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Effect of *n*-Butyl Bromide on the Composition of Cracking Products of Maltenes from Heavy Oil

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Abstract

The effect of *n*-butyl bromide on thermal transformations of maltenes from heavy oil of the Usinskoye oil field (Komi Republic) was explored. The cracking of maltenes was performed at 450 °C for 2 h in the isothermal mode in the presence of the initiating additive, *n*-butyl bromide. The data for the mass balance of the process and the composition of liquid cracking products were acquired. Variations in the hydrocarbon composition of the cracking products were investigated. As demonstrated, the addition of *n*-butyl bromide (0.7 mass % of the mass of raw materials) led to a 1.8 times increase in the yield of distillate fractions boiling up to 360 °C compared to cracking without the additive. As determined, along with the profound destruction of resins, oils were exposed to transformation upon the cracking of maltenes with *n*-butyl bromide due to dealkylation and dehydration reactions.

Key words: heavy oil, maltenes, cracking, *n*-butyl bromide, cracking products, hydrocarbons, composition

INTRODUCTION

As the reserves of light and middle oil are depleted, heavy high-viscosity oil and natural bitumen become an important source of raw materials to meet growing needs for fuel. Their world resources significantly exceed the reserves of light oil and are assessed in more than 810 billion t. Canada and Venezuela, together with Mexico, the USA, Russia, Kuwait, and China possess large reserves of natural bitumen [1]. One of the major issues related to processing heavy hydrocarbon feedstock (HHF) is that it has a high content of asphaltenes and resins prone to coke formation and the poisoning of catalysts [2–5].

The advanced processing of HHF is premised on the development of transformation methods for high-molecular resinous-asphaltenic components into valuable products (distillate fractions). Upon thermal transformations of HHF, there is a high yield of coke, which is due to a high content of as-

phaltenes. Their molecules are highly condensed systems that contain aromatic and naphthenic rings.

The search for new conversion methods of high-molecular oil compounds different from traditional hydrotreating requires the research on cracking reactions both without it and in the presence of additives different according to their impact. In order to increase the deepness of the destruction of resinous-asphaltenic components, their initiating additives are used.

As demonstrated in [6], chemical modification, in particular, the halogenation of oil components leads to the synthesis of lighter products due to the breakage of chemical bonds. Paper [7] explored the process of the catalytic cracking of a model mixture with various compounds, such as methanol, *n*-butyl bromide, and acetic acid. As demonstrated, *n*-butyl bromide makes a strong-acid medium in this process that, as it is known, facilitates cracking reactions. Papers [8, 9] examined the effect of halogens on coke formation

upon heavy oil ennobling, and also on the partial demetallization of raw materials.

The aim of this research was to explore the effect of *n*-butyl bromide on the directionality of thermal transformations of maltenes.

EXPERIMENTAL

Research object

Naphthenic oil from the Usinsk field of the Timan-Pechora oil-gas basin was selected as the research object. The oil is heavy (a density of 967 kg/m³), high-sulphur (S_{tot} of 1.98 mass %), and highly resinous (18.0 %), and also contains asphaltenes in large amounts (8.1 %). The deasphaltized oil containing 80.4 % of oils and 19.6 % of resins was exposed to cracking.

Cracking conditions

The cracking was performed in the stationary mode in 12 cm³ autoclaves. Maltenes with a mass of 7 g were loaded into the reactor not using solvents. The experiments were carried out in air at 450 °C, a time of 120 min. Butyl bromide (C₄H₉Br) was introduced in an amount of 0.7 mass % of the mass of raw materials. This quantity was determined as optimum in the early experiments.

The mass balance of the process was assessed according to the yield of gaseous, liquid, and solid products. "Solid" implies coke-like compaction products that are insoluble in polar organic solvents. Such species were not investigated in this paper.

The yield of gaseous products was determined according to the reactor mass loss after their removal. After decanting the liquid products, the reactor was rinsed with chloroform. Liquid thermolysis products and the chloroform solution were combined and passed through a paper filter to separate solid products. The solvent was evaporated using a rotary evaporator; the liquid products were dried under vacuum, and then their yield was determined.

Determining the material composition of the liquid products

The content of asphaltenes, resins, and oils (the material composition) was determined in the liquid cracking products. In order to analyze asphaltenes, the liquid products were treated with a 40-fold excess of *n*-hexane according to the technique described in [10]. The maltenes derived

after deasphaltization were applied onto ASK silica gel that was loaded into the Soxhlet apparatus. Initially, the oils were extracted with a non-polar solvent (*n*-hexane) and then resins were extracted with a mixture of polar solvents, benzene and ethanol, in a 1 : 1 ratio.

Determination of the fractional composition of the liquid products

The fractional composition was determined by gas-liquid chromatography on the "Crystal-2000M" chromatograph with a flame-ionisation detector utilising a 25 m × 0.22 mm quartz capillary column with the SE54 stationary phase using helium as a carrier gas. The analysis was carried out under temperature linear programming conditions between 50 and 290 °C at a column thermostate heating temperature of 15 °C/min. The identification of hydrocarbons (HC) was performed according to retention times of *n*-alkanes that were a part of the calibrating mixture. After decoding chromatograms, the fractional composition of the liquid products was determined according to the technique described in GOST R 56720–2015.

Defining the group hydrocarbon composition of the liquid products

The group hydrocarbon composition of the oils in the initial raw materials and cracking products was determined by column liquid adsorption chromatography using active Al₂O₃ with the II degree of activity according to Brockman. The chromatography column was filled by the wet method in a 1 : 80 sample/sorbent mass ratio. The sample was mixed with *n*-hexane and equally distributed along the entire surface of the sorbent. Fractions of saturated, mono- and biaromatic hydrocarbons were partitioned using *n*-hexane; triaromatic and polyaromatic HC were eluted with 3 : 1 *n*-hexane/benzene and 1 : 1 ethanol/benzene mixtures by volume, correspondingly. Monitoring over partitioning HC of various classes was carried out *via* electron adsorption spectra of eluates. The spectra were collected using Specord UV-VIS spectrometer. Losses upon distilling off solvents were not higher than 2.5 mass %.

Determining the individual composition of hydrocarbons and sulphur compounds of the liquid products

The gas chromatography–mass spectrometry (GC-MS) analysis of the composition of saturated

and aromatic HC was conducted using GCMS-QP5050A Shimadzu quadrupole system with computer monitoring and data processing. The CR5-MS capillary quartz column with a length of 30 m and an inner pore diameter of 0.25 mm was used for partitioning, using helium as a carrier gas. The split ratio was 1 : 12. The analysis was carried out in the Scan detector operation mode (total ion scanning in the mass range between 50 and 800 amu) upon temperature programming to begin with 80 to 290 °C at a rate of 2 °C/min. The final temperature was maintained constant for 25 min. The ionizing voltage, and also injector and interface temperatures were 70 eV and 290 °C, correspondingly. Data collecting and processing in the SCAN mode was performed with the GCMSsolution software. Compound identification was carried out by comparing the resulting mass spectra with those available in NIST11, NIST02, and Willey229 libraries upon analysing mass fragmentograms according to characteristic ions for alkanes. The ions are as follows: m/z 57 and 183 for alkanes, m/z 55 for alkenes; m/z 69, 83, 191, and 217 for cyclanes; m/z 91, 105, 119, and 133 for alkylbenzene compounds; m/z 128, 142, 156, 170, and 184 for naphthalene and its alkyl-substituted derivatives, m/z 178, 192, 206, 220, and 234 for phenanthrene and its alkyl-substituted homologue; m/z 147, 161, and 175 for benzothiophene, and m/z 184, 198, 212, and 226 for dibenzothiophene derivatives. The assessment of the relative content for each type of compounds was calculated as a ratio of the total intensity to the total amount of areas of all species determined.

RESULTS AND DISCUSSION

Table 1 reports the mass balance of the cracking process of maltenes in the presence of *n*-butyl bromide (C_4H_9Br) as an initiating additive and without it. The cracking of maltenes when *n*-butyl

bromide is present results in the formation of solid products in significant amounts compared to cracking without the additive (see Table 1). These products are coke-like compounds not analysed in this work.

According to the analysis results of the material composition of the liquid products, the asphaltenes that were absent in the composition of maltenes not exposed to cracking and more resins (see Table 1) are generated upon the cracking of maltenes without the addition of C_4H_9Br . The content of the latter compounds is increased by 5.8 % compared to their quantity in the initial mixture (19.2 %). In addition, cracking in the presence of *n*-butyl bromide results in a decrease of the quantity of resins to 10.0 %, which is by 9.2 % lower than that in the initial maltenes and by 15.0 % than in cracking products without the additive. The findings allow the suggestion that *n*-butyl bromide here initiates destruction reactions of resins. The cracking of maltenes in the presence of *n*-butyl bromide also yields asphaltenes. The content of the latter is 2.3 times higher compared to those formed by cracking without the additive.

An increase in destruction depth of resins has an effect on the functional composition of cracking products. For example, upon maltene cracking in the presence of *n*-butyl bromide, there is an increase in the yield of light fractions compared to cracking without the additive. The number of distillate fractions reaches 61.5 % (in the temperature range: initial boiling points (IBP) up to 200 °C – 17.5 %, 200–360 °C – 44.0 %). The yield of the residue boiling above 360 °C, is reduced by about 2 times (Table. 2).

Changes in the group hydrocarbon composition of cracking products of maltenes (an increase or a decrease in the content of individual groups of HC) compared to the those in the initial maltenes take place resulting from the destruction of

TABLE 1

Composition of cracking products of maltenes

Products	Content in cracking products, mass %	
	Without C_4H_9Br additive	With C_4H_9Br additive
Solid	0.3	2.3
Gaseous	2.7	2.7
Liquid:	97.0	95.0
resins	25.0	10
asphaltenes	1.1	2.6
oils	70.9	82.4

Table 2

Fractional composition of liquid cracking products of maltenes

Fraction boiling point, °C	Content in cracking products, mass %	
	Without C ₄ H ₉ Br additive	With C ₄ H ₉ Br additive
IBP–200	5.1	17.5
200–360	33.5	44.0
>360	58.4	33.5

TABLE 3

Hydrocarbon composition of liquid products of maltene cracking

Hydrocarbons	Content, mass %		
	Initial maltenes	In liquid cracking products	
		Without C ₄ H ₉ Br additive	With C ₄ H ₉ Br additive
Saturated	27.6	23.8	26.4
Monoaromatic	12.3	15.2	15.5
Biaromatic	9.8	7.0	9.6
Triaromatic	8.1	9.7	7.5
Polyaromatic	22.7	15.2	23.4

resin molecules or due to condensation reactions that lead to asphaltene formation (Table 3).

The individual hydrocarbon composition of cracking products of maltenes was analysed by GC-MS. Figure 1 lists mass-fragmentograms according to the total ion current of maltenes and their cracking products. As can be seen, chromatograms of maltenes and their cracking products without the additive have weak peaks of *n*-alkanes and isoalkanes in the background of naphthenic humps, whereas there are distinct peaks of pentacyclanes in the high-molecular region (Fig. 1, *a* and *b*). The chromatogram of the products of cracking with *n*-butyl bromide has apparent peaks of *n*-alkanes that form a homologous series (see Fig. 1, *c*). At the same time, there are no peaks of pentacyclanes. An increase in the content of *n*-alkanes is likely due to the destruction of resin molecules owing to the cleavage or aliphatic substituents and/or that of arenes and cyclanes containing long alkyl chains.

Saturated HC of the products of cracking without the C₄H₉Br additive are presented by aliphatic and cyclic compounds, such as *n*-alkanes, alkenes, mono-, tetra- and pentacyclanes. The homological series of *n*-alkanes is comprised of compounds with 12–35 carbon atoms in a molecule; the maximum in the distribution falls on low-molecular C₁₅–C₁₇ homologues (Fig. 2). The ratio value of the total content of low-molecular C₁₂–C₁₉ *n*-alkanes to that of high-molecular ones C₂₀–C₃₁ is 0.97. During the cracking without the additive even C₁₆–C₂₈ *n*-alkenes are formed

Alkyl-substituted benzene (AB) derivatives in these products, as well as in maltenes are presented by the homological series of trimethylalkyl-substituted C₁₃–C₂₁ benzene derivatives (*m/z* 133) (Fig. 3, *a* and *b*). Alkyl-substituted naphthalene derivatives in maltenes and their cracking products without the additive are situated according to concentrations in the following series: trimethyl > dimethyl > tetramethyl > methylnaphthalene derivatives > unsubstituted naphthalene. Phenanthrene and anthracene compounds represent triarene derivatives; dimethyl-substituted phenanthrene homologues are prevailing among them.

Products of cracking with the C₄H₉Br additive have an increased content of *n*-alkanes (see Table 3). Moreover, the content of low-molecular C₁₁–C₁₉ *n*-alkanes is increased to a greater extent (see Fig. 2). The value of the ratio of low-molecular compounds to high-molecular ones is 2.8, while that without the additive is 0.97. The products of cracking with the C₄H₉Br additive do not contain alkenes, tetra- and pentacyclic saturated HC, and also trimethylalkyl-substituted C₁₃–C₂₁ benzene derivatives that are present in maltenes and their cracking products without the additive.

At the same time, alkyl-substituted benzene compounds are mainly presented by low-molecular tetramethyl-substituted benzene compounds of C₈–C₁₀ composition (see Fig. 3). That attests to the decomposition of alkyl-substituted benzene compounds that mainly proceeds at the β-C–C bond in the aliphatic substituent and leads to the

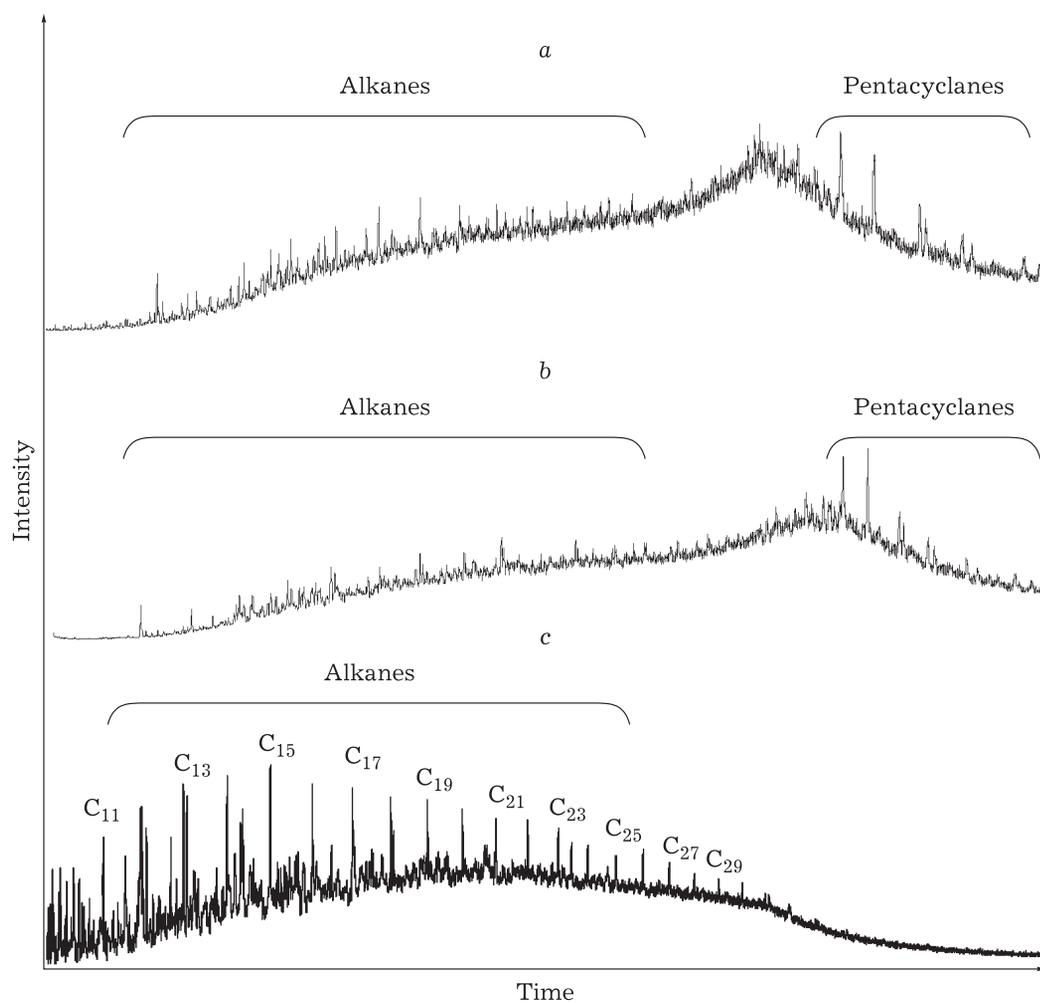


Fig. 1. Mass-fragmentograms according to the total ion current of maltenes (a) and their cracking products without the additive (b) and in the presence of *n*-butyl bromide (c).

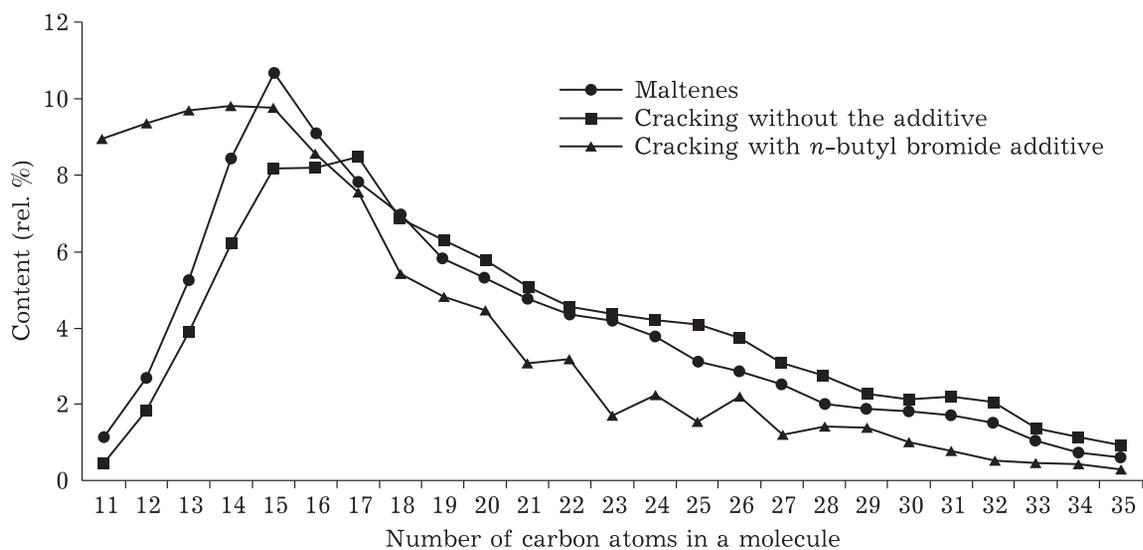


Fig. 2. Molecular mass distribution of *n*-alkanes in initial maltenes and their cracking products.

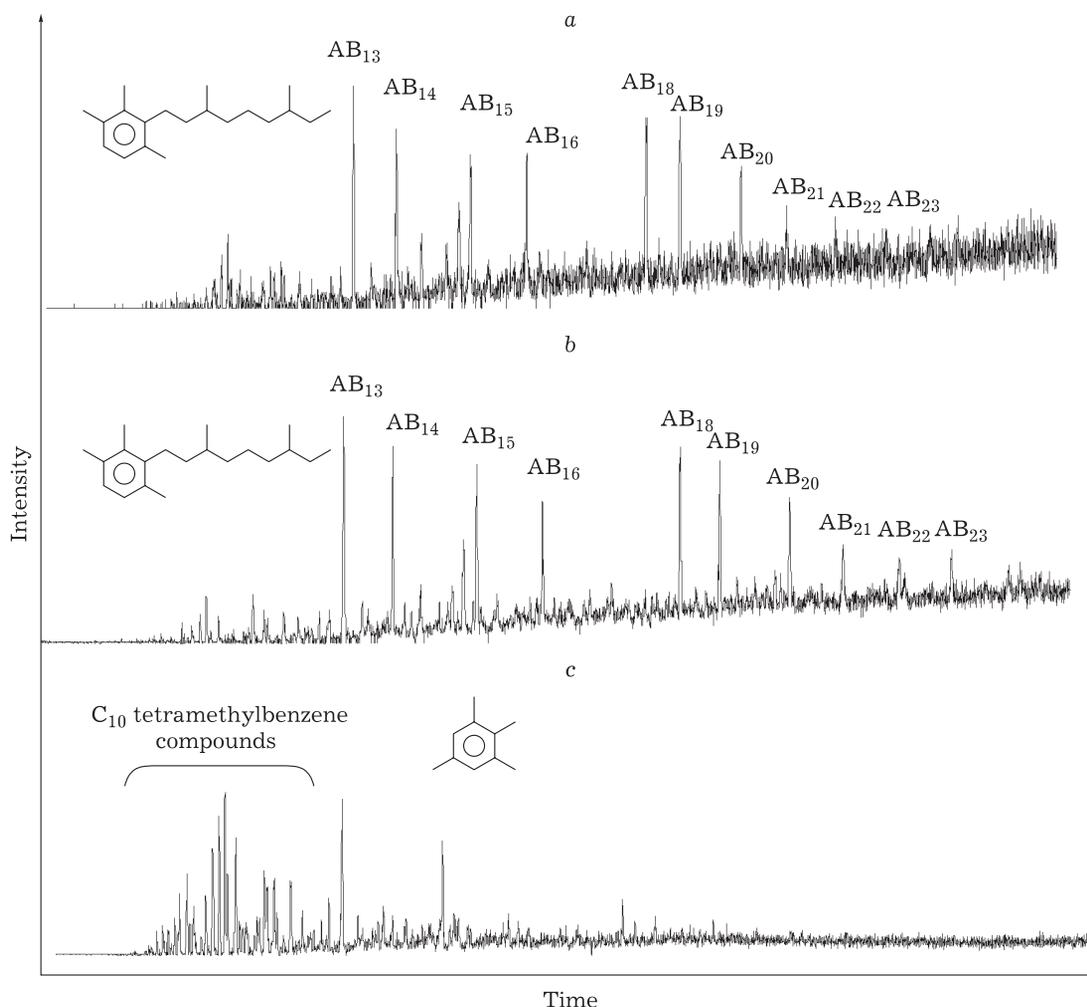


Fig. 3. Mass-fragmentograms of alkylbenzene compounds according to m/z 133 of maltenes (a) and their cracking products without the additive (b) and in the presence of *n*-butyl bromide (c).

formation of saturated HC and methyl-substituted benzene compounds. The lack of tetra- and pentacyclanes in cracking products with *n*-butyl bromide is probably related to their involvement in dehydrogenation reactions to form compounds that may be further structural moieties of asphaltene molecules.

The content of alkyl-substituted naphthalene compounds in cracking products without the additive and its presence is increased from 13.5 to 24.3 rel. %. Their formation is likely to proceed resulting from the destruction of resins due to the recombination of radicals formed upon the decomposition of aliphatic substituents in alkyl-substituted benzene compounds.

The content of unsubstituted naphthalene (from 0.3 to 3.0 rel. %) and methyl-substituted naphthalene (from 0.9 to rel. 4.0 %) derivatives in the composition of the products of cracking with *n*-alkyl

bromide is increased compared to the outcome without the additive. That may indicate the demethylation of polymethyl-substituted naphthalene compounds. The involvement of alkyl-substituted phenanthrene compounds into the formation of coke and asphaltene derivatives results in a reduction of their quantity in the products of cracking with *n*-butyl bromide compared to that without the additive. The decrease is from 11.4 to 9.9 rel. %.

Sulphur compounds in maltenes and cracking products are presented by benzo- and dibenzothiophene homologues. The products of cracking without the additive and with *n*-butyl bromide have an increased content of benzothiophene and dibenzothiophene compounds till 3.7 and 7.0 rel. %, and also 8.5 and 7.0 rel. %, respectively, compared to their levels in maltenes. The increase in their content is apparently related to the destruction of resinous components.

CONCLUSION

The paper explores the effect of an initiating additive (*n*-butyl bromide, 0.7 mass %) upon the cracking of maltenes from heavy oil of the Usinsk oil field on the yield and the fractional composition of the resulting products. As shown, the yield of distillate fractions boiling up to 360 °C is increased by 1.8 times compared to that during cracking without the additive.

As found, in addition to the profound destruction of resins, oils also undergo the transformation during the cracking of maltenes due to dealkylation and dehydrogenation reactions. The products of cracking with the *n*-butyl bromide additive do not contain alkenes, and also tetra- and pentacyclic saturated HC (hydrocarbons). Trimethylalkyl-substituted benzene compounds of C₁₃–C₂₁ composition are completely transformed to methyl-substituted benzene derivatives C₈–C₁₀. Polymethyl-substituted naphthalene derivatives are demethylated forming unsubstituted naphthalene and its methyl-substituted homologues.

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