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Synthesis and properties of naphthalene oligomers polyalkylated with 1-octadecene and 1-hexadecene

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SUMMARY

A one-pot method is described for the synthesis of naphthalene oligomers polyalkylated with 1-octadecene and 1-hexadecene. The synthesis involves two steps: 1) oligomerization of naphthalene using an $AlCl_3$ /$CuCl_2$ catalyst/oxidant system, and 2) polyalkylation with a 1-olefin. Characterization studies include ^1H- and ^{13}C-NMR spectroscopy, GPC and testing methods for lubricants. The degree of alkylation, variations in the alkyl groups, and the position of the substituent on the naphthalene ring were established by ^{13}C NMR spectroscopy. The purified products possess excellent properties for being suitable as a lubricant base stock, lubricant additives and functional fluids.

I. INTRODUCTION

Long-chain alkylnaphthalenes having high viscosity index, low volatility, good thermal, oxidation and hydrolytic stability are useful as lubricants, lubricant additives and functional fluids. It is thus not suprising, thet they have been the subject of much attention (1-7) recently.

The synthesis of a long-chain polyalkylated oligomeric naphthalene has stirred up our interest since such a material would display further improvements in properties.

Our one-pot synthesis involves two steps: 1) oligomerization of naphthalene using $AlCl_3$ as the Lewis-acid catalyst and $CuCl_2$ as the oxidizing agent (8-10), and 2) polyalkylation of naphthalene oligomers with a 1-olefin (as shown in Scheme 1).

Scheme 1

$$\text{Naphthalene} \xrightarrow[\text{-HCl, -CuCl}]{AlCl_3/CuCl_2} \begin{array}{c}\text{Naphthalene}\\ \text{oligomers}\end{array} \xrightarrow{\text{1-olefin}} \begin{array}{c}\text{Polyalkylated}\\ \text{naphthalene}\\ \text{oligomers}\end{array}$$

Naphthalene may be converted into oligomers in quite a good yield when it is allowed to react with $AlCl_3$ without a solvent. However, in the absence of an oxidant, the oligomers contained a substantial fraction with the dihydro structures (8).

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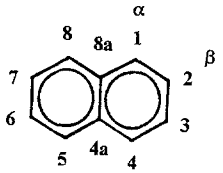
Dehydro coupling of naphthalene using an $AlCl_3$ Lewis-acid catalyst–$CuCl_2$ oxidant combination yields oligomers DP≤6. However, oxidative rearomatization of the dihydro structures to a totally aromatic oligonaphthalene was not complete, and formation of condensed polynuclear structures was apparent. The oligomerization proceeds *via* coupling at positions 1 and 4 of the naphthalene monomer. The initially formed products are then subsequently isomerized in systems containing a sufficiently active catalyst (9).



II. EXPERIMENTAL

a/ Materials

Naphthalene (98%), $AlCl_3$ (98%), $CuCl_2$ (97%), 1-hexadecene (95%), 1-octadecene (92%) and Silica gel (0.063-0.200 mm) for column chromatography were purchased from Merck and Aldrich. The solvents were used in commercial p.a. quality.

b/ Characterization methods

The ^1H and ^{13}C NMR spectra were recorded with a Bruker 200 SY spectrometer in $CDCl_3$. The quantitative NMR spectra were obtained by using the inverse gated mode of decoupling in order to obtain signals without nuclear Overhauser enhancement (11). When necessary, the assigments were checked by ATP (attached proton test), a method for making distinction between primary and secondary, or between tertiary and quaternary carbon atoms (12). The chemical shifts are expressed using the solvent $CDCl_3$ absorption $\delta(^{13}C) = 77.0$ ppm as a secondary standard.

GPC analyses were performed with a Waters instrument equipped with dual RI and UV detectors and five Ultrastyragel columns. The calibration curve was constructed with polystyrene standards of narrow molecular weight distribution.

Testing of the products was based on standardized methods of lubricants (7).

c) Preparative procedures

An intimate mixture of naphthalene (6.41 g, 0.050 mol), anhydrous $AlCl_3$ (6.67 g, 0.050 mol), and anhydrous $CuCl_2$ (6.72 g, 0.050 mol) was mechanically stirred under a nitrogen atmosphere at 35 °C for 3 hours. After cooling to room temperature to the reaction mixture was added dropwise 0.50 mol of the 1-olefin (112 g of 1-hexadecene or 126 g of 1-octadecene). The mixture was stirred for 8 hours at 30 °C then quenched and washed with water until neutral. The crude product was further purified by washing with n-butanol and by column chromatography on Silica gel (eluent: benzene/n-hexane volume ratio 5:95). Finally the solvents were removed by evaporation in vacuum. Yield: 85-88% (based on weights of naphthalene and 1-olefin).

III. RESULTS AND DISCUSSION

In our initial approaches synthesizing naphthalene oligomers under severe reaction conditions (naphthalene/$AlCl_3$/$CuCl_2$ mol ratios 1:1:1, 80 °C and 3 hours reaction time) naphthalene was converted into oligomers in high conversion. The product, precipitated from benzene with n-hexane (benzene/n-hexane volume ratio 5:95), had an $\overline{M}_n$=790 and $\overline{M}_w/\overline{M}_n$=1.76. Several attempts for alkylation of this fraction gave oligomers of the 1-olefin and afforded a small yield of the alkylate, i.e. most of the naphthalene oligomers were recovered unchanged (brown powder). This failure is most likely due to the insolubility of the main fraction of the oligomers in the reaction medium, and thus the inaccessibility to the alkylating agent. This suggests that a lower degree of conversion during the reaction would solve the problem. Therefore, exploration of the conditions for the oligomerization reaction under which a subsequent alkylation proceeded was necessary.

Figure 1. displays a GPC trace of a sample taken from the oligomerization reaction mixture before alkylation. This series of peaks starts with naphthalene (representing 23% of the total area) and the GPC chromatogram shows the formation of oligomers with up to ten naphthalene units (2% of the total area).

To ensure polyalkylation, alkylation was carried out under conditions favourable for polysubstitution: high 1-olefin/naphthalene ratio, high $AlCl_3$/1-olefin ratio and long reaction time.

The purified products (naphthalene oligomers polyalkylated with 1-octadecene (**I**) and 1-hexadecene (**II**)) were analyzed by GPC and NMR spectroscopic methods.

The typical number-average molecular weights ($\overline{M}_n$) and polydispersities ($\overline{M}_w/\overline{M}_n$) are shown in Table 2.

Not surprisingly, in the ^1H NMR spectra the aromatic (6.9-8.3 ppm), as well as the aliphatic region (0.7-3.7 ppm) appear broad and almost unstructured. Weak signals in the region of 6.6-6.9 ppm, indicative of the presence of some reduced structures (i.e. olefinic protons in the dihydro structures), can be observed.

The ^{13}C NMR spectra of the products are very complex (Figure 2a and 2b). The observed multitude of signals is ascribed to the presence of different oligomers, the existence of different variations in the alkyl groups (which is caused by isomerization), the position of the substituents, as well as to the degree of alkylation. In many cases the peaks are almost completely lost in the baseline or in a broad hump.

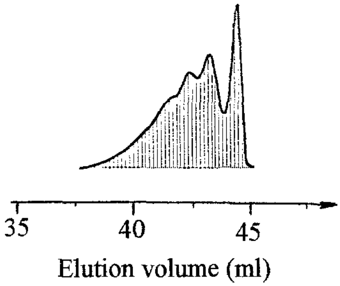


Figure 1. GPC chromatogram of a sample taken from the naphthalene oligomerization reaction mixture preceding the alkylation step

Figure 2b) shows the aromatic region of the APT ^{13}C NMR spectrum of a sample taken from the product of the synthesis of naphthalene oligomers polyalkylated with 1-octadecene (**I**). In this spectrum the phase of signals is positive for the quaternary carbon atoms, and negative for the tertiary carbon atoms.

Due to the lack of relevant model compounds and literature data, the ^{13}C NMR chemical shifts were predicted on the basis of additivity of substituent increments (13-17). A further source of help in the assignments was the comparision of the spectra of the oligomerized 1-octadecene, 1-hexadecene and naphthalene.

The partial assignments of the carbon absorptions in the aromatic region are listed in Table 1.

The major components of products **I** and **II** are most likely the polyalkylated naphthalene oligomers accompanied by the oligomers of the 1-olefin.

The ^{13}C NMR spectra of the products display intensive resonances in the alkyl region, due to the carbon atoms at the terminus of the alkyl chain and the oligomers of

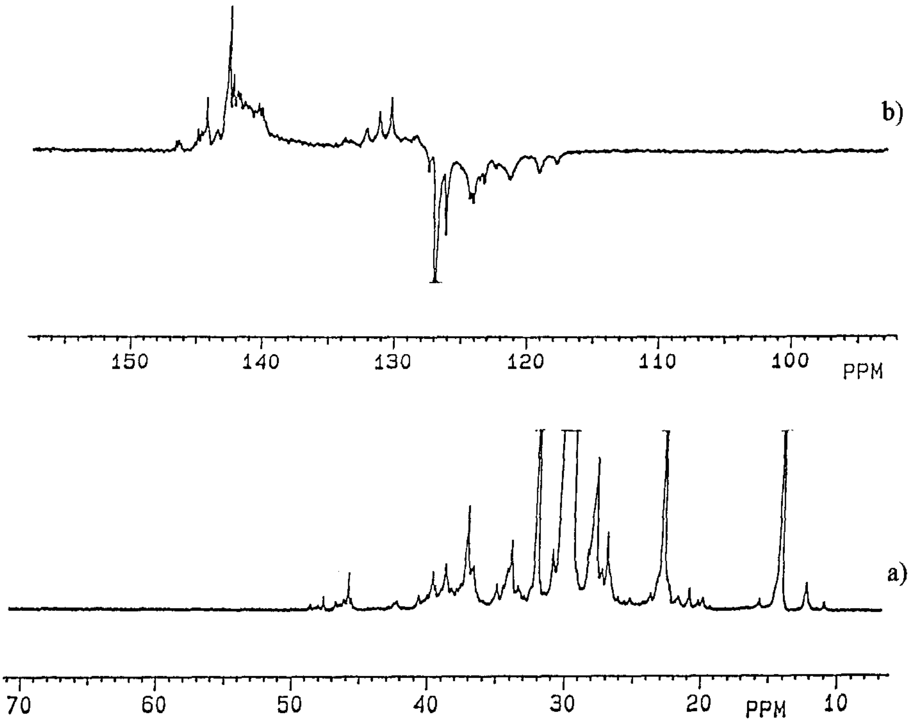
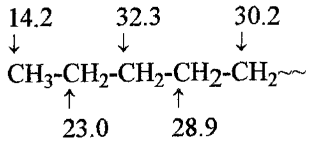
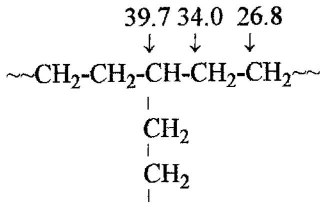


Figure 2. a) Aliphatic region of the ^{13}C NMR spectrum of product **I**, b) Aromatic region of the APT ^{13}C NMR spectrum of a sample of **I**

the 1-olefin (used in excess in the alkylation reaction):



$$\overset{\overset{14.2}{\downarrow}}{CH_3}-\underset{\underset{23.0}{}}{\underset{\uparrow}{CH_2}}-\overset{\overset{32.3}{\downarrow}}{CH_2}-\underset{\underset{28.9}{}}{\underset{\uparrow}{CH_2}}-\overset{\overset{30.2}{\downarrow}}{CH_2}\sim\sim$$



$$\sim\sim CH_2-CH_2-\underset{\begin{array}{c}|\\ CH_2\\ |\\ CH_2\\ |\end{array}}{\overset{\overset{39.7}{\downarrow}}{CH}}-\overset{\overset{34.0}{\downarrow}}{CH_2}-\overset{\overset{26.8}{\downarrow}}{CH_2}\sim\sim$$

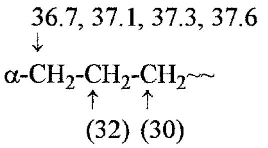
Support for this assigment comes from the ^{13}C NMR spectra of the oligomers of the 1-olefins (obtained with $AlCl_3$), in which all of the alkyl resonances could be observed and identified.

The ^{13}C NMR chemical shifts for the alkyl chains attached to the aromatic nucleus are assigned as shown below:

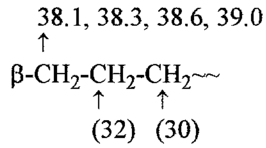
Table 1. Selected ^{13}C NMR chemical shifts ($CDCl_3$, 50 MHz, in ppm) in the aromatic region for structures related to polyalkylated naphthalene oligomers

Structure	Carbon/Position	Chemical shifts
Naphthalene	CH-1,4,5,8 (= α)	127.7*
	CH-2,3,6,7 (= β)	125.6*
	C-4a, 8a	133.3*
Naphthalene oligomers	CH-(1-7) (= α and β)	128.8, 128.4, 128.2, 128.0, 127.9, 127.6, 127.4, 127.2, 126.3, 126.0, 125.9, 125.6, 125.2, 124.9, 122.4, 122.2, 121.9, 121.7, 121.5, 120.5, 120.3, 119.9
	C-(1-7) (= α and β) (in aryl-aryl bonds)	138.9, 138.6, 138.5, 138.3, 138.1
	C-4a, 8a	133.8, 133.7, 133.5, 132.8, 132.6, 132.5, 130.7, 130.5, 130.3
Naphthalene nuclei in poly-alkylated naphthalene oligomers	CH-(1-7) (= α and β)	128.2, 128.0, 127.5, 126.8, 126.1, 125.5, 125.2, 125.0, 124.8, 124.3, 124.0, 123.2, 122.6, 122.0, 119.9, 118.6
	C-(1-7) (= α and β) (alkyl-carrying carbons)	147.4, 147.2, 147.1, 146.2, 145.8, 145.5, 145.1, 145.0, 144.4, 144.3, 144.2, 143.6, 143.2, 142.9, 142.6, 142.3, 141.9, 141.6, 141.2, 140.9, 140.8, 140.6, 140.2
	C-(1-7) (= α and β) (in aryl-aryl bonds)	139.7, 139.5, 138.9, 138.7, 138.3
	C-4a, 8a	134.7, 134.3, 133.0, 132.0, 131.1, 131.0, 130.4, 130.2, 129.9, 129.6, 129.3, 129.0

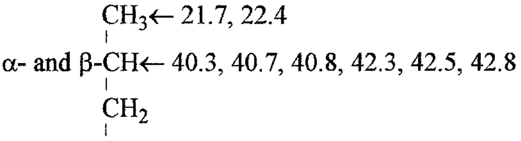
*From Ref.14.



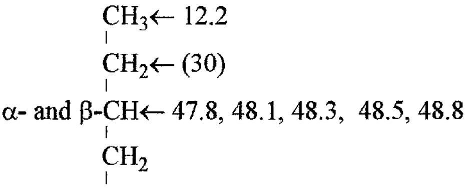
$$\overset{36.7,\ 37.1,\ 37.3,\ 37.6}{\overset{\downarrow}{\alpha\text{-}CH_2}}\text{-}\underset{(32)}{\underset{\uparrow}{CH_2}}\text{-}\underset{(30)}{\underset{\uparrow}{CH_2}}\sim\sim$$



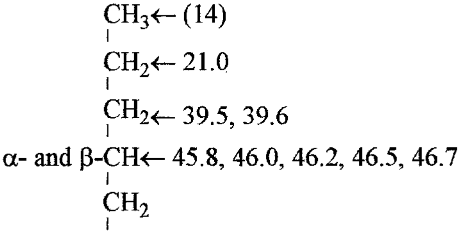
$$\overset{38.1,\ 38.3,\ 38.6,\ 39.0}{\overset{\uparrow}{\beta\text{-}CH_2}}\text{-}\underset{(32)}{\underset{\uparrow}{CH_2}}\text{-}\underset{(30)}{\underset{\uparrow}{CH_2}}\sim\sim$$



$$\begin{array}{rl} & CH_3 \leftarrow 21.7,\ 22.4 \\ & | \\ \alpha\text{- and }\beta\text{-} & CH \leftarrow 40.3,\ 40.7,\ 40.8,\ 42.3,\ 42.5,\ 42.8 \\ & | \\ & CH_2 \\ & | \end{array}$$



$$\begin{array}{rl} & CH_3 \leftarrow 12.2 \\ & | \\ & CH_2 \leftarrow (30) \\ & | \\ \alpha\text{- and }\beta\text{-} & CH \leftarrow 47.8,\ 48.1,\ 48.3,\ 48.5,\ 48.8 \\ & | \\ & CH_2 \\ & | \end{array}$$



$$\begin{array}{rl} & CH_3 \leftarrow (14) \\ & | \\ & CH_2 \leftarrow 21.0 \\ & | \\ & CH_2 \leftarrow 39.5,\ 39.6 \\ & | \\ \alpha\text{- and }\beta\text{-} & CH \leftarrow 45.8,\ 46.0,\ 46.2,\ 46.5,\ 46.7 \\ & | \\ & CH_2 \\ & | \end{array}$$

The chemical shifts in parentheses are due to those overlapped by the main signals.

Although, it is difficult to make reliable intensity measurements on these relatively weak peaks, and some signals are not sufficiently well-resolved from the main signals, the degree of alkylation, the variations in the alkyl chains and the position on the naphthalene ring could be still calculated from the relative intensities.

According to the quantitative ^{13}C NMR spectra a 4:2:1:3 ratio of the peak areas for the hydrogen-bearing carbons (118.0-129.0 ppm), the C-4a and C-8a carbons (129.0-135.0 ppm), the carbons attached to another naphthalene nucleus (137.0-140.0 ppm), and the alkyl-carrying carbons (140.0-148.0 ppm) is measured, which suggests that the average constituent of the products is a hexaalkyl binaphthyl.

From the aliphatic region of the ^{13}C NMR spectra the variations in the alkyl chains and the positions on the naphthalene ring could be determined from the relative peak areas.

	I	**II**
α- CH_2-CH_2-CH_2~~	50%	47%
β- CH_2-CH_2-CH_2~~	24%	25%
α- and β- $CH(CH_3)CH_2$~~	11%	10%
α- and β- $CH(C_2H_5)CH_2$~~	9%	11%
α- and β- $CH(C_3H_7)CH_2$~~	6%	7%

In Friedel-Crafts alkylations of naphthalene the predominantly kinetically controlled reactions give high α/β alkylnaphthalene isomer ratios and an increasing β substitution is indicative of isomerization (18). The above data show kinetically controlled alkylations.

The naphthalene oligomers polyalkylated with 1-octadecene (**I**) and 1-hexadecene (**II**) were tested as lubricants (7) and certain typical properties are summarized in Table 2.

Table 2. Typical properties of the naphthalene oligomers polyalkylated with 1-octadecene (**I**) and 1-hexadecene (**II**)

Property	I	II
Kinematic viscosity, cSt		
at 20 °C,	1044	1000
at 40 °C,	330	325
at 50 °C,	206	203
at 100 °C	37.8	35.3
Viscosity index	161	152
Pour point, °C	17	4
Flash point, °C	>310	>310
High-temperature oxidation test*	1.13	1.09
$\bar{M}_n$, g/mol	1900	1600
$\bar{M}_w/\bar{M}_n$	1.35	1.32

*Oxidation leads to a viscosity increase (7,19). The products (40 ml) were subjected to a high-temperature oxidation test for 2x6 hours, at 200 °C, air flow rate 15 l/h, without catalyst. The number is viscosity ratio: viscosity at 50 °C after oxidation/viscosity at 50 °C before oxidation.

These data indicate that the one-pot synthesis of polyalkylated naphthalene oligomers provides an access to materials with excellent properties to become promising candidates for lubricant base stocks, lubricant additives and functional fluids.

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