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Aromatic Substitution and Dealkylation by Alkanetellurolate Anions[1]

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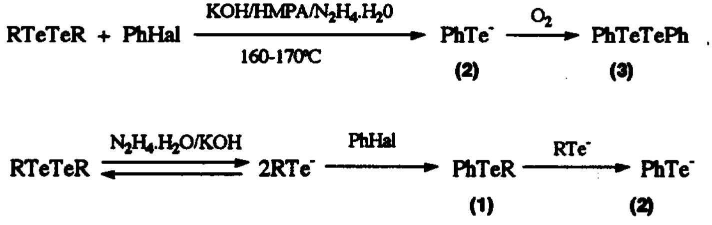
Abstract: Under the action of alkanetellurolate anion phenyl halides undergo aromatic substitution followed by dealkylation of the alkyl phenyl telluride thus formed. The generated benzenetellurolate anion can be either alkylated or oxidized to diphenyl ditelluride, or added to acetylene. Butyl methyl telluride and selenide are demethylated by methanechalcogenolate anions.

The reactions of aromatic substitution of unactivated aryl halides by alkanethiolate and alkaneselenolate anions have been well established.[2] When an excess of these anions is used the obtained alkyl aryl sulfides and selenides are dealkylated to produce arenechalcogenolate anions.

We now report the reactions of aromatic substitution on phenyl halides followed by the dealkylation of alkyl phenyl tellurides by alkanetellurolate anions. As alkanetellurolate anions are extremely oxidizable species, we use the system $KOH/HMPA/N_2H_4.H_2O$ which allows alkanetellurolate anions to be generated *in situ* from dialkyl ditellurides in quantitative yield.[3] The benzenetellurolate anion (2) can be used in various reactions. When the reaction mixture is diluted with water (2) is easily oxidized by air to diphenyl ditelluride (3).



$$RTeTeR + PhHal \xrightarrow[160\text{-}170^\circ C]{KOH/HMPA/N_2H_4.H_2O} \underset{(2)}{PhTe^-} \xrightarrow{O_2} \underset{(3)}{PhTeTePh}\ ,$$

$$RTeTeR \overset{N_2H_4.H_2O/KOH}{\rightleftarrows} 2RTe^- \xrightarrow{PhHal} \underset{(1)}{PhTeR} \xrightarrow{RTe^-} \underset{(2)}{PhTe^-}$$

R= Me, Et, *i*-Pr,   Hal= I, Br, Cl, F

We performed the experiments with various phenyl halides and ditellurides and the highest yield of (3) (70%) was obtained in the case of dimethyl ditelluride and phenyl bromide. When we used phenyl iodide or chloride under the same conditions the yield of (3) ranged between 30-40%. From dimethyl ditelluride and phenyl fluoride (3) was formed but only in traces.

The intermediate alkyl phenyl tellurides (1) were detected in the reaction mixture by GLC comparison with authentic samples. In the case of an equimolar ratio of phenyl bromide and methanetellurolate anion the yield of (1) was very low, suggesting that the dealkylation reaction is faster than the aromatic substitution.

When the reaction is performed under acetylene pressure, (2) adds to the triple bond giving phenyl vinyl telluride (4)[4] in 19% yield. In this case the presence of water is necessary as a proton donor. Treatment of the reaction mixture with alkyl halides leads to the formation of (1) in 64-70% yields.

$$\underset{(4)}{PhTeCH{=}CH_2} \xleftarrow[105\text{-}115^\circ C]{HC{\equiv}CH,\ H_2O} \underset{(2)}{PhTe^-} \xrightarrow[50\text{-}60^\circ C]{RHal} \underset{(1)}{PhTeR}$$

RHal= MeI, EtBr, *i*-PrBr

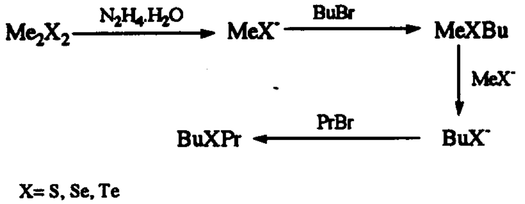
We also found that the system KOH/HMPA(DMSO)/$N_2H_4.H_2O/H_2O$ is very effective for the generation of (2) from (3), and have used (3) in the synthesis of (4) in 95% yield. This method for the preparation of (4) seems to be superior to others known to date.[4]

$$\underset{(3)}{PhTeTePh} + HC{\equiv}CH \xrightarrow[95\text{-}105^\circ C]{KOH/DMSO/N_2H_4.H_2O/H_2O} \underset{(4)}{2PhTeCH{=}CH_2}$$

The dealkylation of substituted alkyl vinyl sulfides and selenides by alkanethiolate and -selenolate anions is a known process.[5] We revealed the divinyl telluride[6] formation (26% yield) in the reaction of nucleophilic addition of methanetellurolate anion to acetylene[7] at 95-115°C under 14 atm pressure. That is understood to be a result of the dealkylation of methyl vinyl telluride followed by the addition of ethanetellurolate anion to acetylene.

$$\begin{tikzcd}
MeTeTeMe + HC{\equiv}CH \arrow[r, "KOH/HMPA/N_2H_4.H_2O/H_2O", "105\text{-}115^\circ C"'] & CH_2{=}CHTeMe \arrow[d, "MeTe^-"] \\
CH_2{=}CHTeCH{=}CH_2 & CH_2{=}CHTe^- \arrow[l, "HC{\equiv}CH"', "H_2O"]
\end{tikzcd}$$

To our knowledge there are no data in the literature concerning the dealkylation of dialkyl chalcogenides by alkanechalcogenolate anions. We found that butyl methyl telluride as well as butyl methyl selenide can be easily demethylated by the corresponding methanechalcogenolate anions on being heated for 5h at 90-95°C in the system KOH/DMSO/$N_2H_4.H_2O$. After the addition of propyl bromide to the reaction mixture butyl propyl selenide and telluride were obtained in 36-40% yield. Butyl methyl chalcogenides were obtained *in situ* by the interaction of butyl bromide with methaneselenolate and -tellurolate anions, which were generated from dialkyl dichalcogenides. Dialkyl sulfides are hardly involved in the dealkylation reaction and when we tested butyl propyl sulfide under the same conditions the yield of butyl propyl sulfide was negligible.



Diphenyl ditelluride (3). A mixture of dimethyl ditelluride (5.8g), KOH (13.2g), hydrazine hydrate (3g), phenyl bromide (1.57g) and HMPA (30 ml) was heated (160-170°C) in a 1 litre steel rotating autoclave for a period of 5h. The mixture was diluted with water and extracted with benzene. the organic layer was dried over K_2CO_3 and benzene was evaporated. The residue was recrystallized from ethanol to give 1.44g (70% yield) of (3) as orange-red powder, m.p. 66°C.

Phenyl vinyl telluride (4). A mixture of (3) (3g), KOH (15g), hydrazine hydrate (5g), water (8 ml), and DMSO (30 ml) was heated (95-105°C) in a 1 litre steel rotating autoclave for a period of 5h under acetylene at pressure (14 atm). The mixture was diluted with water (100 ml) and extracted with ether. The organic layer was washed with water, dried over K_2CO_3 and the ether was evaporated. The distillation of the residue at reduced pressure gave 3.23 g (95% yield) of (4).

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7. The preparation of methyl vinyl telluride by the method[3] from dimethyl ditelluride and acetylene under atmospheric pressure at 60°C does not accompany the divinyl telluride formation.

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