[Contribution from the Chemical Laboratory of Mount Holyoke College]

AN INVESTIGATION OF A SERIES OF DERIVATIVES OF NORMAL HEPTANE. I. PREPARATION, IDENTIFICATION AND PHYSICAL CONSTANTS

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In connection with further investigation of isomeric hydrocarbons similar to those obtained in the case of 2-pentene[2] it was found necessary to prepare and identify certain derivatives of normal heptane. The preparation, purification and identification of these products and the physical constants measured furnish the basis for the present paper. The measurement of the dielectric constants and the determination of the dipole moments of these compounds are given in the following paper. The work involved a study of the four straight-chain alcohols, heptanol-1, heptanol-2, heptanol-3, heptanol-4, the corresponding chloro and bromo derivatives, two of the iodo derivatives, and the aldehyde and the ketones obtained from these alcohols.

Experimental

Determination of Physical Properties

Boiling Point.—All distillations were made at diminished pressure except in a few specified cases. A fractionating column (a modified Vigreux type) 50 cm. in length, was used for these distillations. The receiver was so arranged that fractions could be removed and new receivers put on (evacuated by an auxiliary pump) so that the distillation could be continuous. In the case of distillations at atmospheric pressure the fractionating column was 50 cm. long, of the Crismer type, consisting of a glass spiral fitting closely around an inner tube, the tube and spiral fitting snugly into the column. The thermometers used were of the Anschütz type, calibrated by the Physikalisch-Technische Reichsanstalt, and were placed in the side neck so that the mercury was completely immersed in vapor.

Freezing Point.—The freezing point determinations were made by Professor Jean Timmermans.[3] Approximately 5-cc. samples, in 15–18-cm.

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[1] C. R. B. Fellow, University of Brussels, 1928–1929. The experimental work included in this and the following paper was done at the University of Brussels. The writer wishes to express appreciation to the C. R. B. Educational Foundation for the opportunity given for study and also to acknowledge a very generous grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences which made possible the investigation.

[2] Sherrill, Otto and Pickett, This Journal, **51**, 3027–3033 (1929); Sherrill, Haas and Baldwin, *ibid.*, **51**, 3034–3041 (1929); Carr, *ibid.*, **51**, 3041–3053 (1929).

[3] The author takes this opportunity of expressing appreciation of Professor Timmermans' interest and coöperation.

test-tubes, were cooled in liquid air and the temperature of the freezing point measured by Professor Timmermans' specially calibrated thermometers.

Density.—The density determinations were made in a 14-cc. Sprengel pycnometer and at least three checking determinations were made at each temperature. The measurements at 0° were made by surrounding the pycnometer with finely crushed ice, those at 15° were made in a Dewar flask in which the temperature remained constant within less than 0.1° over several hours, those made at 20° were made in a thermostat regulated constant to at least 0.01°. The weights were reduced to a vacuum basis.

Index of Refraction.—The refractive indices for the three helium lines, at 15 and 20° or at 17.5 and 20° were measured with a Pulfrich refractometer, supplied with a calibrated thermometer graduated in tenths of degrees. The water current through the refractometer came from an accurately regulated thermostat. The temperatures were accurate within 0.05°. Duplicate observations checked closely. The refractive indices for the sodium D line were made with an Abbé refractometer. The water current through the refractometer came from a thermostat.

Following each table of physical data there is a summary of literature data, complete in the case of the halogen derivatives, representative in the case of the other compounds.

Purification of Heptanols.—Three of the heptanols which were the source materials for the work were prepared especially for this problem by R. E. Marker by means of the Grignard synthesis from the corresponding alkyl bromide and alkyl aldehyde. These alcohols were methyl-*n*-amyl carbinol, ethyl-*n*-butyl carbinol and dipropyl carbinol. The fourth alcohol, *n*-heptanol, was obtained from Schering–Kahlbaum. In each case the alcohols were carefully dried and fractionated *in vacuo* in order to diminish any possibility of dehydration which might give a mixture of hydrocarbon and alcohol. Three distillations were made although the alcohols boiled very constantly in the second distillation. The boiling points and indices of the distillates in the second and third distillations were the same. The identity of the alcohols was proved by the oxidation of each and the preparation of the corresponding semicarbazone. In each

TABLE I

CONSTANTS OF HEPTANOLS

	Alc. fract., g.	Const. b. prod. (final dist.), g.	Boiling points					
			°C. ± 0.1°	mm.	°C. ± 0.05°	mm.	$\frac{dt}{dp}$	Mm.
Heptanol-1	535	428	175.9	759.5	84.7	20	0.6°	20–22
Heptanol-2	1100	480	158.7	740.5	66.7	16.5	.4°	16–18
Heptanol-3	963	536	155.9	740.5	65.8	20	.4°	16–20
Heptanol-4	605	184	155.4	755.2	63.8	16	.45°	16–20

TABLE I (*Concluded*)

	F. p., °C.	Density, t°/4° 0°	15°	20°	M. p. of semicarbazone from ox. of alc., °C.
Heptanol-1	.....	0.8359[a]	0.8260	0.8227	109
Heptanol-2	Vitreous	.8315	.8203	.8167	123
Heptanol-3	Vitreous	.8370	.8251	.8210	88
Heptanol-4	−41.5	.8335	.8219	.8183	132

[a] Pycnometer used had a capacity of 6 cc.

Indices of refraction of the heptanols

	Helium red		Helium yellow		D	Helium green	
	15°	20°	15°	20°	20°	15°	20°
Heptanol-1	1.42351	1.42190	1.42627	1.42456	1.4245	1.43043	1.42874
Heptanol-2	1.42059	1.41857	1.42336	1.42125	1.4210	1.42755	1.42527
Heptanol-3	1.42169	1.41967	1.42436	1.42236	1.4222	1.42845	1.42636
Heptanol-4	1.41987	1.41806	1.42256	1.42065	1.4205	1.42665	1.42467

case the semicarbazone *without* purification gave a sharp melting point which checked the most recent literature data.[4,5]

Literature Data

Heptanol-1.—B. p. (760 mm.) 175.8–176.2°, d_4^{25} 0.8187, n_D^{25} 1.4224;[6] b. p. (751.2 mm.) 174.4°, $d_4^{34.6}$ 0.8116;[7] b. p. (755 mm.) 175.5°, d_4^{22} 0.8173; d_4^{32} 0.8106;[8] b. p. (12 mm.) 76°;[9] d_4^{20} 0.8237;[10] b. p. 172.5–173°, $d_4^{22.4}$ 0.8206, $n_\alpha^{22.4}$ 1.42116, n_D 1.42326, $n_\beta^{22.4}$ 1.42843, $n_\gamma^{22.4}$ 1.43281, $d_4^{24.4}$ 0.8190, $n_\alpha^{24.4}$ 1.42043, $n_D^{24.4}$ 1.42242, $n_\beta^{24.4}$ 1.42770, $n_\gamma^{24.4}$, 1.43196.[11]

Heptanol-2.—(a) Inactive, b. p. (762 mm.) 156–157°, d_{20} 0.8193, n_D 1.42131;[12] b. p. 157–158°, d^0 0.8344;[13] b. p. 158–160°;[14]—(b) dextro: b. p. (20 mm.) 73.5°, d_4^{20} 0.8190, n_D^{20} 1.4209;[14]—(c) levo: b. p. (23 mm.) 74.5°, d_4^{20} 0.8184.[14]

Heptanol-3.—(a) Inactive: b. p. (750 mm.) 156.5–157°;[15] b. p. 150–152°;[14] b. p. (745 mm.) 152.7–154°, d_4^{25} 0.8159, n_D^{20} 1.4201, n_D^{25} 1.4175;[16]—(b) dextro: b. p. (18 mm.) 66°, d_0^{13} 0.8248, d_0^{50} 0.7985, d_4^{20} 0.8227.[14]

Heptanol-4.—B. p. 153–154°, d_4^{15} 0.822, n_D^{15} 1.4226;[9] b. p. (767 mm.) 154.5°,

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[4] Mathus and Gibon, *Bull. soc. chim. Belg.*, **34,** 303 (1925).

[5] Harries and Oppenheim, *Chem. Zentr.*, II, 992 (1916); *C. A.*, **11,** 3237 (1917).

[6] Norris and Cortese, THIS JOURNAL, **49,** 2644 (1927).

[7] Verkade and Coops, *Rec. trav. chim.*, **43,** 903–917 (1927); see Ref. 8.

[8] Carrara and Ferrari, *Gazz. chim. ital.*, **36,** I, 424 (1906); summary of data: "Revues Critiques de Constantes Fascicule VI," Union Internationale de la Chemie pure et appliquée par le Bureau International des Étalons Physico-Chimiques Université de Bruxelles, edited by Jean Timmermans, p. 57 (1928).

[9] Vavon, *Ann. chim.*, [9] **1,** 176 (1914).

[10] Lowry, *J. Chem. Soc.*, **105,** 92 (1914).

[11] Eisenlohr, *Z. physik. Chem.*, **75,** 588 (1911).

[12] Henry and de Wael, *Rec. trav. chim.*, **28,** 446 (1909); *Chem. Zentr.*, I, 1854 (1909).

[13] Masson, *Compt. rend.*, **149,** 630 (1909).

[14] Pickard and Kenyon, *J. Chem. Soc.*, **99,** 57, 58, 65 (1911); **101,** 638 (1912); **103,** 1936, 1943, 1957 (1913); **105,** 849 (1914).

[15] Blaise and Picard, *Compt. rend.*, **152,** 446 (1911); *Ann. chim.*, [8] **26,** 286 (1912).

[16] Dillon and Lucas, THIS JOURNAL, **50,** 1711 (1928).

d_4^{20} 0.8183, n_D^{20} 1.4205;[17] b. p. (750 mm.) 155.00 ± 0.04°, d_4^{25} 0.8129, n_D^{25} 1.4178;[18] b. p. (760 mm.) 155.9–156°, d_4^{25} 0.8156, n_D^{25} 1.4184;[6] b. p. (745 mm.) 153.4–154.3°, m. p. −41.5° to −37.2°, d_4^{25} 0.8175; n_D^{20} 1.4199, n_D^{25} 1.4173.[16]

Halogen Derivatives.—Each of the four chlorides and four bromides was prepared; the 3-iodoheptane was prepared; and the 1-iodoheptane (Schering–Kahlbaum) was purified. Especial care was taken in the preparation to prevent a shift of the position of the entering halogen and for the same reason the distillation was carried out under diminished pressure. The products were of very constant boiling point, showing no change on second distillation, and in each case, except for very small cuts at the beginning and the end, the distillate boiled completely within one-tenth of a degree.

The chloro derivatives were prepared by the action of concentrated hydrochloric acid and zinc chloride on the heptanols according to an adaptation of the method of Norris and Taylor.[19] One mole of the heptanol was added to two moles of ice-cold concentrated hydrochloric acid containing two moles of anhydrous zinc chloride. The product was kept in an ice-bath for several hours and vigorously stirred. Then the mixture was gradually allowed to come to room temperature. In the case of 1-chloroheptane the reaction mixture was refluxed gently for one hour and then the oil was slowly distilled off. With the 2-, 3- and 4-chloro derivatives the method was varied as suggested by Lucas,[20] the reaction being carried out at a lower temperature in order to avoid as much as possible any shift of position in the chain. The mixture of heptanol, hydrochloric acid and zinc chloride was kept ice cold for six to eight hours; then it was allowed to come to room temperature. After the mixture had stood from twelve to twenty-four hours, the oil layer was removed and the process repeated. The oil was added to fresh portions of ice-cold concentrated hydrochloric acid (two moles) and zinc chloride (two moles). This was repeated at the end of a second twenty-four hour period. Finally the oil and acid mixture was vigorously shaken.

For purification the chloride layer was separated from the water–acid layer, was washed three times with fresh portions of concentrated hydrochloric acid, four times with ice-cold water, once with 10% sodium hydroxide (ice cold) and twice with cold 15% sodium chloride. The crude oils, very pale yellow in color, were dried over calcium chloride and distilled twice *in vacuo* over phosphorus pentoxide. The crude yields were 77–80% of the theoretical and the yields of constant boiling products were from 60–64% of the theoretical yields. The purified chloro derivatives were perfectly colorless and have remained so for six months.

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[17] Krapiwin, *Chem. Zentr.*, I, 1335 (1910).

[18] Brunel, THIS JOURNAL, **45,** 1334 (1923).

[19] Norris and Taylor, *ibid.*, **46,** 753–757 (1924).

[20] Lucas, *ibid.*, **51,** 249 (1929).

The 1-bromo derivative was prepared according to methods used for similar bromides by Kamm and Marvel,[21] Norris, Watt and Thomas[21] and Simon.[22] Eighty-eight grams of 1-heptanol was refluxed for two and one-half hours with 360 g. of 48% hydrobromic acid to which 92 g. of concentrated sulfuric acid had been added. The oil was separated and washed with water but proved to be lighter than water, so the procedure was repeated and the material was refluxed for three hours. The oil, when separated and washed with concentrated sulfuric acid, with water and with sodium carbonate, was so dark in color that it was distilled from four times its volume of 48% hydrobromic acid, which gave a practically colorless product.

The 2-, 3- and 4-bromo derivatives were prepared by slow saturation of the alcohols with hydrogen bromide.[2] The heptanol was kept at a temperature of about −10° by an ice and salt bath and a slow stream of hydrogen bromide was passed into the alcohol during a period of six to eight hours. The flask was then closed with a capillary tube or a tube carrying a rubber balloon and the mixture was allowed to come to room temperature and left overnight. The process was repeated each day for twelve days.

The bromides were purified as in the case of the chlorides by washing with 48% hydrobromic acid, water and sodium hydroxide and were dried over anhydrous calcium chloride. Then each was distilled twice *in vacuo* over phosphorus pentoxide. The crude yields of bromide were 70% of the theoretical in the case of 1-bromo-, and 85–90% in the case of the other three derivatives. The yields of constant boiling products were from 65–75% of the theoretical. The bromoheptanes so obtained showed no trace of color and have remained colorless for six months.

The 1-iodoheptane was obtained from Schering–Kahlbaum. It was shaken with mercury to remove excess iodine, filtered and distilled *in vacuo*. Eighty per cent. of the distillate was a constant boiling product and the iodoheptane so obtained has remained almost colorless for six months.

The 3-iodoheptane was prepared by a method analogous to that used for the preparation of the chloro derivatives. One hundred and thirty grams of 3-heptanol was treated with 750 g. of hydriodic acid in three separate portions and the mixture left for sixty hours, being agitated frequently. At the end of that time the oily layer was washed and found to be lighter than water so it was put back with the hydriodic acid and zinc iodide and refluxed for two hours at 60–70°. The reaction was still incomplete so gaseous hydrogen iodide was passed into the oily mixture of 3-iodoheptane and 3-heptanol for about five hours. At the end of this time

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[21] Kamm and Marvel, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1921**, Vol. I, p. 7; Norris, Watt and Thomas, THIS JOURNAL, **38**, 1075 (1916).

[22] Simon, *Bull. soc. chim. Belg.*, **38**, 48 (1929).

100 g. of the hydriodic acid (sp. gr. 1.5) and 100 g. of zinc iodide were added and the mixture left for twenty-four hours. The oil was then separated, purified as in the case of the chloro and bromo derivatives and distilled *in vacuo*. The distillation showed that the reaction was not complete, for there were two distinct distillates, one boiling fairly constantly at 75.2–75.6° at 30 mm. for more than an hour; then there was an interval (twenty-five minutes) when there was practically no distillate. Then the temperature rose rapidly to 88.8° at 30 mm. and a second constant boiling product distilled. This product was about 50% of the distillate.

Proof of Position of the Halogen.—In order to test the position of the substituting halogen each of the chloro derivatives was treated in the following manner. Approximately 10 g. of the chloro derivative was refluxed for seven hours with 15 g. of anhydrous potassium acetate and 10 g. of glacial acetic acid. The product was diluted with water and the ester extracted with ether. The ether was then removed by distillation and the ester was hydrolyzed by refluxing for six hours with 50 cc. of alcoholic potash (20% solution). The larger part of the ethyl alcohol was removed by distilling up to 85° (some of the heptanol distilled also, as was evidenced by the odor). Water was then added to the residue and an ether extraction was made. The ether was distilled off and the distillation continued up to 90° to remove all traces of ethyl alcohol. The residue of heptanol (approximately 3 g.) was oxidized by acidified bichromate. A solution of bichromate (2.7 g. in 35 cc. of water) was divided into two portions. Half was added to the heptanol; to the other half, 2.2 cc. of concd. sulfuric acid was added and this acid mixture was poured, drop by drop, into the well cooled mixture of heptanol and bichromate. The entire mixture was refluxed at 70–80° for one hour and a quarter. About 100 cc. of water was then added and the mixture distilled as long as oil distilled over. The ketone (or aldehyde) was separated from the water layer and washed several times with sodium carbonate solution. The ketone (approximately 2 g.) was then transformed into the semicarbazone by treatment with semicarbazide hydrochloride and sodium acetate. The semicarbazones formed were in each case similar in crystal form to those obtained from the original alcohols and they gave, without purification, the same melting points. The semicarbazone from 4-chloroheptane melted slightly lower, 129–130° and less sharply than the one obtained from the original, 132°. Mixed melting points with the original semicarbazones showed no change.

The 2-, 3- and 4-bromo derivatives were esterified, hydrolyzed and oxidized as in the case of the chloro derivatives, and the semicarbazones formed from the ketones were identical with those from the corresponding alcohols, except in the case of the 3-bromo, the semicarbazone from which melted at 96–97°. The amount of ketone obtained was small and the semicarbazone was filtered after standing for several days. The amount obtained was too small for purification. A mixed melting point of equal portions of this semicarbazone and of the pure semicarbazone, m. p. 88–89°, melted at 90–91°, which indicated that it was the semicarbazone of 3-heptanone with some impurity. There are two points of interest to be noted in connection with this: first that Pickard and Kenyon[14] and Michael[23] give values 99–100° and 103° for the melting point of this substance, Mathus and Gibon[4] giving the lower value 89°. Second, in the preparation of the semicarbazone from 3-heptanol a large yield (12 g.) crystallized out instantly and melted at 88–89° sharply. A second precipitate (less than 2 g.) which came out after several days of standing melted at 97–98°. This material mixed with the 88–89° product melted at 90–91°. This seems to indicate that on oxidation of 3-heptanol, in addition to the 3-heptanone, there is a small amount of another ketone or other impurity which on long standing gives a semicarbazone.

Table II

Constants of the Chloroheptanes

	Chloro der. fract., (vac.) g.	Const. b. prod. (final dist.), g.	Boiling points °C. ± 0.05°	Boiling points Mm.	$\frac{dt}{dp}$	Mm.
1-Chloroheptane	170	138	61.4	27	0.5°	25–27
2-Chloroheptane	65	59	46.0	19.5	.5°	19.2–22.5
3-Chloroheptane	75	61	48.3	21	.4°	21–24
4-Chloroheptane	50	38	48.9	21	.5°	20–22

	F. p., °C.	Density, $t°/4°$ 0°	15°	20°	M. p. of semicarbazone from chloro deriv., °C.
1-Chloroheptane	−69.5	....	0.8783	0.8725	108.8–109.2
2-Chloroheptane	..	0.8848	.8725	.8672	123
3-Chloroheptane	..	.8866	.8732	.8690	88–89
4-Chloroheptane	..	.8884	.8751	.8710	129

Indices of refraction of the chloroheptanes

	Helium red 15°	Helium red 20°	Helium yellow 15°	Helium yellow 20°	D 20°	Helium green 15°	Helium green 20°
1-Chloroheptane	1.42381[a]	1.42261	1.42657[a]	1.42537	....	1.43084[a]	1.42964
2-Chloroheptane	1.42170	1.41967	1.42446	1.42246	1.4221	1.42884	1.42675
3-Chloroheptane	1.42251	1.42068	1.42547	1.42336	1.4228	1.42973	1.42755
4-Chloroheptane	1.42270	1.42078	1.42557	1.42346	1.4231	1.42983	1.42765

[a] Temperature, 17.5°.

Literature Data

1-Chloroheptane.—B. p. (750 mm.) 159.2°, d^{16} 0.881;[24] b. p. 159°.[25]

2-Chloroheptane.—Beilstein records that it is unknown in pure form; b. p. 165–170°.[26]

3-Chloroheptane.—B. p. (751 mm.) 143.4–144.4°, n^{20}_{D} 1.4237.[16]

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[23] Michael, This Journal, **41,** 411–424 (1919).

[24] Cross, *Ann.*, **189,** 3 (1877).

[25] Sabatier and Mailhe, *Compt. rend.*, **169,** 124 (1919).

[26] Schorlemmer and Thorpe, *Ann.*, **217,** 152 (1883).

4-Chloroheptane.—B. p. (751 mm.) 143.1–144.4°, n_D^{20} 1.4237;[16] b. p. (758 mm.) 144–145°, d_4^{20} 0.8619, n_D^{20} 1.4199.[4]

Table III

Constants of the Bromoheptanes

	Bromo der. fract. (vac.), g.	Const. b. prod. (final dist.), g.	Boiling points °C. ± 0.05°	Boiling points Mm.	$\frac{dt}{dp}$	Mm.
1-Bromoheptane	80	63	70.6	19	0.7°	19–23
2-Bromoheptane	165	136	66.2	24	.6°	24–25
3-Bromoheptane	135	88	62.0	18	.5°	18–20
4-Bromoheptane	50	38	60.0	18	.7°	18–20

	F. p., °C.	Density, t°/4° 0°	15°	20°	M. p. of semicarbazone from bromo deriv., °C.
1-Bromoheptane	−58.25	1.1596	1.1488	1.1384	.....
2-Bromoheptane	...	1.1493	1.1333	1.1277	122–123
3-Bromoheptane	...	1.1577	1.1415	1.1362	96–97
4-Bromoheptane	...	1.1565	1.1404	1.1351	129–130

Indices of refraction of bromoheptanes

	Helium red 15°	Helium red 20°	Helium yellow 15°	Helium yellow 20°	D 20°	Helium green 15°	Helium green 20°
1-Bromoheptane	1.44934	1.44734	1.45260	1.45049	....	1.45765	1.45546
2-Bromoheptane	1.44673	1.44461	1.44999	1.44789	1.4476	1.45506	1.45295
3-Bromoheptane	1.44954	1.44744	1.45290	1.45069	1.4503	1.45785	1.45575
4-Bromoheptane	1.44894	1.44673	1.45210	1.44989	1.4495	1.45716	1.45496

Literature Data

1-Bromoheptane.—B. p. (750.6 mm.) 178.5°, d^{16} 1.133;[24] b. p. (765 mm.) 175.5–177.5°.[27]

2-Bromoheptane.—B. p. 165° with decomposition;[28] b. p. 165–167°, $d^{17.5}$ 1.422 (*cf.* 1.1422, Beilstein).[29]

3-Bromoheptane.—B. p. (74 mm.) 84.5–85.5°, n_D^{20} 1.4507.[16]

4-Bromoheptane.—B. p. (72–75 mm.) 84.0–85.5°, n_D^{20} 1.4506;[16] b. p. 159–160°, ordinary pressure, b. p. (11 mm.) 55°, d_4^{20} 1.1389, n_D^{20} 1.4472, transformed into mixture by atmospheric distillation.[4]

Bromoheptane (position of bromine uncertain) b. p. (70 mm.) 93°, d_4^0 1.1577.[30]

Table IV

Constants of Iodoheptanes

	Distillate g.	Const. b. prod., g.	Boiling pt. °C. ± 0.05°	Boiling pt. Mm.	$\frac{dt}{dp}$	Mm.	Density,[a] t°/4° 15°	Density,[a] t°/4° 20°
1-Iodoheptane	81	65	97.0	26	0.5°	25	1.3870	1.3774
3-Iodoheptane	115	55	88.9	30	..	..	1.3735	1.3676

Indices of refraction of iodoheptanes

	Helium red 17.5°	Helium red 20°	Helium yellow 17.5°	Helium yellow 20°	Helium green 17.5°	Helium green 20°
1-Iodoheptane	1.48760	1.48689	1.49193	1.49107	1.49867	1.49771
3-Iodoheptane	1.48915	1.48812	1.49346	1.49241	1.50037	1.49923

[a] The densities of the iodo derivatives were measured by M. Cambron at the University of Brussels.

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[27] Bogert, This Journal, **25**, 289 (1903).

[28] Schorlemmer, *Ann.*, **188**, 253 (1877).

[29] Venable, *Ber.*, **13**, 1650 (1880); Wheeler, This Journal, **25**, 532 (1903).

[30] Francis and Young, *J. Chem. Soc.*, **73**, 921 (1898).

Literature Data

1-Iodoheptane.—B. p. (754.8 mm.) 201°, d^{16} 1.346;[24] b. p. (16.5 mm.) 91°;[31] b. p. (20 mm.) 93–95°;[32] 203.8°, ordinary pressure, d_0^0 1.4008.[33]

3-Iodoheptane.—B. p. (8.5 mm.) 64.5°.[15]

Aldehyde and Ketone Derivatives.—The *n*-heptaldehyde, obtained from Schering–Kahlbaum, was distilled *in vacuo;* 82% of the total distillate boiled at a constant temperature. The semicarbazone derivative of the aldehyde was prepared by treating 2 g. of the aldehyde with a water solution of 2 g. of semicarbazide hydrochloride and 2 g. of sodium acetate. Sufficient ethyl alcohol was then added to dissolve the aldehyde and the semicarbazone crystallized out in lustrous plate-like crystals which melted sharply at 109°.

The heptanones (methyl *n*-amyl ketone, ethyl *n*-butyl ketone, di-propyl ketone) were prepared by oxidation of the corresponding heptanols. To one mole of the alcohol, well cooled, was added one-sixth of a mole of potassium bichromate (8% solution). Then to the well-cooled mixture, a sixth of a mole of bichromate solution (8%) containing 1.5 moles of concentrated sulfuric acid was added dropwise. The reaction mixture was refluxed for one hour and a quarter at 70–80°. Water was added and the mixture distilled until all of the oil had distilled over. The oil was separated, washed three times with sodium carbonate and dried over calcium chloride. The crude yields were 85–90% of the theoretical.

The 2-heptanone was purified by making the sodium bisulfite addition product. The ketone was freed from the bisulfite compound by sodium carbonate and then distilled. Neither the 3-heptanone nor 4-heptanone formed sodium bisulfite addition products. The dried ketones were fractionated at atmospheric pressure and 60 to 70% of the products was constant boiling within ±0.05°.

The semicarbazone of 2-heptanone was prepared and crystallized in fine lustrous crystals which, without purification, melted sharply at 123°. The semicarbazone from 3-heptanone crystallized in fine crystals somewhat granular in appearance. The semicarbazone, without purification, melted sharply at 89°. A second small fraction which crystallized out on long standing melted at 97–98°.

The semicarbazone from 4-heptanone crystallized in fine crystals, very similar in appearance to those obtained from 2-heptanone but very much less lustrous. These crystals, without purification, melted sharply at 132°.

Because of insufficient 4-heptanol the amount of 4-heptanone obtained was too small for the complete physical measurements. Dipropyl ketone

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[31] Blaise and Picard, *Ann. chim.*, [8] **25**, 266 (1912); *Chem. Zentr.*, I, 1208 (1912).

[32] Von Braun, *Ann.*, **382**, 24 (1911).

[33] Dobriner, *ibid.*, **243**, 28 (1888).

(purchased from Poulenc Frères) was dried and distilled. The total product boiled within less than one and one-half degrees and 70% was constant boiling within one-tenth of a degree. The boiling point of this compound and the melting point of its semicarbazone were identical with those obtained from the oxidation product of 4-heptanol. The physical constants of this product were measured.

TABLE V

PHYSICAL CONSTANTS

	Distillate, g.	Const. b. prod., g.	Boiling point °C.	Mm.	M. p. semicarbazone, °C.	Density, $t°/4°$ 15°	Density, $t°/4°$ 20°
n-Heptaldehyde	445	350	59.6 ± 0.05	30	108–109	0.8252	0.8219
2-Heptanone	87	58	150.2 ± 0.1	750	123	.0852	.8018
3-Heptanone	140	93	148.2 ± 0.05	756	89	.8222	.8183
4-Heptanone	82	58	144.0 ± 0.05	756	132	.8212	.8175

	Indices of refraction					
	Helium red		Helium yellow		Helium green	
	17.5°	20°	17.5°	20°	17.5°	20°
n-Heptaldehyde	1.41051	1.40941	1.41315	1.41216	1.41748	1.41639
2-Heptanone	1.40760	1.40660	1.41027	1.40927	1.41433	1.41336
3-Heptanone	1.40750	1.40649	1.41017	1.40917	1.41423	1.41316
4-Heptanone	1.40560	1.40459	1.40818	1.40719	1.41218	1.41120

Literature Data

n-Heptaldehyde.—B. p. (748.6 mm.) 152°, d^{16} 0.823;[24] b. p. (760 mm.) 155°, b. p. (20 mm.) 54.4°, b. p. (22.5 mm.) 56.2°;[34] b. p. (10 mm.) 42–43°, d^{20} 0.8250, n_D 1.41655;[36] b. p. (18 mm.) 62°;[35] b..p. 152.2–153.2° (corr.), d_{15}^{15} 0.82264, d_{25}^{25} 0.81578;[37] b. p. 154.2–154.5°, d_4^{20} 0.8495, n_α^{20} 1.42339, n_D^{20} 1.42571, n_β^{20} 1.43094, n_γ^{20} 1.43514;[38] b. p. (759.3 mm.) 152.5–153.5°, $d_4^{19.9}$ 0.81708, $n_\alpha^{19.9}$ 1.41046, $n_D^{19.9}$ 1.41251, $n_\beta^{19.9}$ 1.41789, $n_\gamma^{19.9}$ 1.42236;[11] b. p. 154°, d_{19}^{19} 0.8320, n_α^{19} 1.41105, n_D^{19} 1.41370, n_γ^{19} 1.42312.[5]

Semicarbazone of n-Heptaldehyde.—M. p. 109°.[5]

Heptanone-2.—B. p. 151–152°;[13] b. p. (763 mm.) 151–152°, d^0 0.8366;[39] b. p. (760 mm.) 149.5–150°, d^0 0.8346;[40] b. p. 151–153°, d^{15} 0.8223;[41] b. p. (750 mm.) 148–151°;[42] b. p. 144–145°;[23] b. p. 148–150°;[43] b. p. (760 mm.) 151.45 ± 0.02°, d_0^4 0.83239, d_4^{15} 0.81966, d_4^{30} 0.80680, $n_{\text{He red}}^{15}$ 1.40906, n_D^{15} 1.41156, $n_{\text{He yellow}}^{15}$ 1.41161, $n_{\text{He green}}^{15}$ 1.41577, $n_{\text{He red}}^{25}$ 1.40481, n_D^{25} 1.40729, $n_{\text{He yellow}}^{25}$ 1.40740, $n_{\text{He green}}^{25}$ 1.41154.[22]

Semicarbazone of 2-Heptanone.—M. p. 122–123°;[44] m. p. 122°;[10] m. p. 123°;[14] m. p. 122–123°;[40] m. p. 127°;[23] m. p. 121–123°;[4] m. p. 120°.[43]

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[34] Kahlbaum, *Ber.*, **17,** 1251 (1884); **18,** 2107 (1885).

[35] Schlotterbeck, *ibid.*, **40,** 481 (1907).

[36] Semmler, *ibid.*, **42,** 1161 (1909).

[37] Perkin, *J. Chem. Soc.*, **45,** 477 (1884).

[38] Brühl, *Ann.*, **203,** 28 (1880).

[39] Behal, *Ann. chim.*, [6] **15,** 270 (1888).

[40] Moureu and Delange, *Bull. soc. chim.*, [3] **29,** 674 (1903); *Compt. rend.*, **136,** 753–756 (1903).

[41] Schimmel and Co., *Chem. Zentr.*, I, 1059 (1902).

[42] Johnson and Hager, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1927**, Vol. VII, p. 60.

[43] Weizmann and Garrard, *J. Chem. Soc.*, **117,** 338 (1920).

[44] Dakin, *Am. Chem. J.*, **44,** 46 (1901).

Heptanone-3.—B. p. (742.9 mm.) 147–148°;[45] b. p. 149–150°;[14] b. p. (760 mm.) 147–148°;[23] b. p. 147.4°, m. p. −39°.[46]

Semicarbazone of 3-Heptanone.—M. p. 99–100°;[14] m. p. 103°;[23] m. p. 86–88°.[4]

Heptanone-4.—B. p. (760 mm.) 143.52°;[47] b. p. (760 mm.) 144–145°, d 0.8193, n_{D} 1.414;[48] b. p. 144.2°, m. p. −34°;[46] b. p. (770 mm.) 143–144°;[49] b. p. (755 mm.) 143.5–144.5°;[23] b. p. (68 mm.) 75.1;[50] d_4^{10} 0.8258, d_4^{30} 0.8105;[51] $d_{14.8}^{14.8}$ 0.8210;[52] $d_4^{15.1}$ 0.8205, $n_\alpha^{15.1}$ 1.40818, $n_\beta^{15.1}$ 1.41538;[53] $d_4^{21.7}$ 0.8160, n_α^{22} 1.40521, n_{D}^{22} 1.40732, n_γ^{22} 1.41650;[54] d_4^{20} 0.8217.[10]

Semicarbazone of 4-Heptanone.—M. p. 133°;[55] m. p. 132°;[56] m. p. 132°;[57] m. p. 133°;[49] m. p. 129°;[23] m. p. 125°.[58]

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Summary

The four heptanols (1-, 2-, 3- and 4-), the four corresponding chlorides and four bromides, two of the iodides (1- and 3-), the *n*-heptaldehyde and the three ketones (keto-2, -3 and -4) have been investigated and some of the physical constants determined.

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[45] Ponzio and de Gaspari, *Gazz. chim. ital.*, **28,** II, 272 (1898).

[46] Timmermans, *Bull. soc. chim. Belg.*, **36,** 502–518 (1927).

[47] Louguinine, *Ann. chim. phys.*, [7] **13,** 331 (1898).

[48] Amouroux and Murat, *Compt. rend.*, **154,** 992 (1912).

[49] Henderson, Henderson and Heilbronn, *Ber.*, **47,** 887 (1914).

[50] Rice, *Proc. Roy. Soc.* (London), **91,** 83 (1915).

[51] Morgan and Kramer, This Journal, **35,** 1836 (1913).

[52] Perkin, *J. Chem. Soc.*, **69,** 1173 (1896).

[53] Eijkman, *Rec. trav. chim.*, **12,** 172 (1893); *Rech. Refrac.*, 86 (1919); *cf.* "Revue des Constants," Ref. 8.

[54] Brühl, *J. prakt. Chem.*, [2] **50,** 141 (1894).

[55] Dilthey, *Ber.*, **34,** 2123 (1901).

[56] Staudinger, *ibid.*, **44,** 528 (1911).

[57] Douris, *Compt. rend.*, **157,** 723 (1913).

[58] Lynn, This Journal, **41,** 369 (1919).