ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 8, pp. 1885–1895. © Pleiades Publishing, Ltd., 2015.
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Promoting of Non-Transition Metal Alkylation with Organyl Halides in the Presence of Binary Systems Based on an Organometallic Compound and a Transition Metal Compound: IV.[1] The Effect of Nature of the Organometallic Component of the Binary System on the Rate of the Stationary Process

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Received April 6, 2015

Abstract—Using alkylation of commercial zinc and cadmium powders with organic halides in the presence of the organometallic compound–copper(I) iodide binary systems as an example, it has been demonstrated that the rate of the stationary process can be drastically varied depending on the nature of the organometallic component. Both the nature of the metal and the ligand composition of the organometallic compound were significant factors. Activity of the binary systems in the considered process correlates with the organometallic component reactivity upon its transmetalation with the second compulsory component of the binary system (the transition metal compound).

Keywords: zinc, cadmium, alkyl halide, alkylation, catalysis, mechanism

DOI: 10.1134/S1070363215080162

The earlier proposed [2] scheme of stimulated alkylation of metals with organic halides in the presence of binary mixtures suggests that the rate of the stationary process should depend on the nature of the binary system components. In particular, the nature of the organometallic compound affects the rate of formation of the labile organic derivative of the transition metal upon the interaction of the binary system via transmetalation. On top of that, the organometallic compound can enhance the solubility of the organic derivative of the transition metal in the reaction mixture and stabilize it in the course of the transfer to the surface of the alkylated metal owing to formation of the ate-complex. The influence of the organometallic component nature on the rate and the equilibrium position of other stages of formation of the active surface of the alkylated metal involving the organometallic compound is fairly understandable as well [2]. Therefore, the increase of the transmetalation reactivity of the organometallic component of the binary system towards the transition metal compound (the second component of the binary system) has been expected to increase the active surface area and to accelerate the rate of the stationary direct synthesis.

Solutions of organometallic compounds generally contain the metal-containing particles of different reactivity. For example, organometallic compounds can dissociate to form ion pairs, free solvated ions, ion aggregates, self-associates, and complexes with the Lewis bases if any is present in the solution [2]. Therefore, the reactivity of organometallic compounds is an effective parameter including the overall reactivity of the metal-containing species present in the solution [3]. Reactivity of organometallic compounds in different processes varies fairly significantly, due to a number of possible reasons. It has been suggested in [4] that these reasons can be in the first approximation reduced to a pair of factors: polarity (the fraction of

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[1] For communication III, see [1].

Table 1. Relative reactivity of organometallic compounds in the selected processes as connected with electronegativity of the metal atom in the organometallic compound

Process	Relative reactivity of the organometallic compound[a]	References
Transmetalation RM + M'L ⇄ RM' + ML	Li (0.98) > Mg (1.31) > Al (1.61) > Zn (1.65) > Cd (1.69), Sn (1.96)	[6–9]
Halogen exchange with metal RM + R'Hlg → R'M + RHlg	Li (0.98) > Mg (1.31) > Al (1.61), Hg (2.0), Pb (2.33)	[6–8, 10]
Dehydrohalogenation of organic halide RM+R'Hlg → RH+R'(-H)+MHlg	Li (0.98), Mg (1.31), Al (1.61), Zn (1.65) > Hg (2.0)	[6, 8, 11]
Interaction with organic halides	K (0.82) > Na (0.93) > Li (0.98) > Ca (1.0), Mg (1.31), Al (1.61) > Zn (1.65) > Cd (1.69) > Sn (1.96), Hg (2.0)	[6–8, 12]

[a] The Pauling's electronegativity [5] of the metal atoms are given in parentheses.

ionic character) of the metal–carbon bond and the state of coordination sphere of the metal atom in the organometallic compound (the presence of the free coordination sites at the metal atom and their accessibility for the substrate). Increase of the metal–carbon bond polarity enhances the reactivity of the organometallic compounds in various processes; their examples are given in Table 1. At the same time, alkyl derivatives of aluminum can be more reactive that the etherates and complexes with amines in their reactions with alkenes, alkynes, water, and other species [4, 6, 13], even though the complex formation increases the Al–C bond polarity [4, 13–15]. Hence, the state of the metal atom coordination sphere in the complex can be a decisive factor influencing the reactivity. The solvent effect can be different as well: application of electron-donating solvents enhances the organometallic compounds reactivity in certain reactions, decreasing the reactivity in some other cases (generally, the reactions of rearrangement or addition at the multiple bonds) [3, 8, 15, 16]. In view of this, discussion of the reactivity issues in the cases of organometallic compounds should account for the type and mechanism of the considered process as well as the nature of the metal-containing species and the complex forming agents present in the solution. Importantly, all the known factors determining the reactivity of organometallic compounds are not independent; instead, they are somehow interrelated, making the precise prediction of the organometallic compounds impossible at the current state of the art. As far as transmetalation is concerned (the reaction of primary interest in this work, responsible for the formation of the labile alkyl derivative of the transition metal and, apparently, for the etching of the passivating film at the surface of the alkylated metal), the organometallic compounds reactivity should be reduced with the increasing electronegativity of the metal atom (Table 1) and upon exchange of the full organometallic compounds with the mixed ones [11]. In turn, polarity of the metal–carbon bond in the organometallic compounds is known to grow with introduction of electron-accepting groups at the α-carbon atom and to decrease with introduction of electron-donating groups at this position [8, 17, 18] as well as in the presence of the electronegative substituents (Hlg, OR, –C≡CR, or –CR=CHR') at the metal atom [4, 11, 13, 15, 17, 18]. Consequently, it can be expected that decrease of electronegativity of halogen atom in the mixed organometallic compounds (in the Cl > Br > I series [5]) should result in the following change of the reactivity in transmetalation reaction: I > Br > Cl and the accelerated direct synthesis of organometallic compounds in the Cl < Br < I series, other conditions being the same.

There are at least two more important points to be considered in the discussion. First, the active surface of the alkylated metal is free of the passivating film and contains the potentially catalytically active adatoms, small clusters, and the transition metal subhalides. Its value is determined by the surface area as well as the surface concentration of the catalytically active species. If formation of the active surface is accom-

Table 2. The effect of nature of organometallic component of the binary system with copper(I) iodide on the rate of alkylation of zinc powder with alkyl halide under vigorous forced stirring at 38°C

Exp. series no.	Composition of the initial mixture, mol		Reaction time, h	Induction period (τ_{ind}), min	Number of points in kinetic curve	RZnHlg yield, %	$w \times 10^6$, mol/s (standard error of kinetic curve fitting, mol)
	major components	organometallic compound					
1	1.835 Zn (PTS-3)	0.201 EtZnI	2.3	~0	2	30	67.6±5.4 (0.051)
	1.835 EtBr	0.109 EtZnBr	4.0	21	4	40	58.2±4.5 (0.036)
	0.030 CuI	0.042 $Al_2Et_3Br_3$	4.3	79	3	15	23.6±6.1 (0.020)
		0.028 Et_4Pb	4.5	–	–	~0	~0
2	0.380 Zn (PTS-3)	0.041 EtZnI[a]	2.8	11; 12	8	29	11.7±0.3 (0.004)
	1.299 EtBr	0.025 EtZnBr	3.5	25	5	19	5.8±0.8 (0.006)
	0.003 CuI	0.030 $Al_2Et_3Br_3$	4.5	–	–	~0	~0
		0.030 Et_4Pb	4.5	–	–	~0	~0
		0.030 Et_3Sb	4.5	–	–	~0	~0
3	0.125 Zn (PTS-4)	0.015 MeMgI	4.0	17	4	40	3.76±0.02 (0.0001)
	0.125 BuI	0.015 EtMgI	5.0	41	5	45	3.8±0.3 (0.003)
	0.005 CuI	0.015 BuMgI	4.0	~0	4	46	4.4±0.3 (0.006)
	0.749 Et_2O	0.015 n-C_7H_{15}MgI	4.0	40	4	30	3.2±0.3 (0.002)
		0.015 n-$C_{10}H_{21}$MgI	4.0	17	4	15	1.5±0.3 (0.002)
4	0.380 Zn (PTS-4)	0.030 EtMgI[a]	4.5	33; 35	12	11	2.81±0.04 (0.001)
	0.380 EtBr	0.030 EtZnI	3.8	29	4	5	1.5±0.2 (0.0009)
	0.010 CuI	0.022 EtZnBr	4.5	45	6	4	1.04±0.06 (0.0006)
	0.998 Et_2O						
5	0.500 Zn (PTS-4)	0.080 EtMgBr	4.0	37	4	47	19.0±0.5 (0.005)
	0.500 BuBr	0.080 EtZnBr	5.0	~0	5	8	2.4±0.3 (0.007)
	0.030 CuI						
	1.148 Et_2O						

[a] Two independent experiments.

panied by complete elimination of the passivating film, then the increased reactivity of the organometallic component of the binary mixture can only increase the rate of the direct synthesis up to the state of the adsorption saturation of the alkylated metal surface with the catalytically active particles. Under conditions of the adsorption saturation, the stationary rate of the process should not be sensitive to the reactivity of the organometallic component of the binary system. However, only part of the alkylated metal surface can be liberated of the passivating film in the course of the activation. Since the organometallic component of the binary system can act as both the transmetalation agent responsible for the delivery of the catalytically active species at the surface and the etching agent responsible for the passivating film elimination [19], its nature may somehow affect the surface concentration of the catalytic species as well as the active surface area. Therefore, each of the binary systems exhibits a certain "limiting" rate of the stationary direct synthesis dependent on the nature of the components, the alkylated metal, and the process conditions.

Second, the series of the reactivity of the organometallic compounds in transmetalation coincides with that in the interaction with organic halides (Table 1);

Table 3. The effect of nature of organometallic component of the binary system with copper(I) iodide on the rate of alkylation of cadmium powder with alkyl halide under vigorous forced stirring at 38°C

Exp. series no.	Composition of the initial mixture, mol		Reaction time, h	Induction period (τ_{ind}), min	Number of points in kinetic curve	RCdHlg yield, %	$w \times 10^6$, mol/s (standard error of kinetic curve fitting, mol)
	major components	organometallic compound					
1	0.250 Cd, 0.250 BuI,	0.020 EtMgBr	1.5	1	4	36	16.8±0.5 ($S = 0.001$)
	0.010 CuI, 0.749 Et_2O	0.020 BuCdI	4.0	~0	4	5	1.0±0.1 ($S = 0.002$)
		0.020 EtZnBr	5.0	~0	4	1	0.24±0.03 ($S = 0.001$)
		0.020 BuZnBr	5.0	67	5	1	0.15±0.03 ($S = 0.0003$)
2	0.500 Cd, 0.500 BuBr,	0.080 EtMgBr[a]	5.0	6; 31	10	11	3.05±0.08 ($S = 0.003$)
	0.030 CuI, 1.148 Et_2O	0.080 EtZnBr	4.0	126	3	1	0.5±0.1 ($S = 0.0003$)
3	0.500 Cd, 0.500 BuI,	0.040 BuMgI	5.0	~0	5	30	8.7±0.2 ($S = 0.006$)
	0.020 CuI, 1.148 Et_2O	0.040 BuMgBr	6.0	19	5	30	7.5±0.2 ($S = 0.003$)
		0.040 BuMgCl	6.0	67	4	19	5.0±0.9 ($S = 0.009$)
4	0.500 Cd, 0.500 BuI,	0.040 EtMgI	5.0	24	5	21	6.1±0.3 ($S = 0.003$)
	0.020 CuI, 1.148 Et_2O	0.040 n-$C_7H_{15}MgI$	4.0	~0	4	3	1.1±0.1 ($S = 0.002$)
		0.040 n-$C_{10}H_{21}MgI$	4.5	–	–	~0	~0

[a] Two independent experiments.

therefore, the increase of reactivity of the organometallic compound may result in the acceleration of the direct synthesis as well as faster consumption of the compound in the side reactions involving the organic halide.

In this report we present and discuss the results of experimental verification of the preliminary conclusions stated above: the possibility of acceleration of stationary direct synthesis of organometallic compounds in the presence of the binary systems owing to the certain changes in the organometallic component of the binary system (decreasing electronegativity of the metal atom and the exchange of chlorine with bromine and iodine).

In particular, the process of commercial zinc and cadmium powders alkylation with organic halides in the presence of binary systems: organometallic compound + copper(I) iodide was studied. The results are shown in Tables 2 and 3 as well as in Figs. 1 and 2. In all the cases, the alkylation exhibited the induction period and almost constant rate of the stationary process. The kinetic data was processed as described in [1]. The applied fitting was valid in the cases of the experimental curves.

The rate of the stationary process was noticeably varied with the changing nature of the organometallic component of the binary system. Nature of both the metal atom and the ligand surrounding were significant in determination the compound properties. The results did not contradict the expected the effect of the organometallic component of the binary system on the rate of metals alkylation with organic halides: the discussed process rate should be in general accelerated with the enhancing alkylating ability of the organometallic compound in transmetalation reactions. First, the stationary rate of alkylation was decreased with the increasing electronegativity of the metal atom in the organometallic component of the binary system, other conditions and the ligand composition being the same (cf. Figs. 1a, 1b, 1d, 1e and Figs. 2a, 2c): Mg (1.31) > Zn (1.65) > Al (1.61) > Cd (1.69) > Sb (2.05), Pb (2.33), the values in parentheses being the Pauling's metals electronegativity [5]. $Al_2Et_3Br_3$ was seemingly an exception, since it gave rise to the slower zinc alkylation as compared to EtZnBr (Figs. 1a, 1b). However, it should be kept in mind that correlation of reactivity of metals organic derivatives with the metal electronegativity suits as rough qualitative estimation.

Second, in the case of mixes organometallic compounds the alkylation rate was regularly decreased with the nature of the halogen atom in the ligand

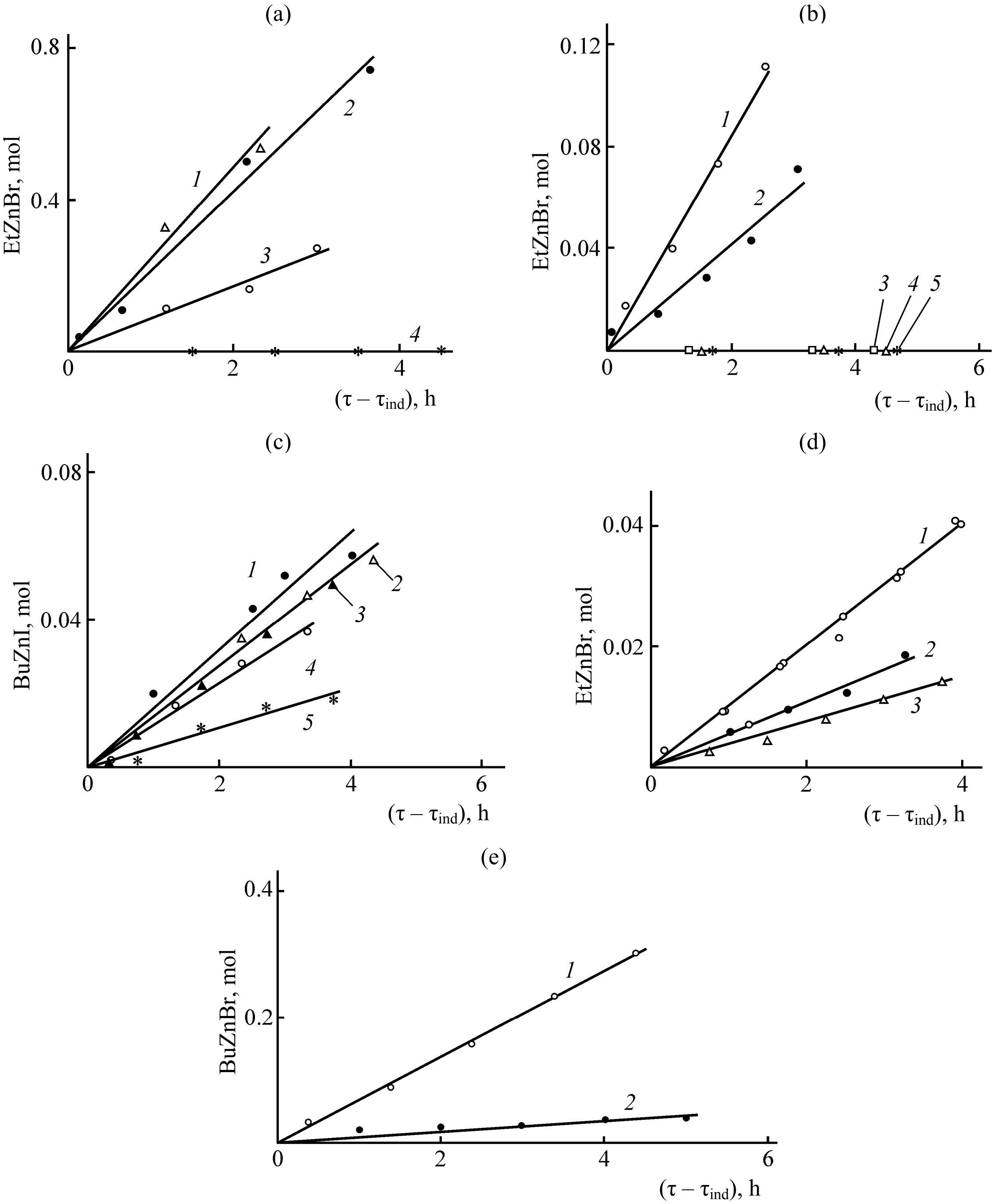

Fig. 1. Influence of the nature of organometallic component of the binary system with CuI on the rate of zinc powder alkylation with organic halides (see experimental conditions in Table 2): (a): (*1*) EtZnI, (*2*) EtZnBr, (*3*) $Al_2Et_3Br_3$, (*4*) Et_4Pb (series 1); (b): (*1*) EtZnI, (*2*) EtZnBr, (*3*) $Al_2Et_3Br_3$, (*4*) Et_4Pb, (*5*) Et_3Sb (series 2); (c): (*1*) BuMgI, (*2*) EtMgI, (*3*) MeMgI, (*4*) n-$C_7H_{15}MgI$, (*5*) n-$C_{10}H_{21}MgI$ (series 3); (d): (*1*) EtMgI, (*2*) EtZnI, (*3*) EtZnBr (series 4); (e): (*1*) EtMgBr, (*2*) EtZnBr (series 5).

following the I > Br > Cl series (Figs. 1a, 1b, 1d, and Fig. 2d). Hence, the results were in line with the expectations.

It was of interest to compare the activity of the organometallic compound–copper(I) iodide systems with the data directly reflecting the organometallic compound reactivity towards transmetalation with CuI. The corresponding data were not found in the literature; therefore, we estimated the alkylating (transmetalating) ability of various organometallic compounds towards CuI under conditions close to those in the kinetic experiments on alkylation of zinc

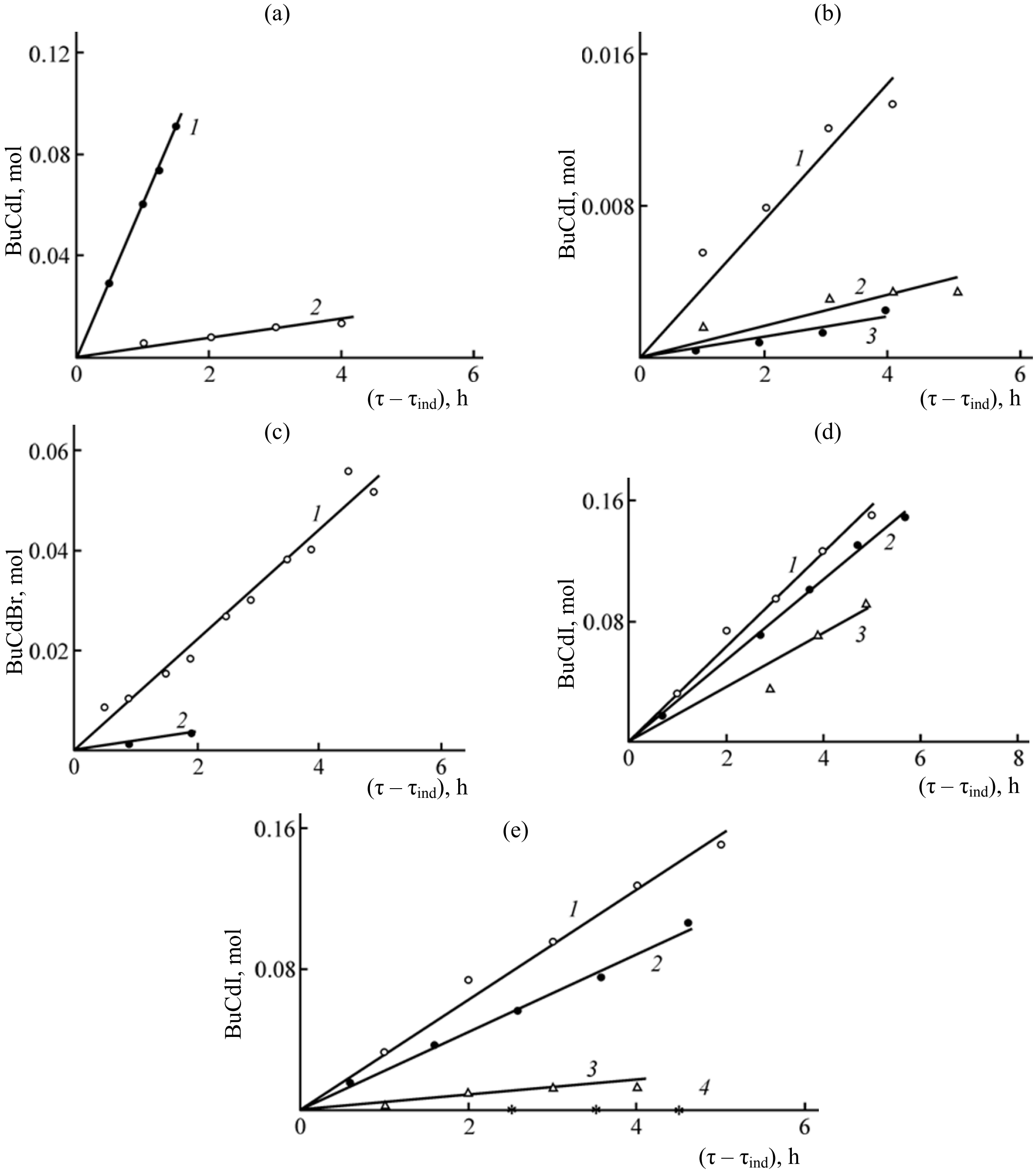

Fig. 2. Influence of the nature of organometallic component of the binary system with CuI on the rate of cadmium powder alkylation with organic halides (see experimental conditions in Table 3): (a): (*1*) EtMgBr, (*2*) BuCdI (series 1); (b): (*1*) BuCdI, (*2*) EtZnBr, (*3*) BuZnBr (series 1); (c): (*1*) EtMgBr, (*2*) EtZnBr (series 2); (d): (*1*) BuMgI, (*2*) BuMgBr, (*3*) BuMgCl (series 3); (e): (*1*) BuMgI (series 3), (*2*) EtMgI, (*3*) n-$C_7H_{15}MgI$, (*4*) n-$C_{10}H_{21}MgI$ (series 4).

and cadmium. Results of the estimation are given in Table 4. The rate of the reaction was judged about from the time required to visually detect the copper metal in the reaction mixture, formed via decomposition of the labile alkylcopper intermediate. The data in Table 4 revealed that the alkylating ability of the organometallic compounds decreased along the following series:

In diethyl ether: MeMgI, EtMgI, EtMgBr, BuMgI > Et_3In > n-$C_7H_{15}MgI$ > n-$C_{10}H_{21}MgI$ > EtZnI, BuCdI > n-$C_7H_{15}CdI$ > EtZnBr > BuZnI > BuZnBr, Et_3Sb.

Table 4. Reduction of copper(I) iodide with organometallic compounds[a]

Exp no.	Organometallic compound	Time to appearance of visually noticeable amount of metallic copper in the reaction mixture, s	
		diethyl ether	ethyl bromide
1	MeMgI	3 (25°C)	–
2	EtMgI	3 (25°C)	–
3	EtMgBr	3 (25°C)	–
4	BuMgI	3 (25°C)	–
5	Et_3In	6 (25°C)	–
6	n-$C_7H_{15}MgI$	120 (25°C)	–
7	n-$C_{10}H_{21}MgI$	600 (25°C)	–
8	Et_2Zn	–	90 (20°C)
9	Me_2Zn	–	600 (20°C)
10	EtZnI	1500 (35°C)	1200 (38°C)
11	BuCdI	1500 (35°C)	–
12	n-$C_7H_{15}CdI$	1800 (35°C)	–
13	EtZnBr	2400 (35°C)	1800 (38°C)
14	BuZnI	4200 (35°C)	–
15	BuZnBr	Not observed within 2 h at 35°C	–
16	Et_3Sb	The same	Not observed within 2 h at 38°C
17	$Al_2Et_3Br_3$	–	The same
18	Et_4Pb	–	"

[a] The reaction mixture consisted of 0.015 mol of CuI, , 0.05 mol of the organometallic compound, and 0.20 mol of the solvent (diethyl ether or ethyl bromide).

In ethyl bromide: $Et_2Zn > Me_2Zn > EtZnI > EtZnBr > Al_2Et_3Br_3$, Et_3Sb, Et_4Pb.

The obtained series were in complete accordance with the series of activity of the same compounds as components of the binary systems promoting zinc and cadmium alkylation with organic halides (Figs. 1 and 2).

We further quantified the efficacy of the organometallic compounds as components of the binary systems for direct synthesis of alkyl derivatives of zinc and cadmium. At the current state of theory of chemical reactivity such estimation is only formally possible taking advantage of correlation equations stating the relationship between reactivity of structurally similar compounds in similar reactions with the substituent(s) effect on the reaction center. The following effects are generally considered: inductive, conjugation, hyperconjugation, and the steric one [20]. Considering the nature of the reaction center of alkyl organometallic compounds (four-coordinate carbon atom bound to the metal), the substituents at this carbon atom can only reveal inductive and steric effects. Consequently, the partial linear correlations can be held between the stationary rate of the direct synthesis of organometallic compounds and the inductive or steric constants of the substituents (the steric or inductive constants, respectively, being constant). The data shown in Tables 5–8 revealed such qualitative correlation in the cases of zinc and cadmium alkylation as well as copper(I) iodide reduction (alkylation) with the organometallic compounds. However, quantitative estimation of the nature of the organometallic component of the binary system as affecting such systems efficacy taking advantage of the correlation equations was complicated. That was owing to the complexity of the state

Table 5. Correlation of the rate of zinc powder alkylation by organic halides with induction constant of the substituent (σ*) in the organometallic compound (a component of the binary system with CuI) (according to data in Table 2)[a]

Series no.	Alkylating agent	Solvent	Organometallic compound	Variable substituent	σ*	$w \times 10^6$, mol/s
1	EtBr	–	EtZnI	–ZnI	–1.04	67.6±5.4
			EtZnBr	–ZnBr	–0.90	58.2±4.5
			$Al_2Et_3Br_3$	–Al(Br)(Et) or $–AlBr_2$	–0.89 to –0.31	23.6±6.1
			Et_4Pb	$–PbEt_3$	0.85	~0
2	EtBr	–	EtZnI	–ZnI	–1.04	11.7±0.3
			EtZnBr	–ZnBr	–0.90	5.8±0.8
			$Al_2Et_3Br_3$	–Al(Br)(Et) or $–AlBr_2$	–0.89 to –0.31	~0
			Et_3Sb	$–SbEt_2$	–0.16	~0
			Et_4Pb	$–PbEt_3$	0.85	~0
3	EtBr	Et_2O	EtMgI	–MgI	–2.85	2.81±0.04
			EtZnI	–ZnI	–1.04	1.5±0.2
			EtZnBr	–ZnBr	–0.90	1.04±0.06
4	BuBr	Et_2O	EtMgBr	–MgBr	–2.76	19.0±0.5
			EtZnBr	–ZnBr	–0.90	2.4±0.3

[a] Hereafter the inductive constant of the substituents in the Taft scale (σ*) were calculated using the additive model [21]. Similar relationships were held in the case of cadmium alkylation (Table 3, series 1–3).

Table 6. Influence of the substituent inductive effect (σ*) in the molecule of organometallic compound on CuI reduction into metal copper (according to data in Table 4)

Series no.	Solvent	Organometallic compound	Variable substituent	σ*	Time to appearance of visually noticeable amount of metallic copper in the reaction mixture, s
1	Et_2O	EtMgI	–MgI	–2.85	3 (25°C)
		EtMgBr	–MgBr	–2.76	3 (25°C)
		Et_3In	$–InEt_2$	–1.21	6 (25°C)
		EtZnI	–ZnI	–1.04	1500 (35°C)
		EtZnBr	–ZnBr	–0.90	2400 (35°C)
		Et_3Sb	$–SbEt_2$	–0.16	>7200 (35°C)
2	EtBr	Et_2Zn	–ZnEt	–1.42	90 (20°C)
		EtZnI	–ZnI	–1.04	1200 (38°C)
		EtZnBr	–ZnBr	–0.90	1800 (38°C)
		$Al_2Et_3Br_3$	–Al(Br)(Et) or $–AlBr_2$	–0.89 to –0.31	>7200 (38°C)
		Et_3Sb	$–SbEt_2$	–0.16	>7200 (38°C)
		Et_4Pb	$–PbEt_3$	0.85	>7200 (38°C)

of the organometallic compounds in the solutions and the special features of direct synthesis of organometallic compounds in the presence of the binary systems. Indeed, the organometallic compounds could exist in a number of solvated co-existing forms in the solutions. The ratio of those forms is determined by the nature of the organometallic compound and the solvent, the components concentration, temperature,

Table 7. Correlation of the rate of copper and zinc powders alkylation with *n*-butyl iodide in diethyl ether and the steric constant (R_S) of alkyl substituent in the organometallic compound (a component of the binary system with CuI) (according to data in Tables 2 and 3)

Alkylated metal	Series no.	Organometallic compound[a]	R_S[b]	$w \times 10^6$, mol/s
Zinc	1	*H*-CH_3MgI	–0.25	3.76±0.02
		Me-CH_2MgI	–1.10	3.80±0.30
		Pr-CH_2MgI	–1.64	4.43±0.27
		n-C_6H_{13}-CH_2MgI	–1.87	3.20±0.30
		n-C_9H_{19}-CH_2MgI	–1.96	1.50±0.30
Cadmium	2	*Me*-CH_2MgI	–1.10	6.10±0.30
		Pr-CH_2MgI	–1.64	8.70±0.20
		n-C_6H_{13}-CH_2MgI	–1.87	1.10±0.10
		n-C_9H_{19}-CH_2MgI	–1.96	~0
	3	*Me*-CH_2ZnBr	–1.10	0.24±0.03
		Pr-CH_2ZnBr	–1.64	0.15±0.03

[a] Hereafter: the variable substituents are given in italics. [b] The steric constants of the substituents were calculated in the frames of the model of frontal steric effect [22].

Table 8. Influence of steric effect of alkyl substituents (R_S) in the molecule of organometallic compound on reduction of CuI into metallic copper in diethyl ether medium (according to data in Table 4)

Series no.	Organometallic compound	R_S	Time to appearance of visually noticeable amount of metallic copper in the reaction mixture, s
1	*H*-CH_2MgI	–0.25	3 (25°C)
	Me-CH_2MgI	–1.10	3 (25°C)
	Pr-CH_2MgI	–1.64	3 (25°C)
	n-C_6H_{13}-CH_2MgI	–1.87	120 (25°C)
	n-C_9H_{19}-CH_2MgI	–1.96	600 (25°C)
2	*Pr*-CH_2CdI	–1.64	1500 (35°C)
	n-C_6H_{13}-CH_2CdI	–1.87	1800 (35°C)
3	*Me*-CH_2ZnI	–1.10	1500 (35°C)
	Pr-CH_2ZnI	–1.64	4200 (35°C)
4	*Me*-CH_2ZnBr	–1.10	2400 (35°C)
	Pr-CH_2ZnBr	–1.64	>7200 (35°C)

and the presence of other complexing species. Hence, the formal approximation of the isolated non-solvated organometallic molecule could only be operative for estimation of the inductive and steric constants in narrow series of congener organometallic compounds. The special features of direct synthesis of organometallic compounds in the presence of the binary systems complicating the quantitative analysis are as follows. First, the direct synthesis reaction is accompanied by the induction period corresponding to decomposition of the passivating film and formation of the active surface of the alkylated metal. Data of [19] have suggested that the organometallic component of the binary system acts as the transmetalation agent and

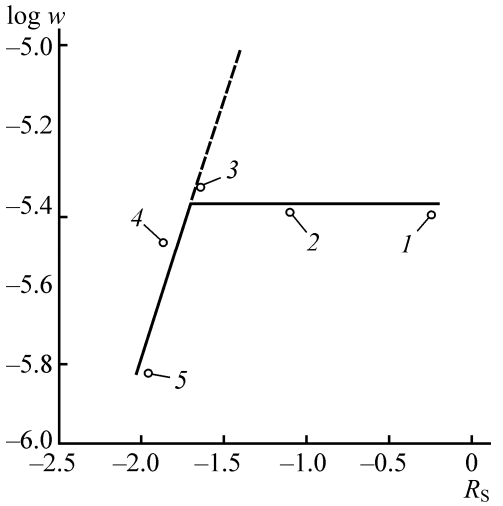

Fig. 3. Correlation between the rate of zinc powder alkylation with *n*-butyl iodide in diethyl ether and the steric constants (R_S) of alkyl substituent R in the R–CH_2MgI (a component of the binary system with CuI) molecule (Table 7). R = H (*1*), Me (*2*), Pr (*3*), *n*-C_6H_{13} (*4*), and *n*-C_9H_{19} (*5*).

favors the passivatibg film etching. On top of that, the ability towards the complex formation with the alkyl derivatives of the transition metal formed via the transmetalation can be an important function of the organometallic compound [2]. The relationships between the mentioned functions of the organometallic compound can be in general fairly complex.

Second, the enhancing reactivity of the organometallic compound can change the kinetic regime of the active surface formation into the diffusion one, and the direct synthesis rate will not be a function of the reactivity of the organometallic component any further.

Third, if practically the whole surface of the alkylated metal is liberated of the passivating film in the course of the activation, the adsorption saturation of the surface with the transition metal-containing catalytic species can be attained. The increase of the reactivity of the organometallic component of the binary system will result in the onset of the plateau of the direct synthesis rate at lower loading of the starting transition metal compound. Above this threshold content, the rate of the direct synthesis will not be a function of the organometallic component activity towards transmetalation, being exclusively determined by catalytic properties of the transition metal species.

The above statements can be illustrated by Fig. 3 showing the logarithm of the rate of direct synthesis of BuZnI in diethyl ether as function of steric constant of the alkyl substituent in the AlkMgI (a component of the binary system). It is to be seen that the logarithm of the reaction rate linearly increased with the decreasing steric constant in the alkyl series from *n*-C_9H_{19} to C_3H_7, remaining nearly constant with the alkyl changing from C_3H_7 to H.

In summary, the results of this work coincided with the scheme of the binary systems action proposed in [2]; the nature of the organometallic component could therefore act as a workable factor governing the direct synthesis of organometallic compounds. Changing the organometallic component nature, it is possible to change the process rate and (likely) optimize the initial loading of the transition metal compound.

EXPERIMENTAL

The following chemicals were used as received: zinc powder of the PTs-3 and PTs-4 grades (GOST 12601-76), cadmium powder (“chemical “pure,”” TU 6-09-02-400-86), magnesium (“technical,” cuttings), indium (grade 0, GOST 10297-75), and copper(I) iodide (“pure,” TU 6-09-02-437-87).

Methyl iodide (“pure,” TU 6-09-3988-83), butyl bromide (“pure,” TU 6-09-240-83), butyl iodide (“pure,” TU 6-09-3971-75), and butyl chloride (“pure,” TU 6-09-1772-72) were dried over calcium chloride and distilled shortly before use. Ethyl iodide (“pure,” TU 6-09-4117-83) was further purified vie rectification with the glass column (20 theoretical plates) at atmospheric pressure and the reflux ratio of 15–20. Ethyl bromide (“pure,” GOST 20181-74) was purified as described in [2]. *n*-Heptyl iodide and *n*-decyl iodide were prepared from the corresponding alcohols (heptanol, TU 6-09-1211-72, and decanol, TU 6-09-1514-72) and hydrogen iodide following the procedure from [18]. The Grignard reagents (MeMgI, EtMgBr, EtMgI, BuMgBr, BuMgI, BuMgCl, *n*-C_7H_{15}MgI, and *n*-$C_{10}H_{21}$MgI), ethylaluminumsesquibromide ($Al_2Et_3Br_3$), tetraethyllead, and triethylantimony were prepared as described in [8]. The full alkyl derivatives of zinc (Me_2Zn and Et_2Zn) and triethylindium as well as mixed zinc (EtZnBr, EtZnI, BuZnBr, and BuZnI) and cadmium (BuCdI and *n*-C_7H_{15}CdI) derivatives were synthesized via the methods described in [23, 24]. Diethyl ether (TU 6-09-1432-76) was dried and distilled over sodium prior to use [25]. Purification of argon (“pure,” GOST 10157-

79) and study of zinc and cadmium alkylation with organic halides were performed as described in [2]. Quantitative determination of zinc, cadmium, and magnesium ions in the reaction mixtures was carried out via titration with disodium ethylenediaminetetraacetate [2, 26].

Copper(I) iodide reduction with the organometallic compounds was performed in a 100 mL flat-bottom conical reactor equipped with a reflux condenser. Copper(I) iodide was loaded into the reactor, the vessel was purged and filled with argon, and the calculated amount of the organometallic compound solution was introduced. The reaction mixture was heated upon stirring (the beginning of heating was taken as the reaction start time). Copper(0) formation was indicated by appearance of characteristic red coloration.

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