tated from the hot mixture, was removed by filtration to give 0.9 g. (95%) of 6,7-epoxy-$\Delta^{9(10)}$-decalin-2,3-dicarboxylic anhydride (V), m.p. 190.5–191.5°.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.50. Found: C, 65.60; H, 5.76.

2,3-Epoxy-1,2,3,4,5,5a,6,11,11a,12-decahydronaphthacene-6,11-dione (VI). To a solution of 0.52 g. (0.0033 mole) of 1,4-naphthoquinone in 25 ml. of dry toluene was added 0.60 g. (0.005 mole) of 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III) and the solution was heated under reflux for 2 days. The solvent was removed by distillation to give a yellow solid. Two recrystallizations from 95% ethanol gave 0.87 g. (70%) of VI as yellow needles, m.p. 165.5–170°, which became slightly discolored on exposure to air.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.00; H, 5.75.

trans-1,2-Dimethylenecyclohexane-4,5-diol (VII). Crude 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III) (33 g.) was treated with a solution of 24 g. of sodium hydroxide in 800 ml. of water for 15 hr. at 40–50°. After the mixture was cooled to room temperature, 15 g. of acetic acid was added and the aqueous solution was extracted continuously with ether for 24 hr. After the ether solution was dried over anhydrous magnesium sulfate and the solvent was removed by distillation, some low boiling liquids were removed from the residue under partial vacuum. The remaining residue was a polymeric resin, which was insoluble in ether, benzene, methanol, and acetone.

Extraction of the residue in hot acetone, followed by filtration of the mixture, gave a white resin, softening point 165–167°. Evaporation of the acetone filtrate gave a white solid, which was dissolved in methanol. Addition of the solution to a large excess of benzene and concentration of this solution to one-half its original volume (essentially removing the methanol) gave 20 mg. of *trans*-1,2-dimethylenecyclohexane-4,5-diol (VII) as a white powder, m.p. 214–215°.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.53; H, 8.63. Found: C, 68.39; H, 8.59.

Emulsion polymerization of 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III). In a 2-oz. screw-cap bottle were placed 2.06 g. of 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III), 0.10 g. of sodium stearate, 0.02 g. of lauryl mercaptan, 0.007 g. of potassium persulfate and 3.80 g. of water. The bottle was rotated in a water bath maintained at 63° for 26 hr., at which time the emulsion had broken. After acidification of the mixture with dilute hydrochloric acid and removal of the solid by filtration, the solid was dissolved in 60 ml. of benzene and a trace of 1,3,5-trinitrobenzene was added as an inhibitor. The benzene solution was poured slowly into 250 ml. of cold methanol with stirring and the white flocculent polymer precipitated. Filtration, followed by drying, gave 0.77 g. (37% conversion) of poly-3,4-dimethylene-7-oxabicyclo[4.1.0]heptane. The polymer did not exhibit a definite softening point, although discoloration and signs of cross linking of the polymer occurred at 180°. The polymer showed signs of considerable discoloration at 230°. This decomposition probably resulted from cross linking of the epoxide groups, as the heated polymer displayed hard, brittle properties which were not present in the original polymer.

Determination of the viscosity of the polymer at 25° in a chloroform solution in an Ostwald viscometer gave an intrinsic viscosity of 0.326.

Combined peroxide-catalyzed and epoxide polymerization of 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III). When 0.57 g. of 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III) was polymerized in bulk with a catalytic quantity of benzoyl peroxide at steam-bath temperature for 13 hr., the resulting polymer was very viscous and displayed some elasticity at room temperature. After a small amount of ethylenediamine was added to this polymer, the mixture was heated for 2 hr. on a steam bath. There resulted a very hard amber-colored resin which adhered to the walls of the glass container.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Cyclopentenes and Cyclopentanes. II. Synthesis from Isophorone[1]

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Received July 13, 1959

Synthesis of 1,1,3,3-tetramethylcyclopentane, 1,1,2,4-tetramethylcyclopentane and 1,1,3,4-tetramethylcyclopentane from isophorone has been accomplished. Several intermediate compounds, tetramethylcyclopentenes, trimethylcyclohexenes polymethyladipic acids, cyclohexanones cyclopentanones and cyclohexanediols were prepared and characterized. The methods described are adaptable to large scale use.

The tetramethylcyclopentanes comprise a little known group of hydrocarbons. Of the seven possible structural isomers only one (1,1,2,3-tetramethylcyclopentane[3]) has been reported as synthesized, and no effort was made to determine the hydrocarbon's geometrical configuration. 1-*trans*-2-*cis*-3-*trans*-4-Tetramethylcyclopentane and 1,1-3-*trans*-4-tetramethylcyclopentane have been identified in a representative petroleum.[4] If all of the geometrical isomers are counted, sixteen different tetramethylcyclopentanes are possible.

Previously,[5,6] isophorone (3,5,5-trimethyl-2-cy-

(1) This paper was abstracted in part from a dissertation presented by George Slomp, Jr., to the Graduate School of the Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The remainder of the work was carried out as a part of the normal research activities of the American Petroleum Institute Research Project 45, which is administered by the Ohio State University Research Foundation.

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(3) J. F. Eykman, *Chem. Weekblad*, **3**, 692 (1906).

(4) F. D. Rossini and A. J. Streiff, Paper presented to Section V of the Fifth World Petroleum Congress, N. Y. (1959).

TABLE I

PHYSICAL PROPERTIES FOR SOME HYDROCARBONS SYNTHESIZED

Compound	F.P., °C.	B.P., °C.	d_4^{20}	n_D^{20}	Purity, Mole %
1,1,3,3-$(CH_3)_4$ Cyclopentane	−88.29	117.96	0.7509	1.4125	99.0 + 0.5
1,1,3,4-$(CH_3)_4$ Cyclopentane (*trans*)	−93.94	121.4–121.6	0.7489	1.4120	98.5 + 0.5
1,1,3,4-$(CH_3)_4$ Cyclopentane (*cis*)	−106.49	132.9–133.0	0.7670	1.4204	98.0 + 0.5
1,1,2,4-$(CH_3)_4$ Cyclopentane (*cis* and *trans*)	−118.91	129.41–129.45	0.7648	1.4194–1.4196	—
3,3,5,5-$(CH_3)_4$ Cyclopentene	−64.23	107.03	0.7484	1.4154	—
3,3,5-$(CH_3)_3$ Cyclohexene	−85.39	131.33	0.7888	1.4386	99.5 + 0.2
3,5,5-$(CH_3)_3$ Cyclohexene	−91.97	133.58	0.7941	1.4406	97.8 + 0.2

clohexenone) had been used as a starting material for a variety of trimethylcyclopentanes. Paper I of our series[7] describes syntheses based on cyclopentadiene. The present work extends the use of isophorone to the synthesis of five tetramethylcyclopentanes (two as a mixture of geometrical isomers), one tetramethylcyclopentene, and, incidentally, two trimethylcyclohexenes.

The synthesis of 1,1,3,3-tetramethylcyclopentane from isophorone was made possible by the discovery of M. S. Kharasch and P. O. Tawney[8a] that, in the presence of cuprous chloride, methyl Grignard reagent undergoes 1,4-addition to isophorone, and 3,3,5,5-tetramethylcyclohexanone is obtained. When this ketone was oxidized by nitric acid it yielded 2,2,4,4-tetramethyladipic acid, which upon destructive distillation was converted to a new ketone, 2,2,4,4-tetramethylcyclopentanone. This ketone was converted to 1,1,3,3-tetramethylcyclopentane in two ways: (1) direct reduction by a modification of the Wolff-Kishner procedure, and (2) reduction by catalytic hydrogenation, dehydration, and re-hydrogenation. The products obtained were of about the same purity. Method 2 produced two new olefins in the dehydration step: 3,3,5,5-tetramethylcyclopentene and another, tentatively identified as 1,3,3,5-tetramethylcyclopentene (which could be formed by retropinacolic rearrangement).

1,1,2,4 - Tetramethylcyclopentane and 1,1,3,4,-tetramethylcyclopentane were synthesized by a similar series of reactions. 3,3,5-Trimethylcyclohexanone and 3,3,5-trimethylcyclohexanol were oxidized by nitric acid to produce a mixture of 2,2,4-trimethyladipic acid and 2,4,4-trimethyladipic acid, which was ketonized without separation or purification, yielding cyclic ketones.

2,2,4-Trimethylcyclopentanone, the lower boiling of the cyclic ketones, was separated in good purity by high-efficiency distillation, and 2,4,4-trimethylcyclopentanone was isolated through its sodium bisulfite addition product. The purified ketones were condensed individually with methyl Grignard reagent to produce 1,2,2,4-tetramethylcyclopentanol and 1,2,4,4-tetramethylcyclopentanol, respectively. Dehydration of the latter and hydrogenation of the resulting olefin mixture produced 1,1,3,4-tetramethylcyclopentanes. The 1,2,2,-4-tetramethylcyclopentanol was treated with anhydrous hydrogen chloride to obtain the corresponding organic chloride which was then reduced with sodium in liquid ammonia to produce 1,1,2,4-tetramethylcyclopentane; some retropinacolic-type rearrangement probably took place during the hydrochlorination but the same hydrocarbon product would result. These quite different methods of reduction were chosen because it was believed that they would produce approximately equimolar mixtures of the geometrical isomers from which each individual isomer might be isolated in quantity.

In the case of the 1,1,3,4-tetramethylcyclopentanes, the mixture was distilled at about 25-plate efficiency to separate it into nearly equal amounts of *trans* isomer and *cis* isomer, with the properties shown in Table I.

The mixture of 1,1,2,4-tetramethylcyclopentanes was fractionated at about 25-plate efficiency, and 94% of the distillate had a boiling range of only 0.04° and a refractive index (n_D^{20}) range of only 0.0002. Inasmuch as both of the possible geometric isomers were undoubtedly present,[8b] it was concluded that the boiling points of the two must be similar. This appears plausible when other such pairs are compared: for example, the two 1,3-dimethylcyclopentanes boil only 0.96° apart and the 1-methyl-3-ethylcyclopentanes 0.6° apart.

An alternative method of synthesizing relatively pure samples of the trimethyladipic acids and pure trimethylcyclopentanones was developed. Dehydration of 3,3,5-trimethylcyclohexanol gave 3,3,5-

(5) S. F. Birch and E. A. Johnson, *J. Chem. Soc.*, 1493 (1951).

(6) George Slomp, Doctoral Dissertation, the Ohio State University, 1949. Also presented before the Organic Division of the American Chemical Society in September, 1950, in Chicago, Ill.

(7) Grant Crane, C. E. Boord, and A. L. Henne, *J. Am. Chem. Soc.*, **67**, 1237 (1945).

(8a) M. S. Kharasch and P. O. Tawney, *J. Am. Chem. Soc.*, **63**, 2308 (1941).

(8b) An equimolar mixture of the *cis* and *trans* isomers of 1,3-dimethylcyclopentane had been obtained by reduction of 1-chloro-1,3-dimethylcyclopentane by sodium in liquid ammonia (unpublished work of this laboratory).

trimethylcyclohexene and 3,5,5-trimethylcyclohexene (new compounds) which were separated by distillation and individually oxidized to the known 2,2,4-trimethyladipic acid and 2,4,4-trimethyladipic acid, respectively, thus establishing their structures. These acids were then converted to ketones separately to produce pure samples of 2,2,4-trimethylcyclopentanone and 2,4,4-trimethylcyclopentanone, respectively.

EXPERIMENTAL

3,3,5,5-Tetramethylcyclohexanone. The procedure followed in this synthesis was similar to one published.[8] To 770 ml. of filtered 2.14*M* methylmagnesium bromide (1.65 moles) contained in a 2-l., three-neck flask fitted with a Hershberg stirrer, thermometer, bulb condenser, and dropping funnel was added 0.0165 mole of cuprous chloride. Redistilled isophorone (Union Carbide Chemicals Co.) was added dropwise while maintaining the temperature at 10–15°, until 191 g. (1.38 moles) had been added. Stirring was continued for 1 hr. longer under reflux, and the mixture was allowed to stand overnight at room temperature. The reaction was quenched by pouring it into a mixture of 100 g. of glacial acetic acid and 800 g. of cracked ice. The ether layer was separated and the aqueous layer was extracted twice with 50 ml. of ether. The combined ether solutions were washed twice with 10% sodium bicarbonate, water, and saturated sodium chloride solution, successively. After drying over anhydrous sodium sulfate, the ether was removed by rapid distillation and the remaining material was fractionated at 10 mm. pressure and 10:1 reflux ratio on a 1.6 × 55 cm. column packed with 3/16-in. glass helices. The fractions boiling at 72–74°, 10 mm. amounted to 162.5 g. (76.5% yield) of tetramethylcyclohexanone. Properties determined were: b.p. 195–196°, n_D^{20} 1.4520–1.4522; (lit.,[8] b.p. 196–197°, n_D^{20} 1.4520).

2,2,4,4-Tetramethyladipic acid. Oxidation of 3,3,5,5-tetramethylcyclohexanone was accomplished in all-glass apparatus consisting of a 1-l., multi-neck flask fitted with a pressure-compensating dropping funnel, a propeller-type stirrer, a multibulb reflux condenser, and a thermometer well. The flask was charged with 480 ml. (5.0 moles) of 50% nitric acid and 1.0 g. of ammonium metavanadate, and the vigorously stirred mixture was heated to 65°. Then, 145.8 g. (0.945 mole) of 3,3,5,5-tetramethylcyclohexanone was dropped in at a carefully controlled rate and an exothermal reaction occurred with foaming and evolution of nitrogen oxides; the temperature was maintained at 60–65° by surrounding the flask with cold water. When about half of the ketone had been added, solid tetramethyladipic acid began to separate. Stirring was continued for 0.5 hr. after addition was complete, while reaction temperature was maintained by surrounding the flask with hot water. By the end of this time, no more gases were evolved, and the spent reaction mixture was allowed to cool to room temperature. The crude 2,2,4,4-tetramethyladipic acid, filtered and washed with water, amounted to 188 g. (98% yield); it melted at 118–119°, neut. equiv. 100.9 (theory 101.1).

A small amount of the acid was purified by recrystallization from water, and this sample (m.p. 119.0–119.5°) had a neut. equiv. of 101.2.

Anal. Calcd. for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97. Found: C, 59.34; H, 8.95.

The di-*p*-toluide of the acid was prepared and it recrystallized as needles (m.p. 125–126°) from ethyl alcohol.

2,2,4,4-Tetramethylcyclopentanone. In a typical run, 177 g. (0.875 mole) of 2,2,4,4-tetramethyladipic acid was converted to the ketone by heating to about 250–255° with 20 g. of manganese carbonate and 20 g. of barium hydroxide. The crude ketone (70% yield), after washing and drying, was distilled at about 20-plate efficiency to produce relatively pure 2,2,4,4-tetramethylcyclopentanone (61% yield). Physical properties determined for a center fraction were: b.p. 165.38°, d_4^{20} 0.8651, n_D^{20} 1.4305, f.p. −55.19° (f.p. range, 2.2°).

Anal. Calcd. for $C_9H_{16}O$: C, 77.08; H, 11.50. Found: C, 77.05; H, 11.48.

Semicarbazone, m.p. 189–189.5°.

Anal. Calcd. for $C_{10}H_{19}ON_3$: C, 60.88; H, 9.71; N, 21.30. Found: C, 60.88; H, 9.68; N, 21.28.

1,1,3,3-Tetramethylcyclopentane by direct reduction. To obtain the hydrocarbon, 107.5 g. (0.756 mole) of the corresponding ketone was reduced with 90 ml. of 85% hydrazine and 120 g. of potassium hydroxide in 600 ml. of diethylene glycol by the modified Wolff-Kishner method of Huang-Minlon.[9] The reactants were combined in a 2-l. round bottom flask which was fitted with a thermometer reaching nearly to the bottom and a reflux condenser with a take-off side arm. After the mixture was refluxed for 1 hr. take-off was commenced and the temperature was maintained at 170–175° by adjusting the rate at which water and hydrocarbon were distilled; the reaction was finished in about 2 hr. and distillation ceased.

The hydrocarbon layer in the distillate was separated and washed with dilute hydrochloric acid, water, and saturated salt solution; the 78 g. of crude product was dried over anhydrous sodium sulfate and fractionated at about 20-plate efficiency to yield 75.5 g. (77.5%) of 1,1,3,3-tetramethylcyclopentane with the properties shown in Table I.

1,1,3,3-Tetramethylcyclopentane by indirect reduction. In a typical run, 67.0 g. (0.477 mole) of 2,2,4,4-tetramethylcyclopentanone was hydrogenated over 10 g. of reduced nickel-on-kieselguhr at 200° and 1900 p.s.i.g. in a 300-ml. rocking autoclave to produce 62 g. (91%) of a compound presumed to be the corresponding 2,2,4,4-tetramethylcyclopentanol (b.p.$_{745}$ 174.4–175.0°, n_D^{20} 1.4431–1.4428). The material crystallized as white needles, m.p. 32.5–33.0° (uncorr.).

The tetramethylcyclopentanol was dehydrated by passing it through a 2.5 × 100 cm. tube filled with 8–14 mesh activated alumina at 300°. From 96.0 g. (0.675 mole) of carbinol, 64 g. (95% yield) of crude olefins was obtained after separation and drying. Distillation at 20-plate efficiency indicated 87% of the olefin mixture was 3,3,5,5-tetramethylcyclopentene: b.p.$_{760}$ 107.03°, n_D^{20} 1.4154. The remaining 13% of the distillate (b.p.$_{744}$ 122°, n_D^{20} 1.430) was rearranged olefin(s), most likely 1,3,3,5-tetramethylcyclopentene. The desired cycloparaffin was produced by hydrogenating 26.8 g. (0.215 mole) of the 3,3,5,5-tetramethylcyclopentene over 5 g. of nickel-on-kieselguhr. The reaction was carried out at 150° and 1900 p.s.i.g. in a 300-ml. rocking autoclave fitted with a 100-ml. glass liner. Distillation at 20-plate efficiency gave 22.5 g. (83% yield) of 1,1,3,3-tetramethylcyclopentane (b.p.$_{745}$ 117.2–117.4°, n_D^{20} 1.4125). A center fraction had virtually the same properties as the previous sample (Table I).

3,3,5-Trimethylcyclohexanol (dihydroisophorol). In a typical run, 1855 g. (13.7 moles) of isophorone was hydrogenated to saturation over 90 g. of nickel-on-kieselguhr at 250° in a 3-l. rocking autoclave at pressures of 1600–2000 p.s.i.g. The product was decanted from the catalyst while warm, and formed white crystalline needles which were not further purified. The yield was nearly quantitative.

3,3,5-Trimethylcyclohexanone (dihydroisophorone). Isophorone was hydrogenated as in the preceding section except that the temperature was held at 95–105° and treatment was suspended when the calculated amount of hydrogen had been absorbed. At this point, the rate of absorption had decreased nearly to zero. The bomb was cooled, and the liquid material was decanted from the catalyst and used without further purification. The yield was nearly quantitative.

Mixed 2,2,4- and 2,4,4-trimethyladipic acids. These acids were produced from a mixture of dihydroisophorone and

(9) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

dihydroisophorol by the same procedure described for 2,2,4,-4-tetramethyladipic acid, but on a larger scale. Presence of the ketone in the mixture prevented crystallization in the addition funnel.

The excess nitric acid was neutralized by a minimum amount of sodium hydroxide, with stirring. A color change from green to orange occurred at the point of equivalency, and the 2,2,4- and 2,4,4-trimethyladipic acids separated as an oil which partially crystallized upon standing; the yields of crude mixed acids were essentially quantitative in several runs.

2,2,4- and 2,4,4-Trimethylcyclopentanones. The crude mixture of trimethyladipic acids was converted to a ketone mixture by dry distillation with 10% of its weight of barium hydroxide. This reaction was performed, without mechanical stirring, in a 5-l. Pyrex flask heated to temperatures (260–290°) at which the trimethylcyclopentanones were formed at a steady rate and distilled off through a Vigreux column. The distillate consisted of the crude trimethylcyclopentanone mixture and a water layer which yielded additional crude ketone when saturated with sodium chloride. Based on the trimethylcyclohexanone-hexanol starting material, 80 to 85% yields of crude ketones were obtained over the two steps.

Pure 2,4,4-trimethylcyclopentanone was obtained from the crude ketone mixture through its sodium bisulfite addition compound (2,2,4-trimethylcyclopentanone does not form such a compound, due to steric hindrance). In a typical run, 400 ml. (355 g.) of the crude ketones was added to 2000 ml. of 40% sodium bisulfite and 300 ml. of absolute alcohol, and the mixture was stirred until a finely crystalline precipitate formed. From the precipitate (filtered, washed with ether, and dried) the 2,4,4-trimethylcyclopentanone was regenerated by steam distillation over an excess of sodium bicarbonate, 20 to 55 g. of ketone being obtained. This yield could have been substantially increased, but the product would have been less pure. Distillation of the product of several such runs gave 2,4,4-trimethylcyclopentanone with the following properties: b.p. 161.29°, d_4^{20} 0.8772, n_D^{20} 1.4312, m.p. −25.64°; semicarbazone m.p. 160.1–160.6°. (Lit.,[5] b.p. 161.5°, d_4^{20} 0.8765, n_D^{20} 1.4313, m.p. −25.6°.)

Even though the 2,2,4- and 2,4,4-trimethylcyclopentanones boil about 5° apart, fractional distillation is not recommended for their separation because considerable self-condensation may occur. In the present work, however, a quantity (8.3 moles) of pure 2,2,4-trimethylcyclopentanone was obtained by distillation of some of the crude ketone mixture at better than 100-plate efficiency. Most of the 2,4,4-trimethylcyclopentanone in the mixture was sacrificed, thereby. The distilled 2,2,4-trimethylcyclopentanone had the following properties: b.p. 156.1°, d_4^{20} 0.8737, n_D^{20} 1.4293, f.p. −40.36°; semicarbazone m.p. 175.1 to 176.0°. (Lit.,[5] b.p. 155.6°, d_4^{20} 0.8730, n_D^{20} 1.4294, f.p. −40.6°.)

1,1,3,4-Tetramethylcyclopentane. The purified 2,4,4-trimethylcyclopentanone (5.05 moles) was condensed with methyl Grignard reagent in the customary manner to produce 1,2,4,4-tetramethylcyclopentanol (4.47 moles, 89% yield); the carbinol after distillation under reduced pressure had the following properties: b.p. 65 to 76°/18 mm., n_D^{20} 1.4411–1.4405.

The distilled carbinol was dehydrated over activated alumina at 325° to produce a mixture (486 g. or 4.4 moles) of crude tetramethylcyclopentenes. After distillation and redistillation at about 20-plate efficiency, there was obtained 271 g. (43% yield from ketone) of tetramethylcyclopentenes with the following properties: b.p. 121.0–126.5°/745 mm., n_D^{20} 1.4331–1.4409.

The tetramethylcyclopentene mixture (271 g.) was hydrogenated to saturation over nickel-on-kieselguhr catalyst at 150°. The hydrogenate was filtered free of catalyst, after which it was treated exhaustively with 10% sodium permanganate solution, and steam distilled; the crude 1,1,3,4-tetramethylcyclopentane (after drying) weighed 190 g., a 30% yield from the ketone. Distillation of the product at 25-plate efficiency separated it into the *trans* isomer (b.p. 121.4–121.6°) and the *cis* isomer (b.p. 132.9–133.0°) in the ratio of 55:45.

1,1,2,4-Tetramethylcyclopentane. The purified 2,2,4-trimethylcyclopentanone (8.3 moles) was condensed with methyl Grignard reagent to produce 1,2,2,4-tetramethylcyclopentanol (b.p. 54–71°/20 mm., n_D^{20} 1.4298–1.4491); the yield of distilled product was 6.8 moles, or 82% (from ketone).

The 1,2,2,4-tetramethylcyclopentanol (6.8 moles) was saturated with anhydrous hydrogen chloride at ice temperature to produce the corresponding chloride; the yield of crude chloride was 1090 g., or 100%.

The 1-chloro-1,2,2,4-tetramethylcyclopentane was converted to the cycloparaffin by sodium in liquid ammonia. The chloride (6.8 moles) was added rapidly to a solution of 17 g.-atoms of sodium in 4 l. of liquid ammonia, in a 12-l. flask equipped with a Dry Ice–cooled reflux condenser, Hershberg stirrer, and dropping funnel. Rapid stirring was continued for 1/2 hr. after addition was complete; then, powdered ammonium nitrate was added from a side-flask to destroy unreacted sodium. The amount of nitrate required (1.8 moles) indicated 5.4 atoms of excess sodium, *i.e.*, that reaction with the chloride had consumed about 85% of the theoretical amount. Then, 7 moles of powdered ammonium chloride was added to neutralize the by-product, sodium amide, and the reaction mixture was quenched with as much water as the reserve capacity of the flask would permit. The hydrocarbon layer was washed twice with water, and then was steam distilled and dried; the yield of crude tetramethylcyclopentane was 59% (from ketone). The crude product was highly unsaturated to bromine, so it was resaturated with anhydrous hydrogen chloride and retreated with sodium in liquid ammonia. The product was agitated with successive portions of potassium permanganate solution until the purple color persisted, when it was again steam distilled; the yield of dried, saturated hydrocarbon was 425 g. (50% from ketone). The olefin-free 1,1,2,4-tetramethylcyclopentane was fractionally distilled at 25-plate efficiency, but was not separated into its geometric isomers thereby, the distillate showing only 0.04° boiling range (Table I).

3,3,5- and 3,5,5-Trimethylcyclohexene. To dehydrate dihydroisophorol, 2.2 kg. of the carbinol (2500 ml., 15.4 moles) was placed with 8 g. of *p*-toluenesulfonic acid in a 3-l. pot attached to a column having about 15-plate efficiency. Enough heat was applied to obtain reflux, and the olefins were distilled, along with water, as they were formed. The organic distillate was dried over anhydrous sodium sulfate to obtain 1.85 kg. (95% yield) of mixed olefins. Fractionation of 5 kg. of such product at better than 100-plate efficiency yielded about 55% of the charge as 3,3,5-trimethylcyclohexene and about 36% as 3,5,5-trimethylcyclohexene; the properties of the two cyclohexenes are shown in Table I. The cyclo-olefins were definitely identified by stepwise oxidation to the corresponding trimethyladipic acids:

3,3,5-Trimethylcyclohexane-1,2-diol. For the oxidation of the cycloolefins, the hydroxylation method of D. Swern *et al.*[10] was followed, with certain modifications. For the hydroxylation of 3,3,5-trimethylcyclohexene, 308 ml. of 87% formic acid was placed in a 1-l., multi-neck flask fitted with an efficient stirrer, a condenser, a thermometer well, and a dropping funnel. Stirring was started, and 155 g. (1.25 moles) of purified 3,3,5-trimethylcyclohexene was added. The mixture was warmed to 45° and 159.5 g. (1.27 moles) of 27% hydrogen peroxide was added as rapidly as possible while maintaining the reaction temperature at 45–47° by cooling with an ice bath. After addition was complete, the mixture was stirred overnight at 40° and at the end of this time, no hydrogen peroxide remained and two

(10) D. Swern, G. N. Billen, and J. T. Scanlan, *J. Am. Chem. Soc.*, **68**, 1504 (1946).

layers were in evidence. The lower (acid) layer was separated and then neutralized with 322 g. of potassium hydroxide. By continuous ether extraction of this layer, 3 g. of material was recovered and added to the upper (mono- and/or diformic ester) layer. The ester material was saponified by refluxing for 5 hr. with 90 g. of potassium hydroxide and 100 ml. of water. Upon cooling to room temperature, the upper (glycol) layer solidified and weighed 199.5 g. The lower (aqueous) layer yielded 4.5 g. of additional glycol on continuous extraction with ether. The glycol (204 g.) was distilled under reduced pressure to yield 152 g., b.p.$_7$ 120–122° and 13 g., b.p.$_7$ 122–125° (combined yield 84%). A small amount of glycol from the 120–122° fraction was recrystallized from benzene, and this sample of 3,3,5-trimethylcyclohexane-1,2-diol melted at 102.4–102.8°.

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.11; H, 10.91.

3,5,5-Trimethylcyclohexane-1,2-diol. 3,5,5-Trimethylcyclohexene (155 g., 1.25 moles) was oxidized in exactly the same manner as its isomer, with 159.5 g. of 27% hydrogen peroxide solution (1.27 moles) in 308 ml. of 87% formic acid. There was obtained 167.3 g. (85% yield) of a mixture of geometrical isomers of the glycol (b.p.$_7$ 120–130°). A small amount of material from a center fraction (b.p.$_7$ 124–125°) was recrystallized to yield white needles; m.p. 58.3–58.7°.

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.77; H, 11.77.

2,2,4-Trimethyladipic acid from 3,3,5-trimethylcyclohexane-1,2-diol. 3,3,5-Trimethylcyclohexane-1,2-diol (158 g., 1.0 mole) was placed with 100 ml. of water in a 3-l. flask fitted with an efficient stirrer and a baffle to aid mixing. The mixture was warmed to 45°, and 400 g. of sodium permanganate in 1800 ml. of water was added, portionwise, with enough cooling to maintain temperature at 45–50°.

The reaction mixture was then made slightly alkaline with 20% sodium hydroxide (about 30 ml. being required), and permanganate solution was added until no more was consumed (about 90 ml. additional required). A small amount of sodium bisulfite was then added (enough to destroy the purple color), and the reaction mixture was filtered, hot, through a Buchner funnel. The filter cake (manganese dioxide) was rinsed with 100 ml. of hot water, then removed from the funnel and leached by boiling with 200 ml. more water, after which it was refiltered. Both batches of filtrate were evaporated (individually) to about one-half volume; they were then cooled and acidified to *p*H 2 with hydrochloric acid. A small amount of carbon dioxide was evolved and the solution became cloudy just before the desired *p*H was reached. The mixtures were held at −5° overnight, to crystallize. The first filtrate yielded 175.5 g. of white crystalline acid and the second filtrate, obtained by leaching the solid manganese dioxide with more water, yielded 10 g. more, corresponding to a 98.7% of crude acids having a neutralization equivalent of 101.1 (theory, 94.11). The acid was recrystallized once from water to yield 170 g. (92% yield) of 2,2,4-trimethyladipic acid; neut. equiv. 94.3, m.p. 100.1 to 100.4°, (lit.[5], m.p. 101.1 to 101.5°).

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.42; H, 8.57. Found: C, 57.45; H, 8.58.

2,4,4-Trimethyladipic acid from 3,5,5-trimethylcyclohexane-1,2-diol. In exactly the same manner as its isomer, 3,5,5-trimethylcyclohexane-1,2-diol (152.1 g., 0.96 mole) was oxidized to yield 120 g. of crystalline acids from the first filtrate and 15.5 g. from the second filtrate. The total yield was 65.8% of crystalline material having a neutralization equivalent of 97.0 (theory, 94.11). The aqueous layers were combined and upon continuous ether extraction yielded 51.4 g. (28.4%) of oil with a neutralization equivalent of 116.0, bringing the total yield of crude acid up to 94.2%. This oily acid did not crystallize when seeded and held at −5° for 1 week. The crystalline acids were recrystallized once from water and there was obtained 115 g. (63.7% yield) of 2,4,4-trimethyladipic acid having a neutral equivalent of 94.3, m.p. 69.7 to 70.0°, (lit.,[5] m.p. 68.6 to 69.2°).

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.42; H, 8.57. Found: C, 57.40; H, 8.56.

Trimethylcyclopentanones from pure trimethyladipic acids. The pure 2,2,4- and 2,4,4-trimethyladipic acids were distilled, separately, with barium hydroxide and manganous carbonate as described under 2,2,4,4-tetramethylcyclopentanone. The yields of purified 2,2,4- and 2,4,4-trimethylcyclopentanone were 67% and 78%, respectively, and the properties of these samples were virtually identical with those of the corresponding ketones isolated earlier from their mixture.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE R & E DIVISION, MONSANTO CHEMICAL COMPANY]

Methylcyclopentadiene Isomers

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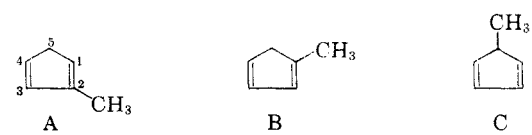
Received October 12, 1959

The three methylcyclopentadiene isomers, 1-, 2-, and 5-methylcyclopentadiene were separated by vapor phase chromatography over 2,4-dimethylsulfolane substrate and identified *via* their ultraviolet absorption maxima. Five methylcyclopentadiene dimer isomers were separated by vapor phase chromatography over silicone oil substrate. They were identified as far as the parent monomers are concerned by dimerizing monomer mixtures of known isomer concentration. Composition of the dimer isomers approaches statistical distribution. Infrared spectra of the monomer isomers are included.

Commercial methylcyclopentadiene is a byproduct of thermal cracking of petroleum hydrocarbons. Pyrolysis of the commercial methylcyclopentadiene dimer yields a mixture of isomeric methylcyclopentadienes and some cyclopentadiene. Three isomers of monomeric methylcyclopentadiene are possible: 2-methyl (A), 1-methyl (B), and 5-methylcyclopentadiene (C). Only Diels-Alder adducts of two of these isomers, presumably those of 1-methyl and 2-methylcyclopentadiene have been separated.[2,3] Structures were not as-



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