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RELATIVE RATES, RELATIVE ACTIVATION PARAMETERS AND SUBSTITUENT EFFECTS OF LITHIUM–METALLOID EXCHANGE REACTIONS

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The relative reactivity of heteroatomic compounds (PhM; M = SeR, SnR_3, TeR, I) towards BuLi was estimated by competitive experiments. The rates of exchange reactions in THF increase in the order I > Te » Sn » Se with a ratio of 1000:300:15:1 at −70 °C when R = Bu. Me_3SnPh underwent exchange much faster than Bu_3SnPh, suggesting that the exchange reaction was largely affected by steric hindrance. The evidence that Bu_3SnPh and BuTePh react with BuLi at almost the same rate in the presence of HMPA and that the relative exchange rates of Li–Te/Li–Sn increase in less polar solvents such as Et_2O and hexane indicates that coordination of solvents towards lithium plays an important role in exchange reactions. Relative activation parameters obtained from competitive reactions of PhTeBu and $PhSnBu_3$ with BuLi showed that Li–Te exchange was favored over Li–Sn exchange by an enthalpy factor. Hammett treatment of Li–Te exchange of ArTeBu with BuLi in THF showed a substantially large positive reaction constant (ρ) of 3·4, indicating that the anion charge was largely distributed on the leaving group in the transition state.

INTRODUCTION

Organic compounds containing a carbon–metal(loid) (Hg, As, Se, Sn, Sb, Te, I, Bi) bond afford corresponding organolithium compounds with the aid of lithium–metal(loid) (hereafter referred to as Li–M) exchange reactions.[1,2] Among these, Li–Sn and Li–Te exchange reactions are especially useful in synthetic reactions when Li–X (X = halogen) exchange cannot be employed.[3,4] Several mechanisms for the exchange reactions have been proposed, such as a single electron transfer (SET),[5] an S_N2 process[6] or via ate complex intermediates,[7] and four- or three-center process.[2e,7f,8] Reich and co-workers[7c,f] have succeeded in detecting Sn, Te and I ate complexes by low-temperature NMR and also suggested that exchange proceeds more rapidly on the heavier and more electronegative elements. Furukawa and co-workers[9] have examined triaryltellurium ate complexes by NMR and reported that the stabilities of triaryl chalcogen ate complexes increase in the order Te > Se > S. Rogers and Houk[2e] and Winkler and Winkler[8] have reported the rates of Li–Br exchange reactions. We report here relative rates of Li–M exchange reactions of aryl-substituted selenium, tin, tellurium and iodine compounds with BuLi along with the effects of solvents and the leaving group on the rate of exchange reactions which proceed via ate complexes [equation (1)].[7]

$$ArM + BuLi \rightarrow [Ar—M—Bu]^- Li^+ \rightarrow ArLi + BuM \quad (1)$$

$(M = SnR_3, TeR, SeR, I)$

RESULTS AND DISCUSSION

Selectivity and reversibility of exchange reactions

In order to examine the selectivity of exchange reactions of aryl-substituted metalloids, a limited amount of BuLi (0·2 mmol) was added to a THF solution of n-$C_6H_{13}TePh$ (HexTePh; 1·0 mmol) and PhCHO (3·0 mmol) at −70 °C. The products obtained were

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Table 1. Reactions of PhM with BuLi in the presence of PhCHO[a]

Run	PhM	GLC yields based on BuLi (%)			
		BuM	Ph_2CHOH	PhRCHOH	PhBuCHOH
1	PhTeHex	12	13	0[b]	87
2	PhSeHex	2	2	0[b]	96
3	$PhSnMe_3$	8	7	0·7[c]	92

[a] BuLi (0.2 mmol), PhM (1 mmol), PhCHO (3 mmol), THF (10 ml), −70 °C.
[b] R = Hex.
[c] R = Me.

PhBuCHOH and Ph_2CHOH (87% and 13%, respectively, based on BuLi used, run 1 in Table 1). No formation of Ph(Hex)CHOH, which can be formed by trapping of HexLi with PhCHO, indicates that HexLi was not generated. Selective generation of PhLi from PhSeBu and from $PhSnBu_3$ was confirmed also under identical conditions (see run 2 for PhSeBu). A similar reaction of $PhSnMe_3$ afforded Ph_2CHOH and PhMeCHOH in 7% and 0·7% yields, respectively, suggesting that generation of PhLi competed with that of MeLi, probably owing to the high thermodynamic stability of MeLi in comparison with alkyllithiums (run 3).

The reverse process to generate alkyllithiums by the attack of PhLi was found to be negligible, being supported by the following evidence. When PhLi was added to an equimolar mixture of Bu_2Te and Hex_2Te in THF at −78 °C, disproportionation of the tellurides was not observed, resulting in the recovery of tellurides unchanged after quenching with MeOH. A similar reaction of a mixture of Bu_4Sn (0·5 mmol) and Me_4Sn (0·5 mmol) with PhLi (0·5 mmol) in THF at −78 °C for 1 min followed by quenching with MeOH afforded only $PhSnMe_3$ in 10% yield, without the formation of $PhSnBu_3$ and $BuSnMe_3$. These results indicate that aryl-substituted metalloids afford only aryllithiums exclusively by the reaction with BuLi and that the reverse reaction is negligible except the case of methyl-substituted compounds.

A possibility suggested by a referee that ate complexes, generated as intermediates of exchange reactions, directly react with trapping reagents can be ruled out because ate complexes are much less reactive than generated aryllithiums which react exclusively with electrophiles.[7a] However, this may not be the case when HMPA is present, where ate complex can do react with electrophiles (see below).[7a]

Estimation of relative rates of Li–M exchange reactions

To examine the rate order of exchange reactions with respect to metalloids, competitive reactions of two kinds of metalloids were carried out using different ratios of mixtures and maintaining the concentration of one of the metalloids at 0·1 M. For example, BuLi (0·2 mmol) was added to a mixture of $PhSnBu_3$ (1 mmol) and a certain amount of PhTeBu in the presence of PhCHO (3 mmol) at −70 °C in THF (10 ml). The plots of the product ratio [Bu_2Te/Bu_4Sn] against the ratio of the substrates used [PhTeBu / $PhSnBu_3$] gave a straight line [Figure 1(a)]. Similar linear correlations were obtained when [PhTeBu] was held constant [Figure 1(b)] and also when other mixtures (PhTeBu/PhI and PhTeBu/PhSeBu) were used. These results indicate that the exchange reaction is pseudo-first-order in each metalloidal compound.

Results of competitive reactions of PhTeBu and PhM are summarized in Table 2 [equation (2)]. Since Li–Se

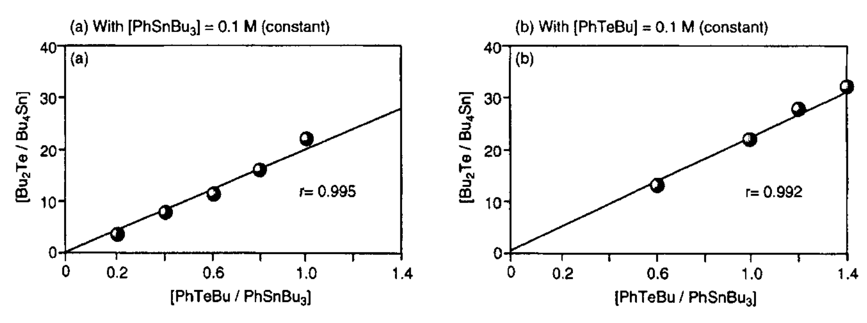

Figure 1. Competitive reactions of PhTeBu and $PhSnBu_3$ at different concentrations at −70 °C in THF

Table 2. Competitive exchange reactions of PhM (M SeBu, $SnBu_3$, $SnMe_3$, TeBu, I) and PhTeBu with BuLi at −70 °C[a]

Run	PhM: M	GLC yields based on BuLi(%)				ratio
		Bu_2Te	BuM	Ph_2CHOH	PhBuCHOH	Bu_2Te/BuM
1	I	7	27	35	66	0·3
2	TeBu	13	13	28	74	1·0
3	$SnBu_3^b$	5	Trace	5	73	~300
4	$SnBu_3^b$	10	0·1	10	85	99
5	$SnBu_3$	13	0·6	13	87	22
6	$SnBu_3^d$	3	2	5	89	1·4
7	$SnMe_3$	9	8	18	80	1·1
8	SeBu	12	Trace	13	86	~300
9[e]	SeBu	7[f]	0·5	8	82	15[g]

[a] Reaction conditions: PhTeBu (1 mmol), PhM (1 mmol), BuLi (0.2 mmol), THF (10 ml), −70.0 °C, 15 min; NH_4Cl_{aq}.
[b] Hexane (10 ml) instead of THF.
[c] Et_2O (10 ml) instead of THF.
[d] In the presence of HMPA (0.8 mmol).
[e] Competitive reaction of $PhSnBu_3$ and PhSeBu.
[f] Yield of Bu_4Sn.
[g] Bu_4Sn/Bu_2Se ratio.

exchange was too slow in comparison with Li–Te exchange (run 8), competitive reaction of Li–Sn and Li–Se exchanges was performed in order to obtain a reliable relative rate as shown in run 9, which indicated that Li–Sn exchange was 15 times faster than Li–Se exchange. From these results, the exchange rates in THF were found to increase in the order Se « Sn « Te < I with a ratio of 1 : 15 : 300 : 1000. This is in accord with qualitative results reported by Reich *et al.*[7]

$$\underset{1\ \text{mmol}}{\text{PhTeBu}} + \underset{1\ \text{mmol}}{\text{PhM}} \xrightarrow[-70\ ^\circ\text{C, solvent (10 ml)}]{\text{BuLi (0.2 mmol)}\ \ \text{PhCHO (3 mmol)}} Bu_2Te + BuM + Ph_2CHPH + PhBuCHOH \qquad (2)$$

M = SeBu, $SnBu_3$, $SnMe_3$, TeBu, I

As for the effect of solvents, comparison of the data for runs 3–5 shows that the relative rate of Li–Te/Li–Sn increases in less polar solvents such as Et_2O and hexane.

Table 3, which lists the results of Li–Te and Li–Sn exchange performed separately under different conditions, indicates that both Li–Te and Li–Sn exchanges become slower in diethyl ether than in THF and that the latter reaction is much more drastically affected than the former by solvents. This may be rationalized by postulating that a strongly coordinating solvent accelerates exchange reactions but with different sensitivities. One may point out a discrepancy between these results with the fact that addition of HMPA lowers the conversion of metalloids (run 6 in Table 2). This effect of HMPA can be explained by hypotheses that HMPA accelerates the addition of BuLi to benzaldehyde and/or that

Table 3. Li–Te and Li–Sn exchange reactions

PhM: M	Solvent	Time (min)	Products (%)[a]	
			PhH	BuM
TeBu	THF	10	98	99
$SnBu_3$	THF	10	97	99
TeBu	THF	1	92	96
$SnBu_3$	THF	1	68	72
TeBu	Et_2O	10	93	95
$SnBu_3$	Et_2O	10	5	5
TeBu	Et_2O	1	64	66
$SnBu_3$	Et_2O	1	<1	<1

[a] GLC yield based on PhM used.

HMPA retards the generation of PhLi from ate complexes stabilized by coordination of HMPA to lithium. In fact, it has been reported that HMPA shifts the equilibrium between Ph_2ILi and PhI + PhLi to the left, resulting in a lowering of the reactivity toward electrophiles.[7a] The very small relative rate of 1·4 observed in run 6 indicates that tellurides and stannanes react with BuLi at almost the same rate in the presence of HMPA, since this process is irreversible in the present case (see above).

Relative activation parameters of Li–Te and Li–Sn exchange

Reich *et al.*[7c] have determined equilibrium constants and changes in enthalpy and entropy (ΔH and ΔS) for ate complex formation from Ph_2Hg, Ph_2Te, and PhI with PhLi.[7c] We attempted to estimate rate constants and activation parameters of exchange reactions, but it was unsuccessful for the following reasons: (i) exchange reactions, especially in the cases of tellurides and iodides, are too rapid even at low temperatures to obtain reliable data using conventional procedures (see Table 3); and (ii) the concentration of active species of BuLi is ambiguous (butyllithium exists in THF as an equilibrium mixture of dimer and tetramer;[10] Reich *et al.*[7c] have reported that PhI and Ph_2Te react only with momomeric PhLi which is in equilibrium with its dimer in THF at low temperatures). Therefore, we calculated relative values of activation parameters by a least-squares treatment using equation (3) from the relative rates of Li–Te and Li–Sn exchange at different temperatures. Figure 2 shows the excellent fit to straight lines and the values obtained are listed in Table 4, which indicates that Li–Te exchange is favored over Li–Sn exchange by an enthalpy factor.

$$\ln(k_{Te}/k_{Sn}) = -\frac{\Delta\Delta H^{\ddagger}_{Te-Sn}}{RT} + \frac{\Delta\Delta S^{\ddagger}_{Te-Sn}}{R} \qquad (3)$$

where

$$\Delta\Delta H^{\ddagger}_{Te-Sn} = \Delta H^{\ddagger}_{Te} - \Delta H^{\ddagger}_{Sn}$$

$$\Delta\Delta S^{\ddagger}_{Te-Sn} = \Delta S^{\ddagger}_{Te} - \Delta S^{\ddagger}_{Sn}$$

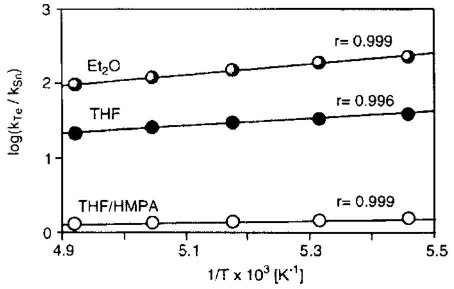

Figure 2. Eyring plots of competitive reactions of PhTeBu and $PhSnBu_3$

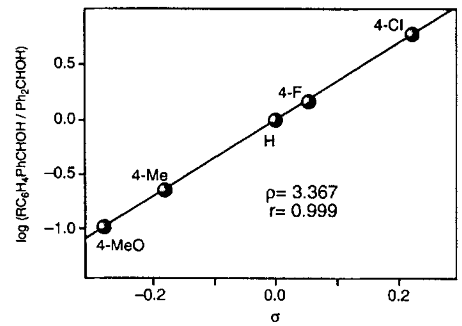

Figure 3. Hammett correlation of Li–Te exchange of RC_6H_4TeBu (R = 4-MeO, 4-Me, H, 4-F, 4-Cl) with BuLi at −70 °C in THF

Hammett plots of Li–Te exchange using ArTeBu

In order to examine the electronic effect of the leaving group (RC_6H_4Li) on the Li–Te exchange reaction [equation (4)], the Hammett correlation was studied using RC_6H_4TeBu (R = 4-MeO, 4-Me, H, 4-Cl, 4-F). When logarithms of the ratios of addition products were plotted against σ,[11] a straight line was obtained as shown in Figure 3, with a good correlation coefficient (r) of 0·999. The large positive reaction constant (ρ) of 3·37 indicates that negative charge is substantially distributed on the leaving group in the transition state of the exchange process. This is in accord with the evidence that thermodynamically the most stable

Table 4. Relative activation parameters of Li–Te vs Li–Sn exchange at −70 °C

Solvent	$\Delta\Delta H^{\ddagger}_{Te-Sn}$ (kJ mol^{-1})	$\Delta\Delta S^{\ddagger}_{Te-Sn}$ (J K^{-1} mol^{-1})	$\Delta\Delta G^{\ddagger}_{Te-Sn}$ (kJ mol^{-1})
THF	−9.27 ± 0.32	−19.9 ± 1.67	−5.23 ± 0.66
THF–HMPA	−1.08 ± 0.04	−2.71 ± 0.22	−0.53 ± 0.10
Et_2O	−13.8 ± 0.20	−29.9 ± 1.04	−7.77 ± 0.41

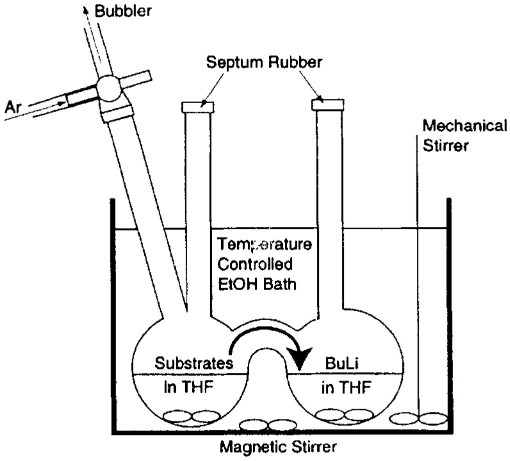

Figure 4. Reaction apparatus for competitive experiments

carbanions are selectively liberated from tellurium ate complexes.[9] A similar study using ArBr and BuLi in hexane gave a much smaller ρ value of *ca* 2.[2e]

$$\mathrm{PhTeBu} + 4\text{-}\mathrm{RC_6H_4TeBu} \xrightarrow[-70\ ^\circ\mathrm{C\ THF\ (10\ ML)}]{\substack{\mathrm{BuLi\ (0.2\ mmol)}\\ \mathrm{PhCHO\ (3\ mmol)}}}$$

$$\mathrm{Bu_2Te} + \mathrm{PhBuCHOH} + 4\text{-}\mathrm{RC_6H_4PhCHOH} + \mathrm{Ph_2CHOH} \qquad (4)$$

EXPERIMENTAL

Solvents and reagents. THF and diethyl ether were distilled from sodium benzophenone ketyl. BuLi in hexane (*ca* 1·6 M), purchased from Kanto Chemical was used after titration.[12] Tellurium and selenium were provided by Mitsubishi Material. Aryl alkyl tellurides and Bu_2Te were prepared from the corresponding tellurolates and alkyl iodides.[13,14] PhSeBu and Bu_2Se were obtained in a similar manner.[14,15] Other chemicals were commercially available and were used after purification based on literature procedures.[16] All reactions were carried out under an argon atmosphere.

Apparatus. All reactions were performed by using a glass vessel as depicted in Figure 4 and a Neslab Cryobath (CB-80) equipped with a Cryotrol. GLC analyses were performed using a Shimadzu G-8A gas chromatograph with a capillary column (silicone OV-1) and a Hitachi model 263-30 gas chromatograph with a stainless steel column packed with silicone OV-17. Product yields were determined based on the limiting substrate using n-$C_{13}H_{28}$ and/or n-$C_{15}H_{32}$ as internal standards, which were added immediately after the reaction.

Typical procedure of competitive experiments. Competitive reaction of PhTeBu and $PhSnBu_3$ with BuLi. Into one part of the dried and cooled (−70 °C) vessel depicted in Fig. 4 was placed a THF solution (5 mL) of BuTePh (1 mmol), PhM (1 mmol) and PhCHO (3 mmol). A 5 ml volume of THF was injected with a syringe into the other part of the apparatus, into which BuLi (0.20 mmol in hexane) was placed after a few minutes. After stirring for 15 min, the two solutions were quickly mixed and stirred for 15 min under the same conditions. The reaction was quenched by addition of a saturated aqueous solution (1 ml) of NH_4Cl and the resulting mixture was analyzed by GLC.

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