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Abstract

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SYNTHESIS OF HIGH-MOLECULAR-WEIGHT HYDROCARBONS OF MIXED STRUCTURE

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Systematic work on the synthesis of individual hydrocarbons and the study of their properties and reactions underlies the new and highly effective methods for the analysis of hydrocarbon mixtures that have recently been developed. Among such new methods are, above all, spectral methods (combination scattering of light, infrared and ultraviolet spectroscopy).

At present, the task of studying the composition, structure, and properties of the highest-molecular-weight portion of petroleum—which, as a rule, constitutes more than half of crude oil—has acquired great importance. The method of isolating individual compounds, successfully used in the study of the light and middle fractions of petroleum, although it may be used in individual cases for solving particular problems, proves extremely laborious and ineffective in studying the composition and properties of complex mixtures of high-molecular-weight petroleum compounds.

In this case one may expect greater success from the use of principles underlying physicochemical analysis, i.e., from establishing quantitative relationships between the principal physical properties of the entire complex system and its chemical composition. But successful application of this principle requires that the dependence of properties on the composition of the system be studied simultaneously both on natural complex systems of unknown structure and on artificial mixtures composed of individual compounds, i.e., on mixtures that, to a certain extent, model the natural systems under investigation. It is precisely this principle that forms the basis of numerous modifications of the method for determining the structural-group composition of petroleum oil fractions.

The molecules of high-molecular-weight petroleum compounds (C_{20} and higher), as studies of recent years have shown, have predominantly a mixed (hybrid) structure. In other words, structural units of various homologous series (paraffins, cycloparaffins, benzene, naphthalene, etc.) participate, to a greater or lesser extent, in the construction of the molecule. The ratio of structural elements of aliphatic and cyclic nature varies within wide limits, depending on the chemical nature of the petroleum. In this connection, it was decided to

synthesize a series of hydrocarbons of composition C_{24}–C_{32}, not described in the literature, with different ratios of carbon atoms in the structural units of the molecule.

The hydrocarbons obtained at present, as well as their properties, are given in Table 1.

In the future we plan both the synthesis of new structures and a more detailed study of the properties of the synthesized hydrocarbons, including viscosity–temperature characteristics, adsorption properties, ultraviolet and infrared spectra, etc. Undoubtedly, a detailed stu-

Table 1

No.	Hydrocarbon	b.p., °C*	n_D^{20}	d_4^{20}	Method of preparation
1	1,1-Diphenyldodecane	208	1.5241	0.9248	From magnesium bromophenide and ethyl laurate
2	1,1-Dicyclohexyldodecane	204	1.4803	0.8758	Hydrogenation of hydrocarbon No. 1

No.	Hydrocarbon	b.p., °C*	n_D^{20}	d_4^{20}	Method of preparation
3	2,11-Diphenyldodecane	200	1.5212	0.9244	From 1,10-diphenyldecanedione-1,10 and magnesium dimethyl. The ketone was synthesized from sebacic acid dinitrile and magnesium bromophenide
4	2,11-Dicyclohexyldodecane	196	1.4802	0.8759	Hydrogenation of hydrocarbon No. 3
5	1,5-Diphenyl-3-heptylpentane	210	1.5206	0.9233	From the magnesium-organic compound of phenylethyl alcohol bromide and ethyl caprylate
6	1,5-Dicyclohexyl-3-heptylpentane	208	1.4776	0.8691	Hydrogenation of hydrocarbon No. 5

No.	Hydrocarbon	b.p., °C*	n_D^{20}	d_4^{20}	Method of preparation
7	1,1-Phenylcyclohexyldodecane	206	1.4980	0.8960	From laurophenone and magnesium bromocyclohexyl. The ketone was synthesized from magnesium bromophenide and lauric acid nitrile
8	1,1-($\alpha\alpha_1$)-Dinaphthyldodecane	254	1.5989	1.0130	From magnesium bromonaphthyl and ethyl laurate
9	1,1-($\alpha\alpha_1$)-Didecahydronaphthyldodecane	252	1.5245	0.9537	Hydrogenation of hydrocarbon No. 8
10	1,1-($\alpha\alpha_1$)-Ditetrahydronaphthyldodecane	243	1.5480	0.9796	Hydrogenation of hydrocarbon No. 8

No.	Hydrocarbon	b.p., °C*	n_D^{20}	d_4^{20}	Method of preparation
11	1,1-α-naphthyl, β-decahydronaphthyldodecane	252	1.5500	0.9662	From lauronaphthone and magnesium bromodecalin. The ketone was obtained simultaneously with hydrocarbon No. 8
12	1,3-($\alpha\alpha_1$)-Dinaphthyl-2-nonylpropane	248	1.5780	1.0044	From magnesium chloromethylnaphthalene and ethyl caprinate
13	1,3-($\alpha\alpha_1$)-Didecahydronaphthyl-2-nonylpropane	244	1.5013	0.9263	Hydrogenation of hydrocarbon No. 12

No.	Hydrocarbon	b.p., °C*	n_D^{20}	d_4^{20}	Method of preparation
14	2,11-($\alpha\alpha_1$)-Dinaphthyldodecane	259	1.5960	1.0193	From 1,10-dinaphthyldecanedione-1,10 and magnesium dimethyl. The ketone was synthesized from sebacic acid dinitrile and magnesium bromonaphthyl
15	2,11-($\alpha\alpha_1$)-Didecahydronaphthyldodecane	256	1.5135	0.9484	Hydrogenation of hydrocarbon No. 14

* Boiling temperatures were obtained at the following pressures: for hydrocarbons Nos. 1-7 at 4 mm Hg, for hydrocarbons Nos. 8-15 at 0.5 mm Hg.

The study of the properties and reactions of these compounds will promote a more rapid investigation of the composition and structure of high-molecular-weight petroleum compounds.

In conclusion, we shall briefly dwell on certain details of the synthesis of the hydrocarbons. The tertiary alcohols obtained by the Grignard method were dehydrated in vacuum over pure aluminum oxide at 280-320° and 1 mm residual pressure. Hydrogenation of the products was carried out in an autoclave in the presence of Raney nickel. Hydrogenation conditions: double bond 50-70°, benzene ring 150°, naphthalene ring in decalin 150°, in tetralin 100°; the pressure in all cases was 100-150 atm.

The hydrocarbons of composition C_{24} obtained were distilled on a special packed vacuum column with an efficiency of 16 theoretical plates. Hydrocarbons of

composition C_{32} were purified by molecular distillation at a pressure of $1 \cdot 10^{-5}$ and a temperature of 170°.

It should also be noted that most of the compounds we synthesized, upon cooling, solidified as glasses at temperatures from −20 to −30° (hydrocarbons of composition C_{24}) and from −5 to −10° (hydrocarbons of composition C_{32}). However, 1,1-dicyclohexyldodecane, after standing for half a year, unexpectedly crystallized at room temperature (m.p. +27°). The possibility of crystallization of other hydrocarbons as well cannot be ruled out, which compels us to approach cautiously the assessment of the vitrification of particular structures. This question will be clarified by us in the future.

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Note: Figure translations are in progress. See original paper for figures.