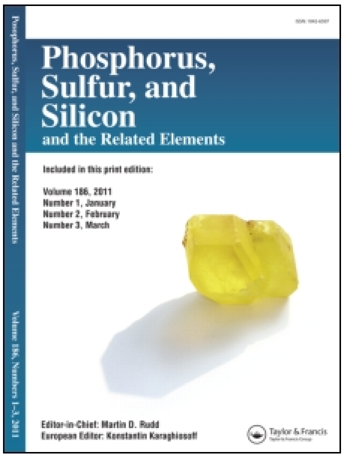

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LITHIUM ORGANYL-POLYCHALCOGENOLATES

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LITHIUM ORGANYL-POLYCHALCOGENOLATES

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Abstract Lithium organyl-selenolates, RSeLi or tellurolates, RTeLi insert further equivalents of chalcogens with formation of selenenyl-selenolates, RSeSeLi or tellurenyl-tellurolates, RTeTeLi (R=Me, n-Bu, s-Bu, t-Bu, Ph). Mixed anions are only formed if the chalcogen insertion order corresponds with an increase of electronegativity, i.e.: RTeSeLi, RTeSLi, RSeSLi and n-BuTeSeSLi. All species have been characterized by 77-Se and 125-Te NMR-spectroscopy. Tellurenyl-tellurolates and tellurenyl-selenolates are stable at room temperature, selenenyl-selenolates and chalcogenyl-thiolates disproportionate. The chemical integrity of the chalcogenyl-chalcogenolates was checked by methylation with methyl triflate. The formed organyl-methyl-dichalcogenides exhibit symmetrization equilibria that are also obtained by mixing the symmetric compounds. Oxidation of tellurenyl-selenolates affords di(organyl-tellurenyl) selenides, $(RTe)_2Se$ (R=Me, n-Bu, t-Bu, Ph, p-MeC_6H_4, 2-thienyl) and $(RTe)_2Se_2$ for R=$(Me_3Si)_3C$. In solution $(RTe)_2Se$ are in equilibrium with R_2Te_2 and $(RTe)_2Se_2$.

INTRODUCTION

Lithium alkyl- and arylselenolates, RSeLi, and -tellurolates, RTeLi, usually prepared by insertion of chalkogen into a carbon-lithium bond and generally used in situ, are important synthons for the preparation of a wide range of organic selenium and tellurium compounds. Surprisingly, the reactions of these chalcogenolates with elemental chalcogens have not been investigated in detail. Exceptions are the 77-Se-shifts of a few selenolates[1] and the alkylation of MeSeSeLi with ethyl iodide[2].

Our recent success in preparing the first diorganyl tritelluride,[3] Tsi_2Te_3 (Tsi=$(Me_3Si)_3C$) by simple H_2O/O_2-oxidation of the reaction product of TsiLi with excess tellurium, prompted us to investigate with 77-Se and 125-Te NMR-spectroscopy the insertion of chalcogens into the Li-C bond of organic lithium compounds, RLi (R=Me, n-Bu, s-Bu, t-Bu, Ph) with respect to molar ratio and insertion order of the chalcogens.

ORGANYL-TELLUROLATES, RTe^-, ORGANYL-TELLURENYL-TELLUROLATES, $RTeTe^-$ AND ORGANYL-SELENENYL-SELENOLATES, $RSeSe^-$

Tellurium and more so selenium dissolve exothermically in a solution of an organic lithium compound in THF. Equimolar amounts of the reagents produce colorless to pale yellow solutions that are stable at room temperature if oxygen is excluded. 125-Te NMR-data for RTe^- are given in Table I.

Competitive equilibria between tellurium and different lithium organyls monitored by 125-Te NMR-spectroscopy give the following order of decreasing insertion tendency:

$$\text{t-BuLi} > \text{s-BuLi} > \text{n-BuLi} > \text{PhLi} > \text{MeLi}$$

This order qualitatively mirrors the metallating strength of the organolithium compounds[4] and with the exception of PhTeLi correlates with the increasing high-field shift of the 125-Te resonances of the tellurolates.

A further equivalent of selenium (tellurium) dissolves smoothly when added to a solution of a selenolate (tellurolate)(eqn.1). The color of the solution changes immediately from colorless to dark-red.

$$RCh^- + Ch \longrightarrow RCh_ACh_B^- \qquad (1)$$
$$Ch_A=Ch_B\text{: Se or Te}$$

Proof for the formation of tellurenyl-tellurolates and selenenyl-selenolates is obtained from 77-Se and 125-Te NMR-spectroscopy (Table I). All species exhibit at room temperature two resonances ($w_{1/2} \sim 30$ Hz) lacking chalcogen satellites. Upon cooling lines broaden first but below 200 K $^1J(Ch_A, Ch_B)$ can be observed with the exception of $PhCh_ACh_B^-$. The resonances are assigned to Ch_A and Ch_B by either observing the coupling pattern due to $^2J(Ch_A,H)$ of $\sim$20 Hz or the concentration dependence of the shift of Ch_A at organolithium - chalcogen ratios intermediate between 1:1 and 1:2. In all anions the carbon-bound chalcogen (Ch_A) resonates at lower field than the chalcogen-bound chalcogen (Ch_B). The chalcogen-chalcogen coupling constants $^1J(Ch_A, Ch_B)$

TABLE I 77-Se and 125-Te NMR-data (193 K) for RTe^-, $RTeTe^-$ and $RSeSe^-$ [a]

R	RTe^-	$RTeTe^-$			$RSeSe^-$		
	δ (125-Te)	δ (125-Te_A)	δ (125-Te_B)	$^1J(Te_A,Te_B)$[b]	δ (77-Se_A)	δ (77-Se_B)	$^1J(Se_A, Se_B)$
Me	-746	-401	-453	2186	+103	-43	323
n-Bu	-520	-289	-546	1932	+ 55	+15	309
s-Bu	-256						
Ph	-127	- 82	-459	-	+171	+60	-
t-Bu	+ 84	+170	-546	1637	+304	-20	267

[a] ppm rel. Me_2Te, Me_2Se, 1 M solutions in THF; [b] AB spin systems.

(Table I) are the highest so far reported.

The tellurenyl-tellurolates have a limited stability at room temperature. Selenenyl-selenolates readily disproportionate (eqn.2). The phenyl derivative is the most stable among the compounds prepared.

$$2\ RSeSe^- \longrightarrow RSeSeR + Se_2^{2-} \qquad (2)$$

ORGANYL-TELLURENYL-SELENOLATES, $RTeSe^-$, ORGANYL-TELLURENYL-THIOLATES, $RTeS^-$ AND ORGANYL-SELENENYL-THIOLATES, $RSeS^-$

Organylchalcogenyl-chalcogenolates with different chalcogens are only formed if the chalcogen to be added has a higher electronegativity than the chalcogen already present in the chalcogenolate. Thus, no reaction occurs between thiolates and selenium or tellurium, and between selenolates and tellurium, whereas tellurolates do react with sulfur and selenium and selenolates with sulfur (eqns.3-6).

$$RS^- + Se \text{ or } Te \quad \text{no reaction} \qquad (3)$$

$$RSe^- + Te \quad \text{no reaction} \qquad (4)$$

$$RTe^- + S \text{ or } Se \longrightarrow RTeS^- \text{ or } RTeSe^- \qquad (5)$$

$$RSe^- + S \longrightarrow RSeS^- \qquad (6)$$

This behavior mirrors the increasing nucleophilicity in the sequence $RS^- < RSe^- < RTe^-$. NMR data for $RCh_ACh_B^-$ ($Ch_A \neq Ch_B$) are listed in Table II. Contrary to the electronegativity criterium, n-BuSe$^-$ reacts with tellurium, but only in the presence of 15-crown-5. The 77-Se (-196 ppm) and the 125-Te (+234 ppm) resonances for n-BuSeTe$^-$ remain broad down to 193 K. Methylation of the anion however leads to the equilibrium characteristic for n-BuSeTeMe, which can also be reached by mixing n-Bu_2Se_2 with Me_2Te_2.

TABLE II 77-Se and 125-Te NMR data (193 K) for $RSeS^-$, $RTeSe^-$, and $RTeS^-$ [a]

R	$RSeS^-$	$RTeSe^-$			$RTeS^-$
	δ (77-Se)	δ (125-Te)	δ (77-Se)	$^1J(Te,Se)^b$	δ (125-Te)
Me		+ 30	-316	738	
n-Bu	+194	+186	-370	731	+415
Ph	+294	+336	-320	481	+545
t-Bu		+588	-349	618	

[a] ppm rel. Me_2Te, Me_2Se, 1M solutions in THF; [b] AX spin systems

The alkylchalcogenyl-chalcogenolates, $RSeS^-$, $RTeS^-$, and $RTeSe^-$ (R=Me, n-Bu, t-Bu) but not the phenylchalcogenyl-chalcogenolates readily undergo internal redox-reactions below room temperature (eqn.7).

$$2\ RTeS^- \longrightarrow R_2Te_2 + S_2{}^{2-} \qquad (7)$$

ORGANYL-POLYCHALCOGENOLATES, $RCh_ACh_BCh_C^-$

Addition of a further equivalent of selenium to a solution of $RSeSe^-$ in THF in an attempt to prepare $RSeSeSe^-$ leads to complex disproportionation reactions. When an equivalent of tellurium is added to $RTeTe^-$ insertion does not occur, unless 15-crown-5 is present to enhance the nucleophilicity of the tellurenyl-tellurolate. For $n\text{-}BuTeTeTe^-$ three 125-Te resonances without satellites are observed at 193 K (+124, -233, -457 ppm). These resonances collapse at room temperature to a broad band centered at -100 ppm.

Addition of first selenium and then sulfur to a solution of n-butyltellurolate in THF produces $n\text{-}BuTeSeS^-$ (eqn.8).

$$n\text{-}Bu^- \xrightarrow[25°C]{+Te} n\text{-}BuTe^- \xrightarrow[-50°C]{+Se} n\text{-}BuTeSe^- \xrightarrow[-80°C]{+S} n\text{-}BuTeSeS^- \qquad (8)$$

The NMR data for n-BuTeSeS$^-$ are:

δ (77-Se) = +70 ppm, δ(125-Te) = +245 ppm, ^{1}J(77-Se, 125-Te) = 460 Hz

METHYLATION WITH METHYLTRIFLATE

To check the chemical integrity of organyl-chalcogenyl-chalcogenolates, they were methylated with methyltriflate. Examples of the observed reactions are shown in eqn.9.

$$\begin{array}{l} \mathrm{RTeCh^-} \\ \mathrm{Ch = Te,\ Se,\ S} \end{array} \xrightarrow{+\ \mathrm{Metfl}} \left\{ \begin{array}{l} \mathrm{RTe - TeMe} \rightleftharpoons \mathrm{R_2Te_2 + Me_2Te_2} \\ (+195)\ (-29) \\ \mathrm{RTe - SeMe} \rightleftharpoons \mathrm{R_2Te_2 + Me_2Se_2} \\ (+645)\ (-14) \\ \mathrm{RTe - SMe} \longrightarrow \mathrm{R_2Te_2 + Me_2S_2} \\ (+809) \end{array} \right. \qquad (9)$$

R = n-Bu; numbers in parentheses are 125-Te or 77-Se shifts.

Whereas the organyl-methyl-chalcogenide-sulfides (R-Ch-S-Me, Ch=S, Se, Te) symmetrize quantitatively at room temperature, all other dichalcogenides reach equilibria that can also be obtained by mixing the symmetric compounds.[5]

OXIDATION: FORMATION OF DI(ORGANYL TELLURENYL)-SELENIDES AND DISELENIDES, $(RTe)_2Se$ AND $(RTe)_2Se_2$

Only the oxidation of tellurenyl-selenolates by H_2O/O_2 was investigated. The products most readily isolated proved to be di(organyl-tellurenyl) selenides,[6] $(RTe)_2Se$ (R=Me, n-Bu, t-Bu, Ph, p-MeC_6H_4, 2-thienyl) as shown by mass spectroscopic and x-ray structural analysis of di(2-thienyl-tellurenyl) selenide.[7] When $(RTe)_2Se$ are dissolved the solutions exhibit 125-Te NMR spectra with the same three resonances that are observed in the original reaction mixtures. Addition of ditelluride to the solution shifts the equilibrium to the left and increases the intensity of the

125-Te resonance of the di(organyl-tellurenyl)selenide. Only $(TsiTe)_2Se$ and $(TsiTe)_2Se_2$ are kinetically stable. The three line spectra indicate that di(organyl-tellurenyl)selenides in solution are in equilibrium with diorganyl ditellurides and di(organyl-tellurenyl)diselenides (eqn.10).

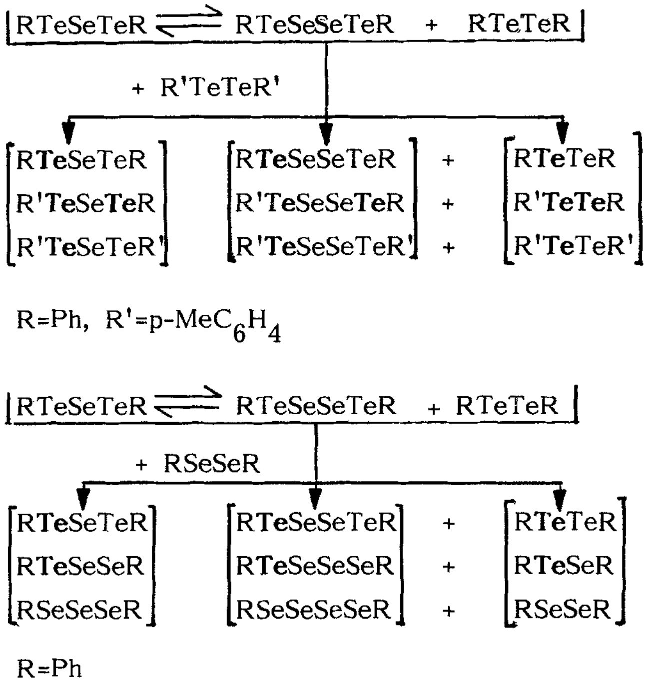
$$2\ RTeSeTeR \rightleftharpoons RTeSeSeTeR + RTeTeR \qquad (10)$$

The above results may explain the report of "exceedingly difficult to purify" aryltellurenyl-tellurinyl-selenides, RTeSeTe(O)R.[6] We obtained identical NMR spectra for "$p\text{-}MeC_6H_4TeSeTe(O)p\text{-}MeC_6H_4$" prepared according to the literature[6] from $(p\text{-}MeC_6H_4)_2Te_2$ and SeO_2 in pyridine and for $(p\text{-}MeC_6H_4Te)_2Se$ prepared by air-oxidation of $p\text{-}MeC_6H_4TeSe^-$ (Table III).

TABLE III 125-Te NMR data for $(RTe)_2Se$ and RTeSeTe(O)R[6] ($R=p\text{-}MeC_6H_4$)

	δ (125-Te)
RTeSeTeR	+1026
RTeSeSeTeR	+ 971
RTeTeR	+ 417
RTeSeTe(O)R	+ 424, +1010
RTe(O)SeTe(O)R or RTeSe(O)Te(O)R	+ 950

Additional equilibria are set up, when diorganyl ditellurides with a different organic group or diorganyl diselenides with an identical organic group are added to an equilibrium as expressed in eqn.10. The species that are present in such a mixture can be enumerated through recombination of all radicals formed by scission of chalcogen-chalcogen bonds (eqn.11). Thus in the first case twelve and in the second case six resonances are indeed observed by 125-Te NMR-spectroscopy.



(11)

The equilibria are actually more complex than shown in eqn.11, because the diorganyl tetrachalcogenides produce new radicals such as RTeSeSe• and RSeSeSe• that recombine as indicated by low-intensity NMR-signals. It is likely, that polychalcogenides with rather long chalcogen chains are present in the solutions.[8]

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