

A novel propargyltitanation of acetylenes. Heteroatom substituent-dependent manifold in intermolecular coupling of allene and acetylene

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Received 9 August 2004; revised 20 October 2004; accepted 5 November 2004

Available online 26 November 2004

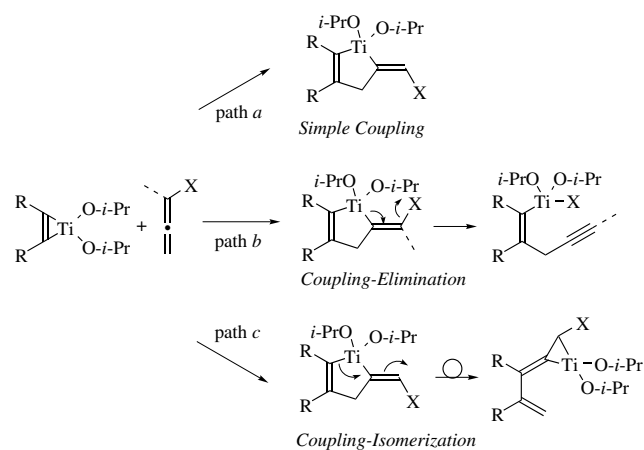
Abstract—Titanium alkoxide-mediated coupling of functionalized allenes and acetylenes afforded various types of products, and the first propargyltitanation of acetylenes was achieved by the appropriate choice of allenes.

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Allenes occupy a unique position in metal-promoted ene–yne coupling reactions.¹ As far as the group 4 metal-mediated coupling reactions are concerned,^{2,3} the behavior of functionalized allenes such as those having a heteroatom substituent has not been focused on in these reactions. We report herein that the reactions of such functionalized allenes proceed in three different ways as formulated in Scheme 1, which involves a simple coupling reaction (path *a*), a coupling–elimination sequence (path *b*), or a coupling followed by isomerization of the molecular structure (path *c*).

Silylacetylene **2** was first titanated with Ti(O-*i*-Pr)₄/2 *i*-PrMgCl (**1**)⁴ to generate acetylene complex **3**,^{4a,b,d} which was then allowed to react with (phenylsulfenyl)allene **4**⁵ or its silylated homologue **8**⁵ at –50 °C (Scheme 2).⁶ Both reactions proceeded in a regioselective manner with respect to the acetylene and allene to give coupling products. However, while nonsilylated allenes **4a,b** afforded 1,4-dienes **6a,b** having a (*Z*)-vinylsulfide moiety after hydrolysis (i.e., Scheme 1, path *a*), the silylated allene **8** experienced elimination of the sulfenyl group to give 1,4-enyne **11** (Scheme 1, path *b*). In the former

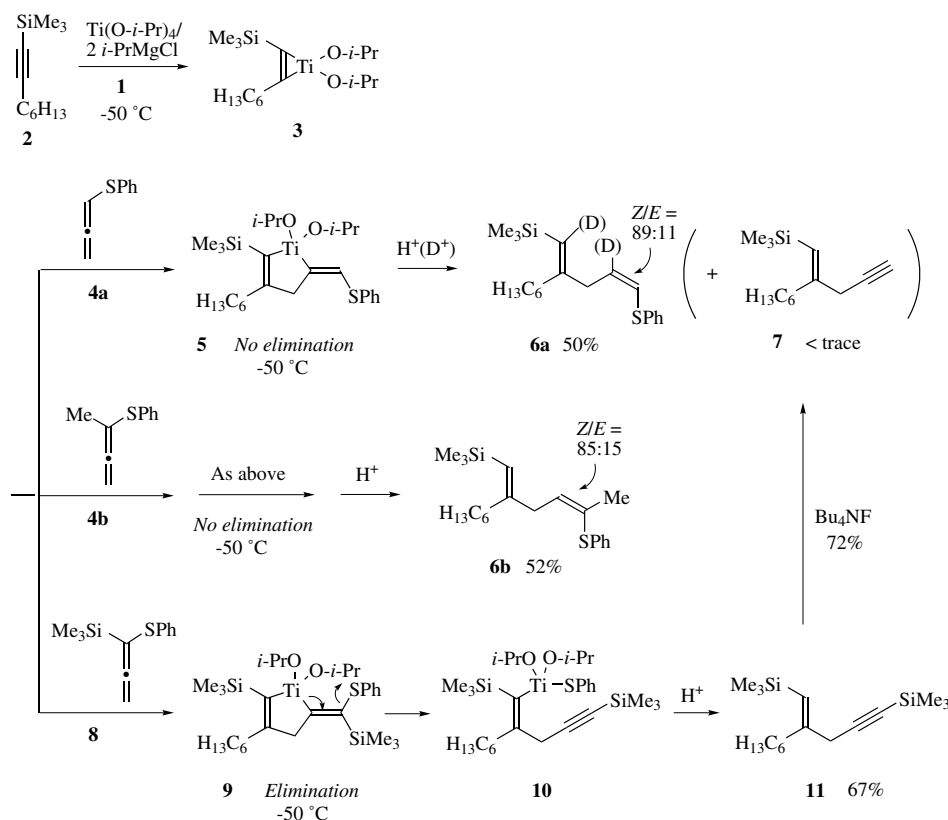
reaction, no elimination product such as **7**, an authentic sample of which was prepared by desilylation of **11**, was detected even under forcing reaction conditions (up to room temperature). The stereochemistry of the olefinic linkage of **6a,b**, and **11** was unambiguously determined by ¹H NMR spectroscopy. Considering the most likely structure of the intermediate **9**, where the bulky silyl group is located *trans* to the titanium atom on the resultant olefin,² we could conclude that the *cis*-elimination from **9** to **10** promoted by the silyl group is a favorable path.



Scheme 1. Variation of reaction patterns.

Keywords: Alkynes; Allenes; Carbometallation; Metallacycle; Titanium and compounds.

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Scheme 2. Stereochemical requirement for elimination.

From the synthetic point of view, the smooth conversion from acetylene **2** to metalated enyne **10** with allene **8** illustrates the first propargyltitanation of acetylenes.⁷ In order to establish the generality of this propargyltitanation, variations of the allenic reagents and acetylenic substrates were examined as summarized in Table 1, where the feasibility and regioselectivity of the reaction were accessed by hydrolytic workup. Actually, bromo-

(silyl)allene **12**^{5,8} is a convenient alternative of **8**, although, in a couple of cases (entries 3 and 5), the regioselectivity (**A**:**B**) is less satisfactory than that attainable by **8**. With the appropriate choice of the allenic reagent, unsymmetrical acetylenes in entries 3, 5, 6, and 7 showed good to virtually complete regioselectivities, which proved that the preparation of various stereo-defined 1,4-enynes is viable.

Table 1. Regiochemistry in the synthesis of skip-type enynes

Entry	R ¹	R ²	X = SPh (8)		X = Br (12)	
			A:B	Yield (%) ^a	A:B	Yield (%) ^a
1	Bu	Bu	—	65	—	70
2	Ph	Ph	—	—	—	90
3	SiMe ₃	C ₆ H ₁₃	Exclusively A	67	71:29	50
4	TBS	C ₆ H ₁₃	—	—	77:23	74
5	Ph	Bu	83:17	76	47:53	59
6	SiMe ₃	Ph	Exclusively A	51	Exclusively A	73
7	SiMe ₃	CO ₂ Bu- <i>t</i>	—	—	Exclusively A	68

^a Isolated yield.

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