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Hydrosilylation of acetylenes with catalytic biscobalthexacarbonyl complex and its application to heteroconjugate addition methodology

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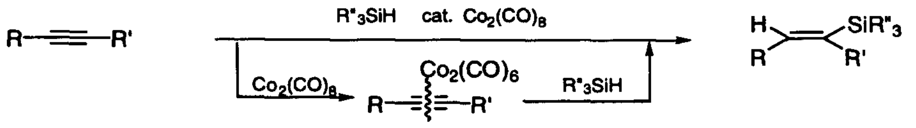
Abstract

The acetylene biscobalthexacarbonyl complex can catalyze hydrosilylation of acetylenes to produce vinylsilanes. The regioselectivity is extremely high with phenylthioacetylenes, while it is hardly selective depending upon the substituents other than the sulfide group. High selectivity with dihydropyranyl-phenylthioacetylene prompted us to establish a practical convenient route to obtain the electrophilic precursor of vinylsulfones in heteroconjugate addition. A new empirical rule for the assignment of *syn*/*anti* stereochemistry of the products can be formulated, the ^{13}C NMR chemical shifts of the *anti*-isomer being higher than those of the *syn*-isomer. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: hydrosilylation; acetylene biscobalthexacarbonyl; heteroconjugate addition; diastereoselectivity.

Biscobalthexacarbonyl complexes of acetylenes[1] are becoming more and more important in synthetic organic chemistry, not only as protection of intermediate-triple bonds[2] but also in bond formation reactions, and sometimes as a key step in natural product syntheses.[3] We have reported a reductive decomplexation of these acetylene biscobalthexacarbonyls with tin or silyl hydride to produce the corresponding olefins or vinylsilanes.[4] Recently, we have succeeded in the hydrosilylation of acetylenes directly to the corresponding vinylsilanes in the presence of a catalytic amount of either biscobaltoctacarbonyl or its acetylene complex as indicated in Eq. 1 without isolating the cobalt complex leading to product formation.



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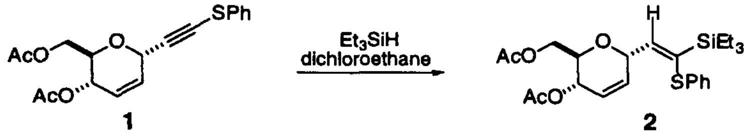
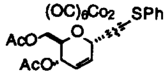
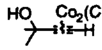
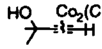
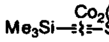
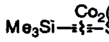
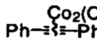
In the hydrosilylation of acetylenes a platinum catalyst (Na_2PtCl_6) has often been used with triethylsilane to produce vinyltriethylsilanes. This reaction usually proceeds by simple heating of the reaction mixture under a nitrogen atmosphere, but occasionally occurred extremely slowly, thus awaiting an alternative method.[5] We reported that the acetylene biscobalthexacarbonyl complex reacted with silanes (Et_3SiH or Ph_3SiH) by heating at 60°C to obtain the corresponding vinylsilanes.[4] After this finding, we searched for conditions to use catalytic amounts of the cobalt reagent.

First of all, we carried out the reaction of **1** under similar conditions as with the platinate catalyst (0.5 mol%, entry 1) with the biscobaltoctacarbonyl (1 mol%, entry 2) and found almost no reaction (Table 1). Use of double amounts of the catalyst gave **2** in 32% yield (entry 3). By applying 5 mol% (entry 4) the reaction became very fast, providing 88% yield. This suggests that trace amounts of $Co_2(CO)_8$ might be decomposed during the early process of operation at a semi-micro laboratory scale. In addition, the inconvenience of handling air-sensitive biscobaltoctacarbonyl reagent might be avoided by employment of a stable acetylene biscobalt complex, so we screened several complexes as exemplified in entries 5–10. Employment of the biscobalthexacarbonyl complex catalyst of thiophenylacetylene (entry 5) or of 2-methyl-3-butyn-2-ol[6] (entries 6, 7) afforded good results. On the other hand, the bistrimethylsilylacetylene complex (entries 8, 9) or diphenylacetylene complex (entry 10) did not provide high yield of the products using catalytic amounts of the catalyst. These results seemed to indicate that the possible exchange of the cobalt between the catalyst and the substrate acetylene would be critical in determining the overall rate of the hydrosilylation.



(2)

Table 1
Effects of the catalysts on hydrosilylation (Eq. 2)

entry	catalyst	amount (mol equiv. %)	temperature (°C)	period (min)	yield (%)
1	Na_2PtCl_6	0.5	70	25	75
2	$Co_2(CO)_8$	1	60	800	5*
3	$Co_2(CO)_8$	2	60	800	32*
4	$Co_2(CO)_8$	5	70	25	88
5		19	60	10	99
6		3	60	30	83
7		2	60	120	61*
8	 $\overset{Co_2(CO)_6}{Me_3Si-\equiv-SiMe_3}$	2.5	60	60	0*
9	 $\overset{Co_2(CO)_6}{Me_3Si-\equiv-SiMe_3}$	100	60	800	39*
10	 $\overset{Co_2(CO)_6}{Ph-\equiv-Ph}$	100	60	60	57*

*The reaction was conducted in dichloroethane as a solvent under nitrogen atmosphere. * Starting material was recovered.*

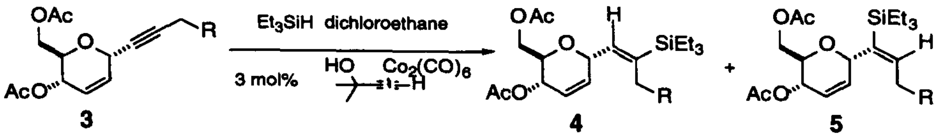
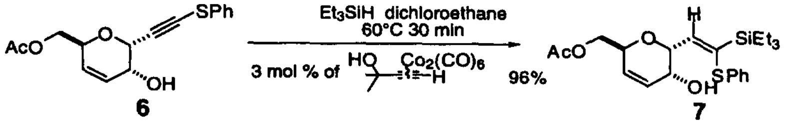
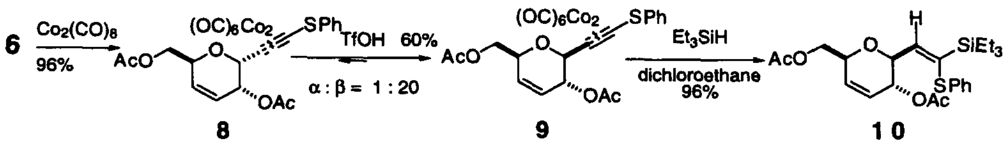
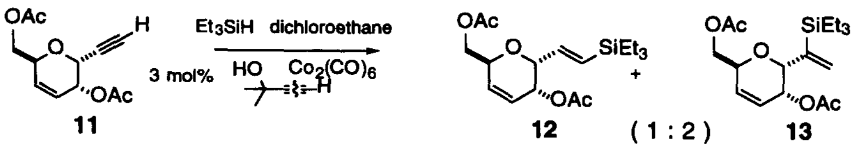

(3)

Table 2
Regioselectivity and yields in hydrosilylation (Eq. 3)

R	OAc	OH	OTBDPS	H	Br
ratio **4** : **5**	14 : 1	8 : 1	3 : 1	7.3 : 1	-
yield (%)	95	92	96	100	0

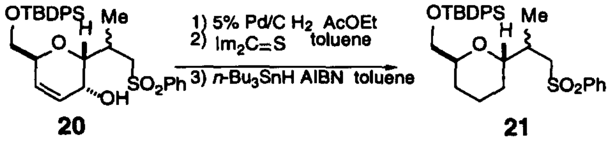

(4)


(5)


(6)

More aspects of this hydrosilylation were studied with reference to the regioselectivity of similar sugar acetylene derivatives **3**, **6**, **9** and **11** (Eqs. 3–6). With the phenylthioacetylenes (**1** and **6**) all of the resultant vinylsilanes were produced in a highly regioselective manner; thus, no trace of the regioisomer was detected under the same catalytic conditions with a 2-methyl-3-butyn-2-ol complex (Eqs. 2 and 4). On the other hand, regioselectivity with **3**, having a C-substituent was examined (Eq. 3). The products **4** and **5** were obtained with variable regioselectivity as presented in Table 2. Another sugar acetylene having a terminal hydrogen (**11**, Eq. 6) afforded a 1:2 mixture of **12** and **13**; thus, the major product **13** had the triethylsilyl group next to the bulkier dihydropyrane ring. These examples exemplified the subtly different effects of steric and electronic factors.

Epimerization of the α-acetylene biscobalthexacarbonyl complex **8** gave the β-isomer **9** as 1:20 equilibrium mixture via trifluoromethanesulfonic acid treatment.[7] The consecutive hydrosilylation provided **10** as a sole product (Eq. 5) and these sulfide products **7** and **10** were used for the following studies.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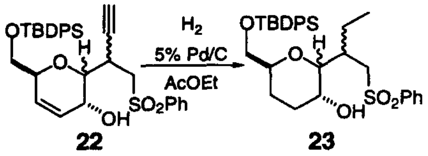
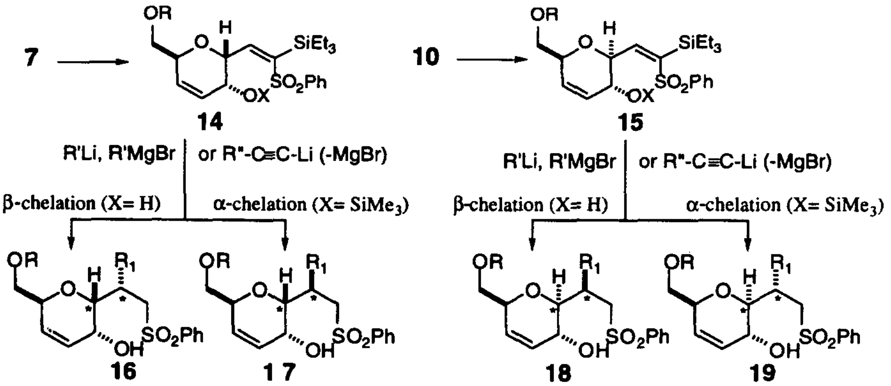


(8)

The results presented above were applied to heteroconjugate addition methodology (Scheme 1); thus, **14** and **15** were prepared (α and β vinylsulfone substituents, respectively). As had been reported previously, the addition of nucleophiles (MeLi, MeMgBr, EtMgBr, $\mathrm{Me_3SiC{+}CLi}$ or $\mathrm{Me_3SiC{+}CMgBr}$) afforded exclusively *syn* or *anti* products after removing the triethylsilyl group. The stereochemistry of the Me adducts (**20**) was assigned via comparison with authentic samples (**21**)[8] after reducing the hydroxy group and the carbon–carbon double bond (**7**), while structures of the alkynyl adducts (**22**) were tentatively assumed only on the basis of the α or β chelation mechanism (Fig. 1).[8] For the ethynyl adducts **22** the stereochemistry was confirmed by conversion into the reduced ethyl derivatives as **23** (Eq. 8). Alternatively, addition of EtMgBr to **14** (X=$\mathrm{SiMe_3}$ or H) and following desilylation with TBAF afforded **16** with exclusive selectivity, and it was further converted into **30** for comparison. An old empirical rule for *syn–anti* assignment was based on the ^{13}C NMR chemical shifts of the carbon of the incoming anionic center; thus, the methyl group usually appears at 14 ppm and 17 ppm for the *syn*- and *anti*-isomer, respectively.[9] Among all of the products with/without 2′-hydroxyl groups higher chemical shifts of the carbon indicated with '*' were observed as illustrated in Table 3. One of the compounds **26** was crystallized and analyzed by X-ray crystallography to prove the *anti* stereochemistry (Fig. 2). These facts established that the stereochemistry of the heteroconjugate addition products can be assigned from ^{13}C NMR; the *anti*-isomer showing higher ^{13}C NMR chemical shifts than *syn*-isomer.



Scheme 1. Synthesis of 4 diastereoisomers

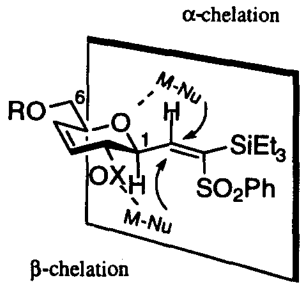
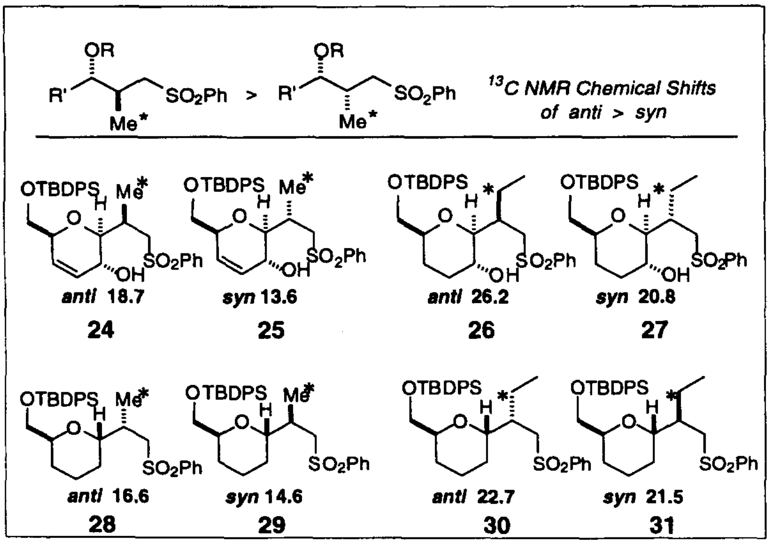


Figure 1. Chelation mechanism in the heteroconjugate addition

Table 3

A new empirical rule of assignment for *syn*/*anti* stereochemistry



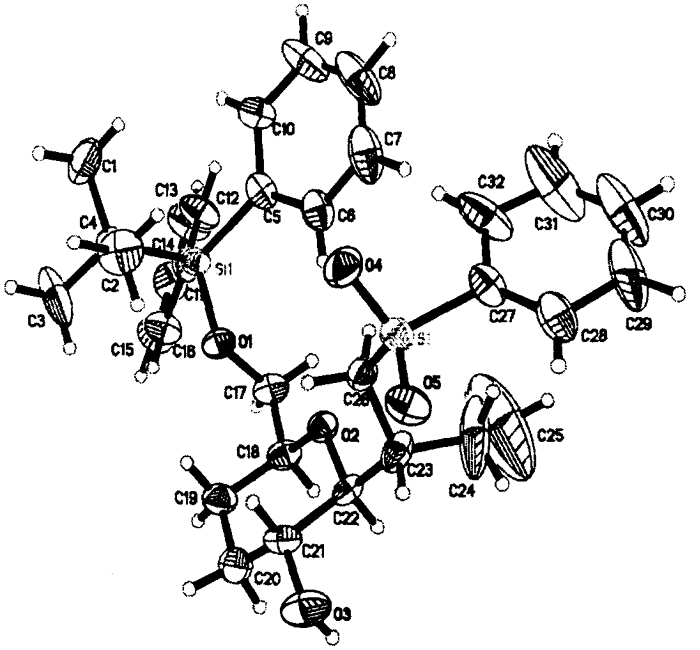


Figure 2. X-Ray structure of **26**

Acknowledgements

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