sults were the same as in experiments in which catalyst was distilled into monomer on a vacuum line and the reaction tubes then sealed in absence of air.

Polymers were worked up and analyzed as described in previous papers, and results of sample experiments are listed in Table III. Results on a number of systems summarized in Table II are omitted since single experiments at 1:1 feed only were carried out. Further, some of these yielded dark, sticky, or insoluble polymers which may have retained some monomer during purification. Accordingly, here only an upper limit to the amount of the least reactive monomer in the polymer is indicated. For the styrene–methacrylate systems catalyzed by light or magnesium perchlorate or carried out in thymol, monomer reactivity ratios were determined graphically in the usual way[2b] and used to calculate the compositions in Table I. For the remainder of the examples given, the analytical results illustrate that no copolymer was formed.

Summary

1. The initial copolymer formed from 1:1 styrene–methyl methacrylate mixtures is shown to be essentially pure polystyrene for the stannic chloride or boron trifluoride-catalyzed reaction and essentially pure polymethyl methacrylate for the reaction in the presence of sodium or potassium.

2. The results are considered as evidence for carbonium ion and carbanion mechanisms respectively for polymerizations in the presence of these two classes of catalysts, and it is suggested that copolymerization studies should provide a sensitive tool for establishing the mechanism of polymerization in the presence of other catalysts.

3. Data are presented on copolymer compositions obtained in the non-radical copolymerizations of some other monomer pairs, and the effects of structure on reactivity in ionic polymerizations are discussed.

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

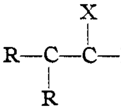
Hydrocarbons. X.[1] Three New Octenes

BY F. C. WHITMORE,[2] H. E. WHITMORE[3] AND N. C. COOK

Introduction

Of the 66 possible structural isomers of the octenes, excluding *cis* and *trans* forms, 63 have been reported. This paper reports the syntheses of the three remaining octenes: 5,5-dimethyl-2-hexene, 2,4-dimethyl-3-hexene and 3-ethyl-4-methyl-1-pentene.

The dimethylhexenes were made as part of a program involving a spectrometric study of olefin types. These olefins were prepared by dehydration of the appropriate alcohols, which were readily synthesized through the Grignard reaction. Separation of the olefins, especially the geometric isomers, required columns of more than 200 theoretical plates.

3-Ethyl-4-methyl-1-pentene was made primarily to complete the octene series. The difficulty of making halides of the type[4]  $R—\underset{R}{C}—\overset{X}{C}—R$ ruled out the probability of making the compound through such a Grignard reagent. After several unsuccessful attempts, a method was developed which involved the acetylation of 2-methyl-2-pentene to give 3-ethyl-4-methyl-4-pentene-2-one. Complete hydrogenation of this ketone, followed by dehydration of the alcohol, gave a 30% yield of 3-ethyl-4-methyl-1-pentene, accompanied by other isomers which were easily separated.

Although all the octene isomers have now been reported, a considerable number should be resynthesized, particularly those having geometric forms. The early investigators were unable to prepare in high purity many of the close boiling isomers because of the lack of precision fractionating equipment. Some work of this nature is in progress in this Laboratory and will be reported in subsequent papers.

Experimental

5,5-Dimethyl-2-hexene.—Ethylene was alkylated with *t*-butyl chloride in the presence of aluminum chloride[5] to give a 65% yield of 3,3-dimethyl-1-chlorobutane.

3,3-Dimethylbutylmagnesium chloride was prepared in 90% yield (20 moles) in a water-jacketed copper Grignard reactor (20-liter capacity), equipped with a motor driven stirrer, dropping funnel and condenser. From the reaction of 867 g. of redistilled acetaldehyde with the Grignard reagent was obtained a 60% yield of fractionated 5,5-dimethyl-2-hexanol, b. p. 166°, $n^{20}D$ 1.4229.

The above alcohol was dehydrated at 360° over Grade F-1, Mesh 4-8 activated alumina (Alorco) at a feed rate of 600 ml. per hour. Fractionation of 1840 g. of the dehydration product through a column of more than 200 theoretical plates,[6] gave 218 g. (cuts 4–12) of 5,5-dimethyl-1-hexene (I), b. p. 103°, $n^{20}D$ 1.4040; the 416 g. of intermediate fractions; 40 g. (cuts 38–41) of a low boiling form of 5,5-dimethyl-2-hexene (II), b. p. 104°, $n^{20}D$ 1.4051; 72 g. of intermediate fractions; and 560 g. (cuts 49–59) of

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[1] For paper IX see, Moersch and Whitmore, THIS JOURNAL, **71**, 819 (1949).

[2] Deceased; Harvard University Ph.D. 1914.

[3] Present address: Universal Oil Products Co., Chicago, Illinois.

[4] Whitmore and Johnston, THIS JOURNAL, **55**, 5020 (1933).

[5] Schmerling, *ibid.*, **67**, 1778 (1945).

[6] Column description: 300 cm. × 1.5 cm., packed with $^1/_{16}''$ stainless steel helices, single turn.

TABLE I

SUMMARY OF PHYSICAL PROPERTIES

	B. p., °C.[a] 760 mm.	dt/dp[b] 760 mm.	$n^{20}D$	dn/dt[c]	d^{20}_4	dd/dt[c]	Viscosity centipoises 20°	30°	40°
5,5-Dimethyl-1-hexene	103.1	0.047	1.4043	0.00049	0.7060	0.00086	0.469	0.417	0.373
low-5,5-Dimethyl-2-hexene	104.1	.046	1.4055	.00050	.7066	.00086	.493	.437	.391
high-5,5-Dimethyl-2-hexene	106.9	.047	1.4113	.00050	.7169	.00088	.525	.466	.417
low-2,4-Dimethyl-3-hexene	107.6	.046	1.4126	.00050	.7145	.00087	.434	.391	.353
high-2,4-Dimethyl-3-hexene	109.0	.045	1.4140	.00051	.7178	.00086	.458	.411	.370
2,4-Dimethyl-2-hexene	110.6	.047	1.4118	.00049	.7213	.00085	.455	.407	.367
3-Ethyl-4-methyl-1-pentene	107.5	.047	1.4097	.00049	.7200	.00083	.452	.405	.365
low-3-Ethyl-4-methyl-2-pentene	114.3	.047	1.4210	.00049	.7350	.00085	.477	.427	.385
high-3-Ethyl-4-methyl-2-pentene	116	.047	1.424	.00049	.739	.00085	.45	.41	.37

[a] None of the compounds had a boiling range greater than 0.05°. [b] Determined from data taken at 760 and 740 mm. [c] Determined from data taken at 20, 30 and 40°.

the high boiling form of 5,5-dimethyl-2-hexene (III), b. p. 106°, $n^{20}D$ 1.4112.

On ozonization I gave formaldehyde and II and III gave acetaldehyde, identified by m. p. and mixed m. p. of their 2,4-dinitrophenylhydrazones.

Additional physical properties of the final olefin products can be found in Table I.

2,4-Dimethyl-3-hexene.—The above described Grignard reactor was charged with 293 g. (27.5 moles) of isobutyryl chloride. To the acid chloride was added 405 g. (25.1 moles) of *s*-butylmagnesium bromide over a five-hour period at 18°, and then stirred overnight. From this reaction was obtained a 70% yield of 2,4-dimethyl-3-hexanone, b. p. 145°, $n^{20}D$ 1.4059. The ketone was hydrogenated in a rocking type bomb (American Instrument Co.) with copper chromite catalyst at 1800 p.s.i. and 175°. The hydrogenated product was fractionated through a 35-plate column giving 2,4-dimethyl-3-hexanol, b. p. 160–162°, $n^{20}D$ 1.4295–1.4300.

2,4-Dimethyl-3-hexanol was also prepared from the reaction of 5760 g. (80 moles) of isobutyraldehyde and 80 moles of *s*-butylmagnesium bromide in 30% yields, b. p. 160°, $n^{20}D$ 1.4316.

The above alcohol, 1700 g., was dehydrated over alumina at 350° and the olefin mixture, 1472 g., fractionated through a >200-plate column,[6] data of which are shown in Fig. 1. The three main components were the low-boiling form of 2,4-dimethyl-3-hexene (IV), high-boiling form of 2,4-dimethyl-3-hexene (V) and 2,4-dimethyl-2-hexene (VI). A small amount of 3,5-dimethyl-2-hexene (VII) was also obtained.

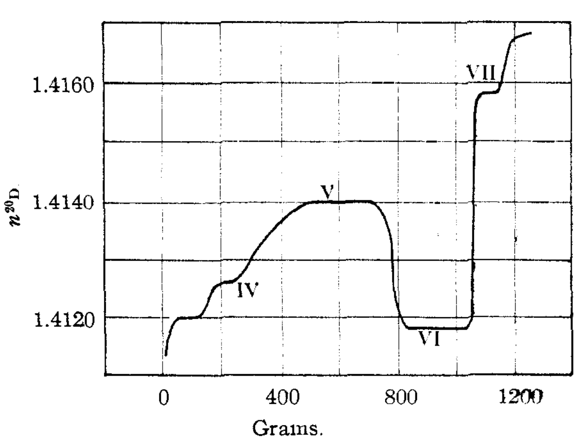

Fig. 1.—Fractionation curve for dehydration products of 2,4-dimethyl-3-hexanol.

The structures of IV and V were established by ozonolyses, and those of VI and VII by comparing the Raman spectra with those of known samples and their physical properties with literature values.[7]

None of the compounds resulting from the rearrangement of the methyl groups were identified. The 3,4-dimethyl-2-hexene and the 2,3-dimethyl-3-hexene were undoubtedly present however in the first and last portions of the fractionation (Fig. 1). Infrared spectra showed a minimum of seven isomers resulting from the dehydration.

3-Ethyl-4-methyl-1-pentene.[8]—Ethylisopropylcarbinol, 2297 g., was dehydrated over alumina. The olefin mixture was fractionated, yielding 951 g. of 2-methyl-2-pentene, b. p. 66°, $n^{20}D$ 1.4001. This olefin was acetylated[9] in the following manner: to a 12-liter round-bottom flask equipped with a motor driven stirrer was added 951 g. (11.3 moles) of olefin and 1390 g. (13.6 moles) of acetic anhydride. To this mixture was added 452 g. of zinc chloride (40 g. per mole of olefin) over a period of two and one-half hours at 17°. The solution was stirred for six hours, after which 2 kg. of ice was added, and the mixture stirred for two more hours. An equal volume of water was added to the decanted organic layer, the mixture neutralized with sodium bicarbonate and the organic layer removed and steam distilled. The resulting product was fractionated giving a 20% yield of unsaturated ketones, b. p. 68–75° at 50 mm., $n^{20}D$ 1.4250–1.4350. Combined fractions (386 g.), boiling between 68–69°, $n^{20}D$ 1.4253–1.4281, were hydrogenated in a rocking type bomb using 19 g. of copper chromite catalyst at 2000 p.s.i., absorbing 2 equivalents of hydrogen per mole. The resulting alcohol mixture was fractionated and gave a yield of 50 g. of 3-ethyl-4-methyl-2-pentanol, b. p. 164°, $n^{20}D$ 1.4331. This alcohol was dehydrated over alumina at 350°, and the resulting olefins fractionated to give a 30% yield of 3-ethyl-4-methyl-1-pentene (VIII) and a 70% yield of the mixed geometric isomers of 3-ethyl-4-methyl-2-pentene (IX) and (X) (Table I).

For the resynthesis of VIII, 2-methyl-1-pentene (Connecticut Hard Rubber Co.) was isomerized to 2-methyl-2-pentene. This conversion was effected by stirring six liters of the 1-olefin with 50% sulfuric acid for five hours at room temperature until the refractive index showed no further

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(7) Doss, "Physical Constants of the Principal Hydrocarbons," 4th edition, 1943.

(8) It was thought possible to make ethylisopropylvinylcarbinol through the use of ethyl acrylate and ethyl and isopropyl Grignard reagents. This alcohol would then have been converted through several steps to the desired olefin. The reaction was attempted in the following manner: normal and reverse addition of ethyl acrylate to a 45–55 mixture of isopropylmagnesium bromide and ethylmagnesium bromide. In each of these procedures the resulting product was a viscous polymerized mass.

An attempt was then made to effect an aldol condensation between methyl isobutyl ketone and acetaldehyde to give 3-ethyl-4-methyl-4-pentene-2-one. Using the method of Landau and Irany, *J. Org. Chem.*, **12**, 422 (1947), two unsuccessful reactions were conducted, recovering 96% of the ketone in each case.

(9) Byrns and Doumani, *Ind. Eng. Chem.*, **35**, 352 (1943).

change (final value 1.4004). Fractionation of the isomerized product gave 4.9 liters (3316 g. 80% yield) of 2-methyl-2-pentene, which was acetylated in the same manner as above, except that the acetylated product was steam distilled without treatment with $NaHCO_3$. Fractionating the acetylation products, 1760 g., gave 350 g. of recovered olefin (most of the recovered olefin was separated during the steam distillation); 566 g. ketonic material, b. p. 60–64° (40 mm.), n^{20}_{D} 1.4113–1.4284; 571 g. of 3-ethyl-4-methyl-4-pentene-2-one,[10] b. p. 64.5° at 48 mm., n^{20}_{D} 1.4285–1.4287 and 500 g. of higher boiling material (residue). The unsaturated ketone was hydrogenated over copper chromite and fractionated (510 g.) to give 175 g. of foreshot-containing ketone and 310 g. of 3-ethyl-4-methyl-2-pentanol, b. p. 165°, n^{20}_{D} 1.4331.

The above alcohol, 310 g., was dehydrated over alumina as previously described, giving 260 g. of olefins which were fractionated to yield 100 g. of 3-ethyl-4-methyl-1-pentene, b. p. 106°, n^{20}_{D} 1.4095, and 150 g. of 3-ethyl-4-methyl-2-pentene, b. p. 114–115°, n^{20}_{D} 1.4210–1.4220. Ozonolysis of VIII gave formaldehyde identified as its 2,4-dinitrophenylhydrazone. No derivative was obtained for the other ozonization product, 3-methyl-2-ethylbutanal, which is unknown. Further proof of structure is based on the fact that the accompanying olefinic products agreed with the physical properties reported for 3-ethyl-4-methyl-2-pentene.[11] Also the infrared spectrum of VIII showed it to be a type I olefin.

Discussion

2,4-Dimethyl-3-hexene.—The method chosen for this synthesis was the dehydration of 2,4-dimethyl-3-hexanol since it was desired to obtain more dehydration data on secondary alcohols. The olefins from the alumina dehydration of 2,4-dimethyl-3-hexanol were found to be a mixture of several isomers as expected. The main portion of the mixture was the desired *cis* and *trans* isomers. Thus, as Fig. 1 shows, the dehydration was slightly more to the secondary butyl group than to the isopropyl group.

Secondary alcohols with double branching on the α-carbon give on dehydration, even with the mildest dehydrating agents, large amounts of rearranged products. Thus pinacolyl alcohol gives only rearranged products with the more acid catalyst and 40% rearranged products over alumina.[12] Secondary alcohols with no α-branching in general give no detectable rearrangement over alumina.[13] However, the dehydration of a secondary alcohol with single branching on the α-carbon leads to rearrangement of the α-hydrogen or alkyl groups in the order of 5%. 2,4-Dimethyl-3-hexanol has branching on both α-carbons and the products from such rearrangements (25%) undoubtedly explain the first and last portions of the curve (Fig. 1).

Summary

The last three of the 66 isomeric octenes have been synthesized, 5,5-dimethyl-2-hexene, 2,4-dimethyl-3-hexene and 3-methyl-4-ethyl-1-pentene. The geometric forms of the first two have also been separated. Three other octenes, 5,5-dimethyl-1-hexene, 2,4-dimethyl-2-hexene, and 3-ethyl-4-methyl-2-pentene (*cis* and *trans*) have also been made in the course of the other preparations. The principal physical properties have been reported on highly purified samples of all the above isomers.

The dehydration of 2,4-dimethyl-3-hexanol has been studied as an example of a secondary alcohol with single branching on both α-carbons. Rearrangements of the order of 25% occurred, most of which resulted in changes of the carbon skeleton.

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[10] The unconjugated double bond position has been assumed from the low refractive index and b. p. as compared with other similar structures that are known.

[11] Reed, Doctor's Dissertation, Ohio State University, 1938.

[12] Whitmore and Meunier, THIS JOURNAL, **55**, 3721 (1933); Cramer and Glasebrook, *ibid.*, **61**, 230 (1939).

[13] Whitmore and Homeyer, *ibid.*, **55**, 4194 (1933).

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

The Reaction of Mesityl Oxide with *t*-Butylmagnesium Chloride

BY FRANK C. WHITMORE,[1] D. P. J. GOLDSMITH,[2] N. C. COOK, J. C. YARZE[3] AND G. G. ECKE

The addition of mesityl oxide to *t*-amylmagnesium chloride[4] gives a 16% yield of the 1,4-addition product, 4,4,5,5-tetramethyl-2-heptanone. Stevens[5] was unable to obtain the corresponding ketone by addition of mesityl oxide to *t*-butylmagnesium chloride at −10 to −20°. We have now obtained this ketone, 4,4,5,5-tetramethyl-2-hexanone in 3% yield by adding mesityl oxide to *t*-butylmagnesium chloride at 35° in conventional glass equipment and in 6.3% yield in a copper reactor at 15–25°. The ketone was degraded by the haloform reaction to 3,3,4,4-tetramethylpentanoic acid, identical with that obtained by the reaction of carbon dioxide with the Grignard reagent of chlorohexamethylethane.[6] The ketone was also converted into the hydrocarbon 2,2,3,3-tetramethylhexane, identical with a sample previously obtained in this Laboratory.

The other products of the reaction were 20% recovered mesityl oxide, 35% of two unrearranged C_{10} dienes and 1% of rearranged C_{10} diene from the dehydration of 2,2,3,5-tetramethyl-4 or 5-hexen-3-ol, 2% of 2,2,3,5-tetramethyl-4 or 5-hexen-3-ol and 10% of residue. A considerable

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[3] Present address: The M. W. Kellogg Co., Jersey City, N. J.

[4] Whitmore and co-workers, THIS JOURNAL, **63**, 650 (1941).

[5] Stevens, *ibid.*, **57**, 1112 (1935).

[6] Whitmore, Marker and Plambeck, *ibid.*, **63**, 1626 (1941).