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Addition of chalcogenolate anions to terminal alkynes using microwave and solvent-free conditions: easy access to bis-organochalcogen alkenes

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Abstract—We present here the reaction of diphenyl dichalcogenides (Se and Te) with propargyl alcohols using alumina supported sodium borohydride under solvent-free conditions. This efficient and improved method is general and furnishes the corresponding vinyl chalcogenide preferentially with a *Z* configuration. We also observed that when the same protocol was applied to phenyl acetylene, the (*E*)-bis-organochalcogen alkenes were obtained in good yields and high selectivity. The use of MW irradiation facilitates the procedure and accelerates the reaction.

Vinyl chalcogenides have been found to be a very useful tool in organic synthesis, since they are very versatile intermediates for the selective construction of isolated or conjugated olefins.[1] Among the vinyl chalcogenides, 1,2-bis-organochalcogen alkenes are very utile synthons in organic synthesis, because they can be used as precursor to enediynes and other functionalized olefins. However, the number of methodologies for accessing 1,2-bis chalcogenide alkenes is limited and the development of protocols for rigorous regio- and stereochemical controlled synthesis of these compounds remains yet a challenge.

Vinyl chalcogenides have been prepared by the addition of organo chalcogenols, or the respective chalcogenolate anions, to acetylenes.[1,2] Besides, it is known that diselenides[3] and ditellurides[4] add to terminal alkynes, in the presence of UV irradiation[3a–d,4] or a transition-metal catalyst[3e,f] to afford the respective 1,2-bis(organylchalcogenide) alkenes in moderate to good yields. Recently, the in situ addition of chalcogenides to propargylic alcohols (alkynyl-lithium species) to afford bis-chalcogenide alkenes (S and Se) in very good yields was described.[5] The authors observed that the presence of the acidic hydrogen from hidroxyl group is essential for the selectivity control of the addition. They also described that with diorganoyl ditelluride the reaction failed completely and in a similar condition, terminal acetylenes afforded the respective tris-organochalcogen alkenes. Due to the increasing use of vinyl chalcogenides,[1,2] the development of new and efficient methods for the preparation of bis-organochalcogen alkenes with defined regio- and stereochemistry is of general interest in organic synthesis.

Looking for cleaner approaches to classical syntheses, we have developed several protocols involving solid supported catalyst under solvent-free conditions[6] and MW irradiation.[7] As a continuation of our studies toward the development of new methods for the synthesis of vinyl chalcogenides,[6,7a] we report herein the results of the hydrochalcogenation of propargylic alcohols and chalcogenolate anion in addition to phenyl acetylene using $Al_2O_3/NaBH_4$ without any solvent (Scheme 1).[8,9]

Initially, we chose propargyl alcohol **1a** (1.5 equiv) and diphenyl diselenide (0.5 equiv) to establish the best conditions for the hydrochalcogenation reaction. We examined the reaction time, the amount of $Al_2O_3/NaBH_4$ (50%) and the use of microwave.[9] It was found that

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Keywords: Microwave irradiation; Solvent-free reaction; Bis(organochalcogen)alkenes; Vinyl chalcogenides.

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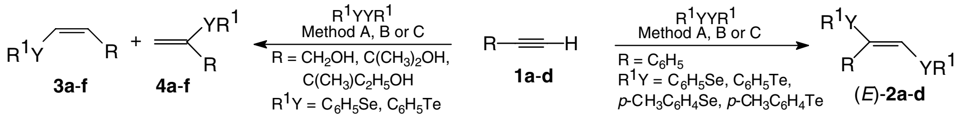


Scheme 1. Method A: $Al_2O_3/NaBH_4$ (50%), stirring, rt, 3–72 h; Method B: $Al_2O_3/NaBH_4$ (50%), MW (548 W), 6–35 min; Method C: $Al_2O_3/NaBH_4$ (50%), stirring, 60 °C (oil bath), 1.5–42 h.

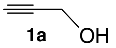
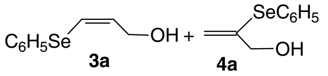
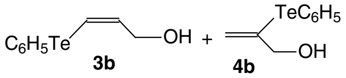
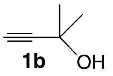
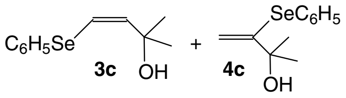
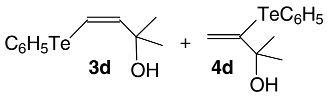
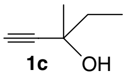
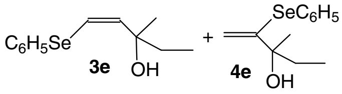
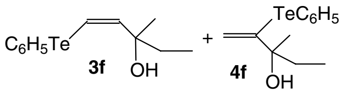
using 0.050 g of $Al_2O_3/NaBH_4$, at room temperature, the reaction proceeded slowly and in 30% yield after stirring for 72 h. However, by using 0.076 g of $Al_2O_3/NaBH_4$, the desired products **3a** and **4a** were obtained in good yield (76%) after 46 h (Table 1, entry 1, Method A). Aiming to reduce the reaction time, the mixture was irradiated with MW (548 W). It was observed there was complete consumption of the starting materials after 10 min and the products were obtained in comparable yield and selectivity (Table 1, entry 2, Method B). When the same protocol was performed at reduced MW power (353 W) it was observed, after 10 min, there was incomplete consumption of diphenyl diselenide, and the product was isolated in 51% yield.

When the reaction was performed in the presence of alumina alone, without $NaBH_4$, no reaction took place in all conditions tested and the starting materials were recovered. By using only $NaBH_4$, the desired products **3a** and **4a** were obtained only in 32% yield.

In order to check the possibility of intervention of specific (non-purely thermal) microwave effects, the reaction with $Al_2O_3/NaBH_4$ (50%) was also examined using a pre-heated oil bath for the same final temperature (60 °C), as measured at the end of exposure during the MW-assisted synthesis (Table 1, entry 3, Method C). However, it was observed that 22 h was required for complete consumption of diphenyl diselenide.

Since the best conditions were established, the protocols were extended to other propargylic alcohols with diphenyl diselenide and also with diphenyl ditelluride (Scheme 1). In all the cases studied, a mixture of **3** and **4** was

Table 1. Synthesis of vinyl chalcogenides **3** and **4** under solvent-free conditions

Entry	Alkyne **1**	$R^1Y)_2$	Products **3** + **4**	Method[a]	Time	Yield[b] (%)	Ratio[c] **3**:**4**
1	 1a	$C_6H_5Se)_2$	 3a 4a	A	46 h	76	75:25
2	**1a**	$C_6H_5Se)_2$	**3a** + **4a**	B	10 min	79	70:30
3	**1a**	$C_6H_5Se)_2$	**3a** + **4a**	C	22 h	77	73:27
4	**1a**	$C_6H_5Te)_2$	 3b 4b	A	72 h	73	80:20
5	**1a**	$C_6H_5Te)_2$	**3b** + **4b**	B	6 min	84	80:20
6	 1b	$C_6H_5Se)_2$	 3c 4c	A	48 h	68	93:07
7	**1b**	$C_6H_5Se)_2$	**3c** + **4c**	B	13 min	71	90:10
8	**1b**	$C_6H_5Te)_2$	 3d 4d	B	15 min	85	90:10
9	**1b**	$C_6H_5Te)_2$	**3d** + **4d**	C	27 h	91	91:09
10	 1c	$C_6H_5Se)_2$	 3e 4e	A	48 h	65	81:19
11	**1c**	$C_6H_5Se)_2$	**3e** + **4e**	B	14 min	82	84:16
12	**1c**	$C_6H_5Te)_2$	 3f 4f	B	13 min	63	91:09
13	**1c**	$C_6H_5Te)_2$	**3f** + **4f**	C	42 h	68	88:12

[a] Method A: The experiments were performed at room temperature. Method B: The experiments were performed at 548 W. Method C: The reaction mixture was heated at 60 °C using an oil bath.[9]

[b] Yields of pure products isolated by column chromatography (AcOEt/hexanes) and identified by mass spectrometry, ^1H, ^{13}C NMR.

[c] Determined by GC of the crude reaction mixture and confirmed after isolation of the individual isomers.