
LITHIUM – HEAVIER ALKALI METAL EXCHANGE IN ORGANOLITHIUM COMPOUNDS INDUCED BY ALKOXIDES OF HEAVIER ALKALI METALS AND REACTIONS OCCURRING IN THIS SYSTEM

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Organolithium compounds of various types undergo an exchange reaction lithium – heavier alkali metal when treated with heavier alkali metal alkoxides. In the presence of a third reactive compound the exchange reaction gives rise to a compound of the third component substituted with the heavier alkali metal. Using this exchange reaction, organic derivatives of heavier alkali metals in the individual state can be easily prepared. The mechanism of such reactions is discussed, and the formation of lithium alkoxide is assumed to contribute significantly to the driving force of the reaction. Organic compounds of heavier alkali metals possess a considerably higher reactivity than organolithium compounds, and are therefore used as reactive intermediates in preparative chemistry, or as polymerization initiators in macromolecular chemistry. This review provides information about the scope and possibilities of this exchange reaction, which has been increasingly widely used in the recent years.

1. INTRODUCTION

Organic compounds of alkali metals are very reactive agents and are often used in organic chemistry. In systems containing these compounds, alkali alkoxides may also appear, either as an impurity due to oxidation, or as a product of a reaction with the substrate (e.g., carbonyl compounds). Interaction may take place between

organic compounds of alkali metals and the respective alkoxides, affecting the properties of the starting compounds.

With organolithium compounds and lithium alkoxides such interaction has been proved by various methods¹⁻⁴; in some cases the products formed could even be isolated, e.g., $[\text{C}_4\text{H}_9\text{Li}(\text{CH}_3)_3\text{COLi}]_n$ (ref.⁴). The interaction was also manifested by a change in the reactivity of the organolithium compounds, e.g. in its addition to the C=C double bond⁵, or to the C=O double bond⁶, in the reaction with tert-butylperoxide⁷, in the anionic polymerization of both polar⁸ and nonpolar^{9,10} monomers, or in a change in the thermal stability of organolithium compounds^{11,12}.

A similar interaction was also expected to occur between organolithium compounds and heavier alkali metal alkoxides, but in such system an additional reaction could be observed, resulting in the exchange of lithium for a heavier alkali metal. This exchange reaction has also been proved to occur with other organic compounds of lithium, i.e. those containing the Li—N< or Li-enolate bond. Its use has considerably increased in the recent years.

In this paper we have summarized most of the existing knowledge regarding the lithium—heavier alkali metal exchange reaction; some new results are reported, and examples of the application of this reaction are given. A more detailed review of applications of the system should be dealt with in another paper. The term “organolithium compound” used throughout this paper applies to compounds in which lithium is bound not only to carbon, but also to nitrogen or to oxygen in the enolate group.

2. PROPERTIES AND REACTIONS OF THE SYSTEM ARISING FROM ORGANOLITHIUM COMPOUND AND HEAVIER ALKALI METAL ALKOXIDE

2.1. Exchange Reaction Lithium – Heavier Alkali Metal

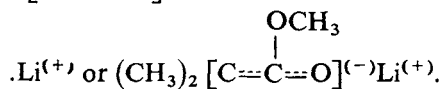
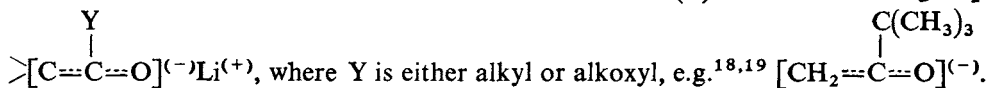
A metal – metal exchange according to the scheme



occurs between an organolithium compound (Z—Li) and a heavier alkali metal alkoxide (ROM), giving rise to an organic compound of the heavier alkali metal and lithium alkoxide.

This reaction has first been described for organolithium compounds containing the C—Li bond, in which Z (see (A)) is an alkyl or aryl, e.g., $\text{C}_4\text{H}_9\text{Li}$ (refs¹³⁻¹⁷), and later it has been reported for other organolithium compounds, such as lithium amides, in which Z (see (A)) is the $\text{R}^1\text{R}^2\text{N}$ group (R^1 being alkyl or aryl, R^2 being alkyl or hydrogen), and which thus contain the >N—Li bond, e.g., $(\text{iso—C}_3\text{H}_7)_2\text{N—Li}$ (ref.¹⁷). Finally, the exchange reaction has also been observed with lithium

enolates of ketones or esters, i.e. Z in the reaction (A) stands for the group



The structure of starting heavier alkali metal alkoxide may also vary considerably, including alkoxides of primary, secondary and tertiary alcohols. Of these, tertiary alkoxides are those most suited for practical application, while methoxides are unsuitable. The exchange reaction also takes place with heavier alkali metal trimethylsilanolates²⁰.

Hence, within the given limits, the exchange reaction is of general validity; some restrictions are given in Part 4. The organic compounds of heavier alkali metals can mostly be isolated in a high yield and purity (Tables I–III). The products obtained have a high content of the heavier alkali metal and only traces of lithium^{13–19,21–26}, thus documenting the lithium–heavier alkali metal exchange. The formation of organic compounds of heavier alkali metals by reaction (A) or (B) has also been proved from the characteristic properties of these compounds, e.g. NMR and EPR spectra^{27,28}, or from the different reactivity of the heavier alkali metal derivatives^{29–32}. However, a different conclusion was reached by the authors³³ in the case of the reaction of metallated pentadiene where participation of the organolithium compound in the reaction is assumed.

2.2. Reaction Between the System Organolithium Compound – Heavier Alkali Metal Alkoxide and a Third Reactive Compound

Organic compounds of heavier alkali metals are considerably more reactive than the corresponding lithium compounds. If the exchange reaction between the organolithium compound and the heavier alkali metal alkoxide takes place in the presence of a third compound of suitable reactivity, substitution of the third compound with the heavier alkali metal is observed (for the mechanism cf. Part 3)^{13–17,32,34a,34b}. Such reactions of the third compound may be of various type, e.g., hydrogen–metal exchange (metallation) (reaction (B)), addition to the multiple C=C or C=O bond (reaction (C)), reaction with alkyl or aryl halides (also nonactivated) (reaction (D)), isomerization of unsaturated compounds or the anionic polymerization of various monomers, e.g. reaction (E) (M = Na, K, Rb, Cs). This does not, of course, exhaust all application possibilities of the reaction, and some further applications may be expected in the future.

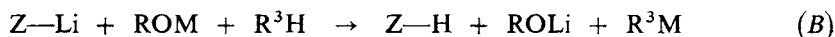


TABLE I

Preparation of organic compounds of heavier alkali metals from organolithium compounds (Z—Li, containing a C—Li bond) and heavier alkali metal alkoxides (ROM) according to reaction (A). Yield of products in mole %, metal content determined by atomic absorption spectrometry

Starting conditions		Isolated precipitate and its analysis								
Z—Li	ROM	[ROM] [Z—Li]	Solvent	°C	Z—M	Yield %	Metal content, %		References	
							M found	M calc.	Li	
CH ₃ Li	(CH ₃) ₃ CONa	0.98	(C ₂ H ₅) ₂ O	25	CH ₃ Na	70	61.6	60.5	1.0	25
	(CH ₃) ₃ COK	0.99	(C ₂ H ₅) ₂ O	-15	CH ₃ K	—	71.1	72.2	1.6	21
	(CH ₃) ₃ CORb	1.1	(C ₂ H ₅) ₂ O	-20	CH ₃ Rb	72	83	85.0	0.45	24
C ₂ H ₅ Li	C ₃ H ₇ C(CH ₃) ₂ OCs	1.1	(C ₂ H ₅) ₂ O	-30	CH ₃ Cs	65	85	89.8	0.55	24
	(CH ₃) ₃ CONa	0.9	C ₅ H ₁₂ + (C ₂ H ₅) ₂ O	-40	C ₂ H ₅ Na	—	42.8	44.16	0.29	22
	(-)(1R)C ₁₀ H ₁₉ ONa ^a	1.3	C ₆ H ₁₂	25	C ₂ H ₅ Na	99	42.9	44.26	0.23	20
C ₄ H ₉ Li	(CH ₃) ₃ CONa	0.77	C ₆ H ₁₂	25	C ₄ H ₉ Na	91	28.30	28.71	0.09	14, 20
	C ₄ H ₉ ONa ^b	0.5	C ₇ H ₁₆	25	C ₄ H ₉ Na	78	27.8	28.71	0.22	20
	(CH ₃) ₃ SiONa	0.77	C ₇ H ₁₆	25	C ₄ H ₉ Na	49	27.0	28.71	0.40	20
	(-)(1R)C ₁₀ H ₁₉ OK ^a	1	C ₇ H ₁₆	25	C ₄ H ₉ K	67	41.95	40.64	0.26	16
C ₆ H ₁₃ Li	C ₂ H ₅ C(CH ₃) ₂ OK	1.3	C ₆ H ₁₄	25	C ₄ H ₉ K	70	39.47	40.64	0.22	20
	(CH ₃) ₃ CONa	0.77	C ₆ H ₁₂	25	C ₆ H ₁₃ Na	58	21.0	21.26	0.05	20
	(-)(1R)C ₁₀ H ₁₉ OK ^a	1	C ₆ H ₁₂	20	C ₆ H ₁₃ K	58	33.4	31.46	0.3	16
C ₈ H ₁₇ Li	(CH ₃) ₃ CONa	0.77	C ₇ H ₁₆	0 → 40	C ₈ H ₁₇ Na	69	17.36	16.89	0.07	14, 20
	(-)(1R)C ₁₀ H ₁₉ OK ^a	1	C ₇ H ₁₆	20	C ₈ H ₁₇ K	86	26.49	25.65	0.40	16
C ₁₂ H ₂₅ Li	(CH ₃) ₃ CONa	0.8	C ₇ H ₁₆	25	C ₁₂ H ₂₅ Na	100	11.06	11.95	0.11	14
	(-)(1R)C ₁₀ H ₁₉ OK ^a	1	C ₇ H ₁₆	20	C ₁₂ H ₂₅ K	61	18.7	18.78	0.15	16
C ₆ H ₅ Li	(CH ₃) ₃ CONa	0.95	C ₆ H ₁₄ + (C ₂ H ₅) ₂ O	4	C ₆ H ₅ Na	82	21.5	23.0	0.30	23
	(-)(1R)C ₁₀ H ₁₉ OK ^a	0.84	C ₆ H ₁₄ + (C ₂ H ₅) ₂ O	-15	C ₆ H ₅ K	84	30.44	33.65	0.60	23

^a Sodium or potassium (-) (1R)-menthoxide. ^b Reaction mixture has been shaken with 3 glass beads for 3 h.

TABLE II

Preparation of substituted heavier alkali metal amides from corresponding lithium amides (Z—Li) and heavier alkali metal tert-butoxides according to reaction (A). Yield as number of moles of all alkali metals in the precipitate relative to the amount of the starting lithium amide in %. Analyses: base determined acidimetrically after hydrolysis and removal of amine by boiling, in % of M; M determined by atomic absorption spectrometry, N according to Kjeldahl. In benzene at room temperature

Z—Li	Starting conditions				Isolated precipitate (Z—M) and its analysis					
	M in (CH ₃) ₃ COM	$\frac{[(\text{CH}_3)_3\text{COM}]}{[\text{Z—Li}]}$	Time h	Yield % mole	Base %	M found	M calc.	Li found	N, % found	calc.
(iso-C ₃ H ₇) ₂ NLi	Na	1	2	68 ^a	18.68	18.80	18.66	0.15	11.26	11.57
iso-C ₃ H ₇ N(Li)C ₆ H ₁₁	Na	1	2	78	14.04	14.78	14.08	0.07	8.21	8.58
(C ₆ H ₁₁) ₂ NLi	Na	1.3	20	91	11.62	11.59	11.31	0.11	6.73	6.89
(C ₄ H ₉) ₂ NLi	Na	1.3	42	93	15.43	13.21	15.20	1.12	9.31	9.26
(iso-C ₃ H ₇) ₂ NLi	K	1.3	2	92 ^b	28.07	28.40	28.06	0.14	9.50	10.06
iso-C ₃ H ₇ N(Li)C ₆ H ₁₁	K	1	2	59	21.70	22.26	21.80	0.25	7.76	7.81
(C ₆ H ₁₁) ₂ NLi	K	1.3	20	74	17.66	17.01	17.82	0.17	6.21	6.38
CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ NLi	K	1.3	30	73	31.81	30.90	31.73	0.36	9.08	11.37
(C ₄ H ₉) ₂ NLi	K	1.3	42	88	23.65	20.44	23.37	1.41	8.17	8.83
(iso-C ₃ H ₇) ₂ NLi	Cs ^d	1	4	73 ^c	68.60	59.22	57.02	0.56	4.98	6.01

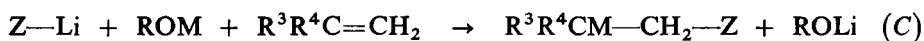
According to refs^{17,20}. Amide content determined by GLC after hydrolysis: ^a 95 mole %, ^b 88 mole %, ^c precipitate contained also some decomposition products of the amide. ^d Cesium 1,1-dimethylbutoxide used.

TABLE III

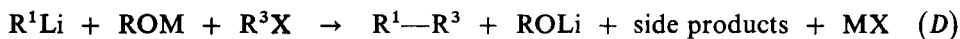
Preparation of heavier alkali metal ester of ketone enolates from the corresponding lithium enolates (Z—Li) and heavier alkali metal tert-butoxides according to reaction (A). Yield of products in mole %, metal content determined by atomic absorption spectrometry, content of components determined by GLC after protolysis (M—E ethyl metalloisobutyrate, M—KE ethyl metalloisobutyrylisobutyrate). In hexane or cyclohexane at room temperature

Starting conditions		Isolated precipitate (Z—M) and its analysis					References		
Z—Li	M in (CH ₃) ₃ COM	$\frac{[(CH_3)_3COM]}{[Z-Li]}$	Yield %	Metal content, %		Content of components, %			
				M found	M calc.	Li		M—E M—KE	
$\begin{array}{c} OC_2H_5 \\ \\ (CH_3)_2[C=C=O]^{(-)}Li^{(+)} \end{array}$	Na	1.2	84	16.05	16.63	0.15	92	7	19
$\begin{array}{c} OC_2H_5 \\ \\ (CH_3)_2[C=C=O]^{(-)}Li^{(+)} \end{array}$	K ^a	1.2	73	23.45	25.32	0.23	74	2	19
$\begin{array}{c} OC_2H_5 \\ \\ (CH_3)_2[C=C=O]^{(-)}Li^{(+)} \end{array}$	Cs	1.0	58	53.3	48.4	0.06	>50	<10	19
$\begin{array}{c} OC(CH_3)_3 \\ \\ (CH_3)_2[C=C=O]^{(-)}Li^{(+)} \end{array}$	K	1.05	68	21.48	21.46	0.29	—	—	19
$\begin{array}{c} C(CH_3)_3 \\ \\ [CH_2=C=O]^{(-)}Li^{(+)} \end{array}$	Na	1.0	29	19.80	18.82	0.8	—	—	18
$\begin{array}{c} C(CH_3)_3 \\ \\ [CH_2=C=O]^{(-)}Li^{(+)} \end{array}$	K	1.0	69	25.20	28.28	0.6	—	—	18

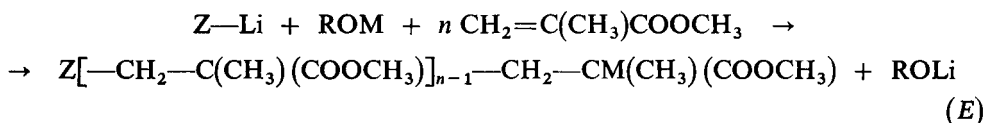
^a Potassium (—)(1*R*)-menthoxide used instead of potassium tert-butoxide.



(structure of the product dependent on the type of substituents R^3 , R^4 and Z)



(R^3X may also be an alkyl or aryl halide of low reactivity)



In these reactions, Z may have a similar meaning as in the reaction (A), but the choice of a suitable Z is determined by the character of the reaction with a third compound and by the structure of the reactants. Thus, e.g., for a successful metallation according to reaction (B), the condition $\text{pK}(\text{Z—H}) > \text{pK}(\text{R}^3\text{H})$ must be satisfied. Alkyl lithium compounds, being the most reactive reagents, are usually applied as an initial organolithium compound. It should be remembered, however, that the selectivity (e.g. regioselectivity) of an agent decreases with its increasing reactivity. For this reason, the choice of a suitable Z—Li for the exchange reaction in the presence of the third component sometimes requires due care. It should also be remembered that the introduction of alkoxide into the system, while strongly increasing the kinetic acidity of weak C—H acids affects their thermodynamic acidity but little³⁵.

An essential feature of all reactions mentioned above ((B)–(E)) is the fact that up to now, the generated derivative of the third compound always contained mostly the heavier alkali metal with an only minor amount of lithium. This indicates that at some reaction stage, an exchange of lithium for the heavier alkali metal must have taken place in the sense of reaction (A). It seems that in some systems (e.g. ref.^{34b}) the lithium content in the product is somewhat dependent on the reaction conditions.

Examples illustrating the reaction of the system organolithium compound – heavier alkali metal alkoxide with a third reactive compound are given in Table IV. They involve various combinations of all three reacting compounds. The yields of isolated products are good, the heavier alkali metal content approaches the calculated value and the lithium content is below 0.5%. In some cases the sum of the alkali metals content is somewhat lower than the calculated value, which might be due to consecutive reactions of the heavier alkali metal derivative formed in the reaction. E.g., metallation of cumene gives rise to higher-molecular weight compounds^{36,37}.

Reactions between organolithium compounds and heavier alkali metal alkoxides with a third reactive compound have been studied also by other authors. In these cases, however, it was mostly not the organometallic compound of the third com-

ponent that was isolated and analyzed, but the reaction product of this compound with some derivatizing agent, e.g., methyl iodide. Schlosser, who independently observed an increased reactivity of butyllithium in the presence of potassium tert-butoxide, should be mentioned here in the first place³⁸. He used this system in successful metallations and derivatizations of a number of various organic compounds, such as aromatic compounds^{38,39}, cyclopropane derivatives^{39,40}, allyl derivatives^{38,41-46}, olefins^{47,48}, dienes^{44,49-51}, enethers⁴⁴, ensulfides⁵², various heterocyclic compounds^{53,54}, and ethers⁵⁴. He has made an important contribution to our knowledge of this reaction.

As a more detailed enumeration of the reactions between the studied system and a third reactive compound is beyond the scope of this paper, only some less typical examples of the reaction are reported below. Thus, using the system organolithium compound - heavier alkali metal alkoxide optimum conditions for the metallation of toluene^{34a} or benzene^{34b} were sought. The purity of phenylpotassium obtained in this metallation is strongly dependent on reaction conditions. It may be considerably improved by addition of small amounts of diethylether^{34b}. Beside these, N-methyldialkylamines were metallated to dialkylaminomethylpotassium⁵⁵, pyridine was metallated to a mixture of 2,3 or 4-potassiopyridines⁵⁶, or 2,3-dimethyl-1,3-butadiene was transformed into the respective dianion^{57,58}. The reactivity of the given system may be further raised in the presence of solvating solvents or additives. Thus, e.g., methyl tert-butyl ether was metallated to tert-butoxymethylpotassium in the excess of this ether⁵⁹, or alkylbenzenes were metallated using a mixture of cesium alkoxide and butyllithium in the presence of hexamethylphosphortriamide⁶⁰, or ethylene was metallated to vinyl potassium in the presence of tetramethylethylenediamine⁶¹ (TMEDA). If the presence of a solvating compound does not interfere, a homogeneous metallation mixture may be obtained by adding TMEDA to the hexane suspension of butylsodium or butylpotassium prepared according to the reaction (A) (refs^{62,63}).

In some reactions of the Z—Li—ROM system with a third reactive compound in a hydrocarbon medium, the generated alkali derivative of the third compound may be contaminated also with the product of the exchange reaction (A) itself, i.e. Z—M (Z = alkyl in this case). Thus, e.g., a mixture of triphenylmethylsodium and butylsodium was formed in the metallation of triphenylmethane with a mixture of butyllithium and sodium tert-butoxide¹⁵. This could be avoided by using 2-ethylhexyllithium as the starting organolithium compound, because the latter forms homogeneous metallation mixtures with both sodium and potassium alkoxides also in the hydrocarbon medium^{34a}. This is why this system is particularly suited for the preparation of unsolvated organometallic compounds.

The exchange reaction lithium - heavier alkali metal was also used in a reaction of an organic halide with an organometallic compound. In a hexane solution of the organolithium compound and a nonactivated organic halide (e.g. butyl bromide)

TABLE IV

Some typical reactions of organolithium compound (Z—Li) and heavier alkali metal alkoxides of the new organometallic compound after isolation. Yield based on Z—Li in mole %. Metal

Starting conditions				
Z—Li	ROM	R ³ H	$\frac{[\text{ROM}]}{[\text{Z—Li}]}$	$\frac{[\text{R}^3\text{H}]}{[\text{Z—Li}]}$
C ₄ H ₉ Li	(-)(1 <i>R</i>) C ₁₀ H ₁₉ OK ^a	C ₆ H ₆	1	28
C ₄ H ₉ CH(C ₂ H ₅)CH ₂ Li	(CH ₃) ₂ C(C ₂ H ₅)OK	C ₆ H ₆	1	5
C ₄ H ₉ Li	(CH ₃) ₃ COK	C ₆ H ₅ CH ₃	0.95	15
C ₄ H ₉ Li	(-)(1 <i>R</i>) C ₁₀ H ₁₉ OK ^a	C ₆ H ₅ CH ₃	1	28
C ₄ H ₉ CH(C ₂ H ₅)CH ₂ Li	(CH ₃) ₂ C(C ₂ H ₅)OK	C ₆ H ₅ CH ₃	1	5
C ₄ H ₉ Li	(-)(1 <i>R</i>) C ₁₀ H ₁₉ OK ^a	C ₆ H ₅ CH(CH ₃) ₂	1	22
C ₄ H ₉ CH(C ₂ H ₅)CH ₂ Li	(CH ₃) ₂ C(C ₂ H ₅)OK	(C ₆ H ₅) ₃ CH	1	2
C ₄ H ₉ Li	(CH ₃) ₂ C(C ₂ H ₅)OK	(C ₆ H ₅) ₂ C=CH ₂	1	1.1
C ₄ H ₉ Li	C ₃ H ₇ C(CH ₃) ₂ OCs	C ₆ H ₅ CH ₃	1	7
C ₄ H ₉ CH(C ₂ H ₅)CH ₂ Li	(CH ₃) ₃ CONa	C ₆ H ₅ CH ₃	1	4
C ₄ H ₉ Li	(CH ₃) ₃ CONa	(C ₆ H ₅) ₃ CH	0.77	0.95
C ₄ H ₉ CH(C ₂ H ₅)CH ₂ Li	(CH ₃) ₃ CONa	(C ₆ H ₅) ₃ CH	1	1.5
C ₄ H ₉ Li	(CH ₃) ₂ C(C ₂ H ₅)ONa	(C ₆ H ₅) ₂ C=CH ₂	1	1.1
(iso-C ₃ H ₇) ₂ NLi	(CH ₃) ₃ COK	C ₆ H ₅ CH ₃	1	46
(CH ₃) ₃ CNHLi	(CH ₃) ₃ COK	C ₆ H ₅ CH ₃	1.3	12

^a Potassium (-)(1*R*)-menthoxide. ^b Content of components after hydrolysis in mole %, dete-
riodide 7 mole % of *m*- + *p*-xylene were found; ^d toluene 95, tert-pentylalcohol 2.8; ^e diisopropyl-
removed by reaction with diethylether and crystallization. ^h Nitrogen content (according to Kjehl-

the Wurtz type reaction is relatively slow, but after the addition of the heavier alkali metal alkoxide an intensive or even vigorous reaction according to reaction (D) takes place⁶⁴. The heavier alkali metal halide separates from the reaction mixture with the simultaneous formation of organic compounds as products of Wurtz "coupling" (under favourable conditions with a yield 60–85%) or of hydrogen halide elimination from the organic halide, along with minor amounts of other compounds (Table V).

The system lithium amide – heavier alkali metal alkoxide was used in reactions with a third reactive compound in those cases where the somewhat weaker basicity of alkali amides compared with compounds containing the C—Li bond was an advantage (p*K*(dialkylamine) c. 33, p*K*(alkane) > 40). Good yields of some heavier alkali metal substituted third components were thus obtained¹⁷ (Table IV). With a two-molar excess of alkoxide the reactivity of the lithium amide – sodium alkoxide

(TABLE IV - Continued)
 (ROM) with a third reactive compound (R^3H) according to reactions (B) or (C) and analysis content determined by atomic absorption spectrometry

New organometallic compound	Yield %	Isolated precipitate and its analysis			References
		Metal content, %			
		M found	M calc.	Li	
C_6H_5K	89	31.2	33.65	0.37	16
$C_6H_5K^{b,c}$	98	29.34	33.65	0.88	34b
$C_6H_5CH_2K$	93	28.35	30.02	0.40	14
$C_6H_5CH_2K$	93	29.1	30.02	0.19	16
$C_6H_5CH_2K^{b,d}$	100	28.3	30.02	0.19	34a
$C_6H_5CK(CH_3)_2^f$	92	22.3	24.70	0.44	16
$(C_6H_5)_3CK$	91	13.25	13.84	0.08	20
$(C_6H_5)_2CK-CH_2C_4H_9$	96	13.75	14.14	0.38	20
$C_6H_5CH_2Cs$	98	61.45	63.29	0.12	20
$C_6H_5CH_2Na$	87	22.60	20.14	0.83	20
$(C_6H_5)_3CNa^g$	44	8.53	8.63	—	15
$(C_6H_5)_3CNa$	57	10.16	8.63	0.19	20
$(C_6H_5)_2CNa-CH_2C_4H_9$	86	—	8.83	—	20
$C_6H_5CH_2K^{b,e,h,i}$	94	27.7	30.02	0.43	17
$C_6H_5CH_2K^{h,j}$	59	30.9	30.02	0.41	17

mined by GLC; ^c benzene 86, tert-pentylalcohol 5.5, after reaction of the product with methylamine 87. ^f Product of lower purity. ^g The precipitate contained also butylsodium which was dahl); ⁱ 0.96%; ^j 1.78%.

system could be further increased¹⁷. An interaction between the sodium amide formed in the reaction and the excess alkoxide obviously took place here, as has been described for unsubstituted amides⁶⁵. A mixture containing potassium diisopropylamide, prepared by the reaction of diisopropylamine with a mixture of butyllithium and potassium tert-butoxide, in which the lithium-potassium exchange had already occurred, was also used in metallations. With this system, 1-(phenylseleno)alkenes or bis(phenylseleno)acetals³¹ as well as various nitrosamines⁶⁶, were smoothly metallated. Lithium diisopropylamide alone did not practically react under comparable conditions.

The anionic polymerization of vinyl monomers can formally also be regarded as a reaction of the organolithium compound - heavier alkali metal alkoxide system with a third reactive compound, as in this reaction, the monomer is repeatedly added to the polymer propagation centre containing an alkali metal. Lithium in the

TABLE V

Products of the reaction $RLi + R'OM + R''X \rightarrow R-R'' + R'OLi + MX +$ by-products ($M = Na, K; X =$ halogen) at starting equimolar ratio of reaction components, in hexane at room temperature. Yield of $R-R''$ (Y) related to RLi . Abbreviations: Bu butyl, *t*-Bu tert-butyl, *t*-Pe tert-pentyl, Oc octyl, EtHex 2-ethylhexyl, Ph phenyl, OcH octane, EtHexH 2-ethylhexane, DodeH dodecane, HxdeH hexadecane, OceH 1-octene, EtHexeH 2-ethyl-1-hexene, PhH benzene, BuPh butylbenzene, PhPh diphenyl, BB unresolved mixture of butane and butene, DiEtDodeH 5,8-diethyldodecane

RLi	R'OM	R''X	Y, mole %	Composition of reaction mixture, mole % (R'OM and MX excluded)																
BuLi	<i>t</i> -PeOK	BuCl	26.2	OcH	26.2	BuCl	3.3	BB	70.5											
BuLi	<i>t</i> -PeOK	BuBr	79.8	OcH	79.8	BuBr	— ^a	BB	17.7											
BuLi	<i>t</i> -PeOK	BuI	80.6	OcH	73.6	BuI	0.6	BB	25.8											
BuLi	<i>t</i> -PeOK	OcBr	62.1	HxdeH	7.1	OcBr	2.1	DodeH	54.3	OceH	7.8	OcH	14.1	BB	14.7					
BuLi	<i>t</i> -PeONa	OcBr	61.3	HxdeH	5.8	OcBr	3.1	DodeH	54.1	OceH	5.8	OcH	14.1	BB	17.0					
BuLi	<i>t</i> -PeONA	OcBr	61.3	HxdeH	4.4	OcBr	3.9	DodeH	54.0	OceH	5.2	OcH	14.1	BB	18.5					
BuLi ^b	<i>t</i> -PeOK ^b	OcBr ^b	77.3	HxdeH	13.0	OcBr	26.7	DodeH	25.5	OceH	2.8	OcH	6.4	BB	35.5					
BuLi ^c	<i>t</i> -PeOK ^c	OcBr ^c	61.4	HxdeH	4.1	OcBr	46.0	DoDeH	29.2	OceH	4.4	OcH	7.5	BB	8.8					
BuLi	<i>t</i> -PeOK	OcBr	56.3 ^d	HxdeH	6.8	OcBr	2.2	DodeH	47.1	OceH	10.1	OcH	15.8	BB	18.0					
BuLi	<i>t</i> -PeOK	OcBr	39.7 ^e	HxdeH	9.4	OcBr	0.5	DodeH	39.7	OceH	— ^a	OcH	— ^a	BB	20.9					
BuLi	<i>t</i> -PeOK	PhBr	63.1	PhPh	1.3	PhBr	0	BuPh	54.0	PhH	22.2	OcH	5.8	BB	16.7					
EtHexLi	<i>t</i> -PeOK	EtHexBr	86.4	DiEtDodeH	76.7	EtHexBr	0.8	EtHexeH ^f	7.9	EtHexH	14.6									

^a Undetermined. The other values in this experiment are related to the starting amount of BuLi. ^{b,c} [BuLi] : [t-PeOK] : [OcBr] = ^b 1 : 0.5 : 1, ^c 1 : 1 : 2. ^d Reaction temperature —45 to —50°C. ^e In THF at —40 to —45°C. ^f Probably.

starting organolithium initiator can be exchanged for a heavier alkali metal by reacting with ROM, thus affecting the course of polymerization, e.g. methacrylate ester polymerization can be started by lithium enolates (particularly by esters of α -lithioisobutyric acid or by α -lithiopinacoline) and it can be affected by various alkoxides^{8,32} (cf. reaction (E)). Polymerization parameters, such as the limiting monomer conversion, molar mass distribution and microstructure of the polymer may be changed by the alkoxide. After the addition of a heavier alkali metal alkoxide to the polymerization initiator the microstructure of poly(methyl methacrylate) assumed a character typical of the propagation centre with a heavier alkali metal³² (Table VI), thus confirming the exchange lithium – heavier alkali metal also in this system. Similar changes have been observed in the polymerization of nonpolar monomers, e.g., 1,3-butadiene^{67,68}. Thus, by adding a heavier alkali metal alkoxide, it is possible to control the microstructure, and thus also the physical properties of the polymer formed.

2.3. Reactions Accompanying the Exchange Lithium – Heavier Alkali Metal

The lithium – heavier alkali metal exchange reaction is accompanied by some other reactions, to an extent depending on the structure of the participating compounds; these reactions affect the nature of the product of the exchange reaction.

One of the important decomposition reactions of organic compounds of heavier

TABLE VI

Influence of alkali metal alkoxides on methyl methacrylate polymerization initiated by metalated isobutyrate esters (according to ref.³²). Polymerization conditions: [MMA] 0.63 mol/l, toluene, [MMA]/[(Li, Na, K)—EtiB] = 120, 20°C, 1 h; abbreviations: (Li, Na, K)—EtiB ethyl-(lithio, sodio, potassio)isobutyrate, t-BuO(Li, Na, K) lithium, sodium or potassium tert-butoxide

Initiating system	Obtained PMMA			
	Yield, %	Microstructure ^a , %		
		I	H	S
Li—EtiB	46	71	21	8
Li—EtiB + t-BuOLi	53	74	19	7
Na—EtiB	65	54	36	10
Li—EtiB + t-BuONa	88	50	34	16
K—EtiB	96	28	51	21
Li—EtiB + t-BuOK	92	28	51	21

^a Content of triads (I isotactic, H heterotactic, S syndiotactic).

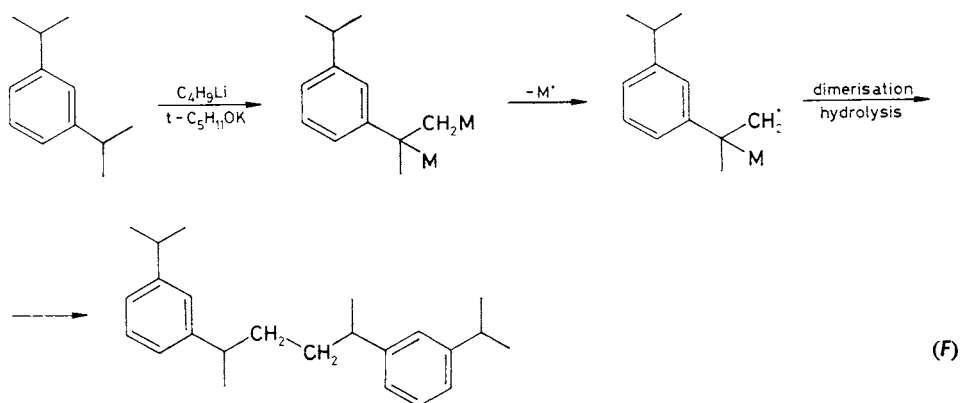
alkali metals is the elimination of the metal hydride resulting in olefin formation^{12,69-71}. The tendency to the elimination of the metal hydride increases in the series from lithium to cesium and is generally lower with compounds having the metal bound to the primary carbon atom than with those where the metal is bound to the secondary or tertiary carbon atom. Thus, in the majority of organolithium compounds in a hydrocarbon solution, the decomposition at room temperature is negligible within one week, similarly to organosodium compounds with the metal bound to the primary carbon atom. In secondary organosodium compounds prepared "in situ" via reaction (A) the decomposition reaction was completed within a few hours, while in tertiary derivatives the reaction was still faster. The isolated product of decomposition had a high sodium content in this case (60–90%) and contained a large amount of sodium hydride²⁰. Organometallic compounds in which potassium is bound to a primary carbon atom undergo a relatively rapid spontaneous decomposition: e.g., butylpotassium in the isolated solid state was deeply transformed within 100 h (ref.¹⁶). In solutions of organopotassium compounds the transformation proceeds even more quickly: from a solution obtained by mixing hexane solutions of 2-ethylhexyllithium and potassium tert-pentoxide (cf.^{34a,72}), a brown-black decomposition product began to separate already after 15 m; when isolated, it had a high potassium content, but lithium was present in traces only. In this process, compounds containing an unpaired electron are also formed, as has been demonstrated by EPR spectra^{34a}.

Olefins obtained by the elimination of metal hydride or of metal methyllide (CH_3M) may be again metallated by a still undecomposed organometallic compound; the process of hydride elimination and remetalation can be repeated. Moreover, isomerizations or molecular transformations may also occur, so that the final product of spontaneous decomposition of organic compounds of heavier alkali metals may be a varied mixture of compounds^{69,70,73}. This is why alkylpotassium compounds should be stored for a short time only, and at reduced temperature, if possible. It is known that lithium alkoxides accelerate the thermal decomposition of organolithium compounds^{11,12}, and a similar catalytic effect in the case of compounds of heavier alkali metals prepared by the (A) or (B) exchange reactions cannot be ruled out, as they may contain small quantities of alkali alkoxides.

Elimination of the metal hydride may also be a desirable reaction, however. Thus, Schleyer et al.^{74,75} used a combined metallation and elimination of the hydride in the preparation of cyclic polyolefins from cyclic monoolefins by using the butyllithium-potassium tert-pentoxide system. In this way they obtained, e.g., benzene from cyclohexane in a 55% yield, or (α -²H₁-) toluene in a 100% yield from 1-methylcyclohexene after the reaction with the system and deuteriolysis.

A different side reaction was observed when ethyl- or isopropylbenzene was treated with the butyllithium and potassium tert-pentoxide system. With a fourfold amount of the agent, these compounds were dimetallated in the α - and β -position,

after which a spontaneous homolytic splitting off of the C_{β} -metal bond took place, yielding the corresponding anion radical, which dimerized by radical recombination (cf. reaction (F))^{36,37}. With various substrates also other reactions may be expected to occur which change the structure of the organic substituent.



For substituted lithium amides a spontaneous decomposition has been reported, starting by the elimination of lithium hydride, using the hydrogen in the α -position with respect to nitrogen, and leading to imines, similar to the decomposition of compounds with a C-metal bond⁷⁶. It is quite likely that such reactions will be more frequent in the case of substituted heavier alkali metal amides being the cause of their limited stability.

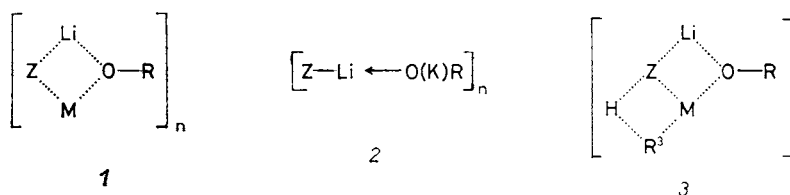
The spontaneous decomposition of alkali enolates of carboxylic acid esters proceeds in the sense of the Claisen ester condensation, yielding β -ketoesters. This reaction accompanies the exchange reaction of lithium enolates and is more rapid with sodium or potassium enolates⁷⁷. In this case, however, the presence of alkali metal alkoxides has a different, i.e., retarding effect on the rate of alkali enolate autocondensation⁷⁷⁻⁷⁹.

Another type of accompanying reactions has been observed with organopotassium compounds (having the C-K bond), viz., formation of nonstoichiometric adducts with one of the starting components, when the latter was used in the reaction in a major excess. Thus, e.g., from a mixture of butyllithium and potassium tert-butoxide in hexane (molar ratio 4 : 1), an adduct $[C_4H_9K \cdot x C_4H_9Li]_n$ was isolated, where $x \cong 1.65$ (ref.¹⁴), or, contrariwise, in the reaction of butyllithium and potassium tert-pentoxide with toluene (molar ratio 1 : 3 : 5) an adduct of the composition $[C_6H_5CH_2K \cdot x C_5H_{11}OK]_n$ was formed with $x \cong 0.6$ (ref.^{34a}, cf. ref.^{34b}).

3. MECHANISM OF THE EXCHANGE REACTION LITHIUM - HEAVIER ALKALI METAL, ALSO IN THE PRESENCE OF A THIRD REACTIVE COMPOUND

So far, only partial views exist regarding the mechanism of reaction between organolithium compounds ($Z-Li$) and heavier alkali metals alkoxides (ROM), alternatively also with a third reactive component. The situation is moreover complicated by the fact that organic compounds of alkali metals exist in the form of their supermolecular aggregates formed by means of "coordination bonds" $(O, N)C \cdots M \cdots C(N, O)$ (ref.⁸⁰). The stability of these aggregates is mostly high and the concentration of monomer compounds is very low, so that at least some of their reactions involve more or less aggregated particles. The degree of aggregation (α) of organic compounds of alkali metals and their reactivity depend on the type of solvent. Thus, in nonsolvating solvents (hydrocarbons) α often lies between 4 and 8, in solvating solvents (e.g., ethers) we usually have $\alpha \leq 4$. Interactions with electron-donating compounds (also with alkoxides) are reflected in a similar manner.

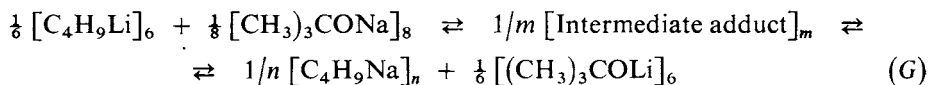
The reaction $Z-Li$ with ROM is initiated by the formation of an intermediate adduct^{13,14,38}, for which the structures of type 1 (refs^{81,82}) or 2 (ref.³⁸) (Scheme 1)



SCHEME 1

have been suggested. This adduct probably also exists in the form of higher mixed aggregates. For an analogous lithium alkoxide adduct $[C_4H_9Li \cdot (CH_3)_3COLi]_\alpha$ the aggregation degrees of α equal to 3.7 (benzene) and 1.8 (tetrahydrofuran, THF)⁸³ have been found in agreement with the NMR spectra of these mixtures³.

In the following reaction step the intermediate adduct splits into an organic heavier alkali metal compound and lithium alkoxide. These processes may be illustrated by reaction (G) (in cyclohexane).



In the case of the system butyllithium with sodium tert-pentoxide in hexane, an intermediate adduct was observed at $-70^\circ C$, and only at a temperature about $0^\circ C$ is it transformed into the final products in the sense of the exchange reaction (G) (ref.²⁰).

For the reaction of the system $Z-Li-ROM$ with a third reactive component (reactions of the (B) through (F) types), various routes may be suggested for the transition from the initial to the final state. In the case of R^3H metallation these routes can be defined as follows: according to route *a*, the intermediate adduct is decomposed to lithium alkoxide and an organic compound of a heavier alkali metal, which in the further step, "in statu nascendi", metallates R^3H to R^3M . On the other hand, however, the intermediate adduct of type 1 (Scheme 1) may also react with R^3H directly, yielding R^3M by way of a transition state, the possible structure of which is schematically represented by formula 3 (Scheme 1) (route *b*). For the intermediate of type 2, activation of the organolithium compound with heavier alkali metal alkoxide is assumed, by a solvation similar to that of electron-donor solvents (e.g., THF)³⁸. In such case the reaction with R^3H should produce a lithium derivative R^3Li . If a really isolated derivative of heavier alkali metal is to result, an additional exchange between lithium and the heavier alkali metal must be assumed, with the participation of a heavier alkali metal alkoxide (route *c*). Finally, other mechanisms, e.g. those involving more strongly charged particles or a "single electron transfer", cannot be completely ruled out either (route *d*). Recently, compounds with an unpaired electron have been shown to be present in reactions of organic alkali metal derivatives^{34a,36,84}, cf. also⁸⁵.

In the metallation of toluene with a mixture of 2-ethylhexyllithium (EtHexLi) and potassium tert-pentoxide (t-PeOK), it was found that in a wide concentration range (t-PeOK/EtHexLi = 0.1 to 1.0), benzylpotassium containing only traces of lithium is formed, and that the amount of benzylpotassium after isolation exactly corresponds to the amount of the potassium alkoxide used^{34a}. Hence, we may assume that potassium alkoxide participated in the reaction with toluene in a stoichiometric amount, and not only as a catalyst. As soon as potassium alkoxide had been consumed, no further metallation of toluene took place, although the organolithium compound was still present. If potassium alkoxide acted only as the activator of the organolithium compound (which by itself is not capable of reacting with toluene to such an extent under the given conditions), the metallation of toluene should be less dependent on the concentration of potassium alkoxide. Thus, the results reported above favour the routes *a* or *b*.

When trying to decide which of the possible reaction mechanisms might be correct, it should be remembered that the system is rather complex and involves a number of partial reactions (including solvation and aggregation equilibria). It is quite likely that the rate and equilibrium constants in the various steps specifically depend on the given conditions (i.e. on the structure of reactants, reaction conditions and character of the reaction mixture (mostly heterogeneous)). Hence, one mechanism may predominate under certain conditions and the importance of another may increase under other circumstances. The results obtained in the metallation of cumene under various conditions support such view⁸⁵. Certain differences observed there

in the composition of the reaction products under various conditions are understandable in view of the complexity of the reaction mechanism. However, irrespectively of the actual pathway for the reaction of the $Z\text{---Li} + \text{ROM}$ system with a third reactive compound, the lithium – heavier alkali metal exchange represented in the reaction (A) must take place at some stage in all cases.

The exchange reaction proceeds against the assumed direction, because it leads to a product containing a more electropositive metal (Na, K, Rb, Cs) bound to a less electronegative atom than oxygen in alkoxide (i.e., to carbon, nitrogen, or the enolate group). For this reason, the problem of the driving force of the lithium – heavier alkali metal exchange is a very important one. The exchange process as suggested above is certainly supported by a shift of the reaction equilibrium caused by the separation of the least soluble component, which in hydrocarbons most often is the heavier alkali metal compound. Some other effects, however, such as the Li---O bond formation in lithium alkoxide, are probably also operative in this case. Lithium alkoxide appears to be the thermodynamically most stable component of the system²⁸ and appears in all types of the exchange reaction (A) reported above. The higher thermodynamic stability of lithium alkoxides compared with heavier alkali metals alkoxides could also be due to the strength of their supermolecular aggregates (cf. the weaker effect of various aprotic solvents on the degree of aggregation of lithium tert-butoxide compared with sodium tert-butoxide⁸⁶, or the fact that lithium alkoxides prefer autoaggregation to the formation of an adduct with phenyl- or benzylpotassium, while potassium tert-pentoxide readily forms such an adduct^{34a,b}).

4. EXPERIMENTAL CONDITIONS FOR THE EXCHANGE REACTION LITHIUM – HEAVIER ALKALI METAL

Experimentally, the reaction between an organolithium compound and a heavier alkali metal alkoxide, possibly in the presence of a third reactive component, is very simple. The initial compounds are mixed in a suitable solvent, mostly as molar solutions and at room temperature, and the reaction is completed with stirring within one or several hours, depending on the nature of the initial mixture. The insoluble product of the exchange reaction is isolated by filtration or centrifugation; its yield and purity are usually high. Organic compounds of heavier alkali metals extremely readily react with oxygen and water, so that the protective argon or nitrogen atmosphere or the so-called vacuum technique must be used. The conditions given in Tables I–IV were not optimized in most cases.

In order to ensure a smooth exchange reaction and an easy isolation of the product, both initial components (or at least one of them) should be soluble in the solvent used. A soluble heavier alkali metal alkoxide is usually chosen, because in such cases also the lithium alkoxide formed is soluble and isolation of the product is quite simple. Heavier alkali metal alkoxides with a branched chain (preferentially alko-

xides of tertiary alcohols) are generally more soluble in hydrocarbons and other aprotic solvents than alkoxides of primary alcohols. The following alkoxides (solubility in both aliphatic and aromatic hydrocarbons $\geq 1 \text{ mol l}^{-1}$ at room temperature) are most frequently used: sodium tert-butoxide (only in cyclohexane and methylcyclohexane), sodium or potassium tert-pentoxide, sodium or potassium (-) (1*R*)-menthoxide. Rubidium tert-butoxide and cesium 1,1-dimethylbutoxide possess some solubility in diethyl ether²⁴. In reactions with organolithium compounds potassium tert-butoxide is also often employed: its solubility in aliphatic hydrocarbons is low, but that of lithium tert-butoxide obtained by the exchange reaction is sufficiently high (about 1 mol l^{-1}). The alkoxides used must be quite pure, and above all, free of alcohol (purification by sublimation or crystallization⁸⁷).

For the reaction of the Z—Li—ROM system with a third reactive compound similar rules are valid. Here the problem of regioselectivity of attack may be of importance. The reactivity of the required attack site must distinctly differ from that of the other parts of the molecule. If a monosubstituted derivative of a third compound containing several sites of equivalent reactivity is needed, a large excess of the third compound must be used, e.g., five-molar. For metallations of third reactive compounds with subsequent derivatization also ether solvents (e.g. THF) at low temperatures (about -78°C) are often used.

These general conditions may be supplemented for the individual types of compounds: organolithium compounds containing the C—Li bond (Tables I and IV) are mostly used as solutions in aliphatic hydrocarbons. Organolithium compounds not soluble in these solvents are employed either as suspensions (sometimes with poorer results), or they are solubilized by the addition of diethyl ether. The latter solvent, however, is suitable for the less reactive organolithium compounds, such as methyl- or phenyllithium, and the reaction of the organometal with ether must be suppressed by lowering the temperature²¹⁻²⁵. Aromatic hydrocarbons are unsuitable as solvents in most cases, because they react with alkyl derivatives of heavier alkali metals. The initial organolithium compound must be pure, i.e. it should not contain other organolithium compounds, otherwise the nonuniformity is sensitively reflected in the product of the exchange reaction. The molar ratio of the heavier alkali metal alkoxide and the organolithium compound is chosen in the range 0.77–1.3, mostly equal to 1, exceptionally to 0.5 (e.g., with insoluble sodium butoxide, cf. Table I).

With substituted lithium amides (compounds with the N—Li bond) the exchange reaction proceeds smoothly with amides soluble in the solvent used (Tables II and IV). In some cases of insoluble amides, however, the lithium— heavier alkali metal exchange was incomplete even after very long reaction times. The most suitable solvents for the metal—metal exchange in lithium amides are aromatic hydrocarbons, benzene in the first place. Alkylbenzenes are less suited because of the danger of metallation under certain conditions¹⁷. In aliphatic hydrocarbons the exchange reaction proceeds slowly and incompletely, ethers are less suitable due to the possibility of a re-

action with heavier alkali metal amides. The molar ratio between heavier alkali metal alkoxide and lithium amide for the exchange reaction is chosen in the range 1.0–1.3. The mixture of lithium tert-butyl amide and potassium tert-butoxide forms a solution in benzene which is highly reactive towards the third component, and is therefore suited for the preparation of its potassium derivative¹⁷. The required lithium amides can be readily prepared, either by reacting butyllithium with the respective amine, or some amides are obtained by reacting lithium powder with amine in toluene in the presence of a hydrogen acceptor (styrene, isoprene, and the like)⁸⁸.

The exchange reaction between the lithium enolates of ketones or esters and the heavier alkali metal alkoxides proceeds most readily in hydrocarbons; in some cases, enolate may be used in the form of a suspension. Analyses of the products (Table III) suggest a somewhat lower purity of the heavier alkali metal enolates formed in the reaction. The exchange reaction in the case of the lithium enolates has a rather theoretical meaning, because the enolates of the heavier alkali metals may be readily prepared by metallation of the parent carbonyl compounds by using hexamethyldisilazylsodium or potassium¹⁹.

Valuable instructions for the use of the system $Z-Li + ROM$ in preparative chemistry have appeared recently in ref.⁸⁹.

5. CONCLUSION

By the lithium–heavier alkali metal exchange reaction, organic compounds of heavier alkali metals may conveniently be prepared and isolated with high degree of purity. The exchange reaction may alternatively be performed in the presence of a third reactive component, in which case a heavier alkali metal derivative of the third component is formed. The products thus obtained serve as reactive agents or intermediates in preparative chemistry, or as polymerization initiators in macromolecular chemistry.

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