to 350°, depending upon the pressure of ethylene. Because of these facts ethylene is not suitable for use as an hydrogen acceptor during the dehydrogenation of hydroaromatic compounds over Raney nickel.

MADISON, WISCONSIN RECEIVED AUGUST 19, 1940

[CONTRIBUTION FROM THE SUN OIL COMPANY, EXPERIMENTAL DIVISION, NORWOOD, PA.

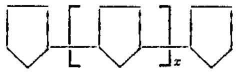
The Synthesis of Multicyclopentyls[1]

BY GILBERT E. GOHEEN

It has been well established that natural petroleum oils consist mainly of a mixture of aliphatic, naphthenic and aromatic hydrocarbons or chemical combinations of these types in various proportions. Relative to the naphthenic or saturated ring portion, the average number of rings per molecule can be determined by known methods of ring analysis.[2] For lubricating oils the values generally range from one to five or more rings per molecule.

With respect to the size of the rings present, some evidence has caused several investigators to assume that six-carbon membered (cyclohexane) rings predominate in the naphthenic portion.[2] However, more recent indications are that five-carbon membered (cyclopentane) rings may be present and may even, in many cases, be in the majority.[3] This latter theory is also supported by the fact that cyclopentane rings have generally been found in the naphthenic acids occurring in petroleum.[4]

Attempts to solve this problem have been hindered by the absence of physical data on pure multicyclic compounds containing cyclopentane rings. Only bicyclopentyl itself has been investigated to any great extent.[5] Important additions to the field of dicyclopentyl and bicyclopentyl derivatives have been made recently by several investigators[6a,b,c] but practically nothing is known concerning hydrocarbons containing more than two cyclopentyl rings in the molecule. In the present communication there are described the synthesis and physical properties of three saturated multicyclopentyls[7] of the type



where x = 0, 1, and 2.

The series of reactions selected for the synthesis of the multicyclopentyls is outlined in Fig. 1. A search of the literature indicated that these intermediates would be free from possible rearrangements to six-carbon membered rings under the conditions necessary for their preparation. The reactions as a whole were carried out at relatively low temperatures and under mild conditions. Two starting compounds were used, cyclopentanone (II) which was prepared from adipic acid (I), and cyclopentadiene (VI), from dicyclopentadiene (V). The first series of reactions consisted in the catalytic hydrogenation of cyclopentanone (II) to cyclopentanol (III) and conversion of this to cyclopentyl bromide (IV) by means of phosphorus tribromide at 0°. The unsaturated bicyclic compound, 1-cyclopentylcyclopentene-2 (VIII) was then produced by the reaction of the Grignard reagent of cyclopentyl bromide with 1-chlorocyclopentene-2 (VII) also at 0°. Catalytic hydrogenation of VIII then produced bicyclopentyl whose physical constants corresponded with those given in the literature for bicyclopentyl prepared by other methods. Thus, the procedures up to this point were proven to be satisfactory.

By the addition of hydrobromic acid to the cyclopentylcyclopentene (VIII) at room temperature, there was obtained 3-bromobicyclopentyl (IX) whose chemical structure has been investigated by von Braun, Kamp and Kopp.[6a]

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(1) Presented before the Division of Petroleum Chemistry of the American Chemical Society, Detroit, Mich., Sept. 11, 1940.

(2) Vlugter, Waterman and van Westen, *J. Inst. Petroleum Tech.*, **21**, 661–676 (1935); **18**, 735–750 (1932); Grosse, *Refiner Natural Gasoline Mfr.*, **18**, 149–157 (1939); Grosse and Mavity, Div. of Petroleum Chem., Am. Chem. Soc. Meeting, Boston, 1939.

(3) Kurtz and Lipkin, Div. of Petroleum Chem., Am. Chem. Soc. Meeting, Boston, 1939; Lipkin and Kurtz, *ibid.*, Detroit, 1940; Rossini, *Proc. Am. Petroleum Inst.*, **18**, III, 51 (1937); Glasgow, *J. Research Natl. Bur. Standards*, **24**, 509–529 (1940).

(4) Harkness and Bruun, *Ind. Eng. Chem.*, **32**, 499–502; Goheen, *ibid.*, **32**, 503–508 (1940); Hancock and Lochte, THIS JOURNAL, **61**, 2448–2452 (1939); Shive and Bailey, Div. of Petroleum Chem., Am. Chem. Soc. Meeting, Cincinnati, 1940.

(5) Evans, *J. Inst. Petroleum Tech.*, **24**, 548, 551 (1938).

(6) (a) Von Braun, Kamp and Kopp, *Ber.*, **70B**, 1750–1760 (1937); (b) Suida and Gemassmer, *ibid.*, **72B**, 1168–1173 (1939); (c) Zelinskiĭ, Mikhlina and Eventova, *ibid.*, **66B**, 1422–1426 (1933).

(7) Class name suggested by Dr. Austin M. Patterson.

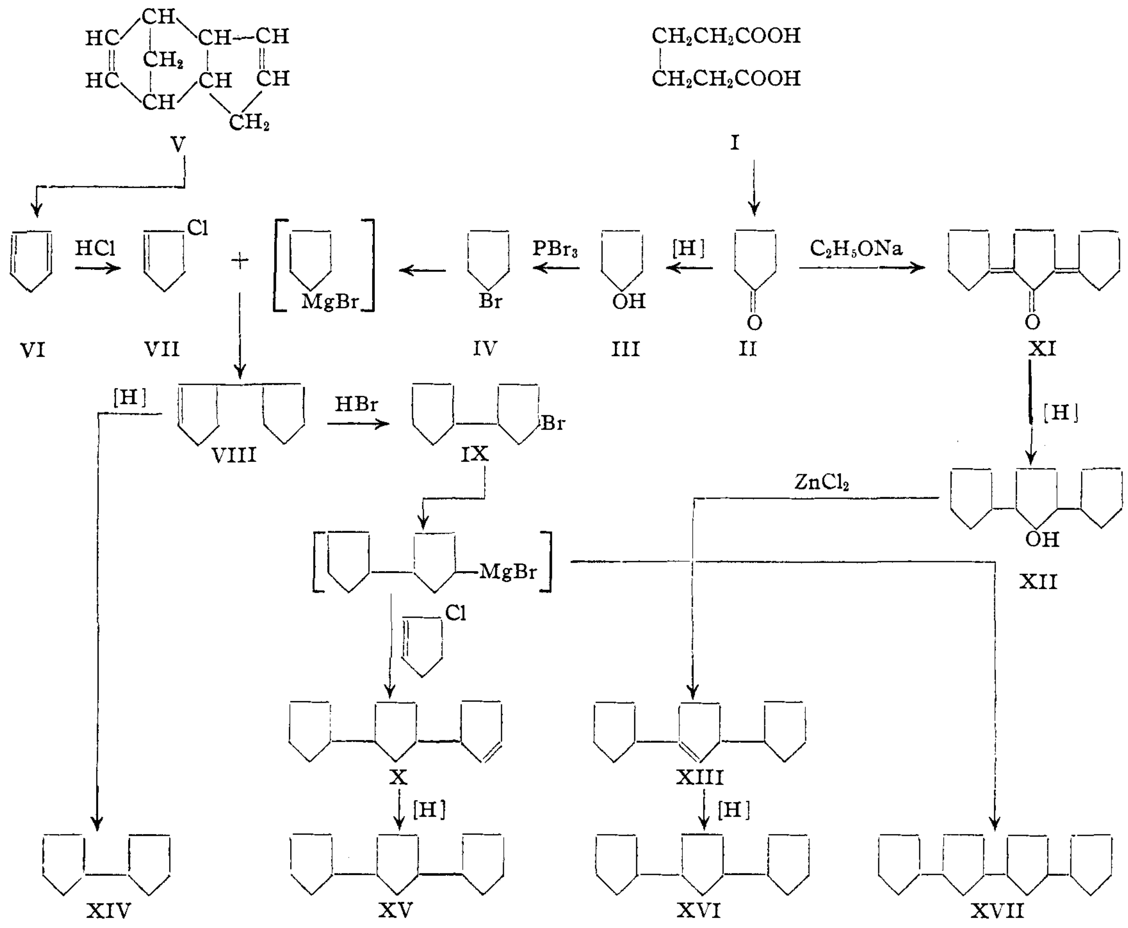

Fig. 1.—Synthesis of Multicyclopentyls.

They proved that the bromine atom entered the ring at the 3-position by transforming the product to 3-cyclopentylcyclopentanone.

The Grignard reagent of 3-bromobicyclopentyl gave with 1-chlorocyclopentene-2 a small yield of the tricyclic unsaturated hydrocarbon, 3-(cyclopenten-2-yl)-bicyclopentyl (X). The catalytic reduction of X then resulted in the first tercyclopentyl: 1,3-dicylopentylcyclopentane (XV).

In order to substantiate the structure of XV, a second series of reactions was carried out. This consisted in the condensation at room temperature of three molecules of cyclopentanone to yield 1,3-dicyclopentylidenecyclopentanone (XI) which was catalytically reduced at 160–170° to give a good yield of 1,3-dicyclopentylcyclopentanol-2 (XII). Dehydration of this tricyclic alcohol took place smoothly with zinc chloride at 180°. The 1,3-dicyclopentylcyclopentene (XIII) thus obtained gave upon reduction a 1,3-dicyclopentylcyclopentane (XVI), whose properties differed only slightly from those of XV. Since no attempts were made in the present investigation to separate geometric isomers, the small deviations observed are probably due to differences in the proportion of the two isomers in the two samples. All evidence indicates that they both have the structure assigned to them.

The quatercyclopentyl, 3,3′-dicylopentylbicyclopentyl (XVII) was obtained in small yield by a Wurtz reaction of the Grignard reagent of 3-bromobicyclopentyl (IX).

Synthesis of Intermediates

Cyclopentanone (II).—This compound was prepared by the distillation of adipic acid according to the method of Thorpe and Kon.[8] By this procedure 7790 g. of adipic acid was transformed to 3047 g. of cyclopentanone. A sample boiling at 130.7–130.8° (765 mm.) had n^{20}_{D} 1.43704, d^{20}_{4} 0.9487, *MR* 23.21 (calcd. 23.11).

Cyclopentanol (III).—The reduction of cyclopentanone to cyclopentanol was effected by hydrogenation in an

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[8] Thorpe and Kon, "Organic Syntheses," Coll. Vol. I, 1932, p. 187.

Adkins apparatus in the presence of Raney nickel catalyst. Each charge consisted of 252.3 g. (3.0 moles) of cyclopentanone and 12 g. of Raney nickel. The hydrogenation was carried out at 60–80° for five hours under 1000–1600 lb. per sq. in. pressure. The combined product of several runs was distilled through a 20-plate bubble-cap column of the Bruun type and the cyclopentanol boiling at 139–140° was collected. The yields were as high as 94% of the theoretical amount. A sample boiling at 139.7° at 748 mm. had n^{20}_{D} of 1.4533, d^{20}_{4} 0.9469, *MR* 24.59 (calcd. 24.62).

Cyclopentyl Bromide (IV).—The action of phosphorus tribromide on cyclopentanol according to the procedure of Noller and Adams[9] produced cyclopentyl bromide. Runs were made using 258 g. (3.0 moles) of cyclopentanol and 308 g. (1.14 moles) of phosphorus tribromide. After the product had been separated from the steam distillate, it was shaken vigorously with two 25-ml. portions of 48% hydrobromic acid. This method of purification of bromides is recommended by McCullough and Cortese.[10] It finally was washed with 10% sodium carbonate and water and dried over calcium chloride with frequent agitation. In the first distillation, the product was collected at 136–138°. Upon redistillation the main portion boiled at 136.7–137.7° (760 mm.); n^{20}_{D} 1.4885.

1-Chlorocyclopentene-2 (VII).—This compound was prepared in a manner similar to that described by Kraemer and Spilker[11a] and Noeldechen.[11b] Dry hydrogen chloride gas was passed into freshly distilled cyclopentadiene at −25°. The cyclopentadiene was obtained by heating dicyclopentadiene.[12]

After the cyclopentadiene had been saturated with the hydrogen chloride, the reaction mixture was vacuum distilled at 11 mm. pressure. The colorless chlorocyclopentene passed over for the most part at 25–29°. It was collected at −40°. From 99 g. (0.75 mole) of dicyclopentadiene there was obtained 119 g. (77.3%) of chlorocyclopentene. Since the product undergoes slow decomposition on standing for even a short time, it was kept at the low temperature until needed and was used within several hours after its preparation.

1-Cyclopentylcyclopentene-2 (VIII).—This compound was prepared by the reaction of 1-chlorocyclopentene-2 with cyclopentylmagnesium bromide.[6a] To the Grignard reagent prepared from 171 g. (1.15 moles) of freshly distilled cyclopentyl bromide in 375 ml. of anhydrous ether and 28 g. of magnesium turnings was added dropwise at 0° a solution of 102.5 g. (1 mole) of freshly prepared chlorocyclopentene-2 in 125 ml. of anhydrous ether. After standing overnight at room temperature, the reaction mixture was refluxed for two and one-half hours. It was finally decomposed with dilute hydrochloric acid. The purified and dried ethereal solution was freed of solvent by distillation of the latter through a column. The yellow-colored residue was refluxed for an hour over sodium metal and finally distilled over sodium through a short Vigreux column. The portion boiling at 183–188° weighed 99.7 g. or 73.2% of the theoretical amount based on the chlorocyclopentene. Upon redistillation the product boiled for the most part at 185–186° (760 mm.), n^{20}_{D} 1.4760, d^{20}_{4} 0.8827 and *MR* 43.53 (calcd. 43.51).

Although bicyclopentyl is a possible by-product in this reaction, no evidence of it was found. The refractive indices of the higher boiling fractions deviated little from those of the main body of liquid.

3-Bromobicyclopentyl (IX).—This compound was prepared in the manner described by von Braun, Kamp and Kopp[6a] by shaking cyclopentylcyclopentene-2 with fuming hydrobromic acid for sixty hours: b. p. 95–98° (2 mm.), yield 89.3%. The product slowly darkened on standing. For this reason it was always freshly distilled before being used. Upon redistillation, the main portion boiled at 96° (1 mm.), n^{20}_{D} 1.51175, d^{20}_{4} 1.2576, *MR* 51.76 (calcd. 51.74).

Anal. Calcd. for $C_{10}H_{17}Br$: Br, 36.82. Found: Br, 36.69.

The lower boiling fraction had a slightly higher refractive index, n^{20}_{D} 1.5121, while the higher boiling fraction had a somewhat lower value, n^{20}_{D} 1.5112.

3-(Cyclopenten-2-yl)-bicyclopentyl (X).—This tricyclic unsaturated hydrocarbon was prepared by the reaction of 1-chlorocyclopentene-2 with the Grignard reagent of 3-bromobicyclopentyl using the same procedure as described for the preparation of 1-cyclopentylcyclopentene-2 (VIII). The compound is not mentioned in the literature. To the Grignard reagent prepared from 14.1 g. of magnesium metal and 126 g. (0.58 mole) of freshly distilled 3-bromobicyclopentyl in 275 ml. of anhydrous ether was slowly added at 0° 101 ml. of an ethereal solution containing 47 g. (0.46 mole) of freshly prepared chlorocyclopentene-2. After working up the reaction mixture, the crude product was gently heated over sodium metal for one and one-half hours. It was then fractionally distilled under diminished pressure. There were obtained three different fractions each of which was separately redistilled. The first fraction boiled for the most part at 63–65° (10 mm.). It represented 44% of the product and was apparently cyclopentylcyclopentene. The second fraction, representing 42% of the product, gave upon redistillation the desired 3-(cyclopenten-2-yl)-bicyclopentyl: b. p. 140–141° (10 mm.), n^{20}_{D} 1.4993, d^{20}_{4} 0.9318, *MR* 64.42 (calcd. 64.40). The yield was 28.3 g. or 30% of the theoretical amount. Due to the fact that the carbon and hydrogen content of a sample was found to decrease upon standing, a satisfactory combustion analysis was not obtained. However, the saturated hydrocarbon obtained by hydrogenating the main portion of the product gave a satisfactory analysis (see XV).

The higher boiling (third) fraction representing about 14% of the product of the reaction and boiling at 190–200° (12 mm.) was 3,3′-dicyclopentylbicyclopentyl (XVII). It is described in a subsequent part of this section.

1,3-Dicyclopentylidenecyclopentanone-2 (XI).—This tricyclic unsaturated ketone was prepared by the condensation of cyclopentanone in the presence of sodium ethylate.[13a,b,c] The sodium ethylate was formed from 750 ml.

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[9] Noller and Adams, THIS JOURNAL, **48**, 1084 (1926).

[10] McCullough and Cortese, *ibid.*, **51**, 225–228 (1929).

[11] (a) Kraemer and Spilker, *Ber.*, **29**, 554 (1896); (b) Noeldechen, *ibid.*, **33**, 3348 (1900).

[12] The author appreciates the kindness of Drs. N. K. Chaney and A. L. Ward of the United Gas Improvement Company in furnishing a sample of pure dicyclopentadiene.

[13] (a) Wallach, *Ann.*, **389**, 183 (1912); (b) Wallach, *Ber.*, **29**, 2964 (1896); (c) Zelinskiĭ and Shuĭkin, *ibid.*, **62B**, 2180–2186 (1929).

of commercial anhydrous ethyl alcohol and 46 g. of sodium metal in a two-liter, three-necked, round-bottomed flask equipped with a reflux condenser and a mercury-sealed stirrer. To the cooled sodium ethylate solution was then added dropwise 252.3 g. (3 moles) of cyclopentanone over a period of four to five hours. The condensation was effected at room temperature with continuous mechanical stirring. The mixture finally stood overnight. The reaction mixture was diluted and extracted with ether. The ethereal solution was washed with water and dried over anhydrous potassium carbonate. After removal of the ether from the filtered solution, the residue was recrystallized from a small volume of methyl alcohol: yellow crystals, m. p. 82°; yield 76.9 g. By steam distilling the mother liquor and extracting with ether the residue not volatile with steam, there was obtained an additional 23.6 g. of the crystalline dicyclopentylidenecyclopentanone. The total yield was therefore 100.5 g. or 46.3% of the theoretical amount. From the steam distillate there was separated 80 g. or 36% of the theoretical amount of monocyclopentylidenecyclopentanone (b. p. 102–103° at 5 mm.).

1,3-Dicyclopentylcyclopentanol-2 (XII).—This tricyclic alcohol was synthesized by the catalytic hydrogenation of 1,3-dicyclopentylidenecyclopentanone in ethyl alcohol and with Raney nickel catalyst. The reduction was complete in five to six hours at 160–170° and 1500 lb. per sq. in. pressure. The product was recrystallized from low boiling petroleum ether: white crystals of m. p. 68–69°. The yields were about 87%. No effort was made to identify geometric isomers. The preparations described in the literature were made by reduction in sodium and ethyl alcohol.[6b,13a,13b]

If the catalytic hydrogenation was carried out at 70–90°, the intermediate dicyclopentylcyclopentanone was obtained.

1,3-Dicyclopentylcyclopentene (XIII).—The unsaturated tricyclic hydrocarbon was produced by dehydrating the tricyclic alcohol with zinc chloride according to the method of Wallach.[13a] After heating the crude product over sodium for several hours, it was fractionally distilled under diminished pressure. The yield of unsaturated hydrocarbon boiling at 150–152° (12 mm.) was 79.5%. The product was redistilled: b. p. 125–127° (1 mm.), n^{20}D 1.5089, d^{20}_4 0.9448, *MR* 64.57 (calcd. 64.40).

Synthesis of Multicyclopentyls

Bicyclopentyl (XIV).—This hydrocarbon has been prepared by the action of sodium metal on cyclopentyl bromide in ether[5,14a,14b] and by the reduction of 1-cyclopentylcyclopentene-1,[15] which had been obtained from cyclopentyl-2-cyclopentanol.

In the present investigation the bicyclopentyl was prepared by the catalytic hydrogenation of 1-cyclopentylcyclopentene-2 (VIII) in ethyl alcoholic solution and with Raney nickel catalyst. The reduction was carried out for five hours at 100° and under 1800–1900 lb. per sq. in. pressure. The product was freed from alcoholic solvent and was diluted with a low-boiling pure paraffin hydrocarbon (isohexane) fraction which had been distilled in a 100-plate Bruun column and which boiled at 60.0–60.3°. The resulting solution was thoroughly extracted with 70%, 80% and concentrated sulfuric acid in turn. The extraction with concentrated acid was repeated with three fresh portions of acid. It was finally washed with water, 10% sodium carbonate solution and water in turn and dried over calcium chloride. After removal of the solvent from the filtered solution by distillation over sodium, the bicyclopentyl was gently refluxed over sodium for an hour and finally distilled at atmospheric pressure; b. p. 190.0–190.5° (761.8 mm.), n^{20}D 1.46415, d^{20}_4 0.8646, *MR* 44.14 (calcd. 43.98), yield 62%. These values correspond very closely to those obtained by Zelinskiĭ and Shuĭkin.[15]

Anal. Calcd. for $C_{10}H_{18}$: C, 86.88; H, 13.12; H/C (atomic ratio), 1.800; no. of rings, 2. Found: C, 86.55; H, 13.12; H/C, 1.806; no. of rings; from H/C, 1.97; from r^{20}D, 1.93.

1,3-Dicyclopentylcyclopentane (XV) and (XVI).—This tricyclic hydrocarbon has not been described in the literature. In the present investigation it was prepared by two separate methods. Geometric isomers were not identified.

(a) From 3-(Cyclopenten-2-yl)-bicyclopentyl (X).—The catalytic hydrogenation of 24 g. of 3-(cyclopenten-2-yl)-bicyclopentyl (X) in 50 ml. of isohexane and 3 g. of Raney nickel was effected in five hours at 135–140° and 2200–2300 lb. per sq. in. pressure. The filtered reaction mixture was thoroughly extracted once with dilute sulfuric acid, then with three portions of concentrated acid, followed by two portions of 98% acid and finally with two portions of concentrated acid. The dicyclopentylcyclopentane (XV) was then isolated from the colorless solution in the manner described above for XIV: b. p. 158° (16 mm.), yield 70%, n^{20}D 1.49010, d^{20}_4 0.9177, *MR* 65.02 (calcd. 64.87).

Anal. Calcd. for $C_{15}H_{26}$: C, 87.30; H, 12.70; H/C (atomic ratio), 1.733; no. of rings, 3. Found: C, 87.39; H, 12.57; H/C, 1.714; no. of rings; from H/C, 3.14; from r^{20}D, 2.91.

(b) From 1,3-Dicyclopentylcyclopentene (XIII).—The catalytic hydrogenation of 1,3-dicyclopentylcyclopentene (XIII) was carried out in the same manner as described above in (a). The resulting 1,3-dicyclopentylcyclopentane (XVI) boiled at 147–148° (12 mm.): yield 65%, n^{20}D 1.49355, d^{20}_4 0.9223, *MR* 65.09 (calcd. 64.87).

Anal. Calcd. for $C_{15}H_{26}$: C, 87.30; H, 12.70; H/C (atomic ratio), 1.733; no. of rings, 3. Found: C, 87.23; H, 12.67; H/C, 1.731; no. of rings; from H/C, 3.02; from r^{20}D, 2.87.

3,3′-Dicyclopentylbicyclopentyl (XVII).—Although this quatercyclopentyl has been reported in the literature by von Braun, Kamp and Kopp,[6a] the only physical property given was the b. p. 205–207° at 9 mm. In the present work the compound was obtained partly as a by-product in the preparation of 3-(cyclopenten-2-yl)-bicyclopentyl (X) and partly by the action of silver bromide upon the Grignard reagent of 3-bromobicyclopentyl according to the method of Gardner and Borgstrom[16a] and Joseph and Gardner.[16b] The yield by the latter method was hardly

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[14] (a) Meiser, *Ber.*, **32**, 2054 (1899); (b) Zelinskiĭ, Titz and Fateev, *ibid.*, **59B**, 2581–2584 (1926).

[15] Zelinskiĭ and Shuĭkin, *J. Russ. Phys.-Chem. Soc.*, **62**, 1343–1354 (1930); *Chem. Zentr.*, **102**, I, 1098–1099 (1931).

[16] (a) Gardner and Borgstrom, THIS JOURNAL, **51**, 3375 (1929); (b) Joseph and Gardner, *J. Org. Chem.*, **5**, 61 (1940).

TABLE I

PHYSICAL CONSTANTS OF THE MULTICYCLOPENTYLS

Hydrocarbon	Number	Formula	B. p. °C.	B. p. Mm.	Aniline point (°C.)	d^{25}_4[a]	n^{25}_D	$n - d/2$ (20°)[b]	r^{20}_D[c]	Sp. disp.[d]
Bicyclopentyl	XIV	$C_{10}H_{18}$	190.0–190.5	762	36.5	0.8608	1.46195	1.0319	0.3193	96
1,3-Dicyclopentylcyclopentane	XV	$C_{15}H_{28}$	293–294	760	54.8	.9143	1.48820	1.0312	.3151	97
1,3-Dicyclopentylcyclopentane	XVI	$C_{15}H_{28}$	296–297	761	54.9	.9190	1.49155	1.0324	.3154	100
3,3′-Dicyclopentylbicyclopentyl	XVII	$C_{20}H_{34}$	369–370	761	67.8	.9534	1.50745	1.0310	.3123	101
1-Cyclopentylcyclopentene-2	VIII	$C_{10}H_{16}$	185–186	760	8.6	.8787	1.4740	1.0346	.3195	111
3-(Cyclopenten-2-yl)-bicyclopentyl	X	$C_{15}H_{24}$	...	...	21.5	.9283	1.4974	1.0334	.3153	108
1,3-Dicyclopentylcyclopentene	XIII	$C_{15}H_{24}$	300–301	760	37.5	.9414	1.5070	1.0365	.3160	114

[a] All densities were corrected for air buoyancy. [b] Refractivity intercept at 20°: see Ward and Kurtz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 559–576 (1938). [c] Lorenz–Lorentz specific refractivity, $(n^2 - 1)/(n^2 + 2) \times (1/d)$. [d] Specific dispersion, $(n_f - n_c)/d \times 10^4$.

TABLE II

VISCOSITY DATA ON MULTICYCLOPENTYLS

Hydrocarbon	Number	Kinematic viscosity (centistokes) 20°C. 68°F.	25°C. 77°F.	37.8°C. 100°F.	54.4°C. 130°F.	98.9°C. 210°F.	V. I.[a]	Density (d_4) 37.8°C.	54.4°C.	98.9°C.
Bicyclopentyl	XIV	1.652	1.543	1.304	1.092	0.7134	173	0.8514	0.8388	0.8053
1,3-Dicyclopentylcyclopentane	XV	5.349	4.774	3.658	2.720	1.494	158	.9058	.8946	.8651
1,3-Dicyclopentylcyclopentane	XVI	7.405	6.489	4.734	3.358	1.704	133	.9105	.8994	.8702
3,3′-Dicyclopentylbicyclopentyl	XVII	44.75	34.68	19.78	11.085	3.927	103	.9452	.9346	.9071

[a] Calculated from the equations of Dean, Bauer and Berglund, *Ind. Eng. Chem.*, **32**, 102–107 (1940).

more than 24% of the theoretical, the main product being cyclopentylcyclopentene. To obtain a pure sample of the quatercyclic hydrocarbon, the crude products were diluted with isohexane and thoroughly extracted with portions of dilute, concentrated and 98% sulfuric acid until no further coloration of the extract was obtained. The product was isolated from the solution as described for bicyclopentyl and after a brief period of heating over sodium metal was again subjected to a concentrated sulfuric acid treatment. The remainder of the above process was repeated and the dried product was fractionally distilled under diminished pressure: b. p. 183–185° (3 mm.), n^{20}_D 1.50920, d^{20}_4 0.9564 and *MR* 85.72 (calcd. 85.76).

Anal. Calcd. for $C_{20}H_{34}$: C, 87.51; H, 12.49; H/C (atomic ratio), 1.700; no. of rings, 4. Found: C, 87.56; H, 12.43; H/C, 1.691; no. of rings; from H/C, 4.09; from r^{20}_D, 4.04.

Determination of Physical Properties

In Table I are collected several physical constants of the multicyclopentyls which are not given above in the text. The boiling points at atmospheric pressure were determined by distilling 6–8 ml. of the sample in a 25-ml. distilling flask heated by a Wood's fusible alloy bath.

For the determination of the aniline points, the following procedure was used. A small test-tube (15 × 150 mm.) of 15-ml. capacity was fitted with a cork stopper carrying a small thermometer of the Anschütz type and a small glass tube to serve as a bearing for a spiral wire hand stirrer. The thermometers used were graduated to divisions of 0.2°, but could be easily read to 0.1°. A heating bath of dibutyl phthalate in a 400-ml. beaker equipped with a mechanical stirrer and thermometer was used. In cases in which the aniline point was below room temperature either a water or acetone bath was used. Cooling was effected by adding small pieces of ice or dry-ice, respectively.

The aniline was freshly distilled under diminished pressure and was colorless. It had a m. p. −6.2° and d^{20}_4 1.0217. Equal volumes of the hydrocarbon and aniline at 20° were used as determined by weighing. About 2.0 g. of aniline was used. The tube was flushed out with dry nitrogen to preclude the presence of moisture. The temperature of sudden appearance of turbidity throughout the clear mixture with slowly descending bath temperature was taken as the aniline point. By this procedure a sample of *n*-heptane gave an aniline point of 70.4°.

Evans[5] found an aniline point of 35.8° for bicyclopentyl. The aniline points for the other hydrocarbons given in Table I are not recorded in the literature.

Densities were determined in pycnometers[17] of 3–5 ml. capacity constructed of capillary tubing bent in the form of a U with a bulb blown on one arm. Both arms were graduated. The instruments were calibrated with distilled water. All values were corrected for the buoyancy of the air. The densities at the standard viscosity temperatures of 100, 130 and 210° F. also were determined for the saturated hydrocarbons and are given in Table II.

The refractive indices were determined on a Valentine Abbe type refractometer which was calibrated with a glass test plate and with distilled water. The calculated molecular refractivities (*MR*) were obtained by the use of Eisenlohr's atomic refractivities. The specific dispersion was estimated from the drum reading of the refractometer.

Kinematic viscosities were determined on the hydrocarbons at five different temperatures (Table II) using modified Ostwald viscosimeters.[18] The tubes were calibrated with aniline using the data of Steiner.[19] The values for bicyclopentyl are only slightly higher than those given by Evans.[5]

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(17) Designed by Mr. S. S. Kurtz, Jr.

(18) Am. Soc. Testing Materials, Designation D-445-39T.

(19) Steiner, *Ind. Eng. Chem., Anal. Ed.*, **10**, 582–584 (1938).

Conclusions

The saturated multicyclopentyls were found to have physical properties which in most cases increased in almost a linear relationship with respect to their boiling points at atmospheric pressure. The kinematic viscosity increased linearly when the boiling points were plotted on a uniform scale as the abscissa and the kinematic viscosities in centistokes at the different temperatures were plotted on the ordinate scale of an A. S. T. M. viscosity–temperature chart. A straight line was also obtained by plotting the boiling points against the logarithm of the number of rings per molecule. Thus some approximate physical properties of unknown saturated hydrocarbons containing five or more rings per molecule in this series may be estimated. An exact determination of the properties of these unknown compounds, of course, cannot be made in this manner since possible geometric isomers need still to be synthesized and characterized.

The viscosity index was found to decrease as the number of rings increased. However, the quatercyclic hydrocarbon still had a viscosity index of more than one hundred.

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Summary

For the purpose of establishing the physical properties characteristic of multicyclic five-carbon membered rings in the light of any probable relationship to the chemical structure of petroleum products, there has been synthesized a series of multicyclopentyls.

Bicyclopentyl, 1,3-dicyclopentylcyclopentane and 3,3′-dicyclopentylbicyclopentyl have been synthesized from cyclopentadiene and cyclopentanone. 1,3-Dicyclopentylcyclopentane has also been synthesized from cyclopentanone itself.

The physical properties determined were boiling point at atmospheric and reduced pressure, refractive index at two temperatures, density at five temperatures, specific dispersion, kinematic viscosity at five temperatures and aniline point.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Secondary and Tertiary Amines from Nitro Compounds

BY WILLIAM S. EMERSON AND C. A. URANECK

Since the reductive alkylation of aromatic nitro compounds in a basic medium was known to give secondary amines in good yield,[1] it seemed likely, by analogy with the known alkyl reduction of the corresponding primary amines, that in an acid medium tertiary amines might be obtained. The reductive alkylation of primary amines by such acid reducing agents as formic acid[2] and zinc and hydrochloric acid[3] produces good yields of tertiary amines. Although unhindered aromatic primary amines yield polymers when treated with aldehydes in the presence of acids,[2b,4] this factor should not interfere with the preparation of tertiary amines from aromatic nitro compounds, since Vavon and Crajcinovic[5] have shown that when nitrobenzene is reduced in the presence of benzaldehyde, the reduction goes only as far as phenylhydroxylamine, which then condenses with the aldehyde as fast as it is formed, so that at no time would there be any aromatic primary amine in the reaction mixture.

It was found that, on treatment of an alcoholic solution of one equivalent of nitrobenzene and three of *n*-butyraldehyde with hydrogen and Raney nickel in the presence of trimethylamine hydrochloride, a 63% yield of N,N-di-*n*-butylaniline was obtained. The yield rose to 69% when acetic acid and platinum oxide were used instead of the trimethylamine hydrochloride

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[1] Emerson and Mohrman, THIS JOURNAL, **62**, 69 (1940).

[2] (a) Wallach, *Ann.*, **343**, 54 (1905); (b) Clark, Gillespie and Weisshaus, THIS JOURNAL, **55**, 4571 (1933).

[3] Emerson, Dorf and Deutschman, *ibid.*, **62**, 2159 (1940).

[4] Emerson and Walters, *ibid.*, **60**, 2023 (1938).

[5] Vavon and Crajcinovic, *Compt. rend.*, **187**, 420 (1928).