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Interaction of alkoxides

XVI *. New properties of complex bases formed from butyllithium and heavier alkali metal t-pentoxides at various alkoxide concentrations. Reaction with organic halogenides

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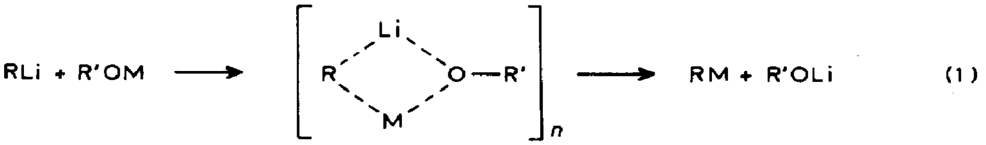
Abstract

Complex bases from organolithium compounds (RLi) and heavier alkali metal alkoxides (R′OM) possess high reactivities. The dependence of their properties on the ratio R′OM/RLi have been investigated. The rates of model reactions between complex bases and organic halides increase with increasing concentration of alkoxide in the complex base by a factor of up to 90. Variation of the concentration of alkoxide also affects the relative yields of the various products in these model reactions, because it affects differently the rates of the competing reactions. Thus in the reaction of the complex base [$C_4H_9Li + x$ t-$C_5H_{11}ONa$] with octyl bromide, the yield of dodecane (a product of C–C coupling) increases from 50 mol% for $x = 1$ to 86 mol% for $x = 4$. However, the effect of the alkoxide concentration is markedly dependent on the reactants and on the reaction conditions. The availability of new types of complex bases increases the possible uses of reagents of this general type in organic synthesis, and they may be regarded as a second generation of complex bases.

Introduction

A mixture of an organolithium compound (RLi) and a heavier alkali metal alkoxide (R′OM) reacts according to eq. 1 in which M = Na, K, Rb, Cs and RLi is a



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compound containing a C–Li, N–Li bond or a Li–enolate of ketones or esters. Such lithium–heavier alkali metal exchange is therefore very general. If the reaction takes place in the presence of a third compound of a suitable reactivity, a compound is formed from the third component and a heavier alkali metal [2–9; for a review see ref. 10]. Reactions between various substrates and a mixture of an organolithium compound and potassium alkoxide have also been described by Schlosser [11,12] and other authors, e.g. Schleyer [13], Brandsma [14,15], and Gordon III [16,17]. The complex bases mentioned above also react readily with organic halides [18], in accord with eq. 2, where R″X may also be a non-activated organic halide, preferably a bromide or iodide, since chlorides predominantly give products formed by a β-elimination of hydrogen chloride.

$$[\mathrm{RLi} + \mathrm{R'OM}] + \mathrm{R''X} \rightarrow \mathrm{R'OLi} + \mathrm{MX} + \mathrm{R{-}R''} + \text{by-products} \qquad (2)$$

Other research on complex bases has focussed on the dependence of their properties on the ratio [R′OM]/[RLi]. Although some particular observations have been reported, e.g. for the anionic polymerization of methylmethacrylate [19] or the metallation of polybutadiene [20] or toluene [6,21], no systematic information has previously been made available.

Experimental part

All operations involving organometallic compounds were carried out under purified argon. Sodium and potassium t-pentoxides were prepared as described in ref. 21. Butyllithium was obtained from lithium and butylchloride in heptane. Organic halides were distilled from calcium hydride.

Reaction procedure

Reactions of complex bases with organic halides were carried out in ampoules; specific conditions are indicated in Table 1. Heptane solutions of butyllithium, of sodium or potassium t-pentoxide, and of the GLC internal standard were mixed at −30 °C. The mixture was shaken at a constant rate for 2 h, care being taken that the temperature of the mixture never exceeded the chosen value. (The amount of BuLi in the ampoule was 0.002 mol; negligible heat was evolved by its reaction.) An organic halide was then added, and at appropriate intervals the ampoules were opened and the contents treated with a mixture of acetic acid, methanol, and water (1 + 1 + 1 by vol.). The alkali halides formed were quantitatively extracted by repeated shaking with water, and their amounts determined by titration with mercury(II) perchlorate in dilute ethanol with diphenylcarbazone as the indicator. The organic phase in the ampoule was analyzed by GLC with a Perkin–Elmer 8310 apparatus, fitted with the following columns: (a) for the reaction of octyl bromide (decane as the internal standard): length 1.8 m, Ø2 mm, 15% GEXE-60 on Chromosorb AW-DMSC 80/100 mesh; (b) for the reaction of butyl chloride (decane as the internal standard) and bromobenzene (dodecane as the internal standard): length 1.8 m, Ø1.8 mm, 15% Apiezon L on Chromosorb W 80/100 mesh.

Results

Dependence of the rate of the reaction between the complex base and organic halides on the ratio [R'OM] / [RLi]

The complex base [$C_4H_9Li + x$ t-$C_5H_{11}OM$] (M = Na, K) readily reacted with organic halides according to eq. 2 (R″X = octyl bromide, butyl chloride, and bromobenzene); the yields of R–R″ and of other products were markedly dependent on the nature of R″X. Under the conditions used, the reaction of butyllithium itself (BuLi) or of alkali alkoxide with R″X was negligible. The reaction was used in order to examine the effect of changing x (between 1 and 4) on the rate of the reaction of the complex base and on the composition of the products. When BuLi was mixed with heavier alkali metal t-pentoxides (t-PenOM) at −30 °C in heptane a precipitate was formed, and R″X was then added. Several parallel or consecutive reactions take place in the mixture, such as C–C Wurtz-type coupling (e.g. reaction 3), β-elimination of hydrogen halide with formation of olefin (e.g. reaction 4), or halogen–metal exchange (e.g. reaction 5). The products of the halogen–metal exchange may also react further by reactions of type 3 and 4 in all possible combinations [18].

In one stage of this reaction lithium–heavier alkali metal exchange, of the type shown in eq. 1, also occurs. This is corroborated by the IR spectra of the liquid phase of the mixture after the reaction of the complex base with octyl bromide but before the hydrolysis: the spectrum is identical with that of lithium t-pentoxide, even when the starting complex base (x = 1) contained t-PenONa or t-PenOK. The IR spectra of alkali metal alkoxides are distinctly different in the range below 600

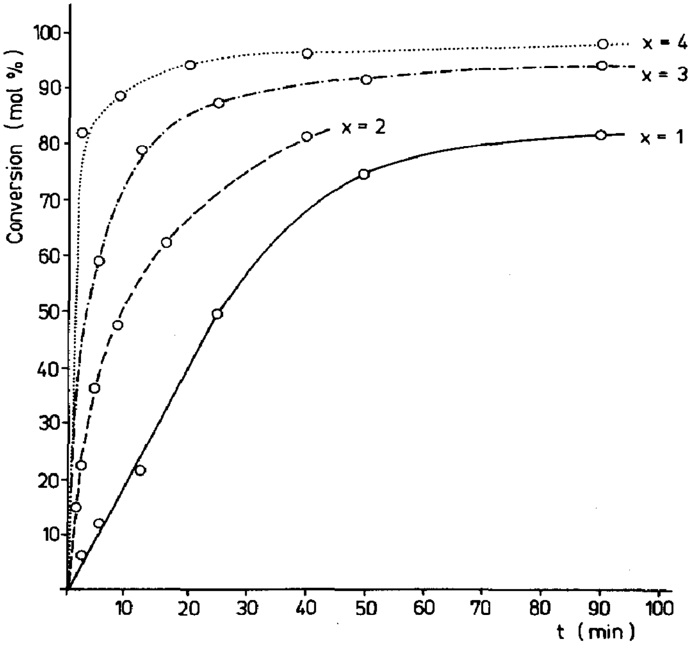

Fig. 1. Rate of formation of Br^- in the reaction between octyl bromide and the complex base [BuLi + x t-PenONa] depending on x. For reaction conditions see Table 1.

Table 1

Reactions of complex bases [BuLi + x t-PenOM] with organic halides (R″X) in heptane at −30 °C. Dependence of the reaction half-time and of the yield of the C–C-coupling product (Bu–R″) on x

Starting concentration (mol/l)						Reaction half-time (min) with respect to		Acceleration factor [a] F	Yield Bu–R″ [b] (mol %)
R″X		BuLi	t-PenOM		x	X⁻	R″X		
$C_8H_{17}Br$	0.442	0.295	t-PenONa	0.295	1	30	31	–	50
	0.442	0.295		0.590	2	9	8	3.5	63
	0.442	0.295		0.885	3	3	3	10	74
	0.442	0.295		1.18	4	0.7	1.3	43	86
	0.287	0.287	t-PenOK	0.287	1	3	4	–	60 [c]
	0.287	0.287		0.861	3	~1.5	4	~2	45 [c]
C_4H_9Cl	0.284	0.284	t-PenOK	0.284	1	68	42	–	15
	0.284	0.284		0.568	2	9	11	7.5	15
	0.284	0.284		0.852	3	9	12	8.5	13
C_6H_5Br	0.442	0.295	t-PenONa	0.295	1	∞	~4	–	3
	0.442	0.295		0.885	3	∞	~2	~2 [d]	3
	0.430	0.287	t-PenOK	0.287	1	44	1	–	18
	0.417	0.278		0.556	2	~0.7	1	~65	24
	0.417	0.278		0.834	3	~0.5	0.5	~90	22

[a] Based on the concentration of X⁻; $F = t_{1/2}(x = 1)/t_{1/2}(x = i)$. [b] Based on amount of R″X consumed 90 min after the beginning of the reaction. [c] The mixture contained a large amount of octane: for (x = 1) 20 mol.% and for (x = 3) 35 mol.%. Octane was formed in the reaction of BuM with BuBr after the halogen–metal exchange. [d] Calculated from the degree of conversion of R″X.

cm^{-1}, and the alkoxides can therefore be readily distinguished [22]. For these reasons, a simplified general notation C_4H_9M is used for the complex base in eq. 3, 4, and 5.

$$C_4H_9M + C_8H_{17}Br \longrightarrow \begin{cases} C_{12}H_{26} + MBr & (3) \\ C_4H_{10} + C_8H_{16} + MBr & (4) \\ C_4H_9Br + C_8H_{17}M & (5) \end{cases}$$

The rate of reaction of R″X with the complex base was determined either by measuring the amount of halide ion formed in the reaction, or the amount of unchanged R″X as indicated by GLC. These procedures gave conversion-time curves from which the half-times $t_{1/2}$ were taken. These are summarized in Table 1, which also shows the initial reaction conditions. The curves for the formation of bromide ions in the reaction between the base [BuLi + x t-PenONa] and octyl bromide at various values of x are shown in Fig. 1. From Table 1 and Fig. 1 it can be seen that the rate of formation of bromide ions increases with increasing concentration of alkoxide. The acceleration of the reaction is indicated by the factor $F_i = t_{1/2}(x = 1)/t_{1/2}(x = i)$, and the value of F_i was as much as 90. Hence, raising the concentration of alkoxide can cause a substantial rise in the reactivity of complex bases.

The half-times of the reaction between R″X and the complex base determined by the two procedures described above were in good agreement for some alkyl halides e.g. octyl bromide, while for some of the halides, e.g. bromobenzene, they differed considerably from each other (Table 1). This is due to the different influence of the concentration of alkoxide on the rates of the competing reactions. It is noteworthy that in some of them halide ion is released (C–C coupling or β-elimination), while in the halogen–metal exchange R″X is consumed without production of halide ion.

Dependence of the yields of the separate products of the reaction between the complex base and organic halides on the ratio [R″OM] / [RLi]

The results reported above indicate that the concentration of heavier alkali metal alkoxides may affect differently the competing reactions, thus causing a change in the relative amounts of the various products. The amounts of the separate products of the reaction between R″X and the complex base were thus determined by GLC after various times of reaction. In this way, yield–time curves were obtained for the separate products. Of the halides R″X used, octyl bromide was the best suited for the formation of a new C–C bond by Wurtz coupling (reaction 3). It was found that in the reaction of the base [BuLi + x t-PenONa] the yield of dodecane depended

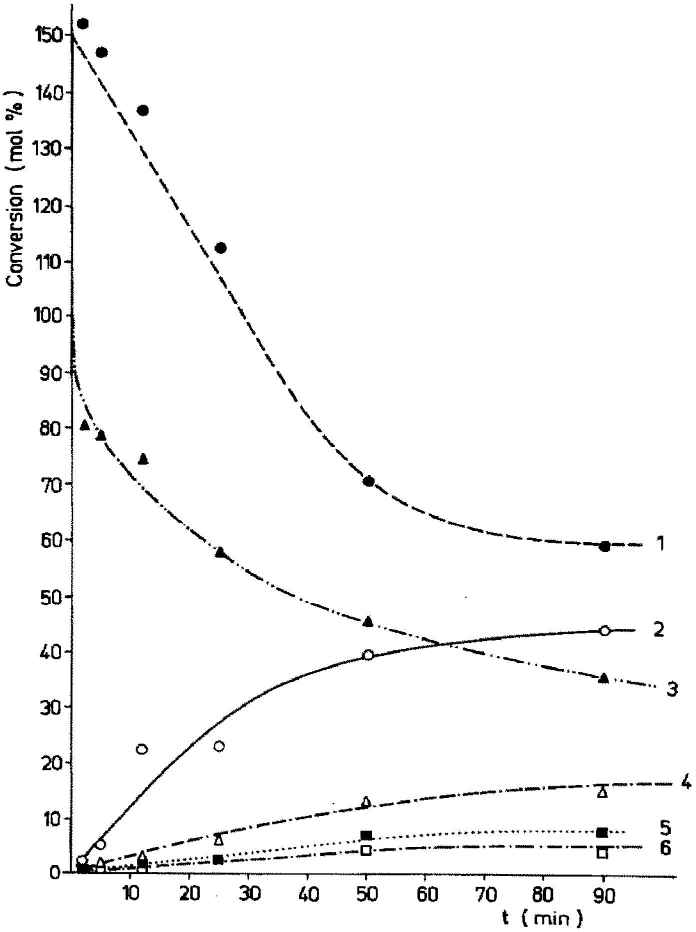

Fig. 2. Variation with time of the composition of the mixture from the reaction of octyl bromide with the complex base [BuLi + x t-PenONa] (x = 1). For the reaction conditions see Table 1. Curves: 1, octyl bromide; 2, dodecane; 3, unresolved mixture of butane and butene; 4, octane; 5, octene-1; 6, hexadecane.

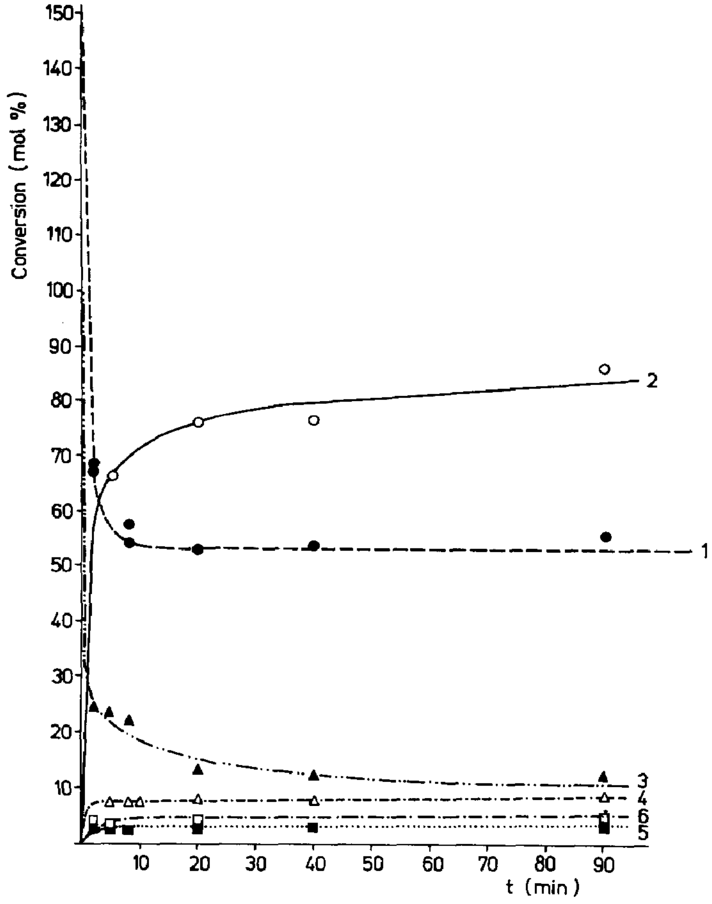

Fig. 3. The same as Fig. 2, but with $x = 4$.

markedly on the value of x. Figure 2 shows the composition of the reaction mixture for $x = 1$ and Fig. 3 that for $x = 4$. From these Figures and from Table 1 it can be seen that the yield of dodecane increased almost twofold after the change in the concentration of alkoxide at the expense of products of β-elimination and of halogen–metal exchange. Hence, by varying the [t-PenONa]/[RLi] ratio, it is possible to bring about pronounced changes in the composition of the products.

In the reaction with octyl bromide, of the complex base containing potassium alkoxide, a change in the concentration of alkoxide had a weaker effect on the relative amounts of the various products; this may be due to a lower selectivity of the derived complex base, associated with the fact that organopotassium compounds are generally more reactive than the corresponding sodium derivatives. Also, the poorer ability of organopotassium compounds to form coordinate bonds may play a part. The effects on the separate competing reactions are evidently rather sensitive to the reaction conditions and the character of the reagent.

Butylchloride shows a marked tendency to undergo β-elimination of hydrogen halide (reaction of type 4) (cf. [18]). Thus, not surprisingly, the reaction between butylchloride and the base [BuLi + x t-PenOK] gave only a small quantity of the coupling product (octane), the yield of which was virtually independent of x (Table

1). The main product was a mixture of hydrocarbons C_4, the yield of which increased somewhat with the concentration of alkoxide (after 90 min of the reaction the theoretical yields were 71% for $x = 1$ and 78% for $x = 3$ (a 100% theoretical yields corresponds to 200 mol%.)).

In the reaction of bromobenzene with alkyl alkali metal compounds halogen–metal exchange (reaction of type 5) plays an important role, depending on the stabilities of the carbanions involved. This was evident in the reaction between bromobenzene and the base [BuLi + x t-PenONa], in which under the conditions used the mixture formed contained, after hydrolysis, 85 mol% of benzene, 65 mol% of the butyl bromide, and small quantities of butylbenzene and hydrocarbons C_4 (below 10 mol%). Its composition remained the same after 600 min; thus, a small quantity of bromide ions was formed at the beginning of the reaction, and afterwards remained constant (Table 1). These results can be explained in terms of a rapid halogen–metal exchange, involving formation of phenylsodium, with which the organic halides present react only very slowly. The situation did not change when the concentration of t-PenONa was increased. For the reaction between bromobenzene and the base [BuLi + x t-PenOK] the same observations are valid, but phenylpotassium formed in this case is more reactive, and products of coupling and β-elimination were therefore detected along with the expected bromide ions. In the case of the reaction between bromobenzene and this base a rise in the concentration of potassium alkoxide had only a weak influence on the yield of the coupling product (Table 1), but distinctly increased the amount of β-elimination from the intermediate butyl bromide.

The causes of the change in the behaviour of complex bases with increasing concentration of the heavier alkali metal alkoxide are probably complex. Possibly new species consisting of mixed supermolecular aggregates are formed, especially at the low temperatures used, but the factors could also be simply of physico-chemical origin, such as changes in solubility and/or the degree of aggregation of the reactants. A discussion of the various mechanisms of reaction of complex bases is given in ref. 21. Each mechanism, however, much retain as a component the lithium–heavier alkali metal exchange shown in reaction 1.

The properties of complex bases may also be changed by TMEDA addition [23], which raises their solubility and reactivity. In this case, however, solvated organometallics are formed.

Conclusion

In the reaction of complex bases [BuLi + x t-PenOM] (M = Na, K) with unactivated organic halides an increase in the value of x ($1 \rightarrow 4$) increases the total reaction rate and changes the composition of the product mixture. Hence, bases with $x \geqq 2$ differ in their properties from the usual bases ($x = 1$), and can therefore be regarded as second generation complex bases of the unsolvated type. It is probable that variation of the concentration of alkoxide will also affect reactions of complex bases with other substrates and in other types of reactions, e.g., metallations. The availability of the new complex bases extends the possible application of the alkali metal reagents in organic synthesis and in anionic polymerization. It must be emphasized, however, that the effects of higher concentrations of heavier alkali metal alkoxides are markedly dependent on the nature of the reactants and on the reaction conditions.

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