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TELLURIUM AMIDES AS A NEW TELLURATING AGENT

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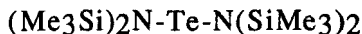
Abstract Two types of tellurium amides have been prepared by the treatment of ArTeI or TeCl_4 with LiNR_2 in THF, and their reaction with acetylenes gave vinyl tellurides and dialkynyl tellurides.

INTRODUCTION

The chemistry of acyclic organotellurium compounds containing Te(II)-N bond have rarely been disclosed in spite of their potential utility because of the weakness of Te-N bond. Recently, we have found that two types of tellurium amides bearing silyl groups on nitrogen atom (**1** and **2**) can be isolated under an inert atmosphere, and



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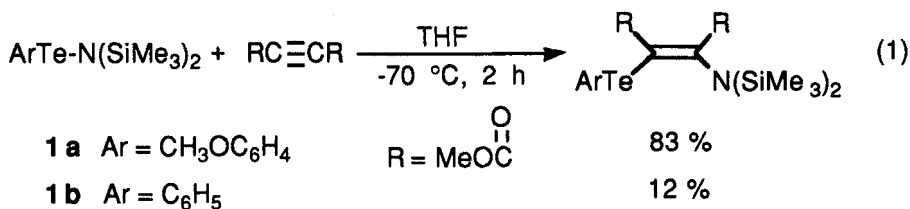


2

their reaction with acetylenes proceeds smoothly to give vinyl tellurides and dialkynyl tellurides in good to high yields.¹⁻³ Herein, we disclose some of these results, and the mechanistic aspects will be discussed.

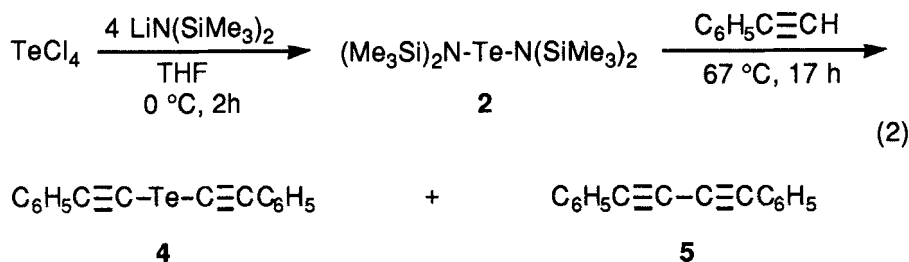
RESULTS AND DISCUSSION

The reaction of dimethylacetylene dicarboxylate (DMAD) with arenetellurenamide **1a**, which was prepared in situ from tellurenyl iodide and lithium *N,N*-bis(trimethylsilyl)amide, was carried out at -70°C (eq. 1). Within two hours, the reaction was complete, and the *Z*-vinyltelluride bearing amino group was stereoselectively



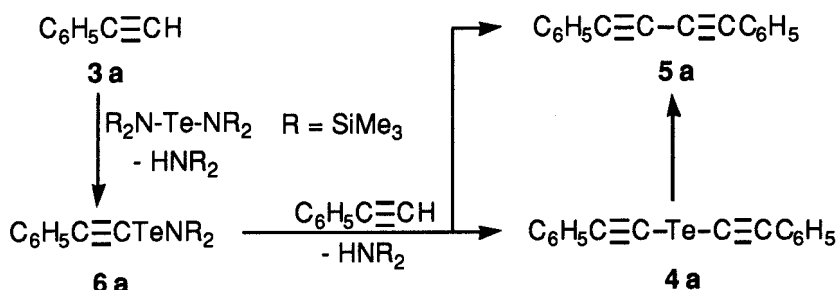
obtained in high yield. 4-Methoxyphenyl group on Te is essential to perform the reaction of eq. 1, since a similar reaction of tellurenamide **1b** with DMAD gave the desired product only in low yield, and C₆H₅TeTeC₆H₅ formed by the decomposition of **1b** was recovered. Based on these results and the fact that the reaction of C₆H₅SeNMe₂ with DMAD proceeds smoothly,⁴ whereas C₆H₅SeN(SiMe₃)₂ was inert, the reactivity of E-N bond (E = Se, Te) toward DMAD can be enhanced by attaching electron donating group either on E atom or N atom.

The reaction of **2** which was formed in situ with phenylacetylene (**3a**) proceeded smoothly under reflux in THF to give bis(phenylethynyl) telluride (**4a**) and 1,4-diphenylbutadiyne (**5a**) in 38 and 12 % yield, respectively. As a solvent, toluene or



dioxane was also used to give the similar results, whereas the black tellurium and **3a** were recovered in n-hexane. However, the formation of **5** could not be suppressed by changing the solvent. The reaction pathway to **4** and **5** are shown in Scheme 1. In the initial step, tellurium amide **2** is probably formed by mixing TeCl₄ and LiN(SiMe₃)₂ in THF. The isolation of **2** by the distillation gave a deep red oil. The ¹H NMR spectrum and microanalysis supported that this oil consists of **2** and one third of HN(SiMe₃)₂ to one molecule of **2**. Recently, **2** was isolated from the

similar reaction in toluene, and its structure was determined by X-ray analysis.⁵ In the next step, tellurium amide **2** may work as a base to abstract proton of **3a** to form tellurium amide **6a**. Then, **6a** reacts with **3a** again to give **4a**. The intermediacy of **6a** may be supported by the formation of butylethynyltelluride (BuTeC≡CPh) in the reaction using **2** and n-BuLi. The product **5a** appears to be formed by the extrusion of Te from **4a**. Alternatively, the direct formation of **5a** from **6a** may be possible since the reaction of **2** with lithium alkynide gave **5a** as a major product.



Scheme 1

A variety of terminal acetylenes were employed as a substrate for the reaction of eq. 2, and the results are listed in Table 1. Generally, the reaction of the terminal acetylenes having electron withdrawing group proceeds quickly, but the product formed decomposes more easily than those bearing electron donating groups. Furthermore, the reaction with propargyl chloride and methyl propiolate gave only intractable black tar.

Finally, the aminotelluration of DMAD using **2** was also carried out (eq. 3). The reaction took place at 0 °C, and the formation of 1 : 1 adduct was confirmed by mass spectrum. But the isolation of the product has not yet been successful.

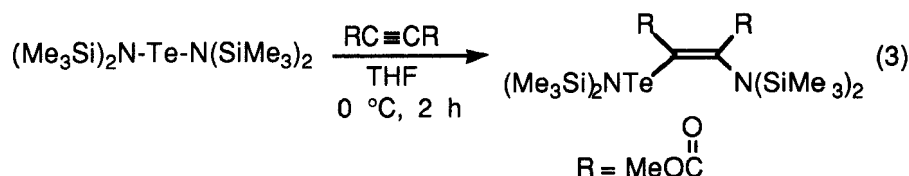


Table I Reaction of terminal acetylenes with in situ formed tellurium amide **2**.

acetylene R	temp. ^a (°C)	time (h)	yield of 4 (%)
4-CH ₃ C ₆ H ₄	0 15	16	61
4-CH ₃ OC ₆ H ₄	0 15	16	59
4-ClC ₆ H ₄	0 15	16	29
Cl(CH ₂) ₃	25	16	54
Me ₃ Si	25	4	53

EXPERIMENTAL

General procedure for the synthesis of dialkynyl telluride from the reaction of terminal acetylenes with lithium amide and TeCl₄. To LiN(SiMe₃)₂ (8 mmol) in THF was added a THF solution of TeCl₄ (2 mmol) at 0 °C, and the mixture was stirred for 2 h at that temperature. Into the resulting orange solution was injected terminal acetylene (4 mmol), and stirred at an appropriate temperature. After the usual workup, the crude product was purified by silica gel column chromatography.

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