amount) of freshly distilled technical grade benzaldehyde. The reaction mixture was hydrolyzed with cold dilute hydrochloric acid and the aqueous layer drained out. After the ether layer was washed successively with cold water, with dilute sodium bicarbonate solution and again with cold

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(1) J. T. Walker, *Ber.*, **5**, 686 (1872).

(2) J. H. Lamneck, Jr., and P. H. Wise, THIS JOURNAL, **76**, 1104 (1954).

(3) J. H. Lamneck, Jr., and P. H. Wise, *ibid.*, **76**, 3475 (1954).

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

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

TABLE I

PHYSICAL PROPERTIES AND ANALYSES OF ETHYLDIPHENYLMETHANES AND ETHYLDICYCLOHEXYLMETHANES

Methane derivative	M.p., °C.	B.p., °C. at 1 atm.	$n^{20}\mathrm{D}$	d^{20}, g./ml.	Heat of fusion, kcal./mole	Estimated purity, mole %	Net heat of combustion, kcal./mole	Isomer in orig. mixt., % approx.	Kinematic viscosity,[a] centistokes				Analyses, %			
									32° F.	100° F.	140° F.	210° F.	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
2-Ethyldiphenyl-	−11.15	290.86	1.5701	0.99213	5.2	99.9	1880	..	11.20	3.43	2.21	1.23	91.78	91.76	8.22	8.17
3-Ethyldiphenyl-	− 9.22	291.54	1.5634	.97976	6.4	99.9	1875	..	6.97	2.71	1.85	1.13	91.78	91.73	8.22	8.25
4-Ethyldiphenyl-	−23.52	297.03	1.5630	.97773	5.2	99.9	1875	..	6.01	2.49	1.75	1.08	91.78	91.65	8.22	8.30
2-Ethyldicyclohexyl[b]-	Glass	280.94	1.4796	.88143	..	..	2150	54	23.72	5.25	3.10	1.63	86.46	86.40	13.54	13.61
2-Ethyldicyclohexyl[c]-	−31.2[d]	282.35	1.4813	.88660	[e]	..	2135	46	25.93	5.68	3.30	1.70	86.46	86.42	13.54	13.53
3-Ethyldicyclohexyl[c]-	Glass	281.35	1.4746	.87046	..	..	2135	80	21.53	5.20	3.09	1.61	86.46	86.43	13.54	13.53
4-Ethyldicyclohexyl[b]-	−24.94	285.91	1.4731	.86749	5.3	99.4	2150	53	20.25	5.28	3.18	1.67	86.46	86.42	13.54	13.58
4-Ethyldicyclohexyl[c]-	Glass	286.15	1.4771	.87774	..	..	2135	47	21.51	5.67	3.40	1.79	86.46	86.40	13.54	13.62

[a] Determined in viscosimeters calibrated with N.B.S. standard viscosity samples and using A.S.T.M. procedure D445-46T. [b] Low boiling isomer. [c] High boiling isomer. [d] Equilibrium portion of melting curve was very short. [e] Failed to crystallize in apparatus.

water, the ether was removed by heating the reactor with steam.

The solution of 2-ethylbenzhydrol from the reactor was heated on a steam-bath to evaporate the remaining ether. When the solution cooled, nearly all the material solidified and was washed with petroleum ether (b.p. 30–60°) to yield 5095 g. of nearly white product. This material was distilled and the colorless fraction amounting to 4840 g. and boiling at 170–175° at 2.5 mm. was collected. The distilled material was washed again with petroleum ether (b.p. 30–60°) and 4460 g. was recovered. This material was recrystallized from petroleum ether (b.p. 60–90°) by dissolving 200-g. portions in 1.2 liters of hot solvent and allowing the mixture to cool to 20–25°. The 2-ethylbenzhydrol precipitated in fine white needles melting at 60.8°. The yield was 3575 g. (44%, based on 38 moles of benzaldehyde).

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.86; H, 7.60. Found: C, 84.84; H, 7.60.

4-Ethylbenzhydrol.—In a 10-gal. water-cooled, glass-lined reactor, the Grignard reagent from 35 moles of *p*-bromoethylbenzene ($n^{20}\mathrm{D}$ 1.5446, m.p. −45.5°) was condensed with 26.25 moles (75% of theoretical amount) of freshly distilled technical grade benzaldehyde. The reaction mixture was hydrolyzed by adding it to a mixture of 75 lb. of cracked ice, 2.9 l. of concd. HCl and 6 l. of cold water in a 30-gal. reactor. (Reference 2 contains a discussion of the reasons for (1) using the hydrolysis procedure mentioned in this preparation and (2) using less than the theoretical amount of benzaldehyde.) After the ether solution was separated and washed with water and dilute sodium bicarbonate solution, the ether was removed by heating the reactor with steam.

The remaining ether in the 4-ethylbenzhydrol solution was evaporated at reduced pressure. The ether-free material was distilled and the fraction amounting to 3908 g. and boiling at 165–175° at 3 mm. was collected. This fraction, which solidified on cooling, was dissolved in hot petroleum ether (b.p. 30–60°) in amounts of 350 g. in 3 l. of solvent and cooled to 5°. The yield of crystallized product was 3342 g. A second crystallization from petroleum ether was carried out in the same manner as the first and 3140 g. (56%, based on benzaldehyde) of white cottony needles (m.p. 42.6°) was obtained.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.86; H, 7.60. Found: C, 84.91; H, 7.61.

2-Ethyl- and 4-Ethyldiphenylmethane.—A solution of 500 g. of ethylbenzhydrol in 200 ml. of absolute alcohol was mixed with 50 g. of copper chromite catalyst in a 3 l. rocking autoclave and hydrogenated for 20 hr. at 225° and an initial pressure of 1500 p.s.i of hydrogen. After the solution was filtered from the catalyst and the solvent removed by distillation, the hydrocarbon was distilled *in vacuo* through a 3-ft. glass column (22-mm. diam.), packed with $^3/_{16}$-inch glass helices, to give a 92–95% yield of ethyldiphenylmethane. Material from several hydrogenations of the same ethylbenzhydrol was further purified by fractional distillation at reduced pressure (18 mm.) through a 6-ft. glass column (30 mm. diam.) packed with $^3/_{16}$-inch glass helices. After approximately 200 ml., consisting of 3 or 4 fractions, was removed, the subsequent individual fractions were of constant refractive index. Several of the purest fractions (highest m.p.) of each compound sufficient to yield the desired 500-ml. quantities, were combined and percolated through silica gel prior to the determination of the final physical properties.

2-Ethyl- and 4-Ethyldicyclohexylmethane.—A solution of 4000 g. of distilled 2-ethyl- or 4-ethyldiphenylmethane in an equal volume of methylcyclohexane was mixed with 400 g. of U.O.P. nickel catalyst in a 20-l. rocking autoclave and hydrogenated for 12 hours at 200° and an initial pressure of 1200 p.s.i. After the solution was filtered from the catalyst and the solvent removed by distillation, the hydrocarbon (95–97% yield) was fractionally distilled *in vacuo* (20 mm.) through a 6-ft. (22 mm. diam.) Podbielniak column. Fractions of the 2-ethyldicyclohexylmethane with constant refractive index and constant density values were combined to obtain the desired quantities of each isomer. These fractions amounted to 29% of the charge for each isomer. Repeated fractionations of the heads and tails of the 4-ethyldicyclohexylmethane produced an 8% yield of pure low boiling isomer (total of three fractionations) and a 7% yield of pure high boiling isomer (total of two fractionations). The yields are based on the charge to the first fractionation. The samples were percolated through silica gel prior to the determination of the final physical properties.

3-Ethylcyclohexanol.—In a typical run a solution of 7500 g. of *m*-ethylphenol (commercial product, distilled; m.p. −3.1°, b.p. 218.27° at 760 mm., d^{20} 1.0115 g./ml., $n^{20}\mathrm{D}$ 1.5339) in an equal volume of methylcyclohexane was mixed with 600 g. of U.O.P. nickel catalyst in a 20-l. rocking autoclave and hydrogenated for 7 hours at 200° and an initial pressure of 1200 p.s.i. After the solution was filtered from the catalyst and the solvent removed by distillation, the 3-ethylcyclohexanol was distilled *in vacuo* (30 mm.) through a 3-ft. glass column (22 mm. diam.), packed with $^3/_{16}$-inch glass helices, to give 7485 g. of 3-ethylcyclohexanol ($n^{20}\mathrm{D}$ 1.4627–1.4629). Fractionation of 1500 g. of this material in a 6-ft. Podbielniak column (22 mm. diam.) yielded 32% of a low boiling isomer (m.p. −14°, b.p. 192.30° at 760 mm., d^{20} 0.9190 g./ml., $n^{20}\mathrm{D}$ 1.4629) and 55% of a high boiling isomer (m.p. glass, b.p. 196.28° at 760 mm., d^{20} 0.9137 g./ml., $n^{20}\mathrm{D}$ 1.4621).

3-Ethylcyclohexanone.—3-Ethylcyclohexanol (7100 g.) was oxidized by adding it to a stirred, cooled solution of 11.4 kg. of $Na_2Cr_2O_7{\cdot}2H_2O$ and 8840 g. of concd. H_2SO_4 in 15 gal. of water in a 30-gal. reactor. The temperature of the solution was kept below 30° during the addition, but cooling was stopped during the 2.5 hours of continued stirring and the temperature rose to 37°. The material remained in the reactor overnight and was cooled but not stirred.

After the acid layer was removed and discarded, the organic layer was washed three times with 5% aqueous caustic solution and with water. The 3-ethylcyclohexanone was filtered through filter-aid and dried with anhydrous magnesium sulfate. The yield of light-amber liquid (n^{20}D 1.4520) was 4268 g. (61%). This product was distilled through the 3-ft. column at a pressure of 34 mm. and 3816 g. (55%) of clear, water-white 3-ethylcyclohexanone was obtained (n^{20}D 1.4514). A further fractionation of 1300 g. of this latter material in a 6-ft. Podbielniak column (22 mm. diam.) yielded 725 g. of constant refractive index and constant density product for physical constants (m.p. −62.27°, b.p. 193.93°, d^{20} 0.9143 g./ml., n^{20}D 1.4515).

1-Benzyl-3-ethylcyclohexanol.—In a 30-gal. water-cooled, glass-lined reactor, the Grignard reagent from 75 moles (25% excess) of benzyl chloride was condensed with 60 moles of 3-ethylcyclohexanone. After the reaction mixture was hydrolyzed with saturated ammonium chloride solution and the clear ether layer siphoned from the precipitated salts, the ether was allowed to evaporate. The residual ether was removed under vacuum by heating with hot water and 11,107 g. (85% yield) of a yellow, oily liquid was obtained. This product was not purified further.

Olefins from Dehydration.—The 1-benzyl-3-ethylcyclohexanol (11,107 g., 50.9 moles) was passed at a rate of 6 ml./min. into a 2.5- by 90-cm. Pyrex column which was packed with 8 to 14 mesh alumina and heated to 250–300°. The alumina was replaced after 2.5-l. of 1-benzyl-3-ethylcyclohexanol had passed through the column. After the water was separated, the product from the dehydration was distilled through the 3-ft. glass column. The material (8385 g.) boiling at 126–140° at 8 mm. was collected. Attempts to separate the individual isomers by fractionation in a 6-ft. Podbielniak column were unsuccessful. The refractive index (n^{20}D 1.5257–1.5460) and density (d^{20} 0.935–0.941 g./ml.) varied continuously from fraction to fraction. However, dibenzyl was separated in this distillation from the higher-boiling olefins, and the yield of dibenzyl-free olefins was 6433 g. (63%).

3-Ethyldiphenylmethane.—Dehydrogenation of 3910 g. of the olefins was accomplished by passing it at a rate of 4 ml./min. into a 2.5- by 90-cm. quartz tube packed with chromia–alumina catalyst and maintained at a temperature of 450–475°. The amber product (3782 g.) was distilled through the 3-ft. column, and the portion distilling at 140–167° at 18 mm. (3197 g.) was fractionated at reduced pressure (3 mm.) in a 6-ft. Podbielniak column. The yield of constant refractive index and constant density 3-ethyldiphenylmethane was 2332 g. (61% based on the amount of olefin dehydrogenated and 17% based on the *m*-ethylphenol). The remainder of the distillation fractions were lower boiling and had lower refractive indices than the desired hydrocarbon. Several of the purest fractions (highest m.p.) of the 3-ethyldiphenylmethane, sufficient to yield the desired 500-ml. quantity, were combined and percolated through silica gel prior to the determination of the final physical properties.

3-Ethyldicyclohexylmethane.—A solution of 1209 g. of olefins in an equal volume of methylcyclohexane was mixed with 120 g. of U.O.P. nickel catalyst in a 4.5-l. rocking autoclave and hydrogenated for 15 hours at 200° and an initial pressure of 1400 p.s.i. The solutions from two runs were filtered from the catalyst and the solvent was removed by distillation. The hydrocarbon was distilled *in vacuo* in the 3-ft. column and 2375 g. (94%) of 3-ethyldicyclohexylmethane (b.p. 133–134° at 8 mm., n^{20}D 1.4753) was obtained. Further purification and separation of isomers was attempted in a 6-ft. Podbielniak column at 2.5 mm. No plateaus of refractive index and density were obtained, and the first 25% (583 g.) and the last 32% (760 g.) of the distilled material were refractionated separately in 6-ft. Podbielniak columns at a pressure of 2 mm. Only the last three fractions (162 g.) of the higher-boiling portion were of constant refractive index and density, and the physical properties listed in Table I were obtained on this material.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF HARVARD UNIVERSITY]

The Oxidation of Tetracyclone with Nitric Acid

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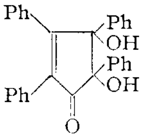
The action of nitric acid on tetracyclone in dioxane is shown to yield a 2,3-dihydroxy-2,3,4,5-tetraphenylcyclopent-4-enone as the main product together with smaller amounts of both diastereoisomeric forms of 2,5-dihydroxy-2,3,4,5-tetraphenylcyclopent-3-enone. The structures of the products obtained by further oxidation of these compounds with lead tetraacetate also have been elucidated. The mode of formation and reactions of the compounds are discussed.

Introduction.—During the course of an extensive study of the chemistry of tetracyclone (tetraphenylcyclopentadienone) and related compounds, Dilthey and his school investigated its oxidation with nitric acid.[2,3] Reaction in either acetic acid or dioxane gave a compound $C_{29}H_{22}O_3$ (I), m.p. 191–192° dec. In addition, when acetic acid was the solvent, 3,4,5,6-tetraphenyl-2-pyrone (II) could be isolated from the mother liquor from the crystallization of I.[4] I was shown by the Zerewitinoff method to have two active hydrogen atoms. It could be converted readily by treatment with acid or base, or by heating briefly above the melting point, to 2-benzoyl-3,4,5-triphenylfuran (III). With acetic anhydride in pyridine, it gave a monoacetate which could be converted by the action of hydrogen chloride in methanol to the pyrone II. Both II and III were obtained by heating I with acetic anhydride alone. On the basis of these facts Dilthey concluded that the compound $C_{29}H_{22}O_3$ must be one of the dihydroxytetraphenylcyclopentenones Ia and Ib, or the hemiketal corresponding to Ia, Ic.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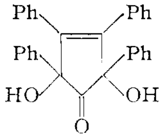
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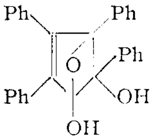
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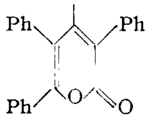
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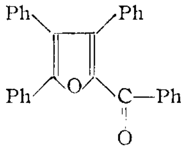
III

In an attempt to distinguish between these struc-

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[1] National Science Foundation Predoctoral Fellow, 1953–1954.

[2] R. Pütter and W. Dilthey, (a) *J. prakt. Chem.*, **149**, 183 (1937); (b) **150**, 40 (1937).

[3] *Cf.* W. Dilthey, S. Henkels and M. Leonhard, *ibid.*, **151**, 97 (1938), for the oxidation of related compounds by other means.

[4] This pyrone was also obtained by peracetic acid oxidation of tetracyclone.