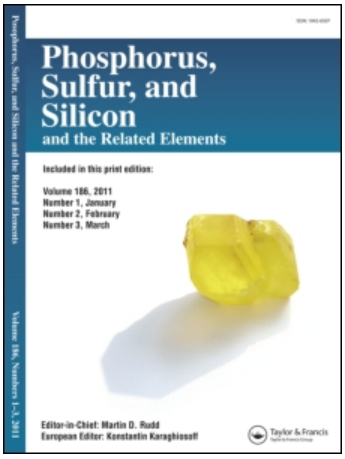

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A New Preparative Method of Organoalkali and Organoalkaline-Earth Metals Using Metal-Tellurium Exchange Reactions

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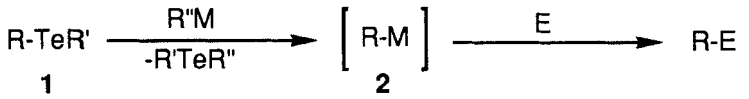
Abstract Diorganyl tellurides (RTeR') undergoes exchange reaction by the treatment with organometallic reagents of alkali and organoalkaline-earth metals (M= Li, Na, K, MgX and CaX) in a fashion that thermodynamically more stable carbanions are formed, which then react with carbonyl compounds to give corresponding addition products in good yields. The scope and limitation of the exchange reactions are also discussed.

Introduction

Organometallic compounds of alkali and alkaline-earth metals are highly useful for carbon-carbon bond formation. We wish to present a new preparative method of organolithium, -magnesium (Grignard reagents), -sodium, -potassium and -calcium compounds by the use of metal-tellurium exchange reactions.

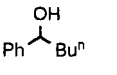
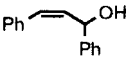
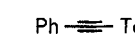
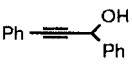
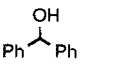
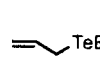
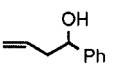
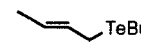
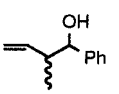
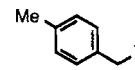
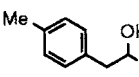
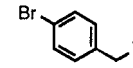
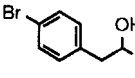
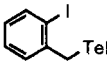
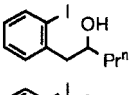
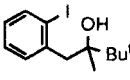
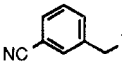
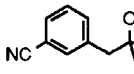


M= Li, Na, K, MgX, and CaX
R= alkyl, alkenyl, aryl, allyl, benzyl
E= aldehyde, ketone

Lithium-, Sodium- and Potassium-Tellurium Exchange Reactions

Allyl- and benzyllithiums are hardly accessible by the conventional lithium-halogen exchange reaction because Wultz-type coupling can not be suppressed under the reaction conditions employed. We have reported that a variety of organolithium compounds can be generated by the use of Li-Te exchange.[1-4] Application of this reaction to some allyl and benzyl substituted tellurides revealed that crotyllithium and 4-methyl- and 4-

Table 1. Reaction of Tellurides with Organoalkali and Organoalkaline-Earth Metal Compounds[a]

entry	telluride	RM	temp, °C	time, h	solv.	electrophile	product, %[b]
1	$^nBu_2Te$	^{t}BuMgCl	20	6	THF[c]	PhCHO	 61
2		PhNa	-70	3	THF	PhCHO	 60
		PhMgCl	20	6	THF[c]		86
		PhCal	-70	3	THF		69
3		PhMgCl	20	6	THF[c]	PhCHO	 96
4		^{n}BuMgCl	20	6	THF[c]	PhCHO	 98
		^{n}BuK	-70	3	THF[c]		77
5		^{n}BuNa	-70	3	THF[c]	PhCHO	 67
		^{n}BuMgCl	20	6	THF[c]		72
		MeCal	-70	3	THF		77
6		^{n}BuLi	-70	0.25	THF	PhCHO	 73[d,e]
		^{n}BuMgCl	20	6	THF[c]		84[d,f]
		^{n}BuCal	-70	3	THF		80[d,g]
7		^{n}BuLi	-70	0.25	THF	^{n}PrCHO	 88
		^{n}BuNa	-70	3	THF[c]		60
		^{n}BuMgCl	20	6	THF[c]		56[h]
		^{n}BuCal	-70	3	THF		76
8		^{n}BuLi	-70	0.25	THF	^{n}PrCHO	 32
			-70	0.25	Et_2O		68
		^{n}BuNa	-70	3	THF[c]		66
		^{n}BuMgCl	20	6	THF[c]		79
		^{n}BuCal	-70	3	THF		33
9		^{n}BuLi	-70	0.25	Et_2O	^{n}PrCHO	 0[i]
			-105	0.25	Et_2O		21
		^{n}BuMgCl	20	6	THF[c]		8
		^{n}BuLi	-105	0.25	Et_2O	pinacolone[j]	 65
10		^{n}BuMgCl	20	6	THF[c]	^{n}PrCHO	0[i]
		^{n}BuLi	-105	0.25	Et_2O	pinacolone	0[i]
			-105	0.25	Et_2O	pinacolone[j]	 96

[a]Reagents: telluride (2 mmol), RM (2 mmol), solvent (5 mL), electrophiles (2 mmol). [b]Isolated yield. [c]In the presence of HMPA (0.5 mL). [d]A mixture of diastereomers (1: 1). [e]Besides, α-addition compound (12 %) was also obtained. [f]Only γ-addition product was formed. [g]A mixture of α– and γ-addition products (5:95). [h]A coupling product $(4\text{-}CH_3C_6H_4CH_2)_2$ was also yielded (22 %). [i]A complex mixture. [j] ^{n}BuLi was added to an Et_2O solution of the telluride in the presence of an equimolar amount of pinacolone at -105 °C.

bromobenzyllithiums could be generated by the reaction of corresponding tellurides with *n*-BuLi in THF at -70 °C. Although 2-iodo- and 3-cyanobenzyllithiums could not be generated under these conditions, they could be successfully generated in ether at -105 °C and trapped with pinacolone to give the addition compounds in good yields. Vinyl-, allyl-, and benzylsodiums and phenylpotassium could be generated by a similar manner when organosodium and -potassium reagents were employed instead of *n*-butyllithium.

Magnesium- and Calcium-Tellurium Exchange Reactions

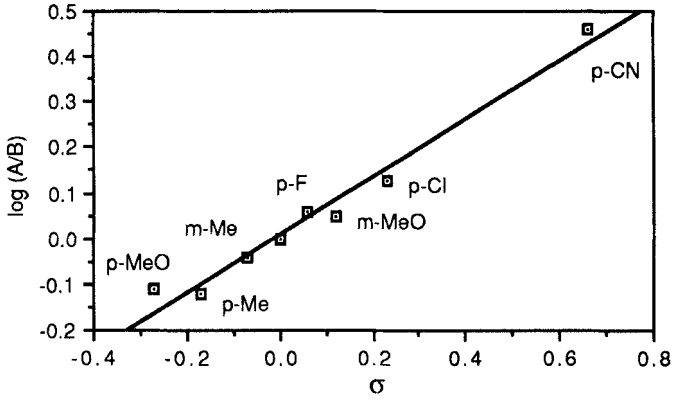
In contrast to the metal-tellurium exchange reactions with organoalkali matals, tellurides did not react with Grignard reagents at -70 °C resulting in the recovery of the tellurides. But when *n*-BuMgCl was allowed to react with allyl *n*-butyl telluride at 20 °C in THF followed by the addition of PhCHO, the Mg-Te exchange reaction did proceed to give the corresponding alcohol in 72 % yield. As shown in Table 1, a variety of Grignard reagents such as alkyl-, alkenyl-, alkynyl-, aryl-, allyl- and benzylmagnesium chlorides could be generated.[5] It is interesting that a simple Grignard reagent, *n*-BuMgCl, could be formed when *t*-BuMgCl was used as a reagent. Although the reactions of 2-iodo- and 3-cyanobenzyl substituted tellurides with *n*-BuMgCl under similar conditions gave complex mixtures (entries 9 and 10), the Mg-Te exchange afforded the best result in the generation of 4-bromobenzyl metals in comparison with other M-Te exchange reactions (entry 8).

Examples of the formation of organocalcium compounds so far reported have been very few.[6,7] Diorganyl tellurides reacted again even at -70 °C with organocalcium halides in THF to provide thermodynamically more stable organocalcium halides. Vinyl-, allyl-, and benzylcalcium halides were prepared by this reaction and trapped with aldehydes in good yields as shown in Table 1.

The Competitive Reactions[8]

We then attempted the competitive reaction in order to shed light on the electronic effect of the leaving group on Li-Te exchange reaction which is likely to proceed via tellurium ate complexes ($RR'R''Te^- Li^+$).[9] When the ratios of addition products formed by trapping with PhCHO of benzyllithiums generated by competitive reactions were plotted against σ, the obtained results fell on a good straight line as shown in Fig. 1 with a reaction constant (ρ) of 0.638 and a correlation coefficient (r) of 0.986. This may suggest that the more stabilized are the benzyllithiums by the electrowithdrawing group, more preferably they are generated, although the effect is not so crucial. The results of these competitive reactions might not simply reflect the relative rate constants of Li-Te exchange process but the overall reaction rates including the equilibrium between benzyllithiums as well as the relative rates of the subsequent reactions of benzyllithiums with PhCHO. The kinetic study on the Li-Te exchange is now in progress.

Fig. 1. A Plot of the Ratio of Addition Products vs. σ



A: $[XC_6H_4CH_2CH(OH)Ph]$

B: $[PhCH_2CH(OH)Ph]$

Conclusion

Metal-tellurium exchange reaction is applicable not only to the generation of organolithium compounds but also to that of organosodium, -potassium, -magnesium (Grignard reagents), and -calcium compounds. This procedure will open up a new field of organoalkali and organoalkaline-earth metal chemistry.

References and Notes

†Present address: Department of Chemistry, Faculty of Engineering, Gifu University, Gifu 501-11, Japan.

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7. T.-C. Wu, H. Xiong, and R. D. Rieke, J. Org. Chem., 55, 5045 (1990).
8. Reaction conditions: $XC_6H_4CH_2TeBu^n$ (0.5 mmol), $PhCH_2TeBu^n$ (0.5 mmol), PhCHO (1.0 mmol), ^nBuLi (0.1 mmol), THF (5 mL), -70 °C, 15 sec, then H_2O (1 mL).
9. H. J. Reich, D. P. Green, and N. H. Phillips, J. Am. Chem. Soc., 113, 1414 (1991) and references cited therein.