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LITHIUM–POTASSIUM EXCHANGE IN ALKYLLITHIUM/POTASSIUM t-PENTOXIDE SYSTEMS

XIV *. INTERACTIONS OF ALKOXIDES

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Summary

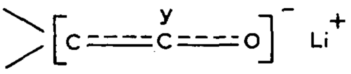
Benzylpotassium containing only traces of lithium compounds is formed in the reaction of alkyllithium, potassium alkoxide and toluene over broad ranges of molar ratios of the reaction components and reaction times. This confirms that metal–metal exchange is occurring under the conditions used. The potassium alkoxide is used in stoichiometric amount for the metallation of toluene and is not only a catalyst. Use of a larger excess of potassium alkoxide leads to formation of its adduct with benzylpotassium. Various mechanisms for the above reaction are considered and formation of lithium alkoxide is assumed to help drive the equilibria towards the observed products.

Introduction

Lithium-heavier alkali metal exchange takes place during the reaction of organic derivatives of lithium with alkoxides of heavier alkali metals:

$$R^1Li + R^2OM \rightarrow R^1M + R^2OLi \ (M = Na, K, Rb, Cs) \qquad (1)$$

This reaction was first described for organolithium compounds containing C–Li bonds [1–4], and later observed for N-substituted amides (involving $>$N–Li bond) [5] and lithium enolates of ketones [6] or esters [7] involving the grouping **A**. This



(A)

(y = alkyl or alkoxyl)

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[*] For part XIII see ref. 30.

exchange reaction gives organic compounds of heavier alkali metals, often pure in high yield [1–10]. If it is carried out in the presence of a third compound with a suitable reactivity, a compound of this third compound with the heavier alkali metal is formed [1–4], e.g.:

$$R^1Li + R^2OK + C_6H_5CH_3 \rightarrow R^1H + R^2OLi + C_6H_5CH_2K \qquad (2)$$

With $R^1Li + R^2OM$ systems, the third component may undergo metallation ($pK(R^1H) > pK(R^3H)$), addition to double bonds, Wurtz-type coupling with organic halides, or polymerization. The formation of organic derivatives of heavier alkali metals via the exchange reactions 1 or of type 2 was confirmed by observation of their characteristic properties (e.g., NMR and EPR spectra, and reactivity [11–17]). The enhanced reactivity of butyllithium in the presence of potassium t-butoxide also was observed by Schlosser [18], who successfully metallated many organic compounds with this system (cf. ref. 19, and references therein).

Although reactions 1 and especially those of type 2 are still much used in organometallic and organic synthesis, the best conditions for their application and their detailed mechanism have not yet been fully established, although recently some new information on these aspects has appeared [17,19,20]. As part of a detailed investigation of these aspects we have examined the effects of variation of the conditions of reaction on the course of reaction 2.

Experimental

All operations involving organic derivatives of alkali metals were carried out under purified argon. Alkali metals were determined by atomic absorption spectrometry. GLC analyses were carried out with a PE 900 or F30 chromatograph fitted with 180 × 0.2 cm columns packed with 15% GEXE-60 (for analysis of the products after hydrolysis) or 10% triethyleneglycol 2,4-dinitrobenzoate (for analysis of the product obtained by treatment with methyl iodide) on Chromosorb W 80–100 mesh. Tetradecane was used as the internal standard. The total base content was determined by titration of the product after hydrolysis.

Starting materials

2-Ethylhexyllithium (EtHexLi) was prepared by treating 2-ethylhexyl chloride with Li powder in hexane with vigorous stirring. Usually the reaction started slowly (sometimes only after an induction period of 10 h) but then became rather vigorous, and rendered a low yield together with some residual 2-ethylhexyl chloride. A portion of the mixture formed was hydrolyzed and then analyzed by GLC, and when necessary, stirring was continued.

Potassium t-pentoxide (t-PeOK) was obtained by gradual addition of 1.8 mol of t-pentyl alcohol to 2.5 mol of K in 1300 ml of boiling heptane with stirring (15 h) when the alcohol had completely reacted (and the initially-formed crystals had dissolved), the clear solution was concentrated and crystallized at −70 °C, to give an 83% yield.

Hexane was purified by shaking with a mixture of H_2SO_4 and P_2O_5 followed by distillation from $LiAlH_4$, and was at least 99.9% pure by GLC. Toluene was dried similarly.

Reaction procedures

(a): To a mixture of 0.015 mol of EtHexLi (0.8 *M* solution in hexane) and a given amount of toluene, the required amount of t-PeOK was added dropwise with stirring at 25 °C (as a molar hexane solution). After the appropriate time the precipitate was isolated by centrifugation, washed, dried, and analyzed.

For hydrolysis a sample of the precipitate was suspended in five volumes of hexane containing the internal standard and a five-fold quantity of water was added with cooling. The mixture was warmed to room temperature with shaking.

For reaction of the precipitate with methyl iodide a similar procedure was used except that a three-fold quantity of methyl iodide was used in place of water.

(b): A solution of EtHexLi was added dropwise to a solution of t-PeOK and toluene, otherwise the conditions were as described under a.

Preparation of the adduct [$PhCH_2K \cdot n$ t-PeOK]. $PhCH_2K$ (0.0067 mol) was shaken with 12.5 ml of a 1.8 *M* solution of t-PeOK (0.023 mol) in hexane for 14 h, during which time the colour of the solid phase changed from orange-red to deep yellow. The yield of the precipitate after 8 washings was 225% based on $PhCH_2K$. Analysis: Total base 30.07% K; after the hydrolysis the toluene content was 30.1 mol% and the t-PeOH content 65.7 mol%.

Results

2-Ethylhexyllithium (EtHexLi) and potassium t-pentoxide (t-PeOK) were chosen for the study of systems formed from organolithium compounds and alkoxides of heavier alkali metal, because they form a homogeneous system in hexane [21]. This permits easy isolation of the product of metallation of a third component. Comparative experiments showed that EtHexLi behaves in the exchange reaction in the way as butyllithium (see Table 1). Toluene was used as the third component because it is metallated readily and with a relatively high regioselectivity. (It should be emphasized that the metallation of other compounds (e.g. of benzene) under similar conditions was not so simple [22].)

A study was made of the effects of the molar ratio of the reaction components and of the reaction time on the composition of the metallated product, which was isolated and analyzed. The analyses comprised the determination of individual alkali metals and of the compounds formed by the reaction with water or methyl iodide. The results are shown in Table 1.

The molar ratio of starting components [t-PeOK]/[EtHexLi] was varied from 0.1 to 3 with a constant excess of the third reactant ([toluene]/[t-PeOK] 5). A high K content was found in the precipitates formed by metallation in all cases, and was close to that calculated for benzylpotassium ($PhCH_2K$) but only traces of Li were present. Analysis of products formed by treatment of the precipitates with water or methyl iodide confirmed that $PhCH_2K$ is a substantial component of the precipitates. The metallation proceeded with a high regioselectivity under the conditions used; ring-metallated species, determined as xylenes after reaction with methyl iodide, usually formed less than 1 mol% of the products.

In view of the low content of Li in the solid product and the small amount of t-pentyl alcohol obtained after hydrolysis, it can be assumed that lithium t-pentoxide (in contrast to t-PeOK, as discussed later) is not bound to $PhCH_2K$ to any significant extent. The yields of $PhCH_2K$ agreed well with the amount of t-PeOK

TABLE 1

CONDITIONS USED FOR THE REACTION SYSTEM EtHexLi + t-PeOK + $PhCH_3$ → EtHexH + t-PeOLi + $PhCH_2K$, AND CHARACTERIZATION OF THE SOLID PRODUCT [a]

Ratio [t-PeOK]/ [EtHexLi]	Ratio [$PhCH_3$]/ [t-PeOK]	Reaction time (h)	Yield $PhCH_2K$ (mol%) [b]	Total basicity [c]	Metal content (%) [d]		GLC after hydrolysis [b]		GLC after reaction with CH_3I		
					K	Li	$PhCH_3$	t-PeOH	EB	o-Xy	To [e]
0.3	5	1	19.6	30.5	27.1	0.61	98.3	2.0	82	0	0.7
0.6	5	1	59.7	30.5	27.6	0.46	96.8	2.0		0.29	1.1
1.0	5	1	103.1	29.1	28.3	0.19	95	2.8	97.7	0.23	2.4
1.3	5	1	103.0	28.9	28.1	0.15	–	–	96.0	0.29	3.4
2.0	5	1	118.8	29.5	28.1	0.25	79.5	17.3	89.3	0.22	3.0
3.0	5	1	138.5	30.4	28.6	0.38	70.1	41.5	63.8	0.23	2.2
1.0	5	97	101.1	29.2	27.7	0.13	91.5	1.6	88.7	0.28	1.7
1.0 [f]	5	1	100.6	29.8	27.7	0.31	98	3.0	89.6	0.3	0.9
1.0	1	1	104.7	30.0	28.8	0.21	84.2	4.8	78	5.0	0.3
1.0	1	5	97.7	29.8	28.2	0.18	90.4	3.0	80.4	2.85	0.8
0.3	5	3	21.9	30.2	27.8	0.40	91.4	0.86	83.9	0.72	0.9
0.3	5	23	28.5	30.3	27.2	0.51	86.2	0.50	87.0	0.22	1.0
0.3	5	100	32.4	30.5	26.3	0.78	97.4	1.0	78.8	0.60	0.8
1 [g]	5	1	98.2	29.83	27.1	0.32	–	–	–	–	–

[a] Procedure (a) was used unless otherwise indicated; abbreviations: t-PeOK = t-$C_5H_{11}OK$, EtHexLi = $C_4H_9CH(C_2H_5)CH_2Li$, EtHexH = $C_4H_9CH(C_2H_5)CH_3$, $PhCH_3$ = toluene, t-PeOH = t-$C_5H_{11}OH$, EB = $C_6H_5C_2H_5$, o-Xy = o-xylene, $PhCH_2K$ = $C_6H_5CH_2K$. [b] Calculated with respect to EtHexLi. [c] Determined acidimetrically after hydrolysis of the solid product. [d] By atomic absorption spectrometry of the solid product after hydrolysis; calc. for $PhCH_2K$: 30.04% K. [e] Product with the same elution time as toluene. Trace quantities of other compounds are also present. [f] Mixing procedure (b) was used. [g] Butyllithium was used instead of EtHexLi.

initially introduced. Thus, the yield of $PhCH_2K$ was 103, 100 and 101% based in the t-PeOK initially taken (after correction for alkoxide in the product) for the initial [t-PeOK]/[EtHexLi] ratios of 0.3, 0.6, and 1.0, respectively. This further confirms the occurrence of reaction 2, i.e., the t-PeOK reacts stoichiometrically and not only as a catalyst; its presence is necessary for metallation of toluene, and after it has been used there is no further metallation of toluene in spite of the presence of the organolithium compound. The results support the view that an organopotassium compound plays a key role in the metallation of toluene, this compound being formed either during the exchange reaction 1 or subsequently (see routes A or B in the Discussion section). If the potassium alkoxide acted as an "activator" only (route C), the extent of metallation of toluene should be much less dependent on the alkoxide.

When the ratio [t-PeOK]/[EtHexLi] was greater than 1.3, the yield of the precipitated product exceeded the theoretical yield of $PhCH_2K$ and a higher t-pentylalcohol content was found after hydrolysis (Table 1). This can be accounted for in terms of the formation of the adduct $[PhCH_2K \cdot n$ t-PeOK] from $PhCH_2K$ and the excess of t-PeOK. The amount and composition of this adduct depend on the actual concentration of t-PeOK. This explanation was confirmed by examining the IR spectra of solid products isolated from reactions carried out with various [t-PeOK]/[EtHexLi] ratios. Furthermore the same adduct was isolated from the reaction of $PhCH_2K$ with a hexane solution of t-PeOK (cf. also ref. 5).

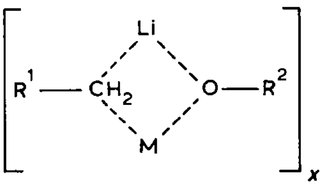
When the toluene was present only in an equimolar ratio to t-PeOK and EtHexLi, the solid product contained a larger amount of ring-metallated products; about 5 mol% of *o*-xylene and only traces of *m*- and *p*-xylene were found after the treatment of the product with methyl iodide. However, the *o*-xylene content fell by about one half when the metallation was carried out for 5 h instead of 1 h, presumably because subsequent reactions of the ring-metallated derivatives gave thermodynamically more stable products. Change in the method of mixing of the reactants corresponding to procedures a and b (see Experimental) did not much affect the product of the metallation.

The effect of the reaction time on the composition of product was investigated with the system [t-PeOK]/[EtHexLi]/[toluene] = 1/1/5. Complete conversion of t-PeOK into $PhCH_2K$ was reached within 1 h, and the product was practically the same as that isolated after 100 h of reaction. However, the reaction proceeded much more slowly in the system [t-PeOK]/[EtHexLi]/[toluene] = 0.3/1/5, for which the limiting conversion of alkoxide was reached only after more than 30 h; nevertheless the composition of the solid product was subsequently substantially unchanged and the Li content remained at 0.3–0.8% during the full period of study (100 h) even under these conditions, which are less suitable for reaction 2 (Table 1).

The optimum [t-PeOK]/[EtHexLi] ratio for the metallation of toluene proved to be 1.0–1.3. This will probably be the case for other systems, but the best concentration of the third reactant will probably depend on its structure [22].

Discussion

Various pathways can be suggested from the starting organic compounds of lithium and alkoxides of heavier alkali metals to the products from reaction of type 2. The process starts with formation of an intermediate complex [1,2,18], with structures suggested to be of types **1** [14,23] or **3** [18], which may also be present in a more or less aggregated form (cf. the complex $[C_4H_9Li \cdot (CH_3)_3COLi]$ forms predominantly tetramers (benzene) or dimers (THF) [24a]; the structures of $[C_4H_9Li \cdot C_4H_9OLi]_2$ and of similar clusters containing bonding of type **1** (M = Li) were determined in THF by NMR spectroscopy [24b], in keeping with the present proposals.



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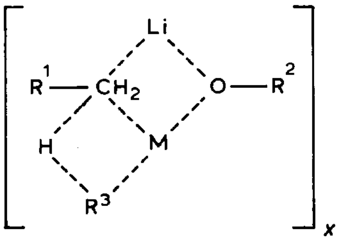

(2)

$$[R^1Li \leftarrow O(K)C(CH_3)_3]_x$$

(3)

In reactions of type 2, the intermediate **1** either decomposes into lithium alkoxide and R^1M, which metallates the third compound R^3H (route A), or reacts directly with R^3H to give R^3M via a transition state, which could have the structure **2** (route B). The intermediate **3** (route C) is an analogue of solvates of organolithium compounds with electron-donor solvents like THF, and it should react with R^3H to give a lithium derivative R^3Li. For formation of the derivative of a heavier alkali metal which was isolated, it is necessary to assume an additional metal exchange with the heavier alkali metal alkoxide. Completely different mechanisms cannot be fully excluded (route D), e.g. those involving participation of strongly ionized species or single electron transfers (SET); SET reactions of organic compounds of alkali metals involving the unpaired electrons were observed recently [21,25,28].

When judging which of the possible reaction mechanisms may be the correct one, it is necessary to note that the system is rather complex and the rate constants and equilibrium constants of the various steps may depend on the structures of the reaction components and reaction conditions and on the physical nature of the mixture, which is mostly heterogeneous. Therefore, one mechanism may predominate under certain conditions, and another under other circumstances. Irrespective of the pathway for reaction 2, the lithium–heavier alkali metal exchange represented in eq. 1, must take place at some stage in all cases. Thus the results favour route A or B.

Both the precipitation of the least soluble compound and the formation of lithium alkoxide may help to drive equilibrium 1 to the right-hand side. One of the reasons for the higher stability of lithium alkoxides compared with those of alkoxides of heavier alkali metals may be the strength of their aggregates in solution (cf. the effect of various solvents on the degree of aggregation of Li, Na, and K alkoxides [29]) or the preference of lithium t-pentoxide for autoaggregation to formation of an adduct with $PhCH_2K$, in contrast with t-PeOK which readily forms such an adduct).

Further investigations of the system formed from organic lithium compound and alkoxides of heavier alkali metals are in progress.

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