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Synthesis of Perspective Hydrocarbons for Synthetic Lubricants with a High Viscosity Characteristic

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ABSTRACT

The alkylation reaction of cyclopentadiene with monoatomic aliphatic alcohols of C_6-C_{10} series in the present of alkaline catalyst, promoted by nano-sized magnesium oxide has been presented. So that, the synthesis of di- and polyalkylcyclopentadienes and cyclopentanes have been conducted. The effect of molar ratio of cyclopentadiene and alcohol, reaction temperature and duration to the yield of synthesized di- and polyalkylcyclopentadiene has been studied. It was established that, the main reaction parameters are temperature and molar ratio of reagents. The structure of synthesized compounds has been proved by modern physico-chemical methods, such as IR-, PMR- and NMR-spectroscopy. It showed that the synthesized compounds have high viscosity properties and can be used as lubricants and additives to mineral oils.

Keywords: cyclopentadiene, alkylation, nano-sized magnesium oxide, viscosity index.

INTRODUCTION

The analysis of modern condition of investigations in the field of synthesis of lubricants and perspectives of their development shows that, for the providing of increased requirements to this materials, it is necessary synthesizing synthetic lubricants with a high viscosity characteristic. It should be noted that, mineral oils even with respective additives not fully satisfied for this requirements. The purposeful synthesis is necessary for the receiving of oils with high operational characteristics [1,2]. However, the investigations in the field of synthesis of efficient synthetic lubricants are studied insufficiently.

Among tested synthetic products from different classes of organic compounds, only three are perspective for this application: synthetic hydrocarbons, organic esters and heteroatom organic compounds [3-7]. As synthetic hydrocarbon oils, polyolefins and alkylaromatic hydrocarbons, received by controlled catalytic polymerization and alkylation have vast applications [8,9].

Recently, the synthesis of novel classes of oil hydrocarbons based on alkylation reaction of cyclopentadiene (CPD) with high aliphatic alcohols has been object of interest for many investigators. Corresponding substituted cyclopentanes with good viscosity-flow properties which creates background for its application as synthetic lubricants, have been synthesized by hydrogenation of obtained alkyl- and polyalkyl-CPD. There are many works devoted to this direction in scientific literature of last year [10-14]. So, in work [10], it is showed that, synthetic lubricant compositions can be received based on alkyl substituted cyclopentadienes, cyclopentenes and cyclopentanes. The structure of synthesized compounds consist of 1-6 alkyl groups, having 4-36 carbon atoms with different form of carbon chain.

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Authors of work [11] marked that, polyalkylcyclopentadienes have lubricant properties and polyalkylcyclopentanes have been obtained.on the base of this compounds.

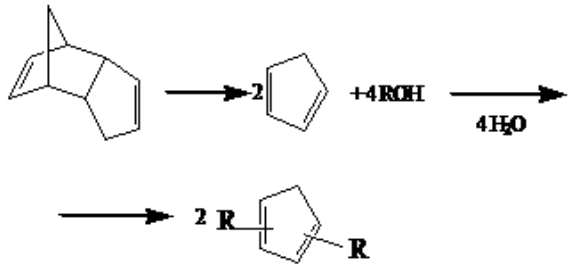
The possibility of application of alkylsubstituted CPD as lubricant components have been showed in work [12]. Polyalkylated cyclopentanes were proposed for using as liquid lubricant oils in rocket apparatus [13].

The lubricants based on alkylcyclopentadienes were offered for tape recorder setting in patent [14]. The aim of the present work is development of worthy and efficient methods for receiving of alkylcyclopentadienes (syntons of synthetic lubricants), determination of purity and rheological properties of target product. Therefore, we carried out the alkylation of cyclopentadiene with monoatomic aliphatic alcohols of C_6-C_{10} series in the present of efficient catalyst.

The recent works show that, catalysts with heavy composition, such as «Adogen-464» (trialkylmethylammonium chloride) have been used in the alkylation of cyclopentadiene with alcohols. In our work [15], the alkaline catalyst promoted by nano-size magnesium oxide with particle size 25-30 nm have been used in the synthesis of dialkylcyclopentadienes.

RESULT AND DISCUSSION

The synthesis of di-n. alkyl-CPD based on alkylation reaction of CPD with aliphatic monoatomic alcohols have been conducted by following scheme:



I, II, III, IV, V

Where I- R=n.C_6H_{13}; II-R=n.C_7H_{15}: III-R=n.-C_8H_{17}; IV-R=n-C_9H_{19}; V-R=n-$C_{10}H_{21}$.

The synthesis method of dialkyl-CPD with the example of alkylation of CPD with n-octyl alcohol is following. Calculated amount of n. octyl alcohol and solution promoted by nano-sized magnesium oxide have been placed in reaction flask equipped by mechanically stirrer, dropping funnel, Din-Stark nozzle with cooler and thermometer. Before heating, determined portion of dicyclopentadiene (DCPD) is added to the flask and temperature is increased to 200^0C. After separation of water in Din-Stark nozzle, the remaining portion of DCPD is added during 1.5 hour.

After completely addition of DCPD, the reaction mixture is heated during 4 hours. After cooling, the mixture is washed by water, hexane, dried by $MgSO_4$, distillated in vacuum and as a result, di-n.octylcyclopentadiene is obtained. The other dialkyl-CPDs (I, II,III,IV, V) are received based on analogical method. The physico-chemical properties of synthesized compounds are given in Table 1.

Table1. *The physico-chemical properties of synthesized compounds (I, II,III,IV, V).*

Indices	I	II	III	IV	V
Molecular weight	234	262	290	318	346
n_d^{20}	1.4310	1.4390	1.4573	1.4590	1.4612
d_4^{20}	0.7912	0.7938	0.8256	0.8176	0.8340
$T_{boiling}$, ^{O}C/mm. Hg	60-62/10	72-75 / 8	118-20 /15	124-26 /15	132-34 /15
Yield, %	62.0	62.5	66.2	68.4	69.7

The effect of main parameters of reaction to alkylation of CPD with monoatomic alcohols have been studied by the example of n.octyl alcohol (Figure1).

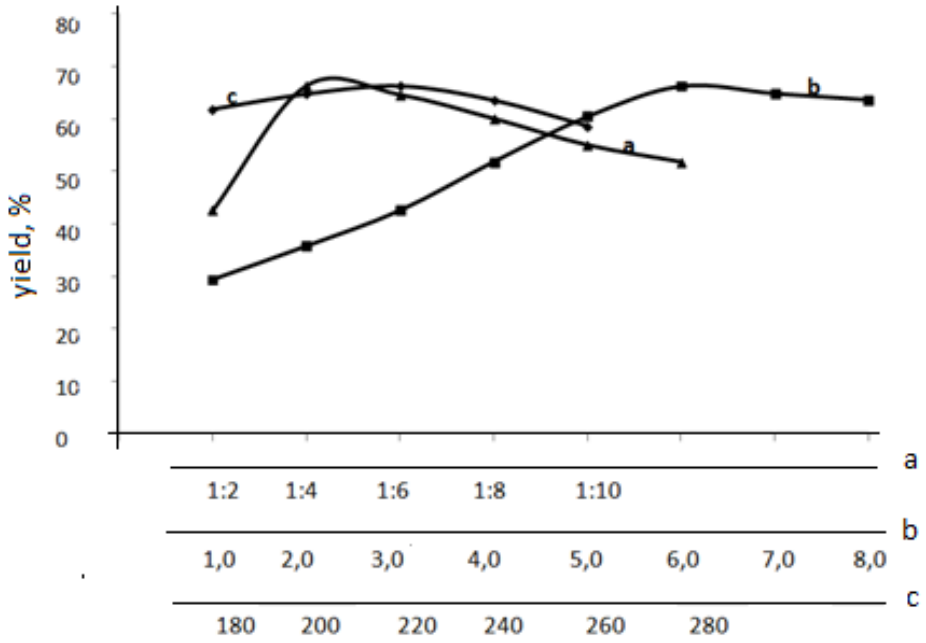


Figure1. *The dependence of dialkyl-CPD yield from:*

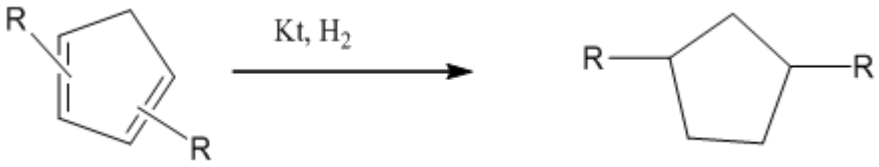
a) molar ratio of CPD : alcohol

b) reaction time, h.

c) reaction temperature, ^0C

As it is seen from Figure 1., the rising of reaction temperature from 180 to 220^{0}C increased the yield of alkyl-CPD. Further increasing of temperature lead to decreasing of yield of target compound . The significant effect to reaction yield was molar ratio of reagent components. In spite of further increasing of molar ratio lead to decreasing of di-n. octyl-CPD yield which is explained by reducing of CPD concentration , the rising of molar ratio from 1:2 to 1:4 results in growing of alkyl-CPD yield (from 40 % to 70 % mass). As it is expected, the increasing of reaction time influenced to reaction yield, significantly. The maximum yield of di-n. alkyl-CPD is obtained in 6 hour of reaction duration.

Synthetic lubricants with high viscosity property could be received by catalytic hydrogenation of synthesized di-n. alkyl-CPD [16]. So that, in our investigation, the synthesis of compound (VI), consisting of 1,3-di-n. hexylcyclopentane (93%) and tri-n.hexylcyclopentane (7 %) have been carried out based on the alkylation reaction of dicyclopentadiene with n.hexyl alcohol in the present of alkaline catalyst. The synthesis of 1,3-di-n.hexyl-(VI) and 1.3-di-n.octylcyclopentane (VII) have been conducted by hydrogenation of according di-n.alkyl-CPD by following scheme:



Where: VI-R= n. C_6H_{13} ; VII-R = n. C_8H_{17}

The physico-chemical properties of synthesized products (VI, VII) are showed at Table 2.

Table2. *The physico-chemical properties of synthesized compounds (VI, VII).*

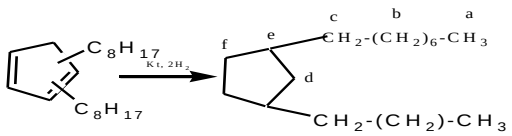
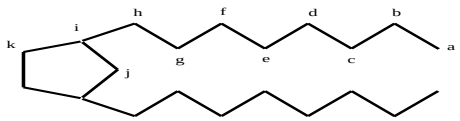
Indices	Compound VI*	Compound VII
n_D^{20}	1.4610	1.4520
Density, q/sm^3	0.8290	0.8170
Viscosity, mm^2/s at 100^{0C}	2.15	2.0
Viscosity, mm^2/s at 50^{0C}	5.82	5.31
Viscosity index	136	159
Solidification temperature, ^{0}C	-45	-60
Flash temperature, ^{0}C	256	245
Acid number, mg KOH/g	neutral	neutral

**- Mark:compound (VI) consist of 93 % of di- and 7,0 % of tri-n-hexylcyclopentane*

IR-spectral analysis of 1,3-di-n.hexylcyclopentadiene (VI) was controlled by UR-20 spectrophotometer in the field 700-4000 sm^{-1}. In IR-spectra, the following adsorbtion stripes are observed: 730 sm^{-1} (CH_2-groups), 1380 sm^{-1} (CH_3-groups), 1480 sm^{-1} (CH_2-groups in cyclopentane ring).

The NMR- and PMR spectra were registered by Fourier 300 impulsive spectrometer *(Bruker Corporation, Germany)* in the solution of deuterated chloroform ($CDCL_3$) at room temperature. The results of NMR-analysis are given at Table 3.

Table3. *The NMR-analysis of 1,3-di-n.hexylcyclopentadiene (VI).*

^{1}H-NMR, δ.m.p.	^{13}C-NMR, δ.m.p.
 a – 0,90; b – 1,26; c – 1,28; d – 1,32; e – 1,40; f – 1,66	 a – 14; b – 22,5; c – 31,8; d – 29,2; e – 29,5; f – 29,8; g – 27,4; h – 33,3; i – 32,1; j - 37,1; k – 29,2

Thus, the synthesized 1,3-di-n.hexylcyclopentadiene has good viscosity characteristics and can be used as a base of synthetic lubricants and also as additives to mineral oils for increasing of their viscosity indexes.

CONCLUSION

The results of investigations showed that, the synthesized compounds (di- and polyalkylcyclopentanes) have efficient viscosity property, high flash temperature and low solidification temperature. Thus, they can be used as components of synthetic lubricants and as additives to mineral oils.

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