(%): I, 37.97; Nd, 21.58. μ_{eff} = 2.8 μ_B (293 K). IR (Nujol), ν/cm^{-1}: 2930, 2879, 1453, 1409, 1189, 1095, 1060, 1035, 860, 548, 480. UV-Vis (DME), λ_{max}/nm: 515. On fast heating, compound **2** decomposes at temperatures above 50 °C.

Compounds **2**—**4** were obtained and isolated similarly. For **1** found (%): I, 37.01; Nd, 18.83. $C_{20}H_{40}I_2NdO_5$. Calculated (%): I, 33.46; Nd, 19.01. For **3** found (%): Dy, 20.16; I, 33.24. $C_{20}H_{40}DyI_2O_5$. Calculated (%): Dy, 20.95; I, 32.67. For **4** found (%): Dy, 22.80; I, 37.36. $C_{12}H_{30}DyI_2O_6$. Calculated (%): Dy, 23.66; I, 36.96.

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Alkylation of naphthalene and toluene by ethylene in naphthalene/alkali metal systems in THF

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We have previously[1,2] found that a reversible hydrogen transfer occurs between naphthalene rings of sodium naphthalene, as well as between sodium naphthalene and THF molecules, in the naphthalene/sodium system in THF at room temperature. Benzene, toluene, ethylene, and even methane undergo similar reactions of exchange of hydrogen atoms with the C—H bonds of naphthalene rings. Taking into account so high an efficiency of this system in C—H bond activation, we studied the possibility of using such systems for the alkylation of hydrocarbons by ethylene under mild conditions. In this work, we report on the first examples of these reactions found by us.

Experiments were carried out at room temperature and atmospheric pressure according to the standard procedure. The amount of naphthalene was 3 mmol, and the volume of THF was 1.5 mL (reaction time 24 h). Alkali metal (Li, Na, or K) was taken, as a rule, in a twofold molar excess with respect to naphthalene. The products formed were analyzed by GLC and GC-MS.

In a typical experiment, sodium (0.138 g, 6 mmol), naphthalene (0.384 g, 3 mmol), and THF (1.5 mL) were placed in a Schlenk tube under an argon atmosphere, and the mixture was stirred under an ethylene atmosphere on a magnetic stirrer at room temperature. A gradual absorption of ethylene was observed in the course of the reaction, and 1-ethylnaphthalene appeared in the solution. After 24 h, the amount of absorbed ethylene was 0.73 moles per mole of naphthalene, and the yield of 1-ethylnaphthalene was 37% based on naphthalene. Along with 1-ethylnaphthalene, small amounts (~3%) of its two dihydro derivatives were also found. The change of THF for 1,2-dimethoxyethane and a decrease in the molar ratio of Na to naphthalene from 2 : 1 to 1 : 1 decreased substantially the efficiency of alkylation. When the reaction was carried out in the presence of 15-crown-5, the products of naphthalene alkylation were formed as traces only.

The naphthalene/potassium system in THF exhibits even higher activity in naphthalene alkylation by ethyl-

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ene. For this system, the yield of 1-ethylnaphthalene is 71%. The reaction products also contain two isomeric dihydro derivatives of 1-ethylnaphthalene in a ~1 : 1 ratio (overall yield ~20%).

When ethylene reacts with the naphthalene/lithium system in THF, butyl- and hexylnaphthalenes (in 13 and 4% yields, respectively) and also dihydro derivatives of ethyl-, butyl-, and hexylnaphthalenes (2, 4, and 3%, respectively) are formed along with 1-ethylnaphthalene (yield 21%). Another distinctive feature of the lithium-containing system is that it absorbs a considerably higher amount of ethylene (~2.4 moles per mole of naphthalene for 24 h) than the systems using sodium and potassium.

Toluene can also be alkylated by ethylene in the naphthalene/alkali systems. The reaction proceeds at room temperature and results in the formation of higher monoalkylbenzenes. For example, when ethylene reacts with toluene in the presence of the naphthalene/lithium system in THF (molar ratio PhMe : $C_{10}H_8$ = 1 : 1), a mixture of *n*-propylbenzene (yield 30%), 3-phenylpentane (7%), *n*-amylbenzene (5%), 3-phenylheptane (5%), and *n*-heptylbenzene (1%) is formed. Naphthalene is also alkylated under these conditions to give 1-ethylnaphthalene (yield 37%), two of its dihydro derivatives (3%), and a mixture of dihydro derivatives of butyl- and hexylnaphthalenes (5 and 16%, respectively). Alkylation of toluene in the naphthalene/sodium system in THF affords *n*-propylbenzene (12%) and 3-phenylpentane (4%), and the products of naphthalene alkylation contain 1-ethylnaphthalene (yield 30%), two isomeric dihydro derivatives of 1-ethylnaphthalene (5%), and diethylnaphthalene (4%). The naphthalene/potassium system in THF in the presence of toluene exhibits a low activity in alkylation of both toluene and naphthalene.

Data on the possibility of using alkali metals (Na, K), their adducts with polycyclic aromatic hydrocarbons (in the absence of a solvating solvent), and graphite-potassium systems for alkylation of toluene and some other hydrocarbons by olefins, including ethylene, have already been published (see, *e.g.*, review[3] and articles[4–6]). However, these reactions occur with noticeable rates at elevated temperatures (90–250 °C) only.

Identification of products. 1-Ethylnaphthalene was identified by GLC and GC-MS using authentic 1-ethylnaphthalene as the standard (the conditions of GLC provided a distinct separation of 1- and 2-ethylnaphthalenes). *n*-Propylbenzene, *n*-amylbenzene, and *n*-heptylbenzene were identified by the same way (using standard authentic compounds). Butyl- and hexylnaphthalenes, as well as 3-phenylpentane and 3-phenylheptane, were identified on the basis of coincidence of their mass spectra with the corresponding published data.[7] The most important parameters of the mass spectra observed for these products are presented below, *m/z* (I_{rel} (%)): butylnaphthalene — 184 $[M]^+$ (62), 142 $[M - C_3H_6]^+$ (46), 141 $[M - Pr]^+$ (100), 115 $[M - Pr - C_2H_2]^+$ (56); hexylnaphthalene — 212 $[M]^+$ (50), 142 $[M - C_5H_{10}]^+$ (35), 141 $[M - C_5H_{11}]^+$ (100), 115 $[M - C_5H_{11} - C_2H_2]^+$ (27); 3-phenylpentane — 148 $[M]^+$ (31), 119 $[M - Et]^+$ (70), 91 $[C_7H_7]^+$ (100); 3-phenylheptane — 176 $[M]^+$ (50), 147 $[M - Et]^+$ (34), 119 $[M - Bu]^+$ (53), 91 $[C_7H_7]^+$ (100). The conclusions on the natures of other products is based on the analysis of their mass spectra.

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