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Highly Chemoselective Calcium-Catalyzed Propargylic Deoxygenation

Vera J. Meyer and Meike Niggemann*[a]

Abstract: A calcium-catalyzed direct reduction of propargylic alcohols and ethers has been accomplished by using triethylsilane as a nucleophilic hydride source. At room temperature a variety of secondary propargylic alcohols was deoxygenated to the corresponding hydrocarbons in excellent yields. Furthermore, for the first time, a catalytic deoxygenation of tertiary propargylic alcohols was generally applicable. The same protocol was suitable for an efficient reduction of secondary as well as tertiary propargylic methyl, benzyl and allyl ethers. Substrates containing an additional keto-, ester or secondary hydroxyl function were reduced with exceptional chemoselectivity at the propargylic position.

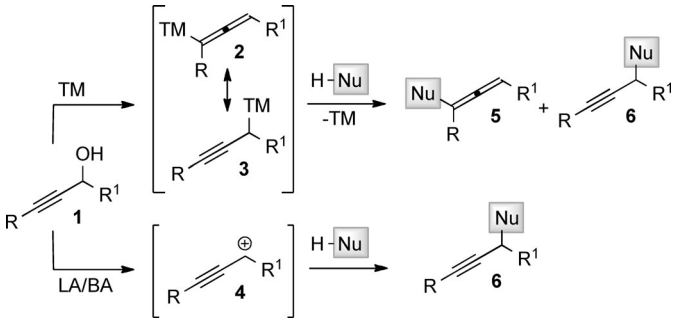
Keywords: alcohols · calcium · chemoselectivity · direct deoxygenation · reduction

Introduction

Within different areas of organic chemistry a frequent final transformation toward a target molecule is the removal of a specific hydroxyl moiety, which is a necessary functional handle at an earlier stage. Due to the high degree of molecular complexity in such advanced substrates, compatible deoxygenation processes must be highly selective and the tolerance of various functional groups is a prerequisite. The radical substitution of xanthenes and thiocarbonates following the Barton–McCombie protocol (and variations thereof) is a versatile and widely employed method for the removal of primary and secondary alcohols.[1,2] However, the deoxygenation of tertiary alcohols remains challenging even nowadays, due to the poor stability of their thionocarbonyl derivatives, which often results in undesired rearrangement and elimination reactions. Therefore, only few procedures have been described.[3] Moreover, from an environmental point of view, the development of mild and catalytic methods for the direct deoxygenation is highly desirable, so that the stoichiometric derivatization of the hydroxyl moiety with an activating group is no longer required. Even though some procedures for the direct reduction of alcohols have been described, several problems remain to be solved, such as limited substrate scope and low functional group tolerance, as most procedures suffer from the necessity of drastic reaction conditions.[2,4,5]

The reduction of one class of alcohols, the propargylic alcohols, is particularly problematic. The Barton–McCombie protocol is applicable in only few cases for secondary propargylic alcohols[6] and essentially one example is known for a tertiary propargylic alcohol.[7] Substitution reactions with a nucleophilic reductant are hampered by the poor leaving-group character of the hydroxyl moiety. Therefore, over-stoichiometric amounts of Brønsted acids or Lewis acids such as trifluoroacetic acid (TFA) or $BF_3{\cdot}Et_2O$ are generally necessary for a direct deoxygenation of the alcohol.[4,8] For cases in which a selective reaction is compulsory, protection of the alkyne with cobalt octacarbonyl is often inevitable.[9] To our knowledge only three protocols have been described for a direct nucleophilic reduction of propargylic alcohols.[10,11] All three reactions are severely limited in substrate scope, and only secondary propargylic alcohols are deoxygenated.

This deficiency in development might be attributed to two main obstacles that are related to the reduction of propargylic alcohols. First, a competing reduction of the alkyne moiety itself, before or after the deoxygenation, is likely to diminish the yield of the desired product.[12] In addition, it is generally difficult to achieve selective substitution reactions of propargylic alcohols and their derivatives with transition-metal catalysts.[13] The reactive species in many of these reactions is assumed to be either a metal allenylidene complex **2** or a metal propargylic intermediate **3** (Scheme 1). Inter-



Scheme 1. Mechanistic pathways of propargylic substitution catalyzed by transition-metal (TM) or Lewis acidic/Brønsted acidic (LA/BA) catalysts.

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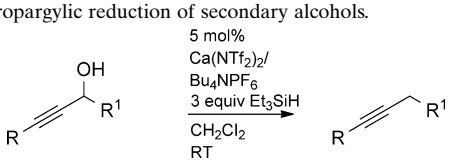
conversion of these two organometallic species results in the predominant formation of the allene derivative **5**. By contrast, Lewis- or Brønsted acid-catalyzed reactions proceed via the intermediary formation of carbocation **4**,[14] which leads effectively to the propargylic substitution product **6**. Hence, a preferentially non-transition-metal Lewis acid-catalyzed direct reduction of a propargylic alcohol should yield the desired product with high selectivity for the acetylene. Surprisingly, no such protocol has hitherto been described.

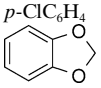
Results and Discussion

Encouraged by our recently published results on propargylic substitution reactions catalyzed by a highly efficacious Lewis acidic calcium catalyst under very mild reaction conditions,[15] we set out to investigate the suitability of our catalyst system for the deoxygenation of propargylic alcohols.

We were pleased to find that the reduction of a variety of secondary propargylic alcohols proceeded smoothly at room temperature in the presence of $Ca(NTf_2)_2$ (5 mol%) and Bu_4NPF_6 (5 mol%) in dichloromethane. An excess of of triethylsilane (three equivalents) was used as an inexpensive and benign hydride source (Table 1). A range of different

Table 1. Propargylic reduction of secondary alcohols.



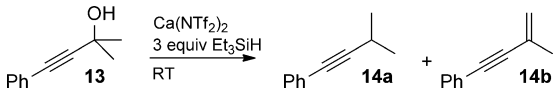
Entry[a]	R	R^1	Product	t [min]	Yield[b] [%]
1	Ph	Ph	7	10	69
2	Ph	pMeOC$_6$H$_4$	8	5	98
3	Ph	p-ClC$_6$H$_4$	9	5	85
4	Ph		10	5	84
5	n-pentyl	Ph	11	5	68
6		Ph	12	10	68

[a] Bu_4NPF_6 (5 mol%) and $Ca(NTf_2)_2$ (5 mol%) were added at room temperature to the alcohol (0.5 mmol) and Et_3SiH (1.5 mmol) in CH_2Cl_2 (1 mL) and stirred for the time indicated. [b] Isolated product yield.

secondary propargylic alcohols, were reduced in reaction times of just 5 to 10 min to give the desired products in good to excellent yields. Interestingly, little impact of the electronic properties of the propargylic substituent on the cation formation was observed; similar results were obtained in the presence of both electron-donating substituents, such as methoxy or methylenedioxy, and electron-withdrawing chloro substituents on the propargylic benzene ring.

However, when we turned our attention to the reduction of tertiary propargylic alcohols, starting with compound **13** as a model substrate, the desired product **14a** was obtained in disappointing 27% yield and the enyne **14b**, isolated in 47% yield, was identified as the major product (Table 2).

Table 2. Optimization of the reaction conditions for tertiary alcohols.



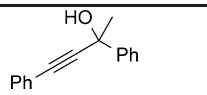
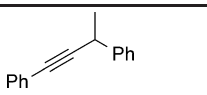
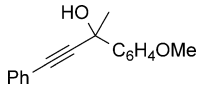
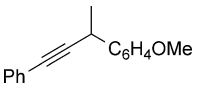
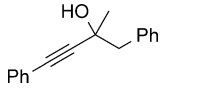
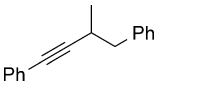
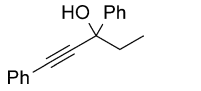
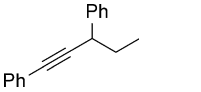
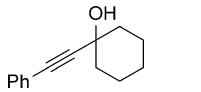
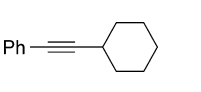
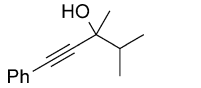
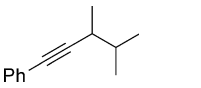
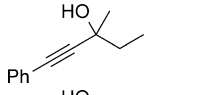
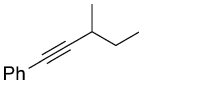
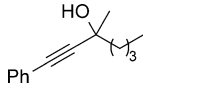
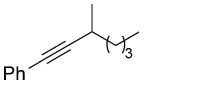
Entry[a]	Additive ([mol%])	Solvent	**14a/14b**	t	Yield[b] [%]
1	Bu_4NPF_6 (5)	CH_2Cl_2	1:1.8	1 h	74
2[c]	Bu_4NPF_6 (5)	CH_2Cl_2	1:2	1 h	80
3[d]	Bu_4NPF_6 (5)	CH_2Cl_2	1:1.8	1 h	42
4	Bu_4NBF_4 (5)	CH_2Cl_2	1:2.4	1 h	75
5	Bu_4NSbF_6 (5)	CH_2Cl_2	1:1.1	1 h	83
6	$PhMe_2NH^+B(C_6F_5)_4^-$ (5)	CH_2Cl_2	1:0.1	5 h	82
7	$PhMe_2NH^+B(C_6F_5)_4^-$ (5)	DCE	1:0.1	4 h	88
8	Bu_4NSbF_6 (5)	toluene	1:8.6	1 h	58
9	Bu_4NSbF_6 (5)	DCE	1:0.7	1 h	71
10[e]	Bu_4NSbF_6 (5)	DCE	1:0.6	5 h	30
11	Bu_4NSbF_6 (5)	$CHCl_3$	1:5.5	1 h	84
12	Bu_4NSbF_6 (5)	$MeNO_2$	1:0.1	1 h	67
13	Bu_4NBF_4 (5)	$MeNO_2$	1:0.1	10 min	66
14	Bu_4NPF_6 (5)	$MeNO_2$	1:0.1	5 min	71

[a] Additive and $Ca(NTf_2)_2$ were added at room temperature to alcohol **13** (0.5 mmol) and Et_3SiH (1.5 mmol) in solvent (1 mL) and stirred for the time indicated. [b] Isolated product yield of the mixture of **14a**/**14b**. [c] 5 equivalents of Et_3SiH. [d] 10 equivalents of Et_3SiH. [e] Reaction at 0°C. DCE = 1,2-dichloroethene.

This undesired elimination reaction was an insurmountable hurdle in ruthenium-catalyzed propargylic reductions.[11]

Increasing the excess of the hydride source to 5 and 10 equivalents did not affect the ratio of reduction versus elimination product (Table 2, entries 2 and 3), and a high concentration of triethylsilane even led to a decrease in overall conversion (entry 3). A screening of different additives revealed their major impact on the outcome of the reaction. In the presence of Bu_4NSbF_6 (Table 2, entry 5) a moderate amelioration of both the yield and the selectivity for the desired product were observed, whereas Bu_4NBF_4 (Table 2, entry 4) did not enhance the results. Even though *N*,*N*-dimethylanilinium tetra(pentafluorophenyl)borate (Table 2, entries 6 and 7) slowed down the reaction rate significantly, from 1 to 5 h, the desired product **14a** was obtained in excellent yield and selectivity. Hence, a first set of optimized reaction conditions was found. Owing to the high cost of this rather particular additive we continued the optimization process. A solvent screening was performed with Bu_4NSbF_6 as the additive, revealing that reaction in nitromethane gave excellent results in terms of selectivity, in a reaction time of just one hour and with an only slightly diminished yield, compared with the reaction in presence of *N*,*N*-dimethylanilinium tetra(pentafluorophenyl)borate. A re-screen of the different additives in nitromethane revealed a second set of optimized reaction conditions for tertiary propargylic alcohols. In presence of the original additive, Bu_4NPF_6, the desired product is obtained in 71% yield after a reaction time of only 5 min (Table 2, entry 14). With the optimized reaction conditions in hand, a series of differently substituted tertiary propargylic alcohols were reduced by using both sets of optimized reaction conditions (Table 3).

Table 3. Propargylic reduction of tertiary alcohols.

Entry[a]	Alcohol		Product		t	Method	Yield[b] [%]
1		**15**		**16**	5 min 15 h	A[c] B[d]	70 68
2		**17**		**18**	5 min 1 h	A B	74 31
3		**19**		**20**	1 h 20 h	A B	70 52
4		**21**		**22**	5 min 15 h	A B	66 69
5		**23**		**24**	5 min 6 h	A B	73 68
6		**25**		**26**	5 min 18 h	A B	76 83
7		**27**		**28**	5 min 6 h	A B	52 52
8		**29**		**30**	5 min 6 h	A B	65 69

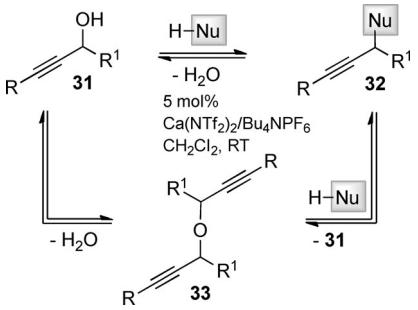
[a] $Ca(NTf_2)_2$ (5 mol%) was added at room temperature to the alcohol (0.5 mmol) and Et_3SiH (1.5 mmol) in solvent (1 mL) and stirred for the time indicated. [b] Isolated product yield. [c] Reaction conditions A: Bu_4NPF_6 (5 mol%) in $MeNO_2$. [d] Reaction conditions B: $PhMe_2NHB(C_6F_5)_4$ (5 mol%) in DCE.

From previous studies it was known that calcium-catalyzed propargylic substitution reactions are generally accompanied by a reversible side reaction. Instead of the desired nucleophile a molecule of the starting material **31** adds to the previously formed carbocationic intermediate, owing to the nucleophilicity of the hydroxyl moiety. Conversion of the thus formed ether **33** to the final product might occur through direct attack, or after the addition of a molecule of water resulting in the regeneration of propargylic alcohol **31** followed by the regular substitution reaction (Scheme 2).

Encouraged by the fact that intermediary-formed ethers are apparently suitable substrates for calcium-catalyzed propargylic substitution reactions, the direct reduction of propargylic ethers was investigated as a synthetically useful extension of our new methodology. Hence we tested the first direct reduction of methyl-, allyl- and benzyl propargylic ethers. Secondary propargylic ethers **34–36** reacted smoothly under the standard reaction conditions, with Bu_4NPF_6 (5 mol%) as the additive in dichloromethane (Table 4).

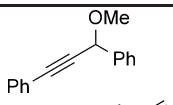
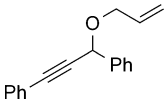
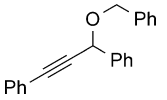
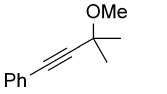
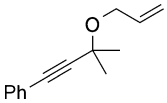
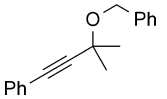
The attempted reduction of the tertiary ethers **37–39** under the same reaction conditions once again gave the enyne **14b** as the major product. However, the same modifications of the reaction conditions that led to an efficient reduction of tertiary alcohols allowed for a successful deetherification of tertiary propargylic ethers **37–39**.

Triethylsilane-mediated reduction of different carbonyl compounds has been described under various reaction conditions.[16] Therefore, the chemoselectivity of the newly developed calcium-catalyzed propargylic deoxygenation was of



Scheme 2. Intermediary formation of self-condensation product **33**.

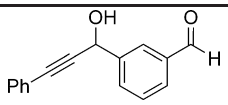
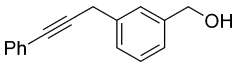
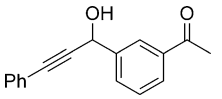
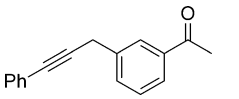
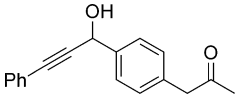
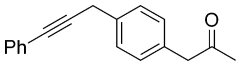
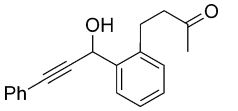
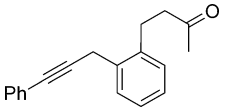
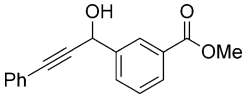
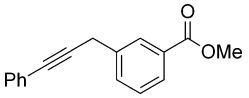
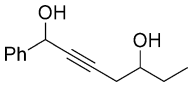
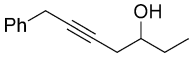
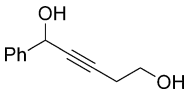
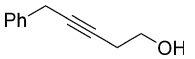
Table 4. Deoxygenation of propargylic ethers.

Entry[a]	Ether		Product	t	Method	Yield[b] [%]
1[a]		**34**	**7**	15 min		46
2[a]		**35**	**7**	15 min		56
3[a]		**36**	**7**	2 h		81
4		**37**	**14a**	1.5 h 5 h	A[c] B[d]	59 33
5		**38**	**14a**	5 min 5 h	A B	84 77
6		**39**	**14a**	5 min 1 h	A B	77 66

[a] Bu_4NPF_6 (5 mol%) and $Ca(NTf_2)_2$ (5 mol%) were added at room temperature to the ether (0.5 mmol) and Et_3SiH (1.5 mmol) in CH_2Cl_2 (1 mL) and stirred for the time indicated. [b] Isolated product yield. [c] Reaction conditions A: Bu_4NPF_6 (5 mol%) in $MeNO_2$. [d] Reaction conditions B: $PhMe_2NHB(C_6F_5)_4$ (5 mol%) in DCE.

major interest to us. Hence, different substrates containing both an aldehyde or a ketone moiety and a propargylic alcohol were synthesized and submitted to the reaction conditions (Table 5).

Table 5. Deoxygenation in the presence of functional groups.

Entry	Alcohol		Product		t [min]	Yield[b] [%]
1[a]		**40**		**41**	5	68
2[a]		**42**		**43**	30	72
3[a]		**44**		**45**	10	76
4[a]		**46**		**47**	5	78
5[a]		**48**		**49**	30	72
6[c]		**50**		**51**	15	72
7[d]		**52**		**53**	15	44

[a] Bu_4NPF_6 (5 mol%) and $Ca(NTf_2)_2$ (5 mol%) were added at room temperature to the alcohol (0.5 mmol) and Et_3SiH (1.5 mmol) in CH_2Cl_2 (1 mL) and stirred for the time indicated. [b] Isolated product yield. [c] Reaction in $MeNO_2$. [d] Reaction at 50°C under microwave conditions.

Different substrates containing benzylic (**42**) and non-benzylic ketone moieties (**44** and **46**), were selectively transformed into the desired deoxygenated products with the carbonyl function remaining intact. Particularly remarkable is the high selectivity for the reduction of the alcohol in presence of the benzylic ketone in **42**, as reduction of such ketones with triethylsilanes under acidic conditions is a standard procedure in organic synthesis. The same excellent chemoselectivity was observed for propargylic reduction in the presence of a methyl ester such as in **48**. Solely, compound **40** containing a benzylic aldehyde yielded the partially reduced compound **41** along with a series of unidentified side products. A second chemoselectivity study was performed using substrates **50** and **52** bearing an additional hydroxyl function. Under the standard reaction conditions, the reduction of compound **50** proceeded cleanly but ceased at about 40% conversion, probably due to a partial poisoning of the calcium catalyst by the secondary hydroxyl function. Nevertheless, changing the solvent to nitromethane proved once more beneficial and the desired product **51** was isolated in 72% yield. Again, no reduction of the secondary hydroxyl function was observed under these slightly modified reaction conditions. The primary alcohol in substrate **52** inhibited the catalyst at room temperature. The reaction proceeded at 50°C under microwave conditions, albeit it was rather sluggish and the desired product could be isolated in a poor yield of just 44%.

In summary, we have developed the first calcium-catalyzed direct deoxygenation of secondary as well as tertiary propargylic alcohols. The corresponding hydrocarbons are obtained under very mild reaction conditions and typical reactions are completed in reaction times of 5 min to a few hours at room temperature. Triethylsilane is used as a convenient, mild, and inexpensive stoichiometric reductant. As anticipated, this propargylic reduction, that is, to our knowledge, the first Lewis acid-catalyzed reaction of this type, yields the desired product with high selectivity and no formation of allene byproducts was observed. In addition, the reduction proceeds with extraordinary high chemoselectivity and carbonyl functions, such as ketone and ester moieties as well as additional hydroxyl groups, remain intact. The remarkable functional group tolerance together with the very mild reaction conditions and the short reaction times renders our new protocol highly suitable for an application in the late stages of the synthesis of a complex molecular target. Furthermore, the same reaction system was applicable to the first direct deetherification of propargylic ethers to the corresponding acetylenes.

Experimental Section

General procedure: The alcohol (0.5 mmol) and the organosilane (1.5 mmol) were dissolved in solvent (1 mL). Next, the additive (5 mol%) and $Ca(NTf_2)_2$ (5 mol%) were added at room temperature and stirred until conversion of the alcohol was complete (monitored by TLC and/or GC). The product was isolated by adding sat. $NaHCO_3$ solution (5 mL), extracting the aqueous phase with dichloromethane, and the combined organic phases were then dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography.

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