



# Activation of C–H bonds of hydrocarbons by the ArH–alkali metal systems in THF (ArH – naphthalene, biphenyl, anthracene, phenanthrene, *trans*-stilbene, pyrene). Alkylation of naphthalene and toluene with ethene

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## ABSTRACT

Systems based on naphthalene and alkali metals (Li, Na, K) in THF are able to induce the alkylation of naphthalene with ethene at room temperature and atmospheric pressure. The highest activity in this reaction is exhibited by the naphthalene–potassium system which converts naphthalene into 1-ethyl-naphthalene (**1**) and small amounts of two isomeric dihydro derivatives of **1** in a yield of 85% (24 h, K:C<sub>10</sub>H<sub>8</sub> = 2:1). The same alkylation products are formed when metallic sodium is used instead of potassium. The interaction of ethene with the naphthalene–lithium system (24 h, Li:C<sub>10</sub>H<sub>8</sub> = 2:1) affords **1** together with 1-*n*-butylnaphthalene (**4**), 1-*n*-hexylnaphthalene (**5**), 1-*n*-oktylnaphthalene (**6**) and dihydro derivatives of **5** and **6** in a total yield of 60%. Alkylation of toluene with ethene in the naphthalene–alkali metal systems leads to the formation of higher monoalkylbenzenes. The greatest toluene conversion (48%, 24 h) is observed on using the lithium-containing system (Li:C<sub>10</sub>H<sub>8</sub> = 2:1), in the presence of which a mixture of *n*-propylbenzene (**11**), *n*-pentylbenzene (**12**), 3-phenylpentane (**13**) and 3-phenylheptane (**14**) is produced from ethene and toluene. On the replacement of lithium by sodium or potassium, only **11** and **13** are obtained. A treatment of biphenyl, phenanthrene, *trans*-stilbene, pyrene and anthracene with alkali metals in THF also gives systems capable of catalyzing the alkylation of toluene with ethene at 22 °C. Of particularly active is the stilbene–lithium system (Li:stilbene = 3:1) which converts toluene into a mixture of **11–14**, *n*-heptylbenzene and 5-phenylnonane in a yield of 58%. In all cases, the rate of the alkylation considerably increases in the presence of the solid phase of alkali metal. The mechanism of the reactions found is discussed.

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## 1. Introduction

Radical anion adducts of alkali metals with naphthalene and other aromatic hydrocarbons (biphenyl, anthracene, *trans*-stilbene, etc.) are widely used in chemical research owing to their ability to efficiently transfer electrons to various organic and inorganic substrates (for reviews, see e.g. [1–3]). They are successfully applied in organic and organometallic synthesis, catalysis and other fields. Of particular importance was the discovery of a high catalytic activity of such adducts in the polymerization of 1,3-dienes and some monoenes to produce “living” polymers.

Previously, we have reported on a new intriguing property of these remarkable reagents [4]. It turned out that on an addition of metallic sodium to a solution of [D<sub>0</sub>]naphthalene and [D<sub>10</sub>]naphthalene in [D<sub>0</sub>]THF a system is formed in which the hydrogen–deuterium exchange between naphthalene rings of sodium naphthalide as well as between sodium naphthalide and THF mol-

ecules takes place at room temperature. An important feature of this interesting reaction is its strong acceleration when the solid phase of the alkali metal is present in the mixture. Under homogeneous conditions, i.e. at a Na:C<sub>10</sub>H<sub>8</sub> molar ratio of 1:1, the rate of the process decreases. A number of other hydrocarbons such as benzene, toluene, ethene and even methane can also be drawn at room temperature into a similar H/D exchange reaction with naphthalene rings, in the case of toluene both the hydrogen atoms of the phenyl core and of the methyl group being involved in the process of the exchange.

Taking into account so high an efficiency of the above naphthalene–sodium system in C–H bond activation, we decided to test systems of such a type as catalysts for the alkylation of hydrocarbons with ethene under mild conditions. In 1971, Watanabe and co-workers described shortly the insertion reaction of isoprene into the C–H bond of the methyl group of toluene under the action of naphthalene–sodium in THF at room temperature [5]. The reaction was conducted at a Na:C<sub>10</sub>H<sub>8</sub> molar ratio of 2:1, i.e. in the presence of an excess of the alkali metal. Later, Carnahan and Closson observed the formation of small amounts (7%) of 1-ethylnaphthalene

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(1) together with its two dihydro derivatives (45%; after hydrolysis) in the interaction of ethene for 1 h with a mixture of naphthalene and excess lithium (Li:C<sub>10</sub>H<sub>8</sub> = 3:1) in tetrahydropyran at 25 °C [6]. It was also demonstrated by Fochi and Nucci in 1991 [7] that the naphthalene–potassium system (K:C<sub>10</sub>H<sub>8</sub> ~ 1.67:1) in 1,2-dimethoxyethane (DME) is capable of catalyzing at room temperature the selective dehydrogenation of 1,4-cyclohexadiene to benzene and molecular hydrogen. Interestingly, when biphenyl and phenanthrene were used instead of naphthalene in this system the concurrent disproportionation of 1,4-cyclohexadiene to benzene and cyclohexene occurred along with the dehydrogenation, and when naphthalene was replaced by anthracene only isomerization of 1,4-cyclohexadiene to its 1,3-isomer took place. The naphthalene–sodium and anthracene–sodium systems proved to be inactive towards 1,4-cyclohexadiene. No transformations of 1,4-cyclohexadiene were also observed on the use of a negatively charged electrode as a source of electrons in place of the above-mentioned arene–alkali metal systems.

In the present article, the reactions of the naphthalene and toluene alkylation with ethene at room temperature in the naphthalene–alkali metal systems in THF are described in detail. The alkylation of toluene with ethene catalyzed by analogous systems based on biphenyl, anthracene, *trans*-stilbene, phenanthrene and pyrene is also reported. The efficiency of the reactions studied depends substantially on the nature of the starting reagents, their ratio and other factors. In all cases, the greatest naphthalene and toluene conversions into alkylation products are observed when an excess of the alkali metal is present in the system. A short preliminary account of a part of this work has been published in [8].

As is known, alkali metals (Na, K), their adducts with polycyclic aromatic hydrocarbons (in the absence of a solvating solvent) as well as graphite–potassium systems are also able to catalyze the alkylation of toluene and some other hydrocarbons with olefins, including ethene [3,9–11]. However, these reactions proceed with noticeable rates only at elevated temperatures (90–250 °C). Recently, Yus and co-workers reported the reactions of some simple terminal and strained internal alkenes (propene, isobutene, norbornene, etc.) with systems based on polycyclic arenes (biphenyl, naphthalene, phenanthrene) and excess lithium metal (Li:arene = 4:1) in THF at 25 °C [12]. Under these conditions, products of the carbolithiation of the above alkenes by the arene dianions are produced after 1–2 h. For other papers concerning addition reactions of organometallic derivatives of alkali metals to alkenes, see [13–16] and references cited therein.

## 2. Results and discussion

In the first experiments, the interaction of ethene with the naphthalene–sodium system in THF was studied. The reactions

were carried out at room temperature and atmospheric pressure. The initial naphthalene concentration was 2 M and a Na:C<sub>10</sub>H<sub>8</sub> molar ratio was 2:1. On using such a ratio of the reagents, half the taken amount of metallic sodium was dissolved to give radical anion of naphthalene while another half remained undissolved, and thus the reaction with ethene was conducted here in the presence of the solid phase of the alkali metal.

The results of the experiments showed that under these conditions a gradual absorption of ethene by the naphthalene–sodium system occurs and 1 appears in the solution. After 24 h, the amount of absorbed ethene reaches 0.73 mol per mol of naphthalene and the yield of 1 is 35% based on naphthalene (Table 1). Along with 1, small quantities (~2%) of its two dihydro derivatives (2 and 3) are also obtained. Further increase in the reaction time (to 48 h) does not increase significantly the amount of absorbed ethene (0.82 mol per mol of naphthalene) and the naphthalene conversion (38%).

A decrease in a Na:C<sub>10</sub>H<sub>8</sub> molar ratio from 2:1 to 1:1 substantially diminishes both the rate of ethene uptake and the efficiency of the alkylation (Table 1). Even stronger retarding effect on ethene absorption and the alkylation reaction is caused by the replacement of THF with DME. On carrying out the reaction in the presence of [15]crown-5 (one mol per mol of naphthalene) only trace amounts of 1 (and no 2 and 3) are produced after 24 h (0.12 mol of absorbed ethene per mol of naphthalene). Similar effects of the nature of an ethereal solvent, a Na:C<sub>10</sub>H<sub>8</sub> ratio and additives of [15]crown-5 have previously been observed in the reactions of the hydrogen–deuterium exchange of hydrocarbons in the naphthalene–sodium system [4]. When a mixture of naphthalene with sodium in THF (Na:C<sub>10</sub>H<sub>8</sub> = 2:1) is held for 3 h under stirring in an argon atmosphere, the activity of the system in the subsequent reaction with ethene only insignificantly lowers.

Even higher efficiency in the naphthalene alkylation with ethene is exhibited by the naphthalene–potassium system in THF (Table 1). On using this system, the conversion of naphthalene into 1 at room temperature reaches 83% after 24 h (K:C<sub>10</sub>H<sub>8</sub> = 2:1). The reaction products contain also small quantities (2%) of 2 and 3. If DME is used as a solvent instead of THF the rate of the alkylation again considerably decreases, even though the amount of absorbed ethene increases. It should be noted that when 1 is introduced into the reaction with the naphthalene–potassium system in THF under Ar (K:C<sub>10</sub>H<sub>8</sub>:1 = 2:1:0.17) no 2 and 3 are formed (22 °C, 24 h). This means that the formation of small amounts of 2 and 3 in the naphthalene alkylation with ethene can not be due to the possible presence of traces of moisture in the system.

In the interaction of ethene with the naphthalene–lithium system in THF at 22 °C (24 h, Li:C<sub>10</sub>H<sub>8</sub> = 2:1), 1-*n*-butylnaphthalene (4) (yield 15%), 1-*n*-hexylnaphthalene (5) (9%), 1-*n*-octylnaphthalene (6) (5%) as well as two dihydro derivatives (7 and 8) of 5 (3%)

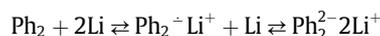
**Table 1**  
Alkylation of naphthalene with ethene in the naphthalene–alkali metal systems in THF and DME.<sup>a</sup>

M	M:C <sub>10</sub> H <sub>8</sub> (mol/mol)	Solvent	Reaction time (h)	Absorbed C <sub>2</sub> H <sub>4</sub>		Yield of alkylation products (%) <sup>b</sup>							C <sub>2</sub> H <sub>4</sub> consumption for alkylation		Naphthalene conversion (%)
				(mmol)	(mol/mol C <sub>10</sub> H <sub>8</sub> )	1	2 + 3	4	5	6	7 + 8	9 + 10	(mmol)	(mol/mol C <sub>10</sub> H <sub>8</sub> )	
Li	2:1	THF	24	5.40	1.80	26	–	15	9	5	3	2	3.60	1.20	60
Na	2:1	THF	2	0.63	0.21	17	–	–	–	–	–	–	0.51	0.17	17
	2:1	THF	4	1.08	0.36	31	–	–	–	–	–	–	0.93	0.31	31
	2:1	THF	24	2.19	0.73	35	2	–	–	–	–	–	1.11	0.37	37
	2:1	THF	48	2.43	0.82	36	2	–	–	–	–	–	1.14	0.38	38
	1:1	THF	24	1.38	0.46	16	–	–	–	–	–	–	0.48	0.16	16
	2:1	DME	24	0.66	0.22	9	–	–	–	–	–	–	0.27	0.09	9
K	2:1	THF	24	2.60	0.90	83	2	–	–	–	–	–	2.55	0.85	85
	2:1	DME	24	3.60	1.20	38	–	–	–	–	–	–	1.14	0.38	38

<sup>a</sup> 22 °C, 1 atm, 3 mmol of naphthalene, [C<sub>10</sub>H<sub>8</sub>]<sub>0</sub> = 2 M.

<sup>b</sup> Based on naphthalene.

and two dihydro derivatives (**9** and **10**) of **6** (2%) are produced together with **1** (26%) in an overall yield of 60% (Table 1). Another distinctive feature of the lithium-containing system is that it absorbs significantly greater quantities of ethene (1.8 mol per mol of naphthalene for 24 h) than the corresponding sodium- and potassium-based systems. Notably, in all of the above naphthalene–lithium and naphthalene–sodium systems, the amount of absorbed ethene noticeably exceeds its consumption for the formation of alkylation products (Table 1), which can be explained by the involvement of ethene in some other reactions, for example, with the alkali metal (activated by naphthalene) to give aliphatic organolithium or organosodium compounds. This assumption is supported by the data of Rautenstrauch [17] who showed that the interaction of ethene with a mixture of naphthalene and biphenyl in dimethoxymethane in the presence of a large excess of lithium metal (Li:C<sub>10</sub>H<sub>8</sub>:Ph<sub>2</sub> = 900:1:5.6) at –10 °C for 20 h affords vinyl lithium, 1,4-dilithiobutane, 1,6-dilithiohexane, 3-butenyllithium, *n*-butyllithium and probably lithium hydride [18]. It has been assumed that biphenyl plays a role of the active “carrier” of the alkali metal in this system, and two possible reaction mechanisms have been proposed. One of them suggests the transfer of electrons and lithium cations to ethene from the radical anion and/or dianion of biphenyl. According to another mechanism, ethene is directly attacked by some active form of lithium, which appears in the solution due to the equilibria (cf. [4]):



In the case of the naphthalene–lithium system in THF, an additional contribution to the observed ethene absorption could be made by the carbolithiation of ethene with the naphthalene dianion [6,12] which is known to be formed in such systems in certain amounts in the presence of an excess of metallic lithium [18d,19].

Toluene can also be alkylated with ethene in the naphthalene–alkali metal systems. The reactions proceed at room temperature and result in the formation of higher monoalkylbenzenes (Table 2). The greatest activity in this process is displayed by the naphthalene–lithium system in THF (Li:C<sub>10</sub>H<sub>8</sub> = 2:1; the C<sub>10</sub>H<sub>8</sub>:PhMe ratio is 1.06:1) which converts toluene into a mixture of *n*-propylbenzene (**11**) (yield 30%), *n*-pentylbenzene (**12**) (5%), 3-phenylpentane (**13**) (8%) and 3-phenylheptane (**14**) (5%) in a total yield of 48% based on toluene (24 h). When the reaction is conducted at a Li:C<sub>10</sub>H<sub>8</sub> ratio of 1:1 the conversion of toluene into alkylation products sharply falls down, and on using DME as a solvent no toluene alkylation occurs at all.

In the presence of toluene, naphthalene is also alkylated with ethene in the naphthalene–lithium system in THF (Li:C<sub>10</sub>H<sub>8</sub> = 2:1). As a result of the reaction, a mixture of **1–8** in 55% overall

yield is produced (Table 3). Here too, a decrease in a Li:C<sub>10</sub>H<sub>8</sub> ratio from 2:1 to 1:1 or the use of DME instead of THF considerably reduces the rate of the process. The amount of ethene absorbed by the naphthalene–lithium system in THF (Li:C<sub>10</sub>H<sub>8</sub> = 2:1) in the presence of toluene is significantly greater (Table 4) than that under the same conditions but in the absence of toluene (Table 1).

Alkylation of toluene with ethene in the naphthalene–sodium system in THF (Na:C<sub>10</sub>H<sub>8</sub> = 2:1) affords 15% of **11** and 3% of **13** after 24 h (Table 2), and products of the naphthalene alkylation contain **1** (33%) along with small quantities (3%) of **2** and **3** (Table 3). The replacement of THF by DME leads again to a strong decrease in the toluene and naphthalene conversion (Tables 2 and 3). The quantity of absorbed ethene decreases also under these conditions (Table 4). If [15]crown-5 (1 mol per mol of naphthalene) is added to the naphthalene–sodium system in THF (Na:C<sub>10</sub>H<sub>8</sub> = 2:1) only traces of products of the toluene and naphthalene alkylation are formed after 24 h and the amount of absorbed ethene drops from 2.77 to 0.37 mol per mol of naphthalene.

The naphthalene–potassium system in THF in the presence of toluene exhibits a low activity in alkylation of both naphthalene and toluene at 22 °C. When the reaction of ethene with this system is carried out for 24 h at a K:C<sub>10</sub>H<sub>8</sub> molar ratio of 2:1, the yield of **1** amounts only to 7% based on naphthalene (Table 3) and the conversion of toluene into alkylation products does not exceed 9% (8% of **11**, 1% of **13**; see Table 2). As mentioned above, the interaction of ethene with the naphthalene–potassium system in THF in the absence of toluene gives **1–3** in a total yield of 85% (Table 1) under similar conditions. Thus, an introduction of toluene in the naphthalene–potassium system leads to a strong inhibition of the process of the naphthalene alkylation. Interestingly, the replacement of THF by DME results here in an increase rather than in a decrease in the toluene and naphthalene conversion.

In the case of the naphthalene–sodium system in THF, an addition of toluene lowers the rate of the naphthalene alkylation as well. For example, if the reaction with ethene is conducted for 4 h (Na:C<sub>10</sub>H<sub>8</sub> = 2:1) the conversion of naphthalene into **1** in the absence of toluene attains 31% (Table 1) while in its presence only 20% of **1** are formed (Table 3). Upon an increase in the reaction time to 24 h, the yields of products of the naphthalene alkylation in the absence and in the presence of toluene become close to each other.

An introduction of toluene in the lithium-containing system in THF (Li:C<sub>10</sub>H<sub>8</sub> = 2:1) increases the yield of **1** but markedly decreases the overall yield of higher monoalkylnaphthalenes and their dihydro derivatives. As a result, the ethene consumption for the formation of products of the naphthalene alkylation in the absence of toluene proves here to be considerably greater than that

**Table 2**

Alkylation of toluene with ethene in the naphthalene–alkali metal systems in THF and DME.<sup>a</sup>

M	M:C <sub>10</sub> H <sub>8</sub> (mol/mol)	Solvent	Reaction time (h)	Yield of products of toluene alkylation (%) <sup>b</sup>				Toluene conversion (%)
				<b>11</b>	<b>12</b>	<b>13</b>	<b>14</b>	
Li	2:1	THF	24	30	5	8	5	48
	1:1	THF	24	9	–	1	–	10
	2:1	DME	24	–	–	–	–	0
Na	2:1	THF	4	6	–	–	–	6
	2:1	THF	24	15	–	3	–	18
	2:1	DME	24	1	–	–	–	1
K	2:1	THF	24	8	–	1	–	9
	2:1	DME	24	11	–	6	–	17

<sup>a</sup> 22 °C, 1 atm, 3 mmol of naphthalene, a C<sub>10</sub>H<sub>8</sub>:toluene molar ratio is 1.06:1, [C<sub>10</sub>H<sub>8</sub>]<sub>0</sub> = 2 M.

<sup>b</sup> Based on toluene.

**Table 3**

Alkylation of naphthalene with ethene in the naphthalene–alkali metal systems in THF and DME in the presence of toluene.<sup>a</sup>

M	M:C <sub>10</sub> H <sub>8</sub> (mol/mol)	Solvent	Reaction time (h)	Yield of products of naphthalene alkylation (%) <sup>b</sup>					Naphthalene conversion (%)
				<b>1</b>	<b>2+3</b>	<b>4</b>	<b>5</b>	<b>7+8</b>	
Li	2:1	THF	24	34	2	13	3	3	55
	1:1	THF	24	20	–	6	–	–	26
	2:1	DME	24	22	–	–	–	–	22
Na	2:1	THF	4	20	–	–	–	–	20
	2:1	THF	24	33	3	–	–	–	36
	2:1	DME	24	8	–	–	–	–	8
K	2:1	THF	24	7	–	–	–	–	7
	2:1	DME	24	29	–	–	–	–	29

<sup>a</sup> 22 °C, 1 atm, 3 mmol of naphthalene, a C<sub>10</sub>H<sub>8</sub>:toluene molar ratio is 1.06:1, [C<sub>10</sub>H<sub>8</sub>]<sub>0</sub> = 2 M.

<sup>b</sup> Based on naphthalene.

in the presence of toluene (see Tables 1 and 4). In all lithium-, sodium- and potassium-based systems, the amount of absorbed ethene in the presence of toluene significantly exceeds the ethene quantity consumed for the alkylation (Table 4). Note also, the

alkylation of naphthalene proceeds, as a rule, more efficiently than the toluene alkylation.

A treatment of biphenyl, phenanthrene, *trans*-stilbene, pyrene and anthracene with alkali metals in THF also gives systems

**Table 4**  
Comparison of the amount of absorbed ethene with its consumption for the formation of products of toluene and naphthalene alkylation in the naphthalene–alkali metal systems in THF and DME.<sup>a</sup>

M	M:C <sub>10</sub> H <sub>8</sub> (mol/mol)	Solvent	Reaction time (h)	Absorbed C <sub>2</sub> H <sub>4</sub> (mmol)	C <sub>2</sub> H <sub>4</sub> consumption for alkylation				Total (mmol)
					Toluene		Naphthalene		
					(mmol)	(mol/mol PhMe)	(mmol)	(mol/mol C <sub>10</sub> H <sub>8</sub> )	
Li	2:1	THF	24	7.25	2.01	0.71	2.40	0.80	4.41
	1:1	THF	24	2.20	0.31	0.11	0.96	0.32	1.27
	2:1	DME	24	1.47	0	0	0.66	0.22	0.66
Na	2:1	THF	4	1.20	0.17	0.06	0.60	0.20	0.77
	2:1	THF	24	2.77	0.59	0.21	1.08	0.36	1.67
	2:1	DME	24	0.94	0.03	0.01	0.24	0.08	0.27
K	2:1	THF	24	1.21	0.28	0.10	0.21	0.07	0.49
	2:1	DME	24	2.84	0.65	0.23	0.87	0.29	1.52

<sup>a</sup> 22 °C, 1 atm, 3 mmol of naphthalene, a C<sub>10</sub>H<sub>8</sub>:toluene molar ratio is 1.06:1, [C<sub>10</sub>H<sub>8</sub>]<sub>0</sub> = 2 M.

**Table 5**  
The effect of the nature of aromatic hydrocarbon (ArH) on the toluene alkylation with ethene in the ArH–alkali metal systems in THF<sup>a</sup>

ArH	M	M:ArH (mol/mol)	Absorbed C <sub>2</sub> H <sub>4</sub> (mmol)	Yield of alkylation products (%) <sup>b</sup>						C <sub>2</sub> H <sub>4</sub> consumption for alkylation		Toluene conversion (%)
				11	12	13	14	15	16	(mmol)	(mol/mol PhMe)	
Biphenyl	Li	2:1	3.87	25	5	2	–	–	–	1.10	0.39	32
		1:1	3.40	21	–	3	–	–	–	0.76	0.27	24
	Na	2:1	2.24	44	–	4	–	–	–	1.47	0.52	48
		1:1	2.62	31	–	2	–	–	–	0.99	0.35	33
Naphthalene	Li	2:1	7.25	30	5	8	5	–	–	2.01	0.71	48
		1:1	2.21	9	–	1	–	–	–	0.31	0.11	10
	Na	2:1	2.77	15	–	3	–	–	–	0.59	0.21	18
		K	2:1	1.21	8	–	1	–	–	0.28	0.10	9
Phenanthrene	Li	3:1	5.41	27	4	3	2	–	–	1.33	0.47	36
	Na	3:1	5.29	10	–	1	–	–	–	0.34	0.12	11
	K	3:1	5.42	12	–	24	–	–	–	1.70	0.60	36
Stilbene	Li	3:1	8.65	30	6	12	6	2	2	2.77	0.98	58
	2:1	6.33	22	–	11	–	–	–	–	1.25	0.44	33
Pyrene	Li	3:1	5.09	36	6	4	3	–	2	2.07	0.73	51
		2:1	2.62	14	–	–	–	–	–	0.40	0.14	14
	Na	2:1	1.20	<1	–	–	–	–	–	<0.03	<0.03	<1
Anthracene	Li	3:1	7.59	34	6	5	4	2	–	2.09	0.74	51
	2:1	4.74	27	4	3	2	–	–	1.33	0.47	36	

<sup>a</sup> 22 °C, 1 atm, 24 h, 3 mmol of ArH, an ArH:PhMe molar ratio is 1.06:1. With the exception of naphthalene, the initial ArH concentration is 1.67 M, [C<sub>10</sub>H<sub>8</sub>]<sub>0</sub> = 2 M.

<sup>b</sup> Based on toluene.

**Table 6**  
The effect of LiI on the toluene alkylation with ethene in the ArH–lithium systems in THF.<sup>a</sup>

ArH	Li:ArH (mol/mol)	[LiI] <sub>0</sub> (M)	Absorbed C <sub>2</sub> H <sub>4</sub> (mmol)	Yield of alkylation products (%) <sup>b</sup>						C <sub>2</sub> H <sub>4</sub> consumption for toluene alkylation		Toluene conversion (%)
				11	12	13	14	15	16	(mmol)	(mol/mol PhMe)	
Biphenyl	2:1	–	3.87	25	5	2	–	–	–	1.10	0.39	32
	2:1	0.28	7.80	34	6	4	3	–	–	1.78	0.63	47
Naphthalene	2:1	–	7.25	30	5	8	5	–	–	2.01	0.71	48
	2:1	0.33	9.61	30	6	5	4	2	5	2.55	0.90	52
Phenanthrene	2:1	–	9.73	33	6	8	5	2	–	2.32	0.82	54
	3:1	–	5.41	27	4	3	2	–	–	1.33	0.47	36
Stilbene	3:1	0.56	6.92	35	6	5	4	2	–	2.12	0.75	52
	3:1	–	8.65	30	6	12	6	2	2	2.77	0.98	58
Anthracene	3:1	0.56	9.61	24	5	17	6	2	2	2.83	1.00	56
	3:1	–	7.59	34	6	5	4	2	–	2.09	0.74	51
	3:1	0.56	6.68	29	4	3	2	–	–	1.39	0.49	38

<sup>a</sup> 22 °C, 1 atm, 24 h, 3 mmol of ArH, an ArH:PhMe molar ratio is 1.06:1. With the exception of naphthalene, the initial ArH concentration is 1.67 M, [C<sub>10</sub>H<sub>8</sub>]<sub>0</sub> = 2 M.

<sup>b</sup> Based on toluene.

capable of catalyzing the alkylation of toluene with ethene at room temperature. As seen from Table 5, in the case of lithium, the activity of the examined aromatic hydrocarbons in the toluene alkylation with ethene falls in the order: stilbene > pyrene ~ anthracene > naphthalene > phenanthrene > biphenyl. The highest efficiency is exhibited by the stilbene-based system which converts toluene into a mixture of **11–14**, *n*-heptylbenzene (**15**) and 5-phenylnonane (**16**) in a yield of 58% (Li:stilbene = 3:1; 24 h). The least alkylation rate is observed for the biphenyl–lithium system.

With metallic sodium, the biphenyl-, phenanthrene- and pyrene-containing systems were tested and it was found that in this case the examined aromatic hydrocarbons are arranged in the following sequence according to their activity in the toluene alkylation: biphenyl > naphthalene > phenanthrene > pyrene. The greatest toluene conversion is reached here for the biphenyl-based system. On using pyrene, the replacement of lithium by sodium leads to a practically full loss of the activity in the toluene alkylation. In all cases, with the exception of biphenyl, the lithium-containing systems are noticeably more efficient than the corresponding sodium-containing systems. In the case of biphenyl, the use of sodium instead of lithium gives markedly higher toluene conversion. In all systems, the presence of the solid phase of alkali metal in a mixture considerably increases the rate of the toluene alkylation.

The efficiency of the alkylation of toluene with ethene in the biphenyl–lithium and phenanthrene–lithium systems in THF can be substantially augmented if the reactions are carried out in the presence of lithium iodide (Table 6). For example, an introduction of LiI into the phenanthrene–lithium system enhances the toluene conversion into alkylation products from 36% to 52% (24 h). In the case of the naphthalene- and stilbene–lithium systems, additives of LiI little affect the alkylation rate. An addition of LiI to the anthracene–lithium system inhibits the process of the alkylation (Table 6).

### 3. Conclusion

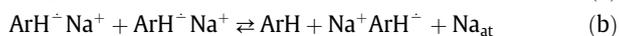
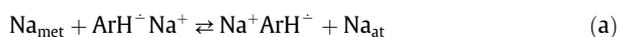
Systems based on naphthalene and metallic lithium, sodium or potassium in THF are able to induce alkylation of naphthalene and toluene with ethene at room temperature. As a result of the reactions, naphthalene is converted into linear 1-alkylnaphthalenes  $C_{10}H_7(CH_2CH_2)_nH$  (Li,  $n = 1–4$ ; Na and K,  $n = 1$ ) and their dihydro derivatives while toluene produces linear and  $\alpha$ -branched higher monoalkylbenzenes. A treatment of biphenyl, anthracene, *trans*-stilbene, phenanthrene and pyrene with alkali metals in THF also yields systems capable of catalyzing the alkylation of toluene with ethene at 22 °C to afford linear and  $\alpha$ -branched monoalkylbenzenes. In all cases, the use of lithium-containing systems favours the formation of products with longer alkyl chains. The greatest activity in the naphthalene alkylation is exhibited by the naphthalene–potassium system which gives 85% naphthalene conversion into alkylation products after 24 h. The stilbene–lithium system shows the highest activity in the toluene alkylation (the toluene conversion is 58% after 24 h). In the case of toluene, the C–H bonds of its methyl group are involved in the reaction with ethene, thereby giving rise to two families of the alkylation products, viz. linear  $C_3$ ,  $C_5$ ,  $C_7$  and  $\alpha$ -branched  $C_5$ ,  $C_7$  and  $C_9$  monoalkylbenzenes. The yields of these products and their ratios depend on the nature of the system used. The process of the alkylation is accompanied by absorption of large amounts of ethene. As is known, THF is splitted in systems of such a type into acetaldehyde enolate and ethene at room temperature [6,18d,20], and, naturally, this autogenously produced ethene can also be involved in the naphthalene and toluene alkylation. The formation of small amounts of 1-ethyl-naphthalene (2%) in the interaction of THF with the naphthalene–lithium system (Li: $C_{10}H_8 = 2.35:1$ ) for 24 h at 25 °C [18d]

supports this conclusion. Benzene is inactive in the alkylation with ethene at room temperature.

A comparison of the alkylation reactions found with the above-mentioned reactions of the H/D exchange of hydrocarbons in the naphthalene–sodium system in THF [4] shows that there is a number of common features between these two types of the processes. The both reactions are strongly accelerated in the presence of the solid phase of alkali metal. In both cases, the replacement of THF by DME in the naphthalene–sodium systems decreases sharply the reaction rate (up to zero in the case of the H/D exchange). Finally, the both processes are dramatically inhibited by additives of [15]crown-5.

On the basis of the results obtained on studying the H/D exchange of hydrocarbons in the naphthalene–sodium system, it has been suggested [4] that this process proceeds through the following main steps:

- (1) Generation of atomic sodium in the  $C_{10}H_8-Na$  system due to the reactions (a),(b),(c):

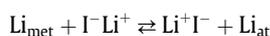


ArH – naphthalene

- (2) Agglomeration of atomic sodium into sodium clusters  $[Na_n]$  stabilized by the formation of surface complexes with naphthalene.
- (3) Reversible cleavage of C–H and C–D bonds of hydrocarbons on the surface of sodium clusters, resulting in the hydrogen–deuterium exchange.

In homogeneous medium, i.e. at a  $C_{10}H_8:Na$  molar ratio of 1:1, atomic sodium could be formed due to reactions (b) and (c). When an excess of the alkali metal is present in a mixture, the conditions for occurrence of reaction (a) are established, which leads to an increase in the content of sodium clusters in the system and, as a consequence, to an increase in the rate of the H/D exchange. A sharp retardation of the H/D exchange reaction on the use of DME instead of THF and also on an addition of [15]crown-5 has been explained by the necessity of the existence of intermediate surface complexes of sodium atoms with naphthalene (or other hydrocarbon molecules) as contact ion pairs. The formation of such ion pairs could provide a direct contact of the reacting hydrocarbon with active metallic centres on the surface of the cluster. As is known, sodium naphthalide in a DME solution, in contrast to sodium naphthalide in THF, exists at room temperature as solvent-separated ion pairs [1,19,21]. A conclusion has also been made that the naphthalene dianion can not play the part of the active species in the H/D exchange because metallic sodium in contrast to lithium metal does not form the corresponding dianion with naphthalene in THF at 22 °C [19].

A similar “cluster” mechanism can be proposed for the above-described reactions of the naphthalene and toluene alkylation with ethene. As in the case of the H/D exchange, this process starts, presumably, with the formation of atomic alkali metal by reactions of the type (a),(b),(c). In the lithium metal-based systems containing lithium iodide, atomic lithium could also be generated due to the reaction between Li and LiI.



This Li–LiI system can be considered as an analogue of the well-known Mg–MgI<sub>2</sub> system in ether wherein the formation of magnesium subiodide MgI was postulated [22,23] in order to explain the activating effect of MgI<sub>2</sub> on metallic magnesium.



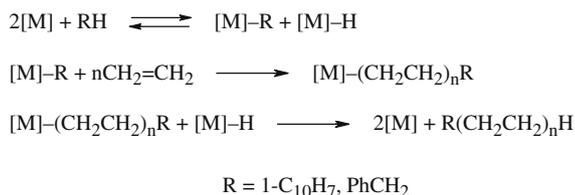
In the next stages, the atomic metal species formed agglomerate into the corresponding clusters which then reversibly cleave the reactive C–H bonds of a hydrocarbon (RH) to afford surface [M]–R and [M]–H groups. The subsequent ethene insertion into the alkali metal–carbon bonds arising on the surface of the clusters gives rise (after the reductive elimination) to the products of the naphthalene and toluene alkylation with linear alkyl chain (Scheme 1).

One may suggest that in the case of toluene, one of the C–H bonds of the benzyl CH<sub>2</sub> group in the resulting linear products, PhCH<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>H, is also able to undergo the metallation, yielding surface [M]–CH(Ph)(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>H and [M]–H moieties. These moieties could be the source of  $\alpha$ -branched higher monoalkylbenzenes in the subsequent reaction with ethene (Scheme 2). The ability of benzyl lithium and phenyllithium as well as primary and secondary alkyl lithium species to add to ethene in THF at room temperature has earlier been reported by Maercker et al. [14,24].

The absence of  $\alpha$ -branched 1-alkylnaphthalenes in products of the naphthalene alkylation can be explained by a strong decrease in the rate of the metallation of the  $\alpha$ -CH<sub>2</sub> group in the linear 1-alkylnaphthalenes, 1-C<sub>10</sub>H<sub>7</sub>(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>H, because of the steric hindrances created by the neighbouring *peri*-hydrogen atom of the naphthalene ring (cf. [25]).

The process of the reductive elimination leads to a termination of the growing alkyl chain due to its coupling with the hydrogen atom of a surface [M]–H group. The appearance of these [M]–H groups on the cluster surface can result from the C–H bond cleavage of the aromatic substrate as well as of the THF and ethene molecules. The occurrence of the hydrogen–deuterium exchange between THF and naphthalene and also between ethene, THF and naphthalene in the naphthalene–sodium system [4] supports this assumption. The surface [M]–H groups could also be a source of hydrogen for the formation of dihydro derivatives of 1-alkylnaphthalenes in the naphthalene alkylation reactions. Another pathway of a termination of a growing alkyl chain in the process of the alkylation might consist in a direct protonation of the surface [M]–(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>R and similar metal organyl moieties with THF (cf. [1]). As is known, alkyl derivatives of alkali metals are unstable in THF at room temperature and, as a rule, rapidly undergo the protolysis with THF molecules to give the corresponding free hydrocarbons (see e.g. [14,26]).

Coupling products of the type R–R and R(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>R either are detected in the reaction solutions only in trace amounts (1,1'-binaphthyl, 1-C<sub>10</sub>H<sub>7</sub>(CH<sub>2</sub>CH<sub>2</sub>)CH<sub>2</sub>Ph (**17**), 1-C<sub>10</sub>H<sub>7</sub>(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>Ph (**18**), dibenzyl) or are not detected at all, which can be connected with a large excess of THF relative to the starting hydrocarbon. Indeed, because THF (along with RH) is proposed to be one of the sources of the [M]–H bonds on the cluster surface, one may assume that the number of such bonds, for the above reason, will be significantly greater than that of the [M]–R bonds, and, correspondingly, the rate of the formation of the alkylation products R(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>H in the reaction with ethene will be significantly higher than that of the coupling products R–R and R(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>R. An additional contribution to the predominant formation of R(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>H could be



Scheme 1.

made by the above-mentioned rapid, direct protonation of the intermediate surface [M]–(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>R species with THF.

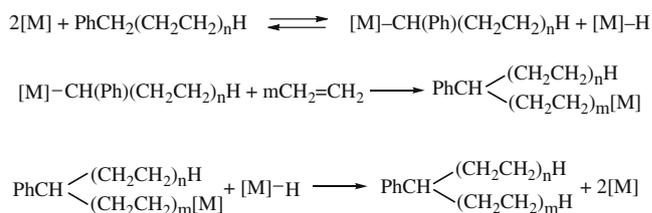
Phenyl ring of toluene, in contrast to toluene methyl group, is not alkylated with ethene in the above ArH–alkali metal systems although both these groups are involved in the H/D exchange with naphthalene rings of sodium naphthalide in THF [4]. This fact can be explained by a competition between ethene and the aromatic substrate for active metallic sites of the clusters. Apparently, in the case of the C–H bonds of toluene phenyl group, which are considerably less acidic than those of toluene methyl group, such a competition with ethene results in a total inhibition of the alkylation reaction. The same reason leads, presumably, to inactivity of benzene in the alkylation despite the fact that benzene also undergoes the H/D exchange with naphthalene rings in the naphthalene–sodium system in THF (see above and [4]).

The formation of alkali metal clusters in the gas phase and in solid inert gas matrices is now well documented (see e.g. [27–30]). Data of quantum-chemical calculations of such clusters are also available (see e.g. [28–33]). Recently, the metal vapour synthesis (MVS) and characterization of the cluster aryl Grignard reagents PhMg<sub>4</sub>X (X = F, Cl, Br) containing four magnesium atoms per one phenyl group and one halogen atom have been reported [34,35]. The clusters are quite stable under usual conditions in a halobenzene solution and are easily transformed into the corresponding cluster alkyl Grignard reagents RMg<sub>4</sub>Cl (R = C<sub>7</sub>H<sub>15</sub>, C<sub>8</sub>H<sub>17</sub>) in the interaction with alkyl chlorides RCl. It has also been shown [36] that under MVS conditions in the magnesium–anthracene system the resulting magnesium clusters are inserted into C–H bonds at the 9- and 10-positions of anthracene to afford cluster anthracenylmagnesium hydrides: 9-C<sub>14</sub>H<sub>9</sub>Mg<sub>4</sub>H and 9,10-C<sub>14</sub>H<sub>8</sub>(Mg<sub>4</sub>H)<sub>2</sub>. These compounds can be considered as models of the aforementioned hypothetical [M]–R and [M]–H species which could be generated from naphthalene and toluene on the surface of alkali metal clusters in the course of the alkylation.

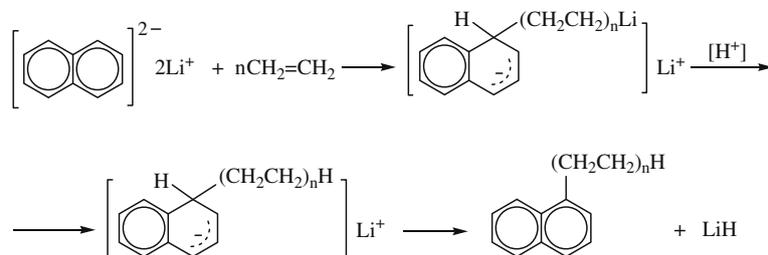
For naphthalene and lithium in THF and for other arenes capable of forming dianionic adducts with alkali metals in this solvent, an alternative reaction mechanism with the participation of the corresponding arene dianion as the active species should also be discussed.

In the case of the naphthalene alkylation, the proposed reaction Scheme 3 is based on the ability of the lithium salts of the naphthalene, biphenyl and phenanthrene dianions to add to some alkenes, including ethene, in THF at 25 °C [6,12]. The mechanism suggests fast protonation of the primary alkyl lithium centre in the resulting products of the ethene insertion with THF [14,26] or/and some other quenchable component of the reaction medium, for instance, with ethene (cf. [12]). For the formation of 1-alkylnaphthalenes in the course of the alkylation, it is necessary also to postulate within the framework of this mechanism the elimination of lithium hydride from the end products of the carbolithiation although it is not quite clear how efficiently such a process might occur under our experimental conditions.

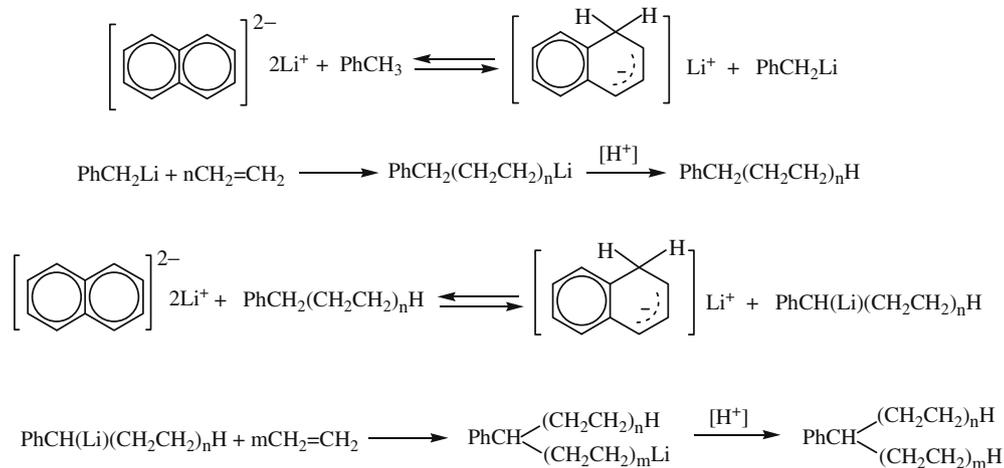
The role of the naphthalene dianion in the toluene alkylation could consist here in the reversible metallation of the toluene



Scheme 2.



Scheme 3.



Scheme 4.

methyl group to give benzyllithium which then reacts with ethene producing linear higher monoalkylbenzenes. The formation of  $\alpha$ -branched monoalkylbenzenes could proceed in a similar fashion (Scheme 4).

It should be noted however that although as a whole this alternative mechanism of the alkylation satisfactorily explains the results obtained for the naphthalene–lithium system, a problem arises in the case of the naphthalene–sodium system because of inability of metallic sodium to form the dianion with naphthalene in THF at room temperature in any detectable amounts [19]. For metallic potassium, there are also no unambiguous evidences for the formation of the corresponding naphthalene dianion in a THF solution at 22 °C. According to Ref. [37], dipotassium naphthalene, prepared by condensation of potassium and naphthalene vapors, instantly and completely decomposes into monopotassium naphthalene and metallic potassium on dissolution in THF. Of course, it must not be ruled out that some tiny quantities of the naphthalene dianion are present indeed in the naphthalene–sodium and naphthalene–potassium systems in THF. However, it is unclear whether such negligible concentrations of the dianion can provide those alkylation rates which were observed at room temperature in our experiments.

For the elucidation of the genuine mechanism of the naphthalene and toluene alkylation in the above-described systems, special studies are required.

#### 4. Experimental

The experiments were carried out in an Ar atmosphere with careful exclusion of air oxygen and moisture using standard Shlenk techniques. THF, DME and toluene were purified in the usual manner and freshly distilled prior to use from sodium/benzophenone

(THF, DME) or over sodium (toluene) under Ar. Commercial naphthalene, biphenyl, phenanthrene, *trans*-stilbene, pyrene and anthracene of high quality as well as [15]crown-5 were used without further purification. Metallic lithium, sodium and potassium were introduced into the reactions in the form of the particles of the size: ca.  $3 \times 2 \times 0.3$  mm in the case of lithium and ca.  $4 \times 3 \times 0.5$  mm in the case of sodium and potassium. Solutions of LiI in THF were prepared by the reaction of metallic lithium with iodine in THF under Ar. The reaction products were analysed by GLC with temperature programming (160 °C, 10 min; 160–300 °C, 10 °C/min; 300 °C, 40 min) on a Crompack CP 9001 chromatograph equipped with a flame ionization detector and a DB5 MS (30 m  $\times$  0.25 mm) capillary column (the internal standard – dodecane). The GLC/MS analyses were performed on a Trio 1000, FISONs instrument. The most part of the experiments was duplicated or triplicated showing reasonably good reproducibility. When the naphthalene–potassium system in THF was used for the naphthalene alkylation in the absence of toluene the reproducibility was somewhat worse and here the results obtained were averaged for five runs (**1** –  $83 \pm 6\%$ ), **2** + **3** –  $2 \pm 1\%$ ).

##### 4.1. Product identification

Compounds **1**, **4**, **5**, **11**, **12** and **15** were identified by GLC and GLC/MS using authentic samples of these compounds. Products **13** and **14** as well as 1,1'-binaphthyl and dibenzyl were identified on the basis of coincidence of their mass spectra with the corresponding literature data [38]. The conclusion on the nature of other products is based on the analysis of their mass spectra. The most important characteristics of the mass spectra recorded for these products are given below. Compound **2**,  $m/z$ : 158 ( $[\text{M}]^+$ , 53%), 129 ( $[\text{M}-\text{Et}]^+$ , 100%), 128 ( $[\text{C}_{10}\text{H}_8]^+$ , 65%). Compound **3**,  $m/z$ : 158 ( $[\text{M}]^+$ , 63%), 129

([M–Et]<sup>+</sup>, 100%), 128 ([C<sub>10</sub>H<sub>8</sub>]<sup>+</sup>, 92%). Compound **6**, *m/z*: 240 ([M]<sup>+</sup>, 12%), 142 ([M–C<sub>7</sub>H<sub>14</sub>]<sup>+</sup>, 28%), 141 ([M–C<sub>7</sub>H<sub>15</sub>]<sup>+</sup>, 100%), 128 ([C<sub>10</sub>H<sub>8</sub>]<sup>+</sup>, 14%), 115 ([M–C<sub>7</sub>H<sub>15</sub>–C<sub>2</sub>H<sub>2</sub>]<sup>+</sup>, 79%). Compound **7**, *m/z*: 214 ([M]<sup>+</sup>, 12%), 185 ([M–Et]<sup>+</sup>, 30%), 157 ([M–Bu]<sup>+</sup>, 22%), 129 ([M–Hex]<sup>+</sup>, 100%), 128 ([C<sub>10</sub>H<sub>8</sub>]<sup>+</sup>, 80%). Compound **8**, *m/z*: 214 ([M]<sup>+</sup>, 8%), 185 ([M–Et]<sup>+</sup>, 14%), 157 ([M–Bu]<sup>+</sup>, 16%), 129 ([M–Hex]<sup>+</sup>, 100%), 128 ([C<sub>10</sub>H<sub>8</sub>]<sup>+</sup>, 86%). Compound **9**, *m/z*: 242 ([M]<sup>+</sup>, 10%), 213 ([M–Oct]<sup>+</sup>, 35%), 185 ([M–Bu]<sup>+</sup>, 11%), 157 ([M–Hex]<sup>+</sup>, 31%), 129 ([M–Oct]<sup>+</sup>, 100%), 128 ([C<sub>10</sub>H<sub>8</sub>]<sup>+</sup>, 93%). Compound **10**, *m/z*: 242 ([M]<sup>+</sup>, 13%), 213 ([M–Et]<sup>+</sup>, 44%), 185 ([M–Bu]<sup>+</sup>, 15%), 157 ([M–Hex]<sup>+</sup>, 42%), 129 ([M–Oct]<sup>+</sup>, 84%), 128 ([C<sub>10</sub>H<sub>8</sub>]<sup>+</sup>, 100%). Compound **16**, *m/z*: 204 ([M]<sup>+</sup>, 8%), 147 ([M–Bu]<sup>+</sup>, 9%), 91 ([C<sub>7</sub>H<sub>7</sub>]<sup>+</sup>, 100%). Compound **17**, *m/z*: 246 ([M]<sup>+</sup>, 15%), 155 ([M–PhCH<sub>2</sub>]<sup>+</sup>, 10%), 142 ([M–PhCHCH<sub>2</sub>]<sup>+</sup>, 38%), 141 ([M–Ph(CH<sub>2</sub>)<sub>2</sub>]<sup>+</sup>, 43%), 128 ([C<sub>10</sub>H<sub>8</sub>]<sup>+</sup>, 15%), 115 ([M–Ph(CH<sub>2</sub>)<sub>2</sub>–C<sub>2</sub>H<sub>2</sub>]<sup>+</sup>, 67%), 91 ([C<sub>7</sub>H<sub>7</sub>]<sup>+</sup>, 100%). Compound **18**, *m/z*: 274 ([M]<sup>+</sup>, 14%), 155 ([M–Ph(CH<sub>2</sub>)<sub>3</sub>]<sup>+</sup>, 12%), 142 ([M–Ph(CH<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>]<sup>+</sup>, 37%), 141 ([M–Ph(CH<sub>2</sub>)<sub>4</sub>]<sup>+</sup>, 64%), 128 ([C<sub>10</sub>H<sub>8</sub>]<sup>+</sup>, 12%), 115 ([M–Ph(CH<sub>2</sub>)<sub>4</sub>–C<sub>2</sub>H<sub>2</sub>]<sup>+</sup>, 70%), 91 ([C<sub>7</sub>H<sub>7</sub>]<sup>+</sup>, 100%).

#### 4.2. Alkylation of naphthalene in the C<sub>10</sub>H<sub>8</sub>–Na system

Naphthalene (0.384 g, 3 mmol), THF (1.5 ml), metallic sodium (0.138 g, 6 mmol) and dodecane (0.0533 g) were placed in the Schlenk tube under Ar. The content of the Schlenk tube was cooled with liquid dinitrogen and, after removal of the argon by evacuation, the mixture was unfrozen to room temperature. Then ethene was introduced from an attached mercury burette and the reaction mixture was stirred at room temperature on a magnetic stirrer. The course of the reaction was monitored based on ethene absorption. After 24 h, when the amount of absorbed ethene attained 0.73 mol per mol of naphthalene (ca. 49 ml, STP), the mixture was diluted with 1.5 ml of THF and analysed by GLC and GLC/MS. The analyses showed the presence of **1** (35% based on naphthalene) together with small amounts (2%) of **2** and **3** in the reaction solution. The overall conversion of naphthalene is 37%.

#### 4.3. Alkylation of toluene and naphthalene in the C<sub>10</sub>H<sub>8</sub>–Li system

Naphthalene (0.384 g, 3 mmol), THF (1.2 ml), metallic lithium (0.042 g, 6 mmol), toluene (0.3 ml, 2.84 mmol) and dodecane (0.0485 g) were charged under Ar in the Schlenk tube and, after replacement of the argon atmosphere by ethene (from an attached mercury burette; see above), the mixture was stirred at room temperature on a magnetic stirrer. After 24 h, when the amount of absorbed ethene reached 2.42 mol per mol of naphthalene (ca. 163 ml, STP), the reaction solution was diluted with 1.5 ml of THF and analysed by GLC and GLC/MS for the content of products of the naphthalene and toluene alkylation. The results of the analyses are as follows: the naphthalene conversion is 55% (34% of **1**,

2% of **2** and **3**, 13% of **4**, 3% of **5**, 3% of **7** and **8**); the toluene conversion is 48% (30% of **11**, 5% of **12**, 8% of **13**, 5% of **14**).

Other experiments on the toluene and naphthalene alkylation were carried out by similar procedures. The results are summarized in Tables 1–6.

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