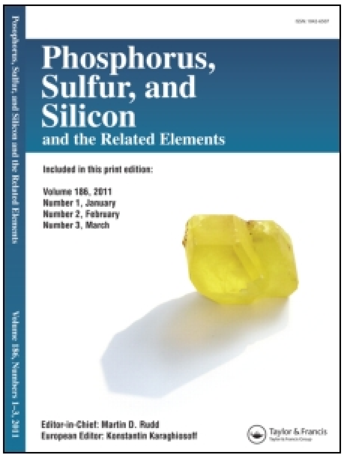

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A Novel Synthesis of α-Tellanyl α,β-Unsaturated Aldehydes Using α-Tellanyl β-Alkoxyalkenyl Lithiums

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A Novel Synthesis of α-Tellanyl α,β-Unsaturated Aldehydes Using α-Tellanyl β-Alkoxyalkenyl Lithiums

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β-Ethoxy-α-phenyltellanylvinyl lithiums were successfully generated in situ *from phenyltellanylacetaldehyde diethyl acetal with lithium 2,2,6,6-tetramethylpiperidide (LTMP) and underwent methylation or nucleophilic addition with aldehydes and ketones. The successive dehydration of the allylic alcohols with trimethylsilyl trifluoromethanesulfonate (TMSOTf) gave α-phenyltellanyl α,β-unsaturated aldehydes, which transformed to some useful compounds.*

Keywords α-Tellanyl α,β-unsaturated aldehydes; β-alkoxyalkenyl lithiums; TMSOTf

INTRODUCTION

Work in our laboratories has been concerned with synthetic organic chemistry using β-alkoxyalkenyl lithiums bearing α-sulfanyl or α-sellanyl groups, which easily generated from β-alkoxyalkenes with BuLi.[1] The reactions with aldehydes and ketones and the successive hydration with acids provided novel two- and four-carbon homologation leading to useful polyene compounds (Scheme 1).[2] Our next attention was on α-tellanyl alkenylation using the α-tellanyl β-alkoxyalkenyl lithiums. While there are a few reports on the syntheses of the α-tellanyl α,β-unsaturated aldehydes,[3] it is of great importance to find new methodology because the α-tellanyl functional groups on the alkenes are easily transformed to the organometalic intermediates such as lithiums,[4] zinc,[5] copper[6] and magnisiums[7] by the Te/metal exchange reactions. Here we preliminarily report a useful synthesis of the α-tellanyl α,β-unsaturated aldehydes from simple aldehydes or ketones.

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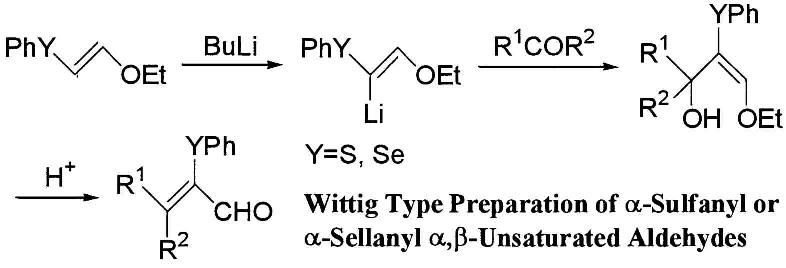
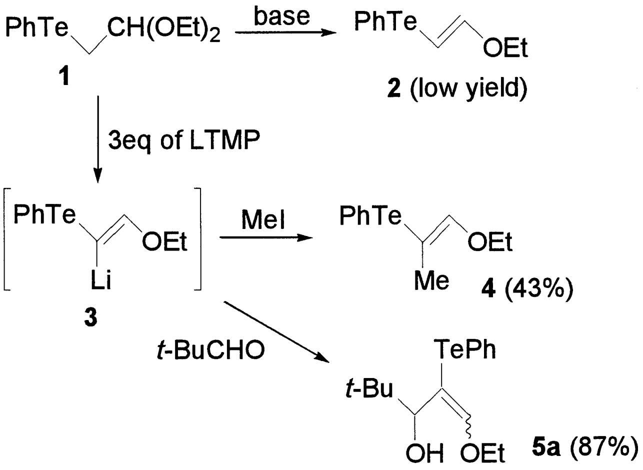


Wittig Type Preparation of α-Sulfanyl or α-Sellanyl α,β-Unsaturated Aldehydes

SCHEME 1

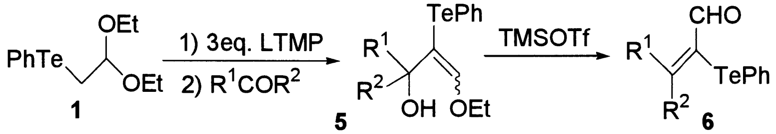
RESULTS AND DISCUSSION

We first examined the preparation of the *β*-ethoxyvinyl telluride **2** from *α*-phenyltellanylacetaldehyde diethyl acetal **1**[8] with some bases; however, the expected alkene **2** was obtained in low yield (Scheme 2). Therefore, we tried to *in situ* generate the *α*-phenyltellanylvinyl lithium **3** with lithium 2,2,6,6-tetramethylpiperidide (LTMP) and the successive trapping with some electrophiles. The reaction with methyl iodide gave the vinylic telluride **4** in 43% yield. Since we found how to successfully generate the *β*-ethoxyvinyl lithiums **3**, we next examined other alkyl halides such as benzyl bromide or cyclohexyl bromide. However, the alkene **2** was obtained as the sole product, and there were no alkylated products. The reaction of **3** with pivaldehyde gave the (*E*)- and (*Z*)-allylic alcohol **5a** in high yield.



SCHEME 2

TABLE I Preparation of α-Phenyltellanyl α, β-Unsaturated Aldehydes

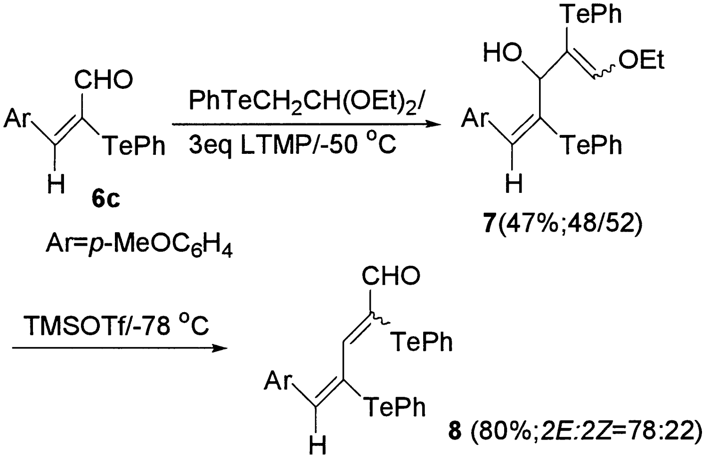


Entry	R^1	R^2	Alcohol (% yield)(Z/E)	Aldehyde (% yield)(Z/E)
1	*t*-Bu	H	**5a** (87)(50/50)	**6a** (84)(0/100)
2	Ph	H	**5b** (54)(87/13)	**6b** (57)(32/68)
3	*p*-$MeOC_6H_4$	H	**5c** (80)(51/49)	**c** (76)(25/75)
4	$(CH_2)_5$		**5d** (47)(40/60)	**6d** (67)
5	$(CH_2)_4$		**5e** (47)(38/62)*1	**6e** (58)

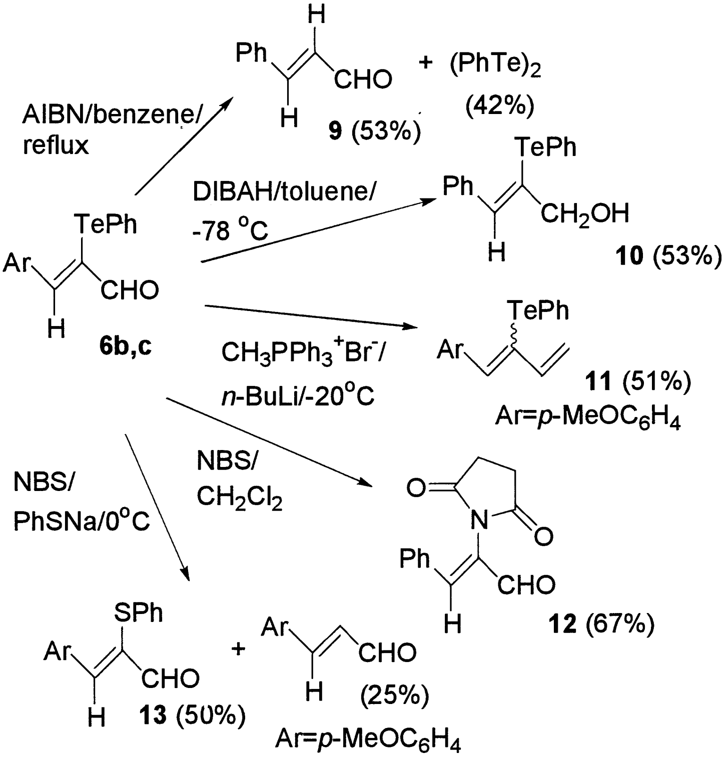
*12-Ethoxy 1-phenyltellanylethene was obtained in 25% yield.

The treatment of the allylic alcohol **5a** with TMSOTf provided the α-phenyltellanyl α,β-unsaturated aldehyde **6a** in 84% yield. The stereochemistries of both **5a** and **6a** were determined by the NOE experiments. It is noteworthy that the stereochemistry of **6a** is different from that of the sulfur or selenium analogs, which were obtained by our previous methods. Some aromatic aldehydes and ketones were also converted to the β-mono- and β,β-disubstituted α,β-unsaturated aldehydes **6b–e** in good to high yields as shown in Table I.

We next performed the tandem alkenylation of **6c** (Scheme 3) and successfully obtained the α,γ-bis(phenyltellanyl)penta-2,4-dienal



SCHEME 3



SCHEME 4

8; however, the third alkenylation failed. In order to characterize the α-tellanyl α,β-unsaturated aldehydes, we finally performed some transformations as shown in Scheme 4. The details of these results will be reported in a full paper.

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