Stoichiometry of Reaction. For all reactions shown in Tables I-III the molarities of the reactants as well as the products were calculated. In addition the molarities of benzene, toluene, biphenyl, di-*p*-tolyl, and 4-methylbiphenyl could be estimated. It was established that for the concentration ranges and temperatures used, the rates of the possible side reactions were too slow to interfere with the rate of halogen-metal interconversion.

Mechanism of Halogen–Metal Interconversion between Aryl Bromides and Aryllithium Compounds. II. Rate Studies

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Abstract: The rates of halogen-metal interconversions between a number of aryllithium compounds and substituted aryl bromides have been measured. Agreement between rate data and equilibrium data for these processes coupled with observations of a salt effect, activation parameters, and solvent effects are discussed relative to the reaction mechanism.

It has not been until recently that rate studies involving organolithium compounds have been reported. One of the difficulties encountered is the complexity of the organolithium species present in solution. This often makes interpretation of rate data subject to an array of assumptions which obscures the significant details of the rate-determining steps.

Halogen–metal interconversions generally have been considered to be extremely fast reactions.[1] This is true of most interconversions and in general the rate decreases along the series I > Br > Cl >> F. More recently the dependence of rate on medium has been demonstrated.[2] It has even been shown that the course of a reaction between an organolithium compound and a halide can be altered by the use of a different solvent.[3]

A study of the solvent effect[4] showed that ethereal solvents have a pronounced effect on the rate-determining consumption of butyllithium in the coupling with 1-bromooctane. The observation that better ion-solvating solvents favor halogen–metal interconversions even of Grignard reagents has recently been published.[5]

In our previous publication[6] it was concluded that halogen–metal interconversions between phenyllithium and aryl bromides were equilibrium processes. The extension of this work deals with a study of the rate processes involved.

Results

It was found that halogen–metal interconversions between aryllithium compounds and aryl bromides in ether proceed at rates convenient for kinetic studies at room temperature. Such systems, furthermore, would be convenient for study because the electronic effects of substituents on the arene nuclei have been systematized.

$$\mathrm{ArLi + Ar'Br \rightleftarrows ArBr + Ar'Li}$$

The techniques used in measuring the rates are described in the first publication of this series.[6] For all reactions mentioned in this study the concentrations of reactants as well as products were estimated at every kinetic point. This was done partly to eliminate possibilities of the side reactions discussed elsewhere[6] and partly to ascertain that the rates measured were indeed the rates of interconversion. The side reaction involving benzyne intermediates has been studied by the rate of lithium halide liberated.[7] From this study it is evident that only for fluoro substituents is the elimination–addition reaction competitive with halogen–metal interconversion.

Table I summarizes the rate data measured for the halogen–metal interconversions between salt-containing phenyllithium and some substituted aryl bromides. The rate constants were evaluated graphically by substituting the concentration *vs.* time data into second-order integrated rate expressions. The data are depicted in Figure 1 showing fair linear agreement between the σ constants for the substituents and log k. From the slope of this line the reaction constant ρ was evaluated to be 4.0.

It was found that the halogen–metal interconversion adhered to second-order rate laws. Table II summarizes the apparent agreement between the independently determined rate constants k_+ and k_- and K_{obsd} found by substitution of equilibrium concentrations. The table also shows that the same results are found for salt-free as for salt-containing aryllithium reagents. This indicates that the equilibrium constant in both cases is dependent on the carbanion stabilities despite differences in mechanisms expected.

Salt Effects. There are indications[8] that salt-free and salt-containing aryllithium compounds are present

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(1) R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 331 (1951).

(2) D. E. Applequist and D. F. O'Brien, *J. Am. Chem. Soc.*, **85**, 743 (1963).

(3) J. F. Eastham and G. W. Gibson, *J. Org. Chem.*, **28**, 280 (1963).

(4) J. F. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, **85**, 2171 (1963).

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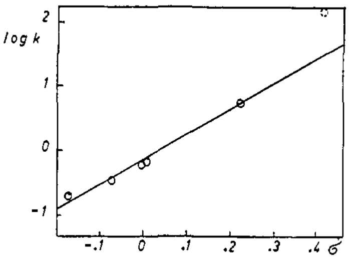

Figure 1. Dependence between substituent constant σ for Z and rate constant for halogen-metal interconversion between phenyllithium and ZC_6H_4Br.

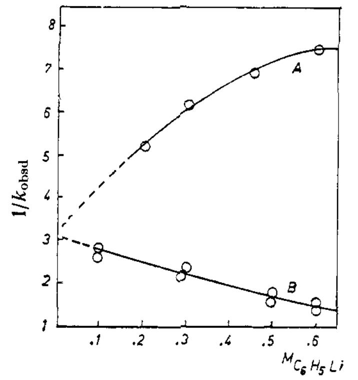

Figure 2. Variation of k_{obsd} with initial concentration of: A, salt-containing and B, salt-free phenyllithium.

in solutions as $(ArLi)_2$ and $(ArLi)_2 \cdot LiBr$, respectively. Some of the evidence was reconfirmed and will be discussed elsewhere. Suffice it here to say that it is apparent that phenyllithium in ether solution is in some way associated with the lithium halide, present in an over-all equimolar amount when the organolithium compound is prepared from an aryl halide. The experiments summarized in Table III show the insensitivity of the magnitude of the equilibrium constant toward lithium halide concentration but also the marked influence of the salt concentration on the rate constant. Already at a molar ratio of 1:2 the rate constant has decreased to that observed for conventionally prepared organolithium reagents (having a 1:1 ratio). The phenyllithium reagent used in experiments 2 and 3 was prepared from diphenylmercury (by route B[6]). To the reaction mixture studied in experiment 2 was added 0.5 mole of lithium bromide per mole of phenyllithium reagent.

Table I. Rates of Halogen-Metal Interconversions between Phenyllithium and Aryl Bromides[a]

Expt no.	Z in BrC_6H_4Z	σ value of Z substituent	k_{obsd}	K_{obsd}
1	p-CH_3	−0.170	0.19	0.60
2	m-CH_3	−0.069	0.34	0.88
3	p-C_6H_5	+0.009	0.65	3.78
4	p-Cl	+0.226	5.4	53
5	m-CF_3	+0.415	170	289
6	p-F	+0.062	b	...
7	p-OCH_3	−0.268	c	...
8	H[d]	0.000	0.59	...

[a] All reactions were performed in ether at 25°, initial concentrations of both reactants 0.3 *M*. [b] Side reaction dominated, metalation *ortho* to F. [c] Side reaction dominated, metalation *ortho* to OCH_3. [d] In this case only, p-tolyllithium was used as organolithium reagent.

Table II. Relation between Rate Constants and Equilibrium Constants

Expt no.	1	2	3	4
Initial concentrations				
C_6H_5Li	0.60	0	0.11	0
p-$CH_3C_6H_4Br$	0.60	0	0.31	0
C_6H_5Br	0	0.50	0	0.32
p-$CH_3C_6H_4Li$	0	0.50	0	0.10
k_+[a]	0.161		0.25	
k_-[a]		0.251		0.51
k_+/k_-	0.64		0.50	
K_{obsd}[b]	0.60	0.67	0.55	0.65
Type ArLi	Salt-containing	Salt-containing	Salt-free	Salt-free

[a] The rate constants are calculated by disregarding the return reaction, *i.e.*, in experiments 1 and 3, k_- is disregarded; in experiments 2 and 4, k_+ is disregarded; rate constants are in units l. mole^{-1} hr^{-1}. [b] The equilibrium constant is defined by the reaction written

$$C_6H_5Li + p\text{-}CH_3C_6H_4Br \underset{k_-}{\overset{k_+}{\rightleftarrows}} C_6H_5Br + p\text{-}CH_3C_6H_4Li$$

Table III. Influence of Lithium Bromide on Initial Rates of Interconversion

Starting materials and concn $M_{C_6H_5Li}$	$M_{p\text{-}CH_3C_6H_4Br}$	M_{LiBr}	k_{obsd}[a]	K_{obsd}
0.25	0.29	0.30	0.21	0.54
0.23	0.30	0.15	0.21	0.59
0.23	0.30	0.00	0.47	0.53

[a] k_{obsd} (l. mole^{-1} hr^{-1}) was evaluated from the initial rates disregarding the return reaction; temperature 25°, solvent ether.

Details of Kinetic Investigations. The halogen-metal interconversion between phenyllithium and p-bromotoluene was chosen for a more detailed study of the kinetics. The exchange proceeds with 1:1:1:1 stoichiometry at a conveniently slow rate. The backward reaction is faster than the forward so that it would be expected to have an appreciable influence on the overall rate. Halogen-metal interconversions involving salt-free and salt-containing phenyllithium were found to obey second-order rate laws and to disobey rate laws for different order reactions. However, an apparent dependency between the simple second-order rate constant and the initial concentrations was soon recognized. This dependency is illustrated in Figure 2 in which the reciprocals of the initial rate constants, calculated by disregarding the backward reaction, are plotted against the initial concentration of the phenyllithium reagent.

The two curves show the dependency of the rate constant for the salt-containing (curve A) and for the salt-free phenyllithium (curve B), respectively. It may be seen that whereas the rate constants increase ($1/k_{obsd}$

Table IV. Evaluation of Rate Constants for Interconversions Involving Salt-Free Phenyllithium[a]

Expt no.	$M_{C_6H_5Li}$	k_{obsd}	k_+	k_+'
1	0.10	0.38	0.65	1.28
2	0.23	0.47	0.55–0.67	1.11
3	0.29	0.55[b]	0.74	1.28
4	0.58	0.73	0.35–0.40	1.19
Method used for calculation[c]		A	C	B
Agreement with rate law		Fair	Fair	Good

[a] All experiments are interconversions between *p*-bromotoluene (initial concentration 0.3 *M*) and phenyllithium. [b] Since initial concentration are alike k_{obsd} was in this case evaluated from the expression $k_{obsd}\,t = x/a(a - x)$. [c] Method used

$$k_{obsd}t = \frac{1}{a-b}\ln\frac{b(a-x)}{a(b-x)} \qquad \text{(A)}$$

$$\frac{dx}{dt} = \frac{k_+'}{2a}\left[(a^2 - x^2)(b - x) - \frac{(a^2 - x_e^2)(b - x_e)}{2ax_e^2 - x_e^3}(2ax^2 - x^3)\right] = \frac{k_+'}{2a}\alpha \qquad \text{(B)}$$

$$\frac{dx}{dt} = k_+(a - x)(b - x) - \frac{k_+}{K_{obsd}}x^2 = k_+\beta \qquad \text{(C)}$$

decreases) with increasing dilution for salt-containing phenyllithium the reverse effect is true for salt-free phenyllithium. It furthermore appears that the two curves approach one value on approaching infinite dilutions. Since the effects are different in character the reactions were studied separately.

A. Halogen–Metal Interconversions of Salt-Free Phenyllithium. It was expected that the backwards portion of an equilibrium process has little effect during the first portion of a reaction proceeding toward an equilibrium. Hence it might be expected that linear agreement of the standard second-order rate plots should be obtainable at least for the first portion of the reaction. This is in general true. However, it may be seen from Table IV how the thus calculated rate constants, k_{obsd}, vary with initial concentrations of the phenyllithium reagent.

The extension of the calculation for simple second-order rate constants involved consideration of the backwards reaction. Unfortunately the differential equation for two opposing second-order reactions is very awkward to integrate when the initial concentrations are not identical. Therefore the differential equation was used for the evaluation of k_+. Although reasonable linear relations resulted from plotting dx/dt *vs.* $[k_+(a - x)(b - x) - (k_+/K_{obsd})x^2]$ the k_+ showed a definite drift.

It was hence that still another refinement was considered. If one makes the reasonable assumption that aryllithium reagents are present almost exclusively in the form of dimeric aggregates[8] and that these are directly involved in the rate-determining steps, then one can write the equation for the halogen–metal interconversion thus

$$(C_6H_5Li)_2 + p\text{-}CH_3C_6H_4Br \underset{k_-'}{\overset{k_+'}{\rightleftarrows}} C_6H_5Br + (C_6H_5Li\cdot p\text{-}CH_3C_6H_4Li)$$

$$(C_6H_5Li\cdot p\text{-}CH_3C_6H_4Li) + p\text{-}CH_3C_6H_4Br \underset{k_-'}{\overset{k_+'}{\rightleftarrows}} C_6H_5Br + (p\text{-}CH_3C_6H_4Li)_2$$

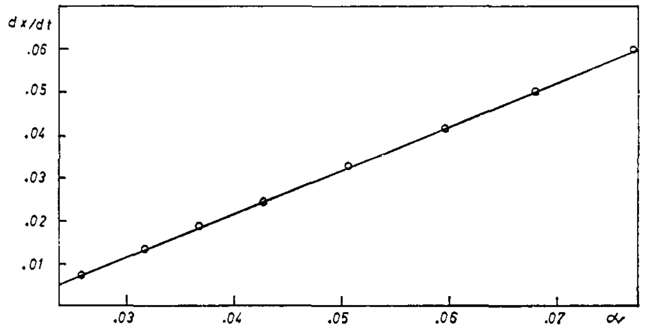

Figure 3. Example of rate constant evaluation from plot depicting $dx/dt = k_+'\alpha/2a$ for interconversion between *p*-bromotoluene and salt-free phenyllithium.

For simplicity the rate constants are assumed equal for the similar forward reactions as well as for the return ones.

The final assumption made is that the aryl groups are distributed randomly among the dimeric complexes. On the basis of these assumptions it is possible to arrive at a differential equation (B) which is obeyed by the experimental concentration *vs.* time data, and more important the k_+' thus derived individually from different reactions appears to be a true constant. This agreement renders the assumptions probable although it does not exclude other explanations. An example of the graphical agreement is given in Figure 3.

B. Halogen–Metal Interconversions of Salt-Containing Phenyllithium. The simplest assumption is to neglect the return reaction and evaluate k_{obsd} for a number of reactions for which the initial concentrations of phenyllithium differed. The results listed in Table V show that despite the good agreement with second-order rate laws the specific rates vary considerably from experiment to experiment. It was again ascertained that other reaction orders were not obeyed.

Table V. Evaluation of Rate Constants for Interconversions Involving Salt-Containing Phenyllithium[a]

Expt no.	$M_{C_6H_5Li}$	k_{obsd}	k_+'	k_+
1	0.60	0.134	0.4–0.9	0.194
2	0.30	0.162[b]	0.6–0.8	0.187
3	0.20	0.212	0.8–2.0	0.173
4	0.19	0.193	0.5–1.0	0.187
5	0.10	0.310	0.1–1.0	0.8–1.25
Method of calculation[c]		A	B	C
Agreement with rate law		Good	Poor	Good

[a] All experiments are interconversions between *p*-bromotoluene (initial concentration 0.3 *M*) and phenyllithium. [b] Since initial concentrations are alike k_{obsd} was in this case evaluated from the expression $k_{obsd}t = x/(a(a - x))$. [c] Same conventions as in Table IV.

The second column of Table V shows the ranges of k_+' which were obtained by evaluating the rate constants for the experiments under the assumptions of dimeric species being involved in the rate-determining step and random distribution of organolithium monomers among possible dimeric species. Very poor agreement was obtained by this approach. It is hence reasonable to conclude that in the presence of

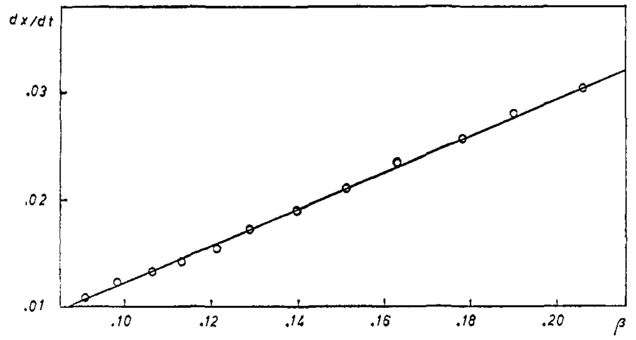

Figure 4. Example of rate constant evaluation from plot depicting $dx/dt = k_+\beta$ for interconversion between *p*-bromotoluene and salt-containing phenyllithium.

lithium bromide the scrambling process is prevented or at least slowed down.

The last column lists the results of the calculation of rate constants using the differential equation which takes the return reaction into account. In this instance good agreement is achieved at all concentrations but the very last in which the result for salt-free phenyllithium is approached. An example of the graphical evaluation is given in Figure 4.

Arrhenius Plot for Halogen–Metal Interconversions. Since the reaction under the conditions of the standard experiments (25°) proceeds at a reasonable rate it was thought possible to study the influence of temperature on the rate of reaction over a range from −10 to +35°. The results of this study is given in Table VI. The experiments were all performed at the same initial concentrations and the rate constants (k_+) were evaluated.

Table VI. Influence of Temperature on Rate of Interconversion[a]

Temp, °C	$1/T$	k_+[b]	Log k_+
−10	0.00380	0.00337	−2.472
0	0.00366	0.0126	−1.898
10	0.00353	0.0342	−1.465
25	0.00336	0.185	−0.737
30	0.00330	0.301	−0.521
35	0.00325	0.490	−0.310

[a] The initial concentrations were approximately $M_{C_6H_5Li} = 0.30$; $M_{p\text{-}CH_3C_6H_4Br} = 0.30$; solvent ether. [b] Evaluated by substitution into the expression $k_+t = [2.3x_e/2a(a - x_e) \log [(x(a - 2x_e) + ax_e)/a(x_e - x)]$, t in hours using the proper values of x_e calculated from K_{obsd} given in ref 6.

The data of Table VI are plotted in Figure 5, showing good linearity within the range studied. The "thermodynamic" activation parameters were evaluated by the usual techniques giving

$$E_a = 16.8 \text{ kcal}, \Delta G^*_{277} = 23.3 \text{ kcal}, \Delta S^*_{277} = -23.6 \text{ eu}$$

Discussion

The results, collected in our previous publication,[6] indicate that the halogen–metal interconversions studied are equilibrium processes. The equilibrium position is governed by an interplay between the relative nucleophilicities of the organolithium reagents (or the carbanions hereof) and the relative electrophilicities of the aryl bromides.

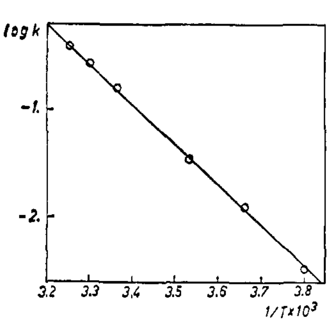

Figure 5. Arrhenius plot for halogen-metal interconversion between phenyllithium and *p*-bromotoluene.

In comparing the relative rates of interconversion between two different bromides and phenyllithium one of the products and one of the reactants are the same. It should hence hold that both the ground-state energy of the aryl bromide reactant and that of the aryllithium product should influence the free-energy changes or the position of the equilibrium.

$$C_6H_5Li + p\text{-}CH_3C_6H_4Br \rightleftarrows C_6H_5Br + p\text{-}CH_3C_6H_4Li$$

$$C_6H_5Li + m\text{-}CF_3C_6H_4Br \rightleftarrows C_6H_5Br + m\text{-}CF_3C_6H_4Li$$

A similar situation exists for the reverse reactions, the comparison of rates of interconversions of two different aryllithium reagents and the same aryl bromide. In this case the two equilibria may be considered to proceed from right to left. It is evident that in general the rate of formation of the organolithium reagent containing the more stable carbanion is faster than the rate of formation of the one containing the less stable one. Viewing the two equilibria as proceeding from left to right establishes at least that the aryl bromide containing the electron-withdrawing substituent is a stronger electrophile than the one containing an electron-releasing substituent, but viewing the processes from right to left shows that the organolithium reagent containing the more stable carbanion is also the poorer nucleophile.

It appears reasonable to interpret the large positive ρ as a buildup of negative charge in the transition state. This is also in accordance with the acceleration of the exchange by better ion-solvating solvents and the negative entropy of activation. In no case could the rates of interconversion between the given bromides and phenyllithium be measured in tetrahydrofuran ($t_{1/2} < 5$ min).

It is conceivable that the rate constants are composite either because the aryllithium reagent reacts as a dimer or because it is in fast equilibrium with a more reactive intermediate. This would, however, not have an influence on the magnitude of ρ unless the composition of the aggregates of aryllithium compounds were different, or unless the equilibrium constants toward the formation of the more reactive species differed significantly among the various aryllithium reagents. Since all organolithium reagents involved are aryllithium compounds neither of these possibilities appear likely.

The apparent agreement between equilibrium data and the fractions of the initial rate constants for the forward and the backward reactions further emphasizes the validity of the conclusions drawn above. Although the agreement holds for both salt-free and salt-containing phenyllithium or *p*-tolyllithium it is evident that the mechanisms by which they react differ. The data listed in Table III show that a drastic change in rate constant is caused by the addition of 0.5 mole of lithium bromide per mole of organolithium reagent but not by further increase of the molar ratio. This is most readily interpreted by postulating the formation of a complex of the formula $(ArLi)_2 \cdot LiBr$ in the solution. This complex is less reactive than the salt-free organolithium reagent.[9]

The following reaction schemes may be suggested (mechanisms A–C) (C may be considered an extreme extension of B).

Mechanism A

$$(ArLi)_2 \overset{\text{fast}}{\rightleftharpoons} 2ArLi$$

$$(Ar'Li)_2 \overset{\text{fast}}{\rightleftharpoons} 2Ar'Li$$

$$(ArLiAr'Li) \overset{\text{fast}}{\rightleftharpoons} ArLi + Ar'Li$$

$$ArLi + Ar'Br \overset{\text{slow}}{\rightleftharpoons} ArBr + Ar'Li$$

Mechanism B

$$(ArLi)_2 + Ar'Br \overset{\text{slow}}{\rightleftharpoons} (ArLiLiAr') + ArBr$$

$$(ArLiLiAr') + Ar'Br \overset{\text{slow}}{\rightleftharpoons} (Ar'Li)_2 + ArBr$$

Mechanism C

$$(ArLi)_2 \overset{\text{fast}}{\rightleftharpoons} Ar^{\ominus} + ArLi_2^{\oplus}$$

$$(Ar'Li)_2 \overset{\text{fast}}{\rightleftharpoons} Ar'^{\ominus} + Ar'Li_2^{\oplus}$$

$$Ar'^{\ominus} + ArLi_2^{\oplus} \overset{\text{fast}}{\rightleftharpoons} (ArLiLiAr') \overset{\text{fast}}{\rightleftharpoons} Ar^{\ominus} + (Ar'Li_2)^{\oplus}$$

$$Ar^{\ominus} + Ar'Br \overset{\text{slow}}{\rightleftharpoons} [Ar....Br....Ar']^{\ominus} \rightleftharpoons ArBr + Ar'^{\ominus}$$

A decision between these is attempted on the basis of the conclusions drawn from the previous[6] and present investigations of the halogen–metal interconversions.

$$ArLi + Ar'Br \rightleftharpoons ArBr + Ar'Li$$

1. The interconversions are equilibrium processes.
2. The position of the equilibrium may be expressed by substituting the concentrations of the aryl bromides and the *total* concentrations of the aryllithium compounds into the common expression for the equilibrium constant (which is independent of initial concentrations).
3. The equilibrium constants are essentially insensitive to the medium although the rates are not, being faster in tetrahydrofuran than in ether.
4. The ratio of the rate constants for the forward and the backward reactions yields the same equilibrium constants.
5. The rates of interconversions of salt-free phenyllithium are decreased by the addition of lithium bromide until a molar ratio of 2:1 and then no further.
6. The rate expression obeyed by data for interconversions involving salt-containing aryllithium reagents is a second-order reversible process, first order in aryl bromide and first order in total concentrations of aryllithium reagents present. This rate expression is not obeyed by data collected for interconversions involving salt-free aryllithium compounds.
7. The latter obey a rate expression derived on two assumptions: the fast, random scrambling of monomeric aryllithium compounds between dimeric aggregates and equal specific rates of interconversion between a given aryl bromide and pure or mixed aggregates. This rate expression is disobeyed by data involving salt-containing phenyllithium.
8. Both equilibrium and rate data for the interconversion of phenyllithium with substituted aryl bromides fit σ–ρ relations with a large positive reaction constant.
9. The rate data yield a straight line in a log k *vs.* $1/T$ plot from which reasonable activation parameters for a second-order reaction may be derived.

Several of the conclusions do not allow a distinction between the mechanism A, B, or C. Thus, conclusions 1 and 2 would not allow a decision between A and B since both involve fast equilibria prior to the rate-determining step. These conclusions alone do not show whether the reacting species are monomers or dimers.

From conclusion 3 follows that either the transition state is favored by solvents with higher dielectric constants or the steady-state concentration of a reactive intermediate is increased. Both 8 and 9 appear to emphasize this conjecture, the large positive reaction constant being interpreted as a sign of buildup of negative charge near the aromatic nucleus in proceeding from the reactants to the transition state. This is best envisioned as nucleophilic attack on bromine by the carbanion of the organolithium reagent.

It is evident that salt-free and salt-containing phenyllithium react by different mechanisms (5, 6, and 7).

Neither can be described by reaction mechanism A which implies a one-half-order dependence in the aryllithium reagents, when we find a first-order dependence.

Mechanism C is improbable for salt-containing aryllithium compounds since fast dissociation prior to the rate-determining step would also be a route for the scrambling process which apparently does not take place. Salt-containing aryllithium compounds thus probably react by mechanism B. Salt-free aryllithium compounds would likewise be expected to react according to mechanism B or its extension C. A clear decision between these cannot at present be made, nor can a clearer picture of the transition state be derived. We are continuing our efforts in this direction.

Experimental Section

For preparation of aryllithium reagent and for general procedure see ref 6.

In all kinetic runs summarized in the tables, the change in concentrations of the two reactants and the two products varied with time as shown by the example given in Figure 1 of ref 6. From this figure and similar plots for other starting concentrations it was concluded that the reaction shows clear 1:1:1:1 stoichiometry.

Calculation of Rate Constants. From the plots of concentration *vs.* time the decrease in concentration of one of the reactants or the increase in concentration of one of the products with time was tabulated, for regular increments of time. *For salt-containing aryllithium* in general, the following integrated rate expressions were used for the evaluation of the rate constants

$$kt = \frac{x}{a(a-x)}$$

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[9] T. V. Talalaeva, A. N. Rodionov, and K. A. Kocheshkov, *Proc. Acad. Sci. USSR Chem. Sect.* (English Transl.), **154**, 47 (1964).

or

$$kt = \frac{1}{a - b} \ln \frac{b(a - x)}{a(b - x)}$$

for equal or different initial concentrations, respectively, disregarding the backward reaction; x is the concentration of the aryl bromide formed by exchange at time t, a is starting concentration of aryllithium reagent, and b is starting concentration of the aryl bromide. For equal starting concentrations of reactants and taking into account the backward reaction, the following integrated rate expression[10] was used.

$$\ln \left(\frac{x(a - 2x_e) + ax_e}{a(x_e - x)} \right) = k \frac{2a(a - x_c)}{x_e} t$$

Integrated rate expressions for reactions of different order did not give linear agreement. For different starting concentrations the differential equation was used: $dx/dt = k_+(a - x)(b - x) - k_-x^2$, the slopes, dx/dt, were evaluated from plots of x *vs.* t; k_- as a function of k_+ and the experimentally determined x_e was substituted into the differential equation.

At equilibrium $dx/dt = 0 = k_+(a - x_e)(b - x_e) - k_-x_e^2$, giving

$$k_- = k_+ \frac{(a - x_e)(b - x_e)}{x_e^2}$$

or

$$\frac{dx}{dt} = k_+ \left[(a - x)(b - x) - \frac{(a - x_e)(b - x_e)}{x_e^2} x^2 \right]$$

Plotting dx/dt *vs.* the expression in the square brackets gave a straight line with slope k_+.

For salt-free aryllithium, a similar approach was used, but the differential equation used for the evaluation of rate constants appears as follows.

$$\frac{dx}{dt} = \frac{k_+'}{2a} \left[(a^2 - x^2)(b - x) - \frac{(a^2 - x_e^2)(b - x_e)}{2ax_e^2 - x_e^3}(2ax^2 - x^3) \right]$$

This is obtained by assuming statistic scrambling of aryllithium monomers between $(\mathrm{ALi})_2$, ArLiAr′Li, and $(\mathrm{Ar'Li})_2$′ the relative concentrations of the three species, for the presence of total aryllithium concentrations, $(\mathrm{ArLi})_{\mathrm{obsd}}$, and $(\mathrm{Ar'Li})_{\mathrm{obsd}}$ being

$$1:2\frac{(\mathrm{Ar'Li})_{\mathrm{obsd}}}{(\mathrm{ArLi})_{\mathrm{obsd}}}:\frac{(\mathrm{Ar'Li})^2_{\mathrm{obsd}}}{(\mathrm{ArLi})^2_{\mathrm{obsd}}}$$

For total aryllithium reagents present

$$(\mathrm{ArLi})_{\mathrm{obsd}} = 2(\mathrm{ArLi})_2 + (\mathrm{ArLi \cdot Ar'Li})$$

and

$$(\mathrm{Ar'Li})_{\mathrm{obsd}} = 2(\mathrm{Ar'Li})_2 + (\mathrm{ArLi \cdot Ar'Li})$$

If x is the concentration of aryl bromide formed by exchange then

$$(\mathrm{ArLi})_{\mathrm{obsd}} = a - x, \ (\mathrm{Ar'\ Li})_{\mathrm{obsd}} = x$$

whch gives

$$(\mathrm{ArLi \cdot Ar'Li}) = \frac{(a - x)x}{a}; \ (\mathrm{ArLi})_2 = \frac{(a - x)^2}{2a}$$

and

$$(\mathrm{Ar'Li})_2 = \frac{x^2}{2a}$$

Assuming the exchange occurring by the reactions

$$(\mathrm{ArLi})_2 + \mathrm{Ar'Br} \underset{k_-'}{\overset{k_+'}{\rightleftharpoons}} (\mathrm{ArLi \cdot Ar'Li}) + \mathrm{ArBr}$$

$$(\mathrm{ArLi \cdot Ar'Li}) + \mathrm{Ar'Br} \underset{k_+'}{\overset{k_-'}{\rightleftharpoons}} (\mathrm{Ar'Li})_2 + \mathrm{ArBr}$$

one arrives, by substitution, at the differential equation given above. Good linear relationships were obtained by calculating the magnitude of the expression in the square brackets for certain times and plotting these against dx/dt for these times. The slope of the line drawn through these points is $k_+'/2a$, from which k_+' can be evaluated.

In the process of deriving the differential equation given above, it is necessary to find a relationship between k_+' and k_-'. This is done by setting $dx/dt = 0$; thus one finds $k_+'/k_-' = x_e^2(2a - x_e)/(a^2 - x_e^2)(b - x_e)$ which can be rearranged to $x_e^2/(a - x_e)(b - x_e)[(a + x_e)/(2a - x_e)]$. If the expression in the square brackets has the magnitude 1 ($x_e = a/2$), then k_+'/k_-' is equal to the classical expression for the equilibrium constant (K_{eq}). That k_+'/k_-' is different from K_{eq} stems from the consideration that all three dimeric species are involved in the halogen-metal interconversion and from the assumptions made in deriving the expression for dx/dt.

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[10] A. A. Frost and R. G. Pearsons, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p 175.