[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE PREPARATION OF CERTAIN HOMOLOGOUS LIQUID HYDROCARBONS[1, 2]

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Received March 24, 1955

In connection with studies on the physical properties of liquids of potential value as lubricating oils, it was desirable to study certain characteristics of a series of singly branched acyclic hydrocarbons. The series comprises homologous alkanes of the type $C_9H_{19}CHRC_{10}H_{21}$ where R includes the normal alkyls from C_5H_{11}- through C_9H_{19}-. An unsymmetrical ketone, 10-eicosanone, was selected as the basis for preparation of a number of such compounds, and the normal alkyl halides from amyl through decyl were employed for the Grignard reaction. The carbinols produced in this manner are new compounds, but since they were of interest only as intermediates in the preparation of the hydrocarbons, no microanalyses were obtained for them.

It is obvious that the dehydration of tertiary carbinols bearing different alkyl groups must lead to mixed alkenes with all possible configurations. Thus, any conclusions as to properties of such alkenes are scarcely of significance except as an indication of gross differences from the saturated hydrocarbons.

Prior to the reported dehydration of the carbinols, attempts were made to reduce them directly to the saturated hydrocarbons with red phosphorus and hydrogen iodide, but only iodine-contaminated alkenes were obtained. Likewise, pyrolysis of the acetate was unsuccessful, affording impure products shown to be highly contaminated with undecomposed esters by the presence of strong carbonyl absorption in the infrared. Ultimately, the carbinols were successfully dehydrated by the method of Whitmore, *et al.* (1) in which the carbinol is heated to 170° over anhydrous copper sulfate in a nitrogen atmosphere.

Various preliminary attempts to reduce the alkenic mixtures proved to be unsatisfactory: with Adams' catalyst at 65°/45 p.s.i. two days were required for complete reaction, and a reaction using the same catalyst at 85°/1000 p.s.i. was not complete in comparable time. The use of Raney nickel (2) clearly afforded the best method of reduction, as reported below.

In reporting the final hydrocarbons, use has been made of the molecular refractivities as criteria of purity for two reasons: first, the allowable errors in carbon-hydrogen analysis may exceed the differences between individual members of the series; and second, the hydrocarbons proved rather difficult to burn completely for such analyses.

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[1] Work done under Contract No. W-33-038-ac-21457, Project MX-982 between the Wright Air Development Center, U. S. Air Force, and the Engineering Research Institute of the University of Michigan.

[2] Abstracted from a portion of WADC Technical Report 54-45, June, 1953. Released for publication by Mr. Harold Rosenberg, Senior Project Engineer, Polymer Section, Organic Materials Branch, Materials Laboratory, Directorate of Research.

EXPERIMENTAL[3, 4]

The experiments described in detail are characteristic, the syntheses being summarized in Table I.

10-Eicosanone. This substance was prepared according to the general method of Gilman (3). To 60 g. (2.5 gram-atoms) of magnesium was added 10 g. of 1-bromodecane in 25 ml. of dry ether. After the reaction started there was added 500 ml. of dry ether, and then a solution of 441 g. (2.5 moles) of 1-chlorodecane in 300 ml. of dry ether was added dropwise with stirring to maintain a steady reflux. Upon completion of the reaction the flask was cooled in an ice-bath and 238 g. (1.3 moles) of cadmium chloride was added with stirring. Next the ice-bath was removed and the stirring was continued for 0.5 hr. The ice-bath then was replaced, and 438 g. of decanoyl chloride was added slowly, the vigor of the reaction being moderated by alternate cooling and warming. At the end of the addition of the acid chloride the mixture was refluxed for 1 hr. and then was poured into a mixture of ice and dilute sulfuric acid. More ether was added to dissolve the ketone, and the ethereal solution was separated and washed successively with water, 5% sodium bicarbonate and water, and then it was dried over magnesium sulfate. After removal of the ether the residue was distilled at 155–162°/1.0 mm. to give 397 g. (58.5%) of 10-eicosanone. The ketone was recrystallized from methanol to give white plates, m.p. 54.0–54.5° uncorr. No derivatives could be readily obtained.

TABLE I

PROPERTIES OF SOME C_{25} TO C_{30} SINGLY BRANCHED ALKANES OF THE TYPE C_9CRC_{10} AND THEIR INTERMEDIATES

(Side Chain Carbons)	Carbinol		Alkene		Alkane			MR_D		Analyses[a]	
	Yield, %	b.p., °C.	Yield, %	b.p., °C.	b.p., °C.	n_D^{25}	sp. gr. 22.5/4	Calc'd	Found	Calc'd	Found
5	66	183–187 0.2 mm.	88.5	164–167 0.3 mm.	161 0.15 mm.	1.4467	0.7981	117.65	117.85	C_{25} 85.15 H_{52} 14.86	84.50 14.38
6	75	188–194 0.2 mm.	65	168–173 0.3 mm.	166 0.15 mm.	1.4481	0.8012	122.27	122.54	C_{26} 85.16 H_{54} 14.85	84.96 14.77
7	71	197–202 0.35 mm.	92	165–168 0.08 mm.	173 0.15 mm.	1.4487	0.8025	126.89	127.09	C_{27} 85.17 H_{56} 14.83	84.83 14.60
8	66	202–206 0.25 mm.	92.5	172–174 0.08 mm.	180 0.15 mm.	1.4496	0.8043	131.51	131.78	C_{28} 85.19 H_{58} 14.81	84.30 14.56
9	69	206–209 0.2 mm.	91	184–187 0.2 mm.	183 0.10 mm.	1.4503	0.8060	136.13	136.33	C_{29} 85.20 H_{60} 14.80	84.73 14.44
10	42	213–217 0.25 mm.	77	213–217 0.25 mm.	193 0.15 mm.	1.4510	0.8070	140.75	141.07	C_{30} 85.22 H_{62} 14.78	85.02 14.71

[a] Microanalyses by Microtech Laboratories, Skokie, Illinois.

Anal. Calc'd for $C_{20}H_{40}O$: C, 81.00; H, 13.60.

Found: C, 80.76; H, 13.80.

10-Pentyl-10-eicosanol. The Grignard reagent from 37.8 g. (0.25 mole) of *n*-amyl bromide and 6.0 g. (0.25 gram-atom) of magnesium in 300 ml. of dry ether was treated with a solution of 60.0 g. (0.203 mole) of 10-eicosanone in 250 ml. of dry ether, and the reaction mixture was worked up with the assistance of 10% hydrochloric acid in the usual manner. Evaporation of the ethereal solution afforded an oil which deposited a few crystals on standing overnight. The oil was distilled at 183–187°/0.2 mm. to give 49.5 g. (66%) of amyldecylnonyl-

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[3] Boiling points are uncorrected.

[4] Microanalyses by Microtech Laboratories, Skokie, Illinois.

carbinol. Inasmuch as each carbinol was converted at once to the hydrocarbon, as described below, microanalyses were omitted.

Dehydration of the carbinols (1). The carbinol (49.5 g.) of the preceding reaction was heated to 170° over 15 g. of anhydrous copper sulfate in a nitrogen atmosphere for 2 hr. Water was readily expelled and was condensed in an air condenser above the reaction flask. The alkenic mixture was decanted from the copper sulfate to which water then was added to effect solution. The resulting mixture was extracted with benzene, and the extract, together with a benzene solution of the decanted alkenes, was passed through a 10-cm. alumina column to remove suspended material and most of the colored impurities. Evaporation of the benzene solution afforded a pale straw-colored oil which distilled at 164–167°/0.3 mm. to give 41.5 g. (88.5%) of the expected alkenes. Infrared analysis showed no hydroxyl absorption, but there was a trace of absorption at 5.92 μ (carbonyl) which was observed only in the case of this particular alkenic mixture. The carbon-carbon double bond frequency at 6.02 μ was well-defined. Redistillation at 147°/0.05 mm. afforded an analytical sample, n_D^{25} 1.4542.

Anal. Calc'd for $C_{25}H_{50}$: C, 85.63; H, 14.37.

Found: C, 85.38; H, 14.47.

Hydrogenation of the alkenic mixtures. The alkenic mixture obtained in the preceding experiment was hydrogenated without solvent, using a Raney nickel catalyst (2) at 85°/100 atm. The uptake of hydrogen was rapid, but the reaction was allowed to proceed for 12 hr. to insure complete hydrogenation. After filtration the product was fractionated in an efficient column to give the expected 10-amyleicosane, b.p. 161–162°/0.15 mm. Analytical and yield data for this and other compounds are summarized in Table I.

SUMMARY

A number of new liquid hydrocarbons (C_{25} to C_{30}) have been prepared by means of the Grignard reaction with 10-eicosanone, dehydration of the carbinols, and hydrogenation of the alkenic mixtures so produced. Certain physical constants for the hydrocarbons are reported.

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REFERENCES

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(3) GILMAN AND NELSON, *Rec. trav. chim.*, **55**, 528 (1936).