to extrapolate the data in order to obtain the correct initial specific rotation of +89.4° in water for alpha *l*-arabinose. The observation of the final specific rotation, +105.1°, provided a check on the purity of the preparation.

TABLE II

MUTAROTATION OF ALPHA *l*-ARABINOSE CALCIUM CHLORIDE TETRAHYDRATE IN WATER

Concn. 4.000%; temp., 20.0 ± 0.5°

Time after soln., min.	$[\alpha]_D^{20°}$	$k_1 + k_2 = \frac{1}{t} \log \frac{r_0 - r_\infty}{r - r_\infty}$
0		
1.0	+ 89.4	
2.0	88.9	
3.0	88.5	
4.0	88.9	
5.0	88.9	
7.0	90.8	0.028
8.5	92.0	.027
11.5	94.6	.030
14.0	96.6	.031
21.0	100.4	.034
25.0	100.9	.029
30.0	101.8	.028
37.0	103.8	.030
24 hrs.	+105.1 (const.)	
		Av. .030

Behavior of the Arabinose–Calcium Chloride Double Compounds when Heated.—Beta *l*-arabinose calcium chloride monohydrate with an initial specific rotation of +202°, and alpha *l*-arabinose calcium chloride tetrahydrate, with an initial rotation of +89° in water, both calculated on the arabinose content, were heated at 95° for four days in an oven. The product in each case was a white powder which gave a clear colorless aqueous solution with an initial specific rotation of +186°, calculated for the arabinose. Evidently the drying of these compounds at elevated temperature changes the arabinose forms contained in them.

Summary

The values of the initial rotation of beta *l*-arabinose recorded in the literature (175–192°) are low; by crystallizing the pure pentose very slowly we find the value $[\alpha]_D^{20}$ +202° in water. This value agrees with that which we find for the arabinose component of Dale's beta *l*-arabinose calcium chloride monohydrate. The alpha form of arabinose has never been crystallized, but its crystalline calcium chloride compound recently discovered by Austin and Walsh exhibits the initial rotation of +89° for its alpha *l*-arabinose component. These observed rotations agree closely with the values that may be calculated for the alpha and beta forms of arabinose from the known rotations of the alpha and beta methyl arabinosides by the isorotation rules.

WASHINGTON, D. C. RECEIVED JUNE 7, 1934

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

The Diamylenes Produced from Methylisopropylcarbinol by Sulfuric Acid[1]

BY NATHAN L. DRAKE, G. M. KLINE AND W. G. ROSE

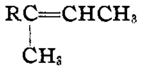
Many investigators have studied the polymerization of amylenes, but to date no *conclusive* proof of the structure of any of the polymers has been offered.[2,3,4,5,6,7]

Previous work on the structures of the decenes produced by sulfuric acid from methylisopropylcarbinol has likewise been inconclusive.[8,9]

The present paper advances evidence that 3,5,5-trimethylheptene-2 and 3,4,5,5-tetramethylhexene-2 result from the action of warm sulfuric acid on methylisopropylcarbinol. These substances are produced in approximately equal quantities, and no evidence of the presence of other decenes has been found.

The formation of 3,5,5-trimethylheptene-2 would be predicted according to the theory advanced by Whitmore[10] to explain the mechanism of the polymerization of olefins by acid catalysts. However, only a radical intramolecular rearrangement of one of the hypothetical intermediates which would be expected according to Whitmore's theory could result in the formation of 3,4,5,5-tetramethylhexene-2.

The proof of the structures of the two decenes was obtained as follows. Ozonolysis yielded acetaldehyde and two ketones, $C_8H_{16}O$, which were demonstrated to be methyl ketones by the haloform reaction. The two decenes must, therefore, possess the structure



$$\underset{\displaystyle CH_3}{RC}{=}CHCH_3$$

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[1] From the Ph.D. dissertations of G. M. Kline and W. G. Rose.

[2] Wischnegradsky, *Ber.*, **8**, 434 (1875).

[3] Schneider, *Ann.*, **157**, 207 (1871).

[4] Michael and Brunel, *Am. Chem. J.*, **41**, 118 (1909).

[5] Michael and Zeidler, *Ann.*, **385**, 252 (1911).

[6] Schindelmeiser, *Chem.-Ztg.*, **45**, 566 (1921).

[7] Norris and Joubert, THIS JOURNAL, **49**, 873 (1927).

[8] Cooke, Dissertation, U. of Md., 1929.

[9] Wheeler, Dissertation, U. of Md., 1931.

[10] Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

Many of the theoretically possible methyl ketones could be eliminated as a result of information available in the literature. The melting point of either the semicarbazone of the ketone, or of the amide or anilide of the seven carbon acids which would be formed from the ketone by the haloform reaction, is recorded for all but three of the theoretically possible eight-carbon methyl ketones. One of these, *viz.*, 4,5-dimethylhexanone-2 has been synthesized in this Laboratory by Wheeler,[9] and found to yield a semicarbazone melting 159–160°. It remained to eliminate one of the three following ketones: 4,4-dimethylhexanone-2,3,4,4-trimethylpentanone-2, and 3-methyl-3-ethylpentanone-2. The last-mentioned ketone has been prepared by Nyberg, who recorded[11] the melting point of its semicarbazone as 168° (*cf.* semicarbazone of (I) below, m. p. 169.5°). Additional evidence in favor of the possible identity of (I) and 3-methyl-3-ethylpentanone-2 is to be found in the fact that Haller and Bauer[12] report that the amide of the related diethylmethylacetic acid melts at 78–79° (*cf.* amide of (V), m. p. 76.5°). Synthesis of 3-methyl-3-ethylpentanone-2, however, proved that it was not identical with ketone (I).

The ketoximes, $R(CH_3)C{=}NOH$, were converted by the Beckmann rearrangement into substituted acetamides, $RNHCOCH_3$, whose hydrolysis yielded the corresponding amines. The latter were identified by comparing several of their derivatives with the same substances prepared synthetically.

Experimental

Methylisopropylcarbinol.—The carbinol was prepared from acetaldehyde and isopropyl bromide.[13]

The Decenes.—The above carbinol was added rapidly from a separatory funnel to one and one-half times its molecular equivalent of 75% sulfuric acid contained in a flask equipped with stirrer and condenser. The temperature *of the mixture* was then raised rapidly to 80° and held there for twenty minutes. Five minutes sufficed to add 200 g. of carbinol to the acid and to raise the temperature of the mixture to 80°; slower addition of the carbinol resulted in a low yield of decenes. After twenty minutes the mixture was cooled, the hydrocarbon layer separated, washed with bicarbonate solution, and with water, and dried over calcium chloride. Distillation of this product through a short column yielded a fraction boiling from 149–169° which was subjected to further purification. The yield was 55–60%. The 149–169° fractions from several experiments were combined, allowed to stand over sodium for about eight hours, then refluxed over sodium for six hours, and allowed to stand in contact with the sodium overnight. The resulting product was distilled through a short column; 1880 ml. of decenes boiling from 147–163° was so prepared, and further fractionated as described below.

Fractional Distillation of the Decenes.—Through the courtesy of the late E. W. Washburn, arrangements were made to fractionate the decene mixture in one of the very efficient columns at the National Bureau of Standards. The column used had been described by Schicktanz,[14] and is capable of separating a 50 mole per cent. mixture of benzene and ethylene dichloride so that 30% of practically pure benzene and 23% of practically pure ethylene dichloride are obtainable by a single distillation.

The decene mixture (1820 ml., n^{25}_{D} 1.4346) was separated into 28 fractions of about 60 ml. each, and a residue of 210 ml. The total volumes, b. p. (215 mm.) and n^{25}_{D} were as follows: Nos. 1–2, 112 ml., to 91.6°, 1.4202–52; Nos. 3–7, 281 ml., to 107.8°, 1.4274–1.4326; Nos. 8–17, 576 ml., to 113.1°, 1.4334–1.4350; Nos. 18–20, 178 ml., to 114.4°, 1.4357–1.4366; Nos. 21–28, 416 ml., to 117.3°, 1.4373–6; residue, 210 ml., above 117.3°, 1.4403.

Indication of the presence of at least two isomers is apparent; the refractive index of one is near 1.4340, that of the other near 1.4375. Since other work had convinced us that it was futile to attempt a separation of pure individuals by further distilling the purest fractions, ozonolyses were carried out on the fractions listed above.[15]

Exploratory Ozonolyses of the Decene Fractions

Fifteen-gram portions of fractions 2, 5, 13, 19, 25, and of the residue, (29), were ozonized and the ozonides decomposed. Acetaldehyde, a trace of formaldehyde, and a mixture of ketones resulted. The ketones were converted into their semicarbazones and the latter fractionally crystallized. *No evidence of more than two semicarbazones was obtained.* Decomposition of the ozonides was effected by several different procedures: the zinc–acetic acid method, the catalytic hydrogenation method,[16] and the zinc–water catalyst method[17] were all used. The most satisfactory results with these particular decenes are obtained by the use of ethyl acetate or petroleum ether as solvent for ozonolysis, and the zinc–water catalyst method for decomposition of the ozonide. Ozonolyses were conducted at −15 to −25°.

Very careful exploratory ozonolyses of representative fractions of a purified specimen of the so-called "Diamylene" marketed by the Sharples Solvents Company of Philadelphia revealed no products other than those mentioned above.[18]

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(11) Nyberg, *Ber.*, **55B**, 1960 (1922).

(12) Haller and Bauer, *Compt. rend.*, **148**, 130 (1909).

(13) "Organic Syntheses," Vol. XII, p. 48.

(14) Schicktanz, *Bur. Standards J. Research*, **11**, 89 (1933); *cf.* also **7**, 852 (1931).

(15) We wish to express our thanks to S. Schicktanz and the others of the Petroleum Research Section of the Bureau of Standards for their valuable assistance in fractionating the decene mixture.

(16) F. G. Fischer, *Ber.*, **65**, 1467 (1932).

(17) Whitmore and Church, THIS JOURNAL, **54**, 3710 (1932).

(18) Space does not permit including the detailed evidence which indicates the absence of any considerable quantity of decenes other than those mentioned above. For detailed evidence the original dissertations of G. M. Kline and W. G. Rose (U. of Md., 1934) should be consulted.

The Eight-Carbon Ketones.—By ozonolysis of fractions 21 to 29, and of fractions 3 to 9, two ketones, (I) and (II) were obtained. The yield of ketones was about 60%. *Both ketones were obtained from all fractions,* but (I) was present in greater abundance in the products of ozonolysis of fractions 21–29, and (II) was present in larger quantity in the products of ozonolysis of fractions 3–9. (I), later shown to be 4,4-dimethylhexanone-2, has the following properties: b. p. (Cottrell)[19] 154.4° at 768 mm.; d_4^{20} 0.829; n_D^{25} 1.4183. (II), later shown to be 3,4,4-trimethylpentanone-2, has the following properties: b. p. (Cottrell) 147.2° at 766 mm.; d_4^{20} 0.826; n_D^{25} 1.4136.

Table I lists the derivatives prepared from ketones (I) and (II).

TABLE I

DERIVATIVES OF KETONES (I) AND (II)

	M. p., °C.	B. p., °C.	Carbon, % Calcd.	Carbon, % Found		Hydrogen, % Calcd.	Hydrogen, % Found	
Semicarbazone of (I)	169.5	....	58.33	58.36	58.60	10.34	10.04	10.28[20]
Semicarbazone of (II)	148	....	58.33	58.53	58.07	10.34	10.20	10.42
2,4-Dinitrophenylhydrazone of (I)	146.5–147	....	54.50	54.14	54.09	6.54	6.29	6.37
2,4-Dinitrophenylhydrazone of (II)	109.5	....	54.50	54.73	54.45	6.54	6.52	6.41
Oxime, (III), of ketone (I)	....	101 (13 mm.)	67.07	66.57		11.97	11.68	
Oxime, (IV), of ketone (II)	....	113 (27 mm.)	67.07	66.97	67.10	11.97	12.22	11.83
p-Nitrophenylhydrazone of (II)	73	....	63.83	64.16	64.30	8.04	7.78	7.97

The Degradation of (I) and (II) to Seven-Carbon Acids.—(I) and (II) were degraded to the corresponding seven-carbon acids by the haloform reaction. The method employed was like that described[21] for the conversion of pinacolone into trimethylacetic acid. The yield of *t*-amylacetic acid (V) from (I) was 45–53%; that of methyl *t*-butylacetic acid (VI) from (II) was 35%. The following properties of (V) and (VI) were observed: (V) boils at 213° at 778 mm. (Cottrell), and distils at 103–104° at 13 mm.; (VI) melts at 24.5°, and distils from 103–104° at 20 mm., or at 76° under 5 mm. pressure; the methyl ester of (V) boils at 49–50° at 17 mm., that from (VI) at 46° under 18 mm. pressure. (VI) has a n_D^{25} 1.4182.

Table II lists the derivatives of (V) and (VI).

TABLE II

THE ACIDS (V) AND (VI) AND THEIR DERIVATIVES

	M. p., °C.	Carbon, % Calcd.	Carbon, % Found		Hydrogen, % Calcd.	Hydrogen, % Found	
Amide of (V)	76.5	65.05	64.98	64.85	11.71	11.75	11.70
Amide of (VI)	106.0	65.05	64.73	64.84	11.71	11.28	11.80
Anilide of (V)	105.5–106.0	76.04	75.93	75.68	9.33	9.40	9.45
Anilide of (VI)	104.5	76.04	76.57	76.68	9.33	9.22	9.32
p-Phenylphenacyl[22] ester of (V)	74	77.73	77.50	77.77	7.46	7.57	7.57
p-Phenylphenacyl ester of (VI)	68.5	77.73	77.67	77.41	7.46	7.29	7.55
t-Amylacetic acid (V)	...	64.54	64.02	7.46	10.84	10.56	
Methyl-*t*-butylacetic acid (VI)	24.5	64.54	64.64	64.09	10.84	10.78	10.62

Synthesis of Diethylmethylacetic Acid and 3-Methyl-3-ethylpentanone-2 and their Derivatives.—Ethyl acetate was treated with ethylmagnesium bromide to yield diethylmethylcarbinol. The chloride of this carbinol was converted into diethylmethylcarbinylmagnesium chloride and treated with carbon dioxide. The resultant acid yielded an amide which melts at 78.5°. A mixture of the synthetic amide with the amide of (V) melted from 52–62°. This acid has been characterized only by its amide; the anilide and *p*-phenylphenacyl ester were consequently prepared for future reference. These substances melt at 88.5 and 76°, respectively.

3-Methyl-3-ethylpentanone-2 was made according to Nyberg's directions. Its semicarbazone melts at 167.5°, but a mixture with the semicarbazone of (I) melted from 136 to 150°. The 2,4-dinitrophenylhydrazones serve well to differentiate 3-methyl-3-ethylpentanone-2 from (I). The melting points of these derivatives are 92–92.5° and 146.5–147° (in the order that the ketones are mentioned).

The Beckmann Rearrangement of the Oximes (III) and (IV).—The oximes (III) and (IV) were rearranged by means of phosphorus pentachloride in dry ether. A typical example is as follows: 25 g. of (III) was dissolved in 220 ml. of ether which had been carefully dried, rendered alcohol free, and finally distilled from ethylmagnesium bromide; 37 g. of phosphorus pentachloride was added to the ethereal solution while the mixture was shaken and cooled to −5°. After addition of the phosphorus pentachloride was completed, the reaction mixture was allowed to stand overnight. The ether was then removed by distillation, and the residue poured over cracked ice. The aqueous solution was made slightly alkaline with sodium hydroxide and extracted thoroughly with ether. The ether extract was dried over sodium hydroxide and the ether removed by distillation. Five grams of amide (VII) boiling at 125° at 13 mm. was obtained. A very similar process resulted in the production of 9 g. of amide (VIII) boiling at 130–131° at 20 mm. from 11.6 g. of (IV). The yield of amide obtainable from (IV) was much better than that from (III). There was always

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[19] Boiling temperatures (Cottrell), and melting points have been corrected, or were taken with standardized Anschütz thermometers.

[20] Analyses reported by Wheeler, Ref. 9.

[21] "Organic Syntheses," Coll. Vol. I, p. 510.

[22] Drake and Bronitsky, THIS JOURNAL, 52, 3715 (1930); Drake and Sweeney, *ibid.*, 54, 2059 (1932).

a very considerable amount of high boiling residue left after distillation of (VII). Rearrangement of (III) through its benzenesulfonyl ester resulted in no increase in yield; the rearrangement takes place smoothly, however. The high boiling residue is probably the result of rearrangement in the other sense.

The Hydrolysis of the Amides.—Both amides (VII) and (VIII) are very stable toward hydrolysis. Boiling them with alkali or sulfuric acid was found to be without any appreciable effect. However, by heating the amides for five hours at 230–240° in a sealed tube with 85% phosphoric acid diluted with an equal volume of water, hydrolysis was effected. After opening the tubes, the acid solution was extracted with ether to remove unhydrolyzed amide and acidic products, and then cooled strongly and saturated with potassium hydroxide. The amine was either separated in a separating funnel and distilled, or distilled directly from the alkaline solution into 1:1 aqueous hydrochloric acid. From 5 g. of (VII) approximately 5 g. of amine (IX) hydrochloride was obtained; 9 g. of (VIII) yielded 5.5 g. of amine (X).

2-Amino-3,3-dimethylbutane (XII).—Pinacolylamine was prepared by the reduction of pinacone oxime by sodium and alcohol.

1-Amino-2,2-dimethylbutane (XI).—Dimethylethylacetic acid was made from *t*-amyl chloride by use of the Grignard reagent and carbon dioxide. The acid was converted into its chloride by means of thionyl chloride and then into its amide; 22 g. of amide was mixed thoroughly with 32 g. of phosphorus pentoxide and heated gently for about ten minutes. The mixture was then heated more strongly until no more nitrile distilled. After washing the nitrile with water and saturated potassium carbonate solution, it was dried and distilled from a bit of phosphorus pentoxide; 15.8 g. of dimethylethylacetonitrile boiling at 128–129° at 760 mm. was obtained, a yield of about 86% of that theoretically possible. The entire quantity of nitrile was dissolved in 250 ml. of absolute alcohol, and 20 g. of clean sodium cut into small pieces was added. The flask was cooled while the reaction was very vigorous, and finally heated under reflux until all the sodium had dissolved. The solution was then cooled and acidified strongly with hydrochloric acid and most of the alcohol removed by distillation. The aqueous residue was next saturated with potassium carbonate and the amine distilled into 1:1 hydrochloric acid. After evaporation of the solution nearly to dryness on the steam-bath, drying was completed in a vacuum desiccator over potassium hydroxide.

Table III lists the derivatives of amines (IX) and (X).

The Comparison of the Derivatives of Table III with the Corresponding Substances from (XI) and (XII).—The synthetic amines (XI) and (XII) were converted into the P and B derivatives of Table III. The resulting substances were identical in melting point with the compounds listed in the table, and a mixture of approximately equal parts of known and unknown melted at exactly the same point. Amide (VIII) was also prepared from amine (XII); analysis and a "mixed melting point" determination proved the synthetic product identical with the substance obtained from oxime (IV).

TABLE III

THE DERIVATIVES[a] OF THE UNKOWN AMINES (IX) AND (X)

		Carbon, %			Hydrogen, %		
	M. p., °C.	Calcd.	Found		Calcd.	Found	
P—IX[b]	88–88.5	46.12	45.97	46.12	5.16	5.17	5.22
P—X	107	46.12	46.29	46.30	5.16	4.94	5.12
B—IX	59–9.5	59.70	59.66	59.68	7.94	7.78	7.82
B—X	96.0	59.70	59.76	59.29	7.94	7.90	7.65
Amide VIII	68–68.5	67.07	67.23	66.74	11.97	11.63	11.95
Chloroaurate X[c]	189, 195d	16.31	16.08	16.48	3.69	3.85	3.72
		Au 44.67	Au 44.88, 44.71				

[a] In the above table N-(2,4,6-trinitrophenyl)-amines are designated by P, and N-benzenesulfonylamines by B. Thus, P—IX is the N-(2,4,6-trinitrophenyl) derivative of the unknown amine (IX). [b] Prepared from the amine and 2% alcoholic picryl chloride. [c] *Cf.* Markownikoff, *Ber.*, **32**, 1448 (1899).

Conclusion

It is apparent, from the structure of amines (IX) and (X), that amides (VII) and (VIII) from which the amines are produced by hydrolysis must be $C_2H_5C(CH_3)_2CH_2NHCOCH_3$ and $(CH_3)_3CCH(CH_3)NHCOCH_3$. The oximes (III) and (IV), therefore, have the structures $C_2H_5C(CH_3)_2CH_2C{=}(NOH)CH_3$ and $(CH_3)_3CCH(CH_3)C{=}(NOH)CH_3$. Ketones (I) and (II), consequently, are $C_2H_5C(CH_3)_2CH_2COCH_3$ and $(CH_3)_3CCH(CH_3)COCH_3$, respectively, and the original decenes are $C_2H_5C(CH_3)_2CH_2C(CH_3){=}CHCH_3$ and $(CH_3)_3CCH(CH_3)C(CH_3){=}CHCH_3$.

Summary

1. The action of 75% sulfuric acid at 80° on methylisopropylcarbinol has been shown to yield 3,5,5-trimethylheptene-2 and 3,4,5,5-tetramethylhexene-2.

2. These same two substances are also present in the "Diamylene" formed as a by-product during the chlorination of mixed pentanes.

3. Whitmore's theory of the mechanism of the polymerization of olefins by acid catalysts accounts adequately for the formation of 3,5,5-trimethylheptene-2, but not for the production of 3,4,5,5-tetramethylhexene-2.

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