butadiene were found to be stable at a temperature of 500°.

2. The pyrolysis of hexachloropropene yielded principally carbon tetrachloride, tetrachloroethylene, and hexachloroethane. Smaller amounts of hexachlorobenzene and a compound C_6Cl_8 (m. p. 43–44°) were obtained under some conditions.

3. The pyrolysis of octachloro-1,3-pentadiene yielded principally carbon tetrachloride, hexachloro-1,3-butadiene and hexachlorocyclopentadiene. Smaller amounts of tetrachloroethylene, hexachloroethane, octachlorocyclopentene, hexachlorobenzene and a compound C_6Cl_8 (m. p. 182–183°) were obtained under some conditions.

4. The pyrolysis of two C_6Cl_8 compounds (m. p. 43–44° and 182–183°) yielded chiefly hexachlorobenzene and chlorine.

5. Hexachloro-1,3-butadiene yielded hexachloroethane slowly on chlorinolysis in sunlight at 10–20°. In the dark, it was found to resist the action of chlorine at a temperature of 500°.

6. Tetrachloroethylene was found to be stable to thermal chlorinolysis at temperatures up to 500°; however, small amounts of hexachloroethane were produced by addition of the halogen.

7. Thermal chlorinolysis of hexachloropropene yielded principally carbon tetrachloride and tetrachloroethylene and smaller amounts of hexachloroethane.

8. Thermal chlorinolysis of octachloro-1,3-pentadiene yielded carbon tetrachloride and hexachloro-1,3-butadiene as the principal products and lesser amounts of hexachlorocyclopentadiene and octachlorocyclopentene. Small amounts of tetrachloroethylene and hexachlorobenzene were also obtained under some conditions.

WASHINGTON, D. C. RECEIVED AUGUST 19, 1948

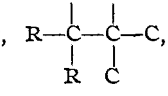
[CONTRIBUTION FROM THE WHITMORE LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Hydrocarbons. IX.[1] 2,2,4-Trimethylheptane, 2,2,4-Trimethyloctane, 2,2,4,6-Tetramethylheptane and 2,2,4,5,5-Pentamethylhexane

BY GEORGE W. MOERSCH[2] AND FRANK C. WHITMORE[3]

In a continuation of previous work the present paper reports the syntheses of a decane and three undecanes containing the neopentyl system, and the determination of several of their physical constants.

With some exceptions, the hydrocarbons were prepared by catalytic hydrogenation of the olefins resulting from dehydration of the tertiary alcohols, 2,2,4-trimethyl-4-heptanol, 2,2,4-trimethyl-4-octanol, 2,2,4,6-tetramethyl-4-heptanol, and 2,2,3,5,5-pentamethyl-3-hexanol. In the case of 2,2,3,5,5-pentamethylhexane, the alcohol was prepared by two different methods and the olefins were also obtained by a Kolbe electrolysis of Butlerow's beta acid, methyl-*t*-butylneopentylacetic acid.

The reactions involved in these syntheses are not of the type usually accompanied by rearrangement[4] except for the dehydration of 2,2,3,5,5-pentamethyl-3-heptanol.[5] Structures similar to the latter,  $R-\overset{OH}{\underset{R}{C}}-\overset{C}{\underset{C}{C}}-C$, always rearrange to a small degree, about 5% under the conditions employed here,[4] and it is therefore reasonable to assume that the 2,2,3,5,5-pentamethylheptane contains some 2,3,3,5,5-pentamethylheptane. This contamination from a closely related isomer could not be expected to affect appreciably the physical properties of the compound. This was substantiated when the electrolysis of Butlerow's beta acid gave material that checked the product made by dehydration of the alcohol.

The decane, 2,2,4-trimethylheptane, is mentioned in the literature[6] in connection with the investigation of impurities in isoöctane. From still residues there was isolated a material of b. p. 151.97° at 760 mm., d^{20} 0.7349, $n^{20}{}_D$ 1.41278. It was suggested that this compound was either 2,2,4- or 2,2,5-trimethylheptane. The physical properties of the 2,2,4-trimethylheptane reported in this paper are not in agreement with the values found for the above material.

Experimental

Distillations were made through columns of the adiabatic, total reflux, variable take-off type, packed with (A) one-eighth inch glass helices, packed section 1.7 × 67 cm., 11 theoretical plates, (B) three thirty-second inch stainless steel helices, 1.0 × 100 cm., 25 theoretical plates, and (C) one-sixteenth inch stainless steel helices, 1.0 × 100 cm., 65 theoretical plates.

2,2,4-Trimethylheptane.—A typical preparation of methyl neopentyl ketone is given.[7] Sodium dichromate

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[1] For previous papers of this series see: Whitmore, Marker and Plambeck, THIS JOURNAL, **63**, 1626 (1941); Whitmore and Southgate, *ibid.*, **60**, 2571 (1938); Whitmore and Orem, *ibid.*, 2573; Whitmore, Fleming, Rank and Larson, *ibid.*, **56**, 749 (1934); Whitmore and Laughlin, *ibid.*, **55**, 5056 (1933); Whitmore and Fleming, *ibid.*, 3803; Whitmore, Stehman and Herndon, *ibid.*, 3807; Laughlin and Whitmore, *ibid.*, 2607.

[2] Present address: Research Department, Parke, Davis and Co., Detroit, Michigan.

[3] Deceased.

[4] Unpublished work, this Laboratory.

[5] Whitmore and Laughlin, THIS JOURNAL, **54**, 4011 (1932).

[6] Brooks, Cleaton and Carter, *J. Research Natl. Bur. Standards*, **19**, 319 (1937).

[7] The authors are indebted to Dr. Sutherland for preparation of the methyl neopentyl ketone: L. H. Sutherland, Ph.D. Thesis, Penn State, 1942.

TABLE I

SUMMARY OF PHYSICAL PROPERTIES

Hydrocarbon	B. p., °C., 760 mm.	dt/dp, 760 mm.	n^{20}_{D}	dn/dt	d^{20}_{4}	dd/dt	Viscosity, centipoises at 20°	30°	40°
2,2,4-Trimethylheptane	149.4	0.05°	1.4092	0.00042	0.7275	0.00076	0.554	0.482	0.421
2,2,4-Trimethyloctane	171.5	.05°	1.4149	.00041	.7381	.00074	.730	.624	.539
2,2,4,6-Tetramethylheptane	162.2	.05°	1.4121	.00041	.7335	.00075	.681	.590	.510
2,2,4,5,5-Pentamethylhexane	166.0	.05°	1.4214	.00041	.7519	.00074	1.045	.876	.741

dihydrate, 59 kg., diisobutylene (Rohm & Haas), 207 kg. and 80 liters of water were charged to a 50-gallon glass-lined Pfaudler kettle. Sulfuric acid, 45 liters, was added over a period of thirty-six hours while cold water was passed through the jacket of the reactor, keeping the temperature at 30–40°. Stirring was continued for an additional two hours and then the oxidation product steam-distilled from the kettle, giving 13.4 kg. of organic material. The oil layer was treated with 1.82 kg. of sodium hydroxide, the neutral products siphoned off, 10.22 kg., and the organic acids regenerated with sulfuric acid, yield 2.85 kg. The neutral products were fractionated to give 8.03 kg. (38%) of methyl neopentyl ketone, b. p. 126°, n^{20}_{D} 1.4030–1.4036.

Five moles, 120 g., of magnesium turnings was weighed into a three-liter flask and four moles, 492 g., of *n*-propyl bromide added in four portions of 500 ml. of anhydrous ether each. Addition was completed in five and a half hours, yield 98%. Two moles, 228 g., of methyl neopentyl ketone was added with stirring during one and a half hours, the mixture refluxed for three hours and then decomposed by pouring into 2 l. of cracked ice. A fine suspension resulted which was coagulated by distilling of about 1.5 l. of ether. The entire mass of precipitated salts was washed by decantation with four portions of ether totalling 2.5 l. The ether solution was concentrated by distillation through a modified Vigreux column. The residue was dried over potassium carbonate and distilled from 10 g. of potassium carbonate through Column A, giving a 58% yield of 2,2,4-trimethyl-4-heptanol, b. p. 119.8° at 100 mm., 59.6° at 7 mm., d^{20} 0.833, n^{20}_{D} 1.4373.

The carbinol, 585 g., was dropped onto a mixture of 25 g. of anhydrous copper sulfate and 10 g. of powdered pumice heated to 200° at 200 mm. After separating the water layer, 35 ml., the olefin product was dried over potassium carbonate and distilled. About half was found to be unchanged carbinol and was dehydrated in Column A by distilling with 25 g. of copper sulfate and 10 g. of pumice at atmospheric pressure. The water layer was 18 ml. The olefin mixture was dried over potassium carbonate and distilled to give 454 g., 88% yield, b. p. 149–150° at 741 mm., n^{20}_{D} 1.4255–1.4277.

The olefin mixture, 202 g., was hydrogenated over 20 g. of UOP nickel on kieselguhr at 110–130° at 1200 p. s. i. The product was filtered and fractionated through Column C and constant index material rehydrogenated and then fractionated again through Column C, giving only constant boiling, constant index material.

2,2,4-Trimethyloctane.—Methyl neopentyl ketone was added to *n*-butylmagnesium bromide in the usual way and the product distilled under reduced pressure to give 57% yield of 2,2,4-trimethyl-4-octanol,[8] b. p. 137.1° at 100 mm., 79.8° at 8 mm., n^{20}_{D} 1.4405, d^{20} 0.835.

The alcohol was dehydrated with copper sulfate and pumice as previously described to give an 84% yield of olefin mixture. Ozonolysis of the product showed no rearrangement of the carbon skeleton.[9]

The olefins were hydrogenated in glacial acetic acid using platinum oxide at 3 atm. and room temperature.

The saturated hydrocarbon was also obtained by hydrogenation of the alcohol over Raney nickel at 200° and 150 atm.

2,2,4,6-Tetramethylheptane.—Methyl neopentyl ketone was added to isobutylmagnesium bromide in the usual way. The product was distilled at reduced pressure to give a 29% yield of 2,2,4,6-tetramethyl-4-heptanol, b. p. 126.8° at 100 mm., 64.0° at 7 mm., d^{20} 0.828, n^{20}_{D} 1.4368.

The alcohol was dehydrated by dropping onto copper sulfate and pumice at 200° giving a 77% yield of olefins, b. p. 159–161°, n^{20}_{D} 1.4260–61. The mixture was ozonized in olefin-free, low-boiling (0–30°) hydrocarbon solvent and the ozonide decomposed with zinc dust and water in the presence of traces of hydroquinone and silver nitrate. The products obtained were: formaldehyde (dimetol deriv. m. p. 189–190°), isobutyraldehyde (dimetol deriv. m. p. 147–148°, 2,4-dinitrophenylhydrazone m. p. 182–183°), methyl neopentyl ketone (semicarbazide m. p. 173–173.5°), and isobutyl neopenyl ketone. Isobutyl neopentyl ketone failed to yield a carbonyl derivative but when reduced with sodium in moist benzene gave isobutylneopentylcarbinol (α-naphthylurethan m. p. 99–100°). Mixed melting points were made in all cases. These products show no rearrangement of the carbon skeleton, the olefins being 2,2-dimethyl-4-isobutyl-4-pentene and 2,2,4,6-tetramethyl-4-heptene.

The olefin mixture was hydrogenated over a nickel-kieselguhr catalyst at 120–135° and 1700 p. s. i.

2,2,4,5,5-Pentamethylhexane.—(A) *t*-Butylacetic acid was prepared in 77% yield by the bromoform reaction with methyl neopentyl ketone.[10] The acid was converted to the chloride in 91% yield with thionyl chloride. The *t*-butylacetyl chloride was treated with *t*-butylmagnesium chloride in equi-molar quantity and the complex then treated with an equal amount of methylmagnesium chloride. The reaction mixture was decomposed and the 2,2,4,5,5-pentamethyl-4-hexanol distilled under reduced pressure, 13% yield, b. p. 124.1° at 100 mm., 60.2° at 7 mm., d^{20} 0.841, n^{20}_{D} 1.4412, m. p. 11.4°. (B) The same alcohol was also prepared by adding methyl neopentyl ketone to *t*-butylmagnesium chloride in the usual way, yield 7.5%.

The alcohol was dehydrated with copper sulfate and pumice at 180° in 98% yield, and the products fractionated through Column C, b. p. 152–162°, n^{20}_{D} 1.4309–1.4333. The olefins were ozonized and the products identified as: formaldehyde (dimetol deriv. m. p. 189–90°), trimethylacetaldehyde (2,4-dinitrophenylhydrazone, m. p. 206–207°), pinacolone (2,4-dinitrophenylhydrazone m. p. 122–124°, semicarbazone m. p. 156–156.5°), and *t*-butyl neopentyl ketone which was identified by reduction with sodium in moist benzene to the corresponding alcohol (phenylurethan m. p. 124–126°). These products indicate the olefins as 4,4-dimethyl-2-*t*-butyl-1-pentene and 2,2,4,5,5-pentamethyl-3-hexene. Hydrogenation of the olefins gave material of b. p. 165°, n^{20}_{D} 1.4216.

Although no rearranged product was identified, it is quite certain that a small amount, about 5%, of 2,3,3,5,5-pentamethyl-1-hexene was formed during the dehydration.

A mixture of these same olefins was obtained by dissolving one mole of Butlerow's beta acid, methyl-*t*-butylneopentylacetic acid,[11] m. p. 125.5–127.5°, in 1.2 moles of potassium hydroxide in 500 ml. of water and electrolyzing between smooth platinum electrodes at 8.2 to 8.5 amp. for eight hours. The oil layer (50% yield) was separated

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[8] Whitmore, Popkin, Whitaker, Mattil and Zech, THIS JOURNAL, **60**, 2461 (1938).

[9] Whitmore and Rohrman, *ibid.*, **63**, 2033 (1941).

[10] Homeyer, Whitmore and Wallingford, *ibid.*, **55**, 4209 (1933).

[11] Whitmore and Laughlin, *ibid.*, **56**, 1128 (1934).

and distilled into two portions, (I) b. p. 156–161, n^{20}_{D} 1.4247–1.4320; (II) b. p. 162–165, n^{20}_{D} 1.4325–1.4380.

Refractionation of the lower boiling fractions (I) through Column A gave material boiling at 152–162°, n^{20}_{D} 1.4297–1.4336. Ozonolysis of this material gave formaldehyde, trimethylacetaldehyde and pinacolone, identified as their 2,4-dinitrophenylhydrazones.[12] Hydrogenation of these lower boiling fractions gave material boiling mainly at 165°, n^{20}_{D} 1.4216.

Refractionation of the higher boiling portion (II) through Column B gave material of b. p. 162–166°, n^{20}_{D} 1.4314–1.4396. This when hydrogenated gave material boiling mainly at 171°, n^{20}_{D} 1.4278–90, having a mol. wt. of 166 (dodecane = 168) and which was insoluble in cold concd. sulfuric acid.

Physical Properties.—The constants determined for the hydrocarbons are given the accompanying table. The boiling points were measured in a Cottrell-type apparatus using a thermometer with 0.2° divisions checked against a Bureau of Standards calibrated Anschutz thermometer. Refractive indices were read on a Valentine No. 454 refractometer. Densities were measured in pycnometers; and viscosities, with the Ostwald-type viscometer recommended by Cannon and Fenske[13] for use with non-viscous liquids.

The physical properties were determined by N. C. Cook and Andrew Carson; some of the hydrogenations were performed by R. E. Meyer and N. C. Cook.

Summary

Four highly branched hydrocarbons, 2,2,4-trimethylheptane, 2,2,4-trimethyloctane, 2,2,4,6-tetramethylheptane, and 2,2,4,5,5-pentamethylhexane have been synthesized and a number of their physical properties determined.

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(12) Identification by H. H. Johnson, Ph.D. Thesis, Penn State, 1940.

(13) Cannon and Fenske, *Ind. Eng. Chem., Anal. Ed.*, **10**, 299 (1938).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF TEMPLE UNIVERSITY]

Substituted 1,10-Phenanthrolines. II. Di- and Tri-methyl Phenanthrolines Related to 5-Methyl-1,10-phenanthroline[1]

BY FRANCIS H. CASE

Continuing the work described in the first article of this series[2] with the object of preparing a series of substituted phenanthrolines which in the form of their ferrous complexes would be suitable for use as oxidation–reduction indicators, all possible di- and tri-methyl-1,10-phenanthrolines were synthesized in which one methyl group is in the 5- or 6- position and each of the others in a different ring, but none adjacent to nitrogen. The quinolines and phenanthrolines described here were synthesized from a substituted aniline or aminoquinoline by a Skraup reaction using arsenic acid as oxidizing agent and either glycerol, α-methylacrolein diacetate (2-methyl-2-propene-1,1-diol diacetate) or methyl vinyl ketone as the second component. In the case of 3,5-dimethyl-8-nitroquinoline this method proved much more satisfactory than that previously described,[3] while with 4,5-dimethyl-8-nitroquinoline no improvement in yield was noted.

Under these conditions 3,5-dimethyl-1,10-phenanthroline (III) was obtained from 6-methyl-8-aminoquinoline[4] (II) and α-methylacrolein diacetate.

The action of α-methylacrolein diacetate and 3-nitro-4-aminotoluene (I) yielded, in a two-step reaction, 3,6-dimethyl-8-aminoquinoline (IV) which with glycerol was converted to 3,6-dimethyl-1,10-phenanthroline (V).

I, with methyl vinyl ketone under Skraup conditions yielded in a two-step reaction 4,6-dimethyl-8-aminoquinoline (VI) from which the following compounds were made: 3,5,7-trimethyl-1,10-phenanthroline (VII) (with α-methylacrolein diacetate); 4,6-dimethyl-1,10-phenanthroline (VIII) (with glycerol); 4,5,7-trimethyl-1,10-phenanthroline (IX) (with methyl vinyl ketone). From 3,5-dimethyl-8-aminoquinoline (XI) and α-methylacrolein diacetate, 3,5,8-trimethyl-1,10-phenanthroline (XII) was obtained. This also resulted in very small yield if 3,6-dimethyl-8-aminoquinoline (IV) were used as the base. From 4,5-dimethyl-8-aminoquinoline (XIII) and glycerol, 4,5-dimethyl-1,10-phenanthroline (XIV) resulted, while if α-methylacrolein diacetate were used as the second component, 3,6,7-trimethyl-1,10-phenanthroline (XV) was formed.

It should be noted that in the synthesis of each substituted phenanthroline two possible methods were available. For example, 4,5-dimethyl-1,10-phenanthroline might theoretically be prepared by the action of 4,5-dimethyl-8-aminoquinoline with glycerol or of 6-methyl-8-aminoquinoline with methyl vinyl ketone. Both methods were tried, but in the latter case, no yield was obtained. The choice of methods was conditioned by the availability of the starting aminoquinoline as well as by the fact that the yield is highest when glycerol is used as the second component, less with α-methylacrolein diacetate and least with methyl vinyl ketone. When both possible methods were attempted this fact is indicated by a footnote in Table I.

All the phenanthrolines described in this paper give a positive ferroin reaction.

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(1) This work was supported by a Grant from the Committee on Research and Publications of Temple University.

(2) Case, THIS JOURNAL, **70**, 3994 (1948).

(3) Manske, *Can. J. Res.*, **20B**, 133 (1942).

(4) Baldwin, *J. Chem. Soc.*, 2959 (1929).