instance three to six hours' boiling gave results from 4.4 to 4.7% high; whereas in the latter case the results were 3.7% high. These quantities, in excess of that demanded by theory, are of the same order of magnitude as those obtained on the products recorded in Table III.

Summary

In the Weishut–Zeisel methoxyl determination, gossypol and some of its derivatives, *although containing no alkoxyl groups*, yield upon prolonged boiling a small quantity of silver iodide.

The silver iodide thus formed is responsible in some cases for the abnormally high values obtained in the Zeisel determination of the methoxyl groups in several oxymethylgossypol derivatives.

The explanation has been advanced that under the conditions of the Weishut–Zeisel determination the gossypol nucleus is disrupted in such a manner as to yield an alkyl iodide. This iodide, however, is not methyl iodide.

A description is given of an apparatus and a procedure for the determination of methoxyl groups in samples of the order of 20 mg. In this method an ordinary analytical balance sensitive to 0.1 mg. is employed.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORY OF THE ETHYL GASOLINE CORPORATION]

THE PREPARATION AND PROPERTIES OF THE ISOMERIC HEPTANES. PART I. PREPARATION[1]

BY GRAHAM EDGAR, GEORGE CALINGAERT AND R. E. MARKER

RECEIVED NOVEMBER 7, 1928 PUBLISHED MAY 6, 1929

I. Introduction

In connection with a study in this Laboratory of certain properties of aliphatic hydrocarbons, it was decided to investigate each of the nine isomeric heptanes. This group includes nearly every type of structure which an aliphatic hydrocarbon may have, and yet is not too large to make its synthesis impracticable.

Only one of the heptanes, the normal, was available in reasonable quantity, from Jeffrey pine oil.[2] The others were synthesized in considerable quantities by methods described below.

Inspection of the literature showed that the data on physical properties of even normal heptane leave much to be desired, although the work of Kremers and others in recent years has increased considerably our knowledge of this hydrocarbon. Few reliable data were available in the older

---

[1] Presented at the Symposium on Organic Chemistry, Columbus, Ohio, December 29, 1927.

[2] E. Kremers, *J. Am. Pharm. Assocn.*, 9, 857 (1920).

literature on the properties of any of the other isomers. Chavanne and his co-workers[3] have recently synthesized several of the isomers and determined some of their properties. The amounts synthesized, however, were small, and the authors scarcely attempted to determine the properties of the compounds beyond what was necessary for identification. It was therefore decided to measure with reasonable accuracy such physical properties of these hydrocarbons as could be conveniently measured in this Laboratory, and to enlist the aid of other laboratories well equipped to measure other properties. From these investigations there has resulted a rather complete collection of data concerning these heptanes. The data are of particular interest in that all of them were obtained on the same actual samples of material. Some of the data have been already published,[4] and other data will be published later.

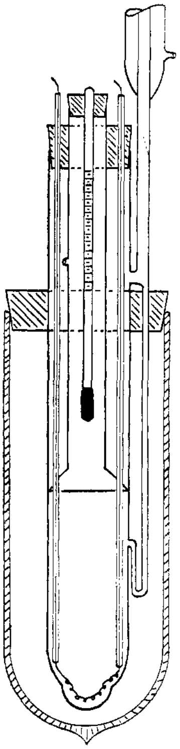

Fig. 1.

Part I of this paper presents the methods of preparation of the heptanes and such physical properties as are commonly employed for purposes of identification. Part II will summarize the entire data, published and unpublished, referred to above, and will discuss the effect of structure upon physical properties in general, and upon certain physical properties in particular.

II. Experimental

(1) **Methods of Synthesis.**—Six of the nine heptanes were prepared by the method which has become classical since its systematic use by Chavanne and his co-workers.[3] It consists in the condensation by means of a Grignard reaction of two suitably chosen radicals, one being present as alkyl halide, the other as aldehyde, ketone or ester. The resulting secondary or tertiary alcohol is dehydrated, and the unsaturated hydrocarbon or hydrocarbons so formed, hydrogenated. This general method had to be modified slightly to fit each individual case. A complete description is given therefore in one case, only the variations being specified for the other preparations.

Of the three other heptanes, the normal is already available from Jeffrey pine oil.[2] The other two, 2,2-dimethylpentane and 3,3-dimethyl-

---

[3] (a) Chavanne and Simon, *Compt. rend.*, **168**, 1324 (1919); (b) Chavanne and Lejeune, *Bull. soc. chim. belg.*, 31, 98 (1922); (c) Chavanne and DeGraef, *ibid.*, **33**, 366 (1924); (d) DeGraef, *ibid.*, 34, 427 (1925).

[4] C. P. Smyth and W. N. Stoops, This Journal, **50**, 1536 (1928); G. W. Stewart, *Phys. Rev.*, **32**, 1153 (1928); Freyer, Hubbard and Andrews, This Journal, **51**, 759 (1929); M. S. Kharasch, *Bureau of Standards Journal of Research*, **2**, 373 (1929).

pentane could not be obtained pure by the general method of preparation (see Note 2, p. 1487) and their synthesis is fully described hereunder.

The main object of the work being the preparation of the heptanes in a state of high purity, comparatively little attention was paid to the intermediate products. The boiling points and specific gravities mentioned here for the alcohols and olefins are to be taken more as indications of the distillation cuts which were used than as accurate physical constants of these compounds. The boiling range given for the heptanes, however, represents the *entire boiling range* of the refractionated sample, temperatures being taken at the top of an efficient column. The alcohols obtained are always individual compounds, while the olefins may be mixtures of two or more isomers, differing only by the position of the double bond. The quantities given here refer to the size of a batch in each preparation, the total amount of heptanes prepared and purified being given at the end. The yields given are those obtained on the preparations as described. No doubt some of them at least could be improved by a careful study of the reaction.

The general method of preparation is fully described in the case of 2-methylhexane. The other preparations are given in tabular form.

2-Methylhexane

(a) **2-Methyl-2-hexanol.**—To a solution of the Grignard reagent prepared from 6.5 moles of magnesium and 6.5 moles of *n*-butyl bromide in 2500 cc. of anhydrous ether was added slowly with stirring 6 moles of very pure acetone in an equal volume of anhydrous ether. After standing overnight, the mixture was decomposed by water and ice. More ice was added and the precipitated magnesium compounds dissolved in 10% hydrochloric acid. The ether layer was separated, washed with dilute sodium carbonate, with distilled water, then dried with anhydrous sodium sulfate and fractionated; yield, 640 g. (92%); b. p. 137–141°; d^{20}_{20}, 0.815.[5]

(b) **2-Methyl-2-hexene.**—A mixture of 580 g. of the carbinol (a) and 1 g. of iodine was slowly distilled, keeping the distilling temperature at 81–83°. The distillate was washed with a sodium thiosulfate solution, with distilled water, then dried with calcium chloride and twice fractionated over metallic sodium; yield, 465 g. (95%); b. p. 94.5–96°.[6]

(c) **2-Methylhexane.**—By means of a nickel catalyst at 150°, 465 g. of the olefin (b) was hydrogenated. One passage over the catalyst gave nearly complete reduction, as shown by titrating a sample with bromate–bromide solution. The product was shaken with several portions of concd. sulfuric acid until a fresh lot of acid showed no yellow color. It was washed with water, then dried over calcium chloride, refluxed over sodium for several hours and then fractionated from sodium; yield 385 g. (82%); b. p. 89.7–90° (760 mm.).

---

[5] The density of the carbinols was determined roughly by means of a Westphal balance.

[6] It was found inadvisable to dehydrate the alcohol by means of *p*-toluenesulfonic acid because the introduction of sulfur compounds caused poisoning of the catalyst. The use of the sulfonic acid also gave a product of much wider boiling range, indicating the presence of isomeric olefins.

Preparation of the Carbinols

The following carbinols were prepared by the Grignard reaction as outlined above.

TABLE IA

REAGENTS

Halide	Moles	Carbonyl compound	Moles
n-Propyl bromide	4	Methylethyl ketone	4
Ethyl bromide	4	Ethyl propionate	2
*Iso*butyl bromide	4.5	Acetone	4
Sec.-butyl bromide	3	Acetone	3
Tert.-butyl chloride	4	Acetone[a]	3

[a] The acetone used must be of very high purity; otherwise polymerization occurs and no alcohol is obtained.

TABLE IB

PRODUCTS AND OTHER DATA

Product	Yield g.	Yield %	B. p., °C.	d_{20}^{20}
3-Methyl-3-hexanol	297	64	137–139	0.823
3-Ethyl-3-pentanol[a]	194	83	140–142	.839
2,4-Dimethyl-2-pentanol	252	54	127–129	..
2,3-Dimethyl-2-pentanol	122	35	129–130.5	.805
2,2,3-Trimethyl-3-butanol[b]	97	28	130	..

[a] This alcohol dehydrates very easily. If it is desired to isolate it pure, it is advisable to avoid entirely the presence of iodine.

[b] The carbinol melts at 17°. It is very hygroscopic and forms a hydrate with m. p. around 80°. When it is distilled in small amounts and without special precautions, only the hydrate is obtained. When larger quantities are handled, the distillate is a mixture of the liquid carbinol and of acicular crystals of its hydrate. The carbinol crystallizes instantly when shaken with a small amount of water. The hydrate loses its water readily when kept in a desiccator over barium oxide.

Preparation of the Olefins

The olefins were prepared from the corresponding carbinols as described above.

TABLE II

REAGENTS, PRODUCTS AND DATA

Carbinol used	G.	Product	Yield, g.	Yield, %	B. p., °C.
3-Methyl-3-hexanol	297	3-Methyl-3-hexene	234	93	93–96
3-Ethyl-3-pentanol	116	3-Ethyl-2-pentene	93	95	95–97
2,4-Dimethyl-2-pentanol	232	2,4-Dimethyl-2-pentene	178	91	81–83
2,3-Dimethyl-2-pentanol	588	2,3-Dimethyl-2-pentene	324	54	92–95
2,2,3-Trimethyl-3-butanol	348	2,2,3-Trimethyl-3-butene	279	95	76–78

Preparation of the Heptanes

The olefins were hydrogenated as described above.

TABLE III

REDUCTION OF OLEFINS

Olefin	G.	Product	Yield, g.	Yield, %	B. p., °C. (760 mm.)
3-Methyl-3-hexene	234	*dl*-3-Methylhexane	206	87	91.4–91.7
3-Ethyl-3-pentene	292	3-Ethylpentane	238	80	93.2–93.5
2,4-Dimethyl-2-pentene	245	2,4-Dimethylpentane	202	81	80.5–81.1
2,3-Dimethyl-2-pentene	360	*dl*-2,3-Dimethylpentane	290	87	89.5–89.9
2,2,3-Trimethyl-3-butene[a]	284	2,2,3-Trimethylbutane	250	86	80.9–81.2

[a] The heptene hydrogenated very readily on one passage through the catalyst tube.

2,2-Dimethylpentane.—To the Grignard reagent prepared from 4 moles each of magnesium and *n*-propyl bromide were added with vigorous stirring 4 moles of *tert.*-butyl chloride and 30 g. of mercuric chloride. Some gas was evolved and the mixture soon settled to a compact solid. After standing overnight the mixture was decomposed as usual. The ether layer was washed, dried and fractionated. The fraction boiling above 50° was washed with cold concd. sulfuric acid several times, with sodium carbonate solution, then dried with calcium chloride, refluxed over sodium for several hours and finally fractionated from sodium; yield, 84 g. (21%); total hydrocarbon prepared, 240 g.; b. p. 78.2–79.5° (760 mm.).

3,3-Dimethylpentane.—This was prepared in a similar way by treating the Grignard reagent from 9 moles of ethyl bromide with 6 moles of *tert.*-amyl chloride and 30 g. of mercuric chloride; yield, 77 g. (13%); total hydrocarbon prepared, 77 g.; b. p. 85.7–86.1° (760 mm.).

NOTE 1.—The low yields obtained with the last two hydrocarbons are due to side reactions giving octane and hexane in one case, and decane and butane in the other, and also to the removal of halogen acid to form olefins in both cases. In a second preparation of 3,3-dimethylpentane a yield of 27% was obtained.

NOTE 2.—Several attempts were made to prepare these two hydrocarbons by the methods employed with the other hydrocarbons. These attempts were unsuccessful due to rearrangements which took place on dehydrating the alcohols.

(a) **2,2-Dimethyl-3-pentanol**, from 5 moles of *tert.*-butyl chloride and 1.65 moles of propionaldehyde by the Grignard reaction; yield, 116 g. (60%); b. p. 136–137°; d^{20}_{20}, 0.826.

(b) Over 400 g. of this carbinol was dehydrated either with iodine, zinc chloride or *p*-toluenesulfonic acid. The corresponding bromide was also changed to the olefin by heating with quinoline. In every case the resulting heptene showed a very wide boiling range (80–90°, mostly 88–90°). No heptane of satisfactory purity could be obtained from it. A study of the physical properties of the product showed it to be a mixture of 2,2-dimethyl- and 2,3-dimethylpentane.

(c) **3,3-Dimethyl-2-pentanol** from 4 moles each of *tert.*-amyl chloride and acetaldehyde; yield, 144 g. (36%); b. p. 147–148°; d^{20}_{20}, 0.829.

(d) Dehydration and hydrogenation again gave a mixture of heptanes, 3,3-dimethyl- and 2,3-dimethylpentane, the latter predominating.

These experiments indicate that on dehydration 2,2-dimethyl-3-pentanol and 3,3-dimethyl-2-pentanol rearrange to a large extent, either by direct migration of a methyl group, or by intermediate formation of a cyclopropane ring. The latter course does not seem unlikely to be the one followed, in light of the rearrangements discussed by Brooks.[7]

Normal Heptane.—This is now available in large quantities from Jeffrey pine oil.[2]

---

[7] Brooks, "The Non-Benzenoid Hydrocarbons," The Chemical Catalog Co., Inc., New York, 1922, p. 70.

A product of this origin was purified from a small amount of terpene and aldehyde either by treatment with iodine[3] or by shaking with sulfuric acid and then with aqueous potassium permanganate. The final product, fractionated over sodium, showed a very sharp boiling point, indicating the absence of other hydrocarbons of the paraffin series. It may also be prepared by either one of the methods outlined above. Another method which has been used successfully by the authors is the reduction of *n*-heptyl bromide by sodium in liquid ammonia, according to the method described elsewhere for the preparation of *n*-butane.[8]

(2) Measurement of Boiling Point, Refractive Index, Specific Gravity, Freezing Point and Critical Temperature of Solution in Aniline

Boiling points were measured in an apparatus outlined in Fig. 1, employing internal electric heating, vapor lagging of the thermometer, protection from radiation losses by a vacuum flask and, of course, appropriate corrections for thermometer error and barometric pressure.

Refractive indices were measured in an Abbé refractometer, employing sodium light. Since the data were later determined with greater precision by Smyth,[4] his data, which agreed very well with those of the authors, have been employed. Specific gravities were determined in a 25-cc. Sprengel pycnometer at two temperatures near 20°. The data are practically identical with those determined later by Smyth and Stoops.[4]

Melting points were determined by Dr. R. N. Pease, of Princeton University, to whom the authors are much indebted for the actual measurements and for permission to include them in this paper. The method employed was the use of a three-junction copper–constantan thermocouple and a sensitive potentiometer carefully calibrated against the melting

Table IV

Physical Properties of the Heptanes

	B. p. (760 mm.), °C.	M. p., °C.	d_4^{20} [a]	n_D^{20}	C.T.S. (aniline), °C.
n-Heptane	98.4	− 90.5	0.6836	1.38777	70.0
2-Methylhexane	90.0	−119.1	.6789	1.38509	74.1
3-Methylhexane	91.8	.....	.6870	1.38873	70.5
3-Ethylpentane	93.3	.....	.6984	1.39366	66.3
2,2-Dimethylpentane	78.9	−125.6	.6737	1.38233	77.7
2,3-Dimethylpentane	89.7	.....	.6952	1.39201	68.1
2,4-Dimethylpentane	80.8	−123.4	.6745[b]	1.38233	78.8
3,3-Dimethylpentane	86.0	−135.0[c]	.6934	1.39114	71.0
2,2,3-Trimethylbutane	80.9	− 25.0	.6900	1.38940	72.4

[a] The average temperature coefficient of specific gravity is 0.00085 per degree.

[b] A later preparation gave a material of d_4^{20}, 0.6731, indicating a possible error in the earlier determination. The difference, however, is, not sufficient to affect any of the conclusions drawn in Part II of this paper.

[c] This value was determined by Dr. George S. Parks, of Stanford University, to whom the authors are very much indebted.

---

[8] G. Calingaert and L. B. Hitchcock, This Journal, **49**, 750 (1927).

points of monochlorobenzene, toluene, carbon disulfide, ethyl ether and the sublimation point of carbon dioxide. Unfortunately four of the isomers could not be frozen, but solidified to a glass. Apparently the increasing viscosity and low melting points of some of the isomers make it very difficult to freeze them, as the same difficulty has been reported by Timmermans.[9] It is hoped that the melting points of all of the isomers may eventually be determined.

Critical solution temperatures in aniline are frequently employed for identification of hydrocarbons and were therefore determined for the isomers in an air-jacketed test-tube, using freshly distilled C. P. aniline and making appropriate thermometer correction.[10] These data are summarized in Table IV.

III. Discussion

(a) **Synthetic Methods.**—While there is nothing particularly novel about the methods employed in the synthesis of these hydrocarbons, the results obtained serve to illustrate the value of the carbinol–olefin–paraffin method. It is theoretically possible to prepare any paraffin by these methods; in most cases the raw materials are available, not too expensive and the reactions direct and clean cut. It is clear, however, from the discussion in Note 2 that care must be taken in interpreting the course of the reactions, particularly when dehydrations are involved of carbinols in which the alcohol group is adjacent to a tertiary group. Rearrangement is usually indicated by a wide boiling range in the dehydrated product, but may be so complete as to be unnoticed. In the present work identification of the compounds was aided by the fact that all of the possible isomers were prepared.

When the raw materials involved are sufficiently inexpensive the present modification of the Würtz synthesis (preparations of 2,2- and 3,3-dimethylpentane) is time saving and fully satisfactory from the standpoint of purity, although the yields are low.

The two preparations in which this synthesis was employed involved the reaction of tertiary halides, and it is not established that other halides will behave similarly. The chlorides of other heavy metals have been employed by the authors for similar syntheses, with varying degrees of success.

(b) **Probable Purity of the Hydrocarbons.**—In a group of hydrocarbons like the heptanes the determination of purity is somewhat difficult. Absence of extraneous substances may be easily assured and the presence of paraffins other than heptanes is usually unlikely; the freedom from isomers is more difficult to detect. There are no specific chemical tests and the ordinary physical properties such as boiling point, refractive index and

---

[9] Timmermans, *Bull. soc. chim. belg.*, **36**, 502 (1927).

[10] These values were determined by Mr. D. T. Flood of this Laboratory.

density, are little separated in some cases. Freezing point measurements would show more variation but these are not available in all cases. For preparations in question the sharpness of boiling points of the purified products, combined with the available data on melting points and other properties, indicates that the compounds were unusually pure and free from other isomers. This makes the data on their physical properties particularly valuable.

(c) **Comparison of the Physical Data with the Literature.**—In general there is good agreement with the most reliable data in the literature, though a few exceptions deserve mention.

3-ETHYLPENTANE

Data of	Konovalow[11]	"Int. Crit. Tables"	Authors
B. p., °C.	95–98	93.8	93.3
d_4^{20}	0.695 (extrapolated)	0.670	0.6984

Konovalow's data agree with those of the authors sufficiently for a product which was admittedly not very pure. The boiling point given in "International Critical Tables" from an unknown source appears to be a little high, while the density is so low as to suggest a typographical error. The detailed discussion of the variation of physical properties with structure, which will be presented in Part II, will show that it is highly improbable that this isomer should have a density lower than that of normal heptane.

2,2-DIMETHYLPENTANE

Observer	DeGraef[3d]	Timmermans[8]	Authors
M. p., °C.		−137.0	−125.6

A private communication from Professor Timmermans has advised the authors that the above figure was in error on account of a faulty thermometer. Professor Timmermans has recalculated his own data and reports the corrected value as −122.5°.

2,4-DIMETHYLPENTANE

Data of	Chavanne and DeGraef[3]	"Int. Crit. Tables"	Authors
B. p., °C.	80.9	83.9	80.8
d_4^{20}	0.6731	0.681	0.6731
M. p., °C.	−119.4	......	−123.4

Here again the figures given in "International Critical Tables" appear to the authors to be of doubtful value. Both the boiling point and density are almost certainly too high. The discrepancy of 4° between the melting point reported by Chavanne and that of the authors does not seem to be accounted for by impurities in the authors' sample because of the nature of the cooling curve obtained, which could not be interpreted so as to change the recorded value by more than one degree.

---

[11] Konovalow, *Chem. Centr.*, I, 2143 (1908).

Summary

The nine isomeric heptanes have been obtained in considerable quantity and excellent purity and have been identified with certainty. One was isolated from a natural product and the other eight were prepared by two methods, alcohol–olefin–paraffin and modified Würtz. Their boiling points, specific gravities, refractive indices and critical solution temperatures in aniline are presented, with the melting points of five of them.

Yonkers, New York

[Contribution from the Chemical Laboratory of the College of Liberal Arts, Northwestern University]

THE REACTION OF ORGANIC MERCURY COMPOUNDS WITH ORGANIC HALIDES. II[1]

By Frank C. Whitmore and E. N. Thurman

Received November 21, 1928 Published May 6, 1929

The present research was undertaken to study the failure of organic halides to react "metathetically" with organic mercury compounds to give lengthened carbon chains according to the equations

$$R_2Hg + R'X \longrightarrow R{-}R' + RHgX$$
$$RHgX + R'X \longrightarrow R{-}R' + HgX_2$$

The original attempt at such a reaction was partly successful.[2] Mercury diphenyl heated with benzal chloride at 150° without a solvent gave some triphenylmethane. Almost all later attempts to extend this reaction have failed. These attempts have been very scattering and no systematic study of the reaction has been made.[3]

For the present study it was decided to treat a representative variety of organic halides with a single mercury compound under comparable conditions to determine the ease of reaction and the nature of the products formed. It seemed best to use an aromatic mercury compound for the following reasons: (1) aromatic mercury compounds being only slightly volatile are less dangerously poisonous, (2) they are more stable toward heat and (3) they give products more easily identified. The most readily available compound was mercury di-*p*-tolyl.[4] In one case mercury di-*n*-butyl was also used. After the projected study had been completed, work appeared which could be interpreted as indicating mercury diphenyl

---

[1] Presented at the First National Symposium on General Organic Chemistry, Rochester, New York, December, 1925. Whitmore and Thurman, This Journal, **45**, 1068 (1923).

[2] Kekulé and Franchimont, *Ber.*, **5**, 907 (1872).

[3] Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, **1921**, pp. 79–83.

[4] Whitmore, Frances Hamilton and Thurman, This Journal, **45**, 1066 (1923).