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

Hydrocarbons. XI. Synthesis of Nineteen Decenes[1]

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The syntheses of the decenes described in this paper were made for the purpose of providing reference olefins for comparison with diamylenes made by polymerization of *t*-amyl alcohol. The polymerization study, to be described in another paper, was made to help resolve an apparent difference in some recent work on the decenes.[4,5]

A second purpose was also achieved in that the study of alcohol dehydration has been extended to highly branched decanols.

Experimental

The Grignard reaction was used to a great extent in the preparation of the decanols. The decanols were prepared in relatively large quantities (up to 2500 g.) in order to permit separation of those decenes which were formed in only small amounts.

Several *cis–trans* pairs were encountered in this work; in most cases one member of the pair was obtained in pure form, while the other was obtained as an impure sample, of sufficiently high concentration to give characteristic Raman lines. No attempt has been made to assign *cis* or *trans* configurations to the isomers.

Equipment.—For the preparation of all Grignard reagents, reactors constructed in the laboratories of the Pennsylvania State College were used. These reactors were of sheet copper, cylindrical in shape, and had external water jackets. The separate reactor tops were equipped with a thermometer well, a stainless steel stirrer (200–800 r. p. m.) and a copper coil condenser.

For the precision distillation of olefin mixtures from carbinol dehydrations, the following columns were used, all with 300 cm. of packed section and all equipped with automatic boiling rate controllers and reflux ratio controllers:

Column	I. d., cm.	Diameter of helices packing, mm.	Approximate theor. plates
44	1.1	1.2 stainless steel	250 or more
45	1.5	1.6 stainless steel	200
46	1.7	2.4 glass	125
47	2.2	2.4 glass	100
48	2.2	2.4 glass	100

Since these distillations took weeks or months to complete, the glass pots were sealed directly to the glass columns, and the columns and receivers were nitrogen-blanketed.

Several smaller columns were used for fractionation of small amounts of olefins and for refractionation of cuts from the larger columns.

Raman spectra were obtained through the courtesy of the Petroleum Refining Laboratory and the Physics Department in a spectrograph developed at the Pennsylvania State College.[6]

Alcohol Syntheses. 2,2,3,4-Tetramethyl-3-hexanol (A).—Butadiene (1140 g., 21.1 moles) was added to a mixture of concentrated hydrochloric acid (5 l.) and zinc chloride (2000 g.) in a 12-l. flask at −30°. The reaction mixture was stirred for ten hours while coming to room temperature. Butadiene which vaporized was collected in a cold trap. The oil layer, 1830 ml., was washed with cold water, dried over sodium sulfate and distilled. From three such preparations was obtained 3856 g. (42.6 moles) or 67% of the two butenyl chlorides, 1-chloro-2-butene and 3-chloro-1-butene, b. p. 70–85°, $n^{20}\text{D}$ 1.4290–1.4356.[7] Reaction with magnesium gave 71 and 85% yields of butenylmagnesium chlorides. Pinacolone reacted with this Grignard reagent to give 2,2,3,4-tetramethyl-5-hexen-3-ol, which was hydrogenated to give a 70% yield of the desired saturated decanol.

2,3,4,4-Tetramethyl-2-hexanol (B).—4,4-Dimethyl-2-hexanone[8] was converted in 22% yield to methyl 2,3,3-trimethylpentanoate by bromination and reaction of the bromoketone with sodium methylate.[9] Addition of methylmagnesium bromide to the ester gave 43% of the desired decanol.

2,3,4,4-Tetramethyl-3-hexanol (C).—2,4,4-Trimethyl-3-hexanone was prepared in 73–87% yield from isobutyryl chloride and *t*-amylmagnesium chloride.[10] This ketone was converted in 50% yield to the desired alcohol by reaction with methylmagnesium bromide.

3,4,4,5-Tetramethyl-3-hexanol (D).—Zinc chloride-catalyzed addition of propionic anhydride to tetramethylethylene gave 48% yield of 4,4,5-trimethyl-5-hexen-3-one (b. p. 95° at 30 mm., $n^{20}\text{D}$ 1.4370; hydrogenation of a small sample gave 4,4,5-trimethyl-3-hexanone, b. p. 168° at 739 mm., $n^{20}\text{D}$ 1.4265, 2,4-dinitrophenylhydrazone, m. p. 117–119°). Addition of methylmagnesium bromide to the unsaturated ketone gave 43% of 3,4,4,5-tetramethyl-5-hexen-3-ol (b. p. 75° at 3 mm., $n^{20}\text{D}$ 1.4620), which was then hydrogenated to the saturated decanol.

3,4,5,5-Tetramethyl-3-hexanol (E).—4,4-Dimethyl-2-pentanone was converted in 42% yield to methyl 2,3,3-trimethylbutanoate (b. p. 44° at 17 mm., $n^{20}\text{D}$ 1.4120–1.4130) by bromination and reaction with sodium methylate.[9] Addition of ethylmagnesium chloride to the ester gave 37% of 4,4,5-trimethyl-3-hexanone (b. p. 90–105° at 55 mm., $n^{20}\text{D}$ 1.4205–1.4214). Reaction of this ketone with methylmagnesium bromide gave only 16% conversion to the desired decanol; the remainder of the ketone was recovered unreacted.

3,5,5-Trimethyl-3-heptanol (F).—The alcohol was prepared in 84% yield by the addition of ethylmagnesium chloride to 4,4-dimethyl-2-hexanone.[8]

Alcohol Dehydrations.—The results of the alcohol dehydrations are given in Table I. Structures of the olefins identified by number in Table III were established by ozonolyses. I gave formaldehyde (dimedon, m. p. 189°, mixed m. p. 189°) and 2,2,4-trimethyl-3-hexanone (2,4-dinitrophenylhydrazone, m. p. 126°, mixed m. p. 126–127°); II gave formaldehyde and a ketone which gave a 2,4-dinitrophenylhydrazone, m. p. 105°; this ketone was presumed to be 3,3,4-trimethyl-2-hexanone, since it was non-identical with other branched C_9 ketones found in this

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(1) For Paper X, see Whitmore, Whitmore and Cook, THIS JOURNAL, **72**, 51 (1950). Paper XXI on Dehydration of Alcohols presented in part before the Organic Division at the New York Meeting of the American Chemical Society, Sept. 15, 1947; for Paper XX, see Dixon, Cook and Whitmore, THIS JOURNAL, **70**, 3361 (1947).

(2) Monsanto Chemical Company, Dayton, Ohio; research work performed during academic leave of absence from Monsanto.

(3) Deceased June, 1947.

(4) Whitmore and Mosher, THIS JOURNAL, **63**, 1120 (1941).

(5) Johnson, *ibid.*, **69**, 146 (1947).

(6) Fenske, Braun, Wiegand, Quiggle, McCormick and Rank, *Ind. Eng. Chem., Anal. Ed.*, **19**, 700 (1947).

(7) The procedure for making the butenyl chlorides was worked out by J. A. Dixon and N. C. Cook of this Laboratory.

(8) Prepared by Mr. James Harvey of this Laboratory by sulfuric acid–dichromate oxidation of a selected fraction of Sharples diamylenes.

(9) Aston, Clarke, Burgess and Greenburg, THIS JOURNAL, **64**, 300 (1942).

(10) Stehman, Cook and Whitmore, *ibid.*, **71**, 1509 (1949).

TABLE I

DEHYDRATION OF ALCOHOLS

Alcohol	Dehydration method	Composition of product
A	Al_2O_3[a]	93% I; 5% II, III and IV
A	H_2SO_4[b]	50% I; 13% II; 37% III and IV
B	Al_2O_3[c]	62% V; 7% VI
C	Al_2O_3[a]	85% VII; 2% VI; 8% VIII, IX and X
D	Al_2O_3[a]	3% (?) VII; 3% (?) VIII; 84% IX and X
E	Al_2O_3[c]	16% III and IV; 9% XII; 63% XIII and XIV
F	Al_2O_3[a]	14% (?) XV; 39% (?) XVI and XVII; 47% XVIII and XIX

[a] Glass tube 22 mm. i. d. having 85 cm. packed with Alorco activated alumina grade F-1, 4–8 mesh. [b] Refluxed with 25% of 25% sulfuric acid, olefin removed as formed. [c] Glass tube 10 mm. i. d. having 25 cm. packed with Alorco activated alumina grade F-1, 14–20 mesh.

work; III gave methyl ethyl ketone (2,4-dinitrophenylhydrazone, m. p. 106°, mixed m. p. 106°) and pinacolone (2,4-dinitrophenylhydrazone, m. p. 119°, mixed m. p. 123°); IV, b. p. 4° higher than III, was not identified by ozonolysis, but from its occurrence with III and from its partially similar Raman spectra lines was tentatively assumed to be the higher boiling geometric isomer of III.

V gave formaldehyde (dimedon, m. p. 189°, mixed m. p. 189°) and 3,4,4-trimethyl-2-hexanone (2,4-dinitrophenylhydrazone, m. p. 112°, mixed m. p. 112°). VI gave acetone (2,4-dinitrophenylhydrazone, m. p. 122°, mixed m. p. 124°) and 3,3-dimethyl-2-pentanone (2,4-dinitrophenylhydrazone, m. p. 110°, mixed m. p. 110°).

VII gave formaldehyde (dimedon, m. p. 188°, mixed m. p. 188°) and 2,4,4-trimethyl-3-hexanone (2,4-dinitrophenylhydrazone, m. p. 116°, mixed m. p. 117°).

VIII on ozonolysis gave 4,4,5-trimethyl-3-hexanone (2,4-dinitrophenylhydrazone, m. p. 117–119°, mixed m. p. 117–118°). IX was not identified by ozonolysis, but from its occurrence along with X and from its partially similar Raman spectra lines is tentatively assumed to be the lower-boiling geometric isomer of X. X gave acetaldehyde (2,4-dinitrophenylhydrazone, m. p. 148°, mixed m. p. 148°) and 3,3,4-trimethyl-2-pentanone (2,4-dinitrophenylhydrazone, m. p. 146–147°, mixed m. p. 146–147°).

TABLE II

DECANOLS

Decanol	B. p., °C., 760 mm.[a]	$n^{20}D$[b]	d^{20}_4[c]	Abs. visc., centistokes[d]	Mol. refraction[e]	Analyses, % found[f] C	H
2,2,3,4-Tetramethyl-3-hexanol (A)[g]	191.8	1.4469	0.8584	6.24	49.26	76.14	13.78
2,3,4,4-Tetramethyl-2-hexanol (B)	180–185[h]	1.4490	....	..	..	75.50	13.58
2,3,4,4-Tetramethyl-3-hexanol (C)[i]	200.6	1.4530	.8745	7.13	48.92	76.02	13.66
3,4,4,5-Tetramethyl-3-hexanol (D)	201.9	1.4533	.8742	5.45	48.96	76.14	13.84
3,4,5,5-Tetramethyl-3-hexanol (E)	194.6	1.4490	.8623	6.87	49.23	75.66	13.82
3,5,5-Trimethyl-3-heptanol (F)[j]	195.6	1.4453	.8558	8.38	49.25	75.81	13.64

[a] Boiling points were determined in a Cottrell apparatus at reduced pressure, and by the Siwoloboff micro method at atmospheric pressure (725–740 mm.). The determined values were plotted, and the boiling points at 760 mm. were read from the curves. [b] Measured on a 5-place Valentine refractometer. [c] Measured in standard pycnometers. [d] Measured at 20° in Cannon type E viscosimeters. [e] Calcd. for $C_{10}H_{21}OH$: 49.90. [f] Calcd. for $C_{10}H_{21}OH$: C, 75.87; H, 14.02. [g] Reported by Nasorov,[11] b. p. 190–193°, d^{10}_4 0.867, $n^{17}D$ 1.4480. [h] Estimated from column head temperatures, 75–78° at 10 mm., uncor. [i] Reported by Nasorov,[11] b. p. 197–199°, d^{18}_4 0.876, $n^{17}D$ 1.4586. [j] Reported by Whitmore and Mosher,[4] b. p. 86° at 30 mm., $n^{20}D$ 1.4455, d^{20}_4 0.8513.

XI gave formaldehyde (dimedon, m. p. 189°, mixed m. p. 189°) and a ketone which produced a 2,4-dinitrophenylhydrazone that could not be crystallized. XI on hydrogenation gave a decane (b. p. 171.2°, $n^{20}D$ 1.4362) unlike any other decane synthesized in this work; mol. wt.: found, 139 and 141; calcd., 142. Thus the structure for XI has not been definitely established; however, the 2,3,4-trimethyl-3-ethyl-1-pentene structure is tentatively assigned on the basis of the high-boiling point of the olefin and the paraffin, and by a consideration of the rearrangement possibilities from the parent alcohol.

XII gave formaldehyde (dimedon, m. p. 189–190°, mixed m. p. 189°), which proved it to be a methylene olefin, and a ketone which produced an oily 2,4-dinitrophenylhydrazone; this olefin was believed to be 3,4,4-trimethyl-2-ethyl-1-pentene. XIII gave acetaldehyde (2,4-dinitrophenylhydrazone, m. p. 147°, mixed m. p. 148°) and 3,4,4-trimethyl-2-pentanone (2,4-dinitrophenylhydrazone, m. p. 110°, mixed m. p. 110°). XIV, b. p. 0.3° higher than XIII, was not identified by ozonolysis, but from its occurrence with XIII and from its partially similar Raman spectra lines, was tentatively assumed to be the higher boiling geometric isomer of XIII.

Certain fractions from dehydration of alcohol F gave formaldehyde (dimedon, m. p. 189°, mixed m. p. 189°), methyl ethyl ketone (2,4-dinitrophenylhydrazone, m. p 112°, mixed m. p. 112°) and 5,5-dimethyl-3-heptanone (2,4-dinitrophenylhydrazone, m. p. 102°, mixed m. p. 98°); these data, with Raman spectra, indicated the presence of XV, XVI and XVII. Ozonolysis of samples of intermediate fractions gave formaldehyde, acetaldehyde and methyl ethyl ketone; the only derivative that could be prepared from the heavier oils from ozonolysis was a 2,4-dinitrophenylhydrazone (m. p. 95–96°; mixed m. p. with known derivative of 5,5-dimethyl-3-heptanone, 97–98°). A sample of higher fractions gave, on ozonolysis, acetaldehyde (2,4-dinitrophenylhydrazone, m. p. 158°, mixed m. p. 156°) and 4,4-dimethyl-2-hexanone (2,4-dinitrophenylhydrazone, m. p. 81–82°, mixed m. p. 75–78°); these data, with Raman spectra, indicated the presence of XVIII and XIX. Raman spectra indicated that at least four and probably five decenes were present; the spectra also indicated that the fractionations had given only incomplete separation of isomers.

Physical Properties of Alcohols and Olefins.—The physical properties of the six decanols and nineteen decenes are given in Tables II and III. The properties of the olefins were determined on small samples refractionated from pure fractions.

Discussion

Unrearranged products predominated in the alcohol dehydrations. Ethylidene olefins were the most readily formed; if they could not be formed without rearrangement, then methylene olefins predominated. This phenomenon was previously noted[12] in the dehydration of tertiary alcohols.

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(11) Nasorov, *Ber.*, **70B**, 599 (1937).

(12) Whitmore and Laughlin, THIS JOURNAL, **54**, 4011 (1932); **55**, 3732 (1933).

TABLE III

DECENES

Decene	No.	B. p., °C. 760 mm.	$n^{20}D$[a]	d^{20}_4[b]	Abs. visc. centistokes[c]	Molar refraction[d]
3-Methyl-2-*t*-butyl-1-pentene	I	148.1	1.4262	0.7560	0.921	47.56
3,4,4-Trimethyl-2-ethyl-1-pentene	XII	149.9	1.4310	.7683	1.071	47.26
3,3-Dimethyl-2-isopropyl-1-pentene	VII	151.0	1.4290	.7620	0.957	47.45
4,4-Dimethyl-2-ethyl-1-hexene	XV	151.5	1.4310	.7647	0.924	47.48
3,4,5,5-Tetramethyl-2-hexene (low b.)[e]	XIII	151.8	1.4361	.7679	1.045	47.77
3,4,5,5-Tetramethyl-2-hexene (high b.)[e]	XIV	152.1	1.4370	.7724	1.088	47.57
2,3,4,4-Tetramethyl-1-hexene	V	155.2	1.4421	....	...	...
3,5,5-Trimethyl-3-heptene (low b.)[f]	XVI	155.8	1.4328	.7641	0.799	47.68
3,5,5-Trimethyl-3-heptene (high b.)[f]	XVII	156	....	....	...	...
3,3,4-Trimethyl-2-ethyl-1-pentene	VIII	157	1.4378	.775	.937	47.34
2,3,3,4-Tetramethyl-1-hexene	II	157	1.4322	.7759	.959	46.91
2,2,3,4-Tetramethyl-3-hexene (low b.)	III	157	1.4375	.7706	1.003	47.73
2,2,3,4-Tetramethyl-3-hexene (high b.)	IV	158	1.434	....	...	...
3,4,4,5-Tetramethyl-2-hexene (low b.)	IX	159	1.4395	.7800	0.976	47.34
3,4,4,5-Tetramethyl-2-hexene (high b.)	X	160.0	1.4430	.7831	1.129	47.48
3,5,5-Trimethyl-2-heptene (low b.)[g]	XVIII	160.6	1.4358	.7744	0.959	47.33
2,3,4,4-Tetramethyl-2-hexene[h]	VI	161	1.4482	....	...	...
3,5,5-Trimethyl-2-heptene (high b.)[g]	XIX	162.1	1.4388	.7756	0.876	47.55
2,3,4-Trimethyl-3-ethyl-1-pentene	XI	171	1.4402	....	...	...

[a] Measured on a 5-place Valentine refractometer. [b] Measured in standard pycnometers. [c] Viscosities were measured at 20° in Cannon type E viscosimeters. [d] Calcd. for $C_{10}H_{20}$: 47.91. [e] Previously reported,[4] b. p. 152° at 746 mm., $n^{20}D$ 1.4360. [f] Previously reported,[13] b. p. 157–157.5° at 759 mm., d^{21}_{21} 0.7729. [g] Previously reported,[4] b. p. 158° at 742 mm., $n^{20}D$ 1.4393. [h] Previously reported, b. p. 45–50° at 15 mm.,[14] $n^{17}D$ 1.4385.[15]

Only small amounts of olefins with double bonds connecting tertiary carbon atoms, and only traces of rearranged products, were formed. Methyl groups from *t*-amyl structures shifted more readily than methyl groups from *t*-butyl structures.

cis and *trans* structures cannot be assigned to geometric isomer pairs found in this work. The assignments on the basis of Raman data[16] would differ in many cases from the assignments on the basis of boiling points. It is believed that chemical reaction rate studies will be necessary before the assignments can be made.

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Summary

Six tertiary decanols were synthesized and dehydrated over alumina to the decenes.

Nineteen decenes were obtained by precise fractionation of the dehydration mixtures. Most of these decenes were characterized by boiling point, refractive index, Raman spectra, density and viscosity, and were defined in structure by ozonolyses.

Dehydration with formation of methylene and ethylidene olefins predominated; only small amounts of the olefins with double bonds connecting tertiary carbon atoms were formed.

Small quantities of products were formed in which a single 1,2-rearrangement of a methyl or an ethyl group occurred; no product was formed involving a 1,3-rearrangement, or involving more than a single shift.

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(13) Kondakow, *J. Russ. Phys. Chem. Soc.*, **28**, 789 (1896); Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939, p. 255.

(14) Norris and Joubert, THIS JOURNAL, **49**, 873 (1927).

(15) Landolt and Jahn, *Z. physik. Chem.*, **10**, 289 (1892); Egloff, ref. 14, p. 256.

(16) Hibben, "The Raman Effect and its Chemical Applications," Reinhold Publishing Corp., New York, N. Y., 1939, p. 168.