Hydroalkylation of 1,1-Diarylalkenes Mediated by Magnesium Hydride in Ethereal Solvents

Nattawadee Chaisan,[a] Eugene Yew Kun Tan,[a] and Shunsuke Chiba*,[a]

[a] School of Chemistry, Chemical Engineering and Biotechnology, Nanyang Technological University, Singapore 637371 (Singapore)
e-mail: shunsuke@ntu.edu.sg

Dedicated to Professor Alois Fürstner, President of the 56th Bürgenstock Conference

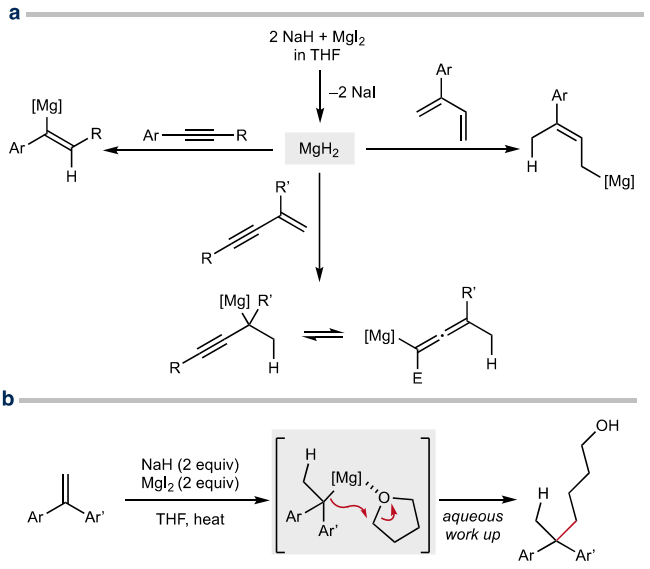
A method for the hydroalkylation of 1,1-diarylalkenes has been developed using magnesium hydride (MgH_2) generated *in situ* by the solvothermal treatment of magnesium iodide (MgI_2) with sodium hydride (NaH) in ethereal solvents. The process is initiated by the hydromagnesiation of 1,1-diarylalkenes with MgH_2 to generate 1,1-diarylethylmagnesium species, which are immediately alkylated with ethereal solvents to construct a diaryl quaternary carbon center in the hydroalkylation products.

Keywords: Hydroalkylation • 1,1-diarylalkenes • magnesium hydride • hydromagnesiation • ethereal solvents

Introduction

Organomagnesium (Grignard) reagents are synthetically valuable organometallic nucleophiles for the construction of various carbon-carbon and carbon-heteroatom bonds.[1,2] They are commonly prepared by the treatment of organic halides with magnesium metal in ethereal solvents such as tetrahydrofuran (THF) and can be stored as a stable solution under an inert atmosphere.[3] The other practical preparation methods involve halogen-magnesium exchange through the reactions of halo(hetero)arenes with alkyl Grignard reagents[4-8] and deprotonative magnesiation of prefunctionalized (hetero)arenes with magnesium amide bases (the Hauser bases).[9,10]

As a distinct mode of approach, the hydromagnesiation of carbon-carbon unsaturated bonds could potentially offer an atom-economical way toward organomagnesium reagents.[11] In this context, our group has recently reported that the solvothermal treatment of magnesium iodide (MgI_2) with sodium hydride (NaH) in THF induces counter ion metathesis to form reactive magnesium hydride (MgH_2), which facilitates the hydromagnesiation of arylalkynes,[12] 1,3-enynes,[13,14] and 2-aryl-1,3-dienes,[15] affording alkenylmagnesium, allenyl/propargylmagnesium and allylmagnesium species, respectively (Scheme 1a). The resulting organomagnesium complexes could be functionalized with various electrophiles, enhancing molecular complexities starting from readily available and simple starting materials. These discoveries motivated us to extend the protocol to the hydromagnesiation of arylalkenes for the generation of benzylmagnesium species. We found that the hydromagnesiation of 1,1-diarylethylenes could proceed in an ethereal solvent, and interestingly, the resulting 1,1-diarylethylmagnesium species underwent nucleophilic alkylation with the ethereal solvent to afford the hydroalkylation products having a diaryl quaternary carbon center (Scheme 1b). The discovery, reaction optimization, and scope & limitation were discussed herein.

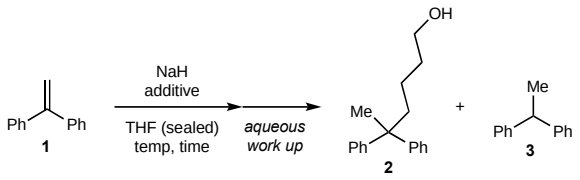


Scheme 1. Hydromagnesiation of unsaturated π-conjugated systems. **a**. Hydromagnesiation of arylalkynes, 1,3-enynes, and 2-aryl-1,3-dienes. **b**. Hydroalkylation of 1,1-diarylethylenes with ethereal solvents through hydromagnesiation (this work).

Results and Discussion

We began our investigation using 1,1-diphenylethylene (**1**) as the model substrate (Table 1). We observed that the treatment of **1** with NaH (1.5 equiv) and MgI_2 (1.5 equiv) in THF at 85 °C (sealed) for 21 h resulted in the formation of 5,5-diphenyl-1-hexanol (**2**) and 1,1-diphenylethane (**3**) in 93% and 4% NMR yields, respectively (entry 1). The hydroalkylation process for the formation of 5,5-diphenyl-1-hexanol (**2**) involves the incorporation of THF to (1,1-diphenylethyl)magnesium intermediate, which could be formed via the hydromagnesiation of **1**. Although THF is utilized as a typical solvent for the preparation of Grignard reagents, there have been several observations that specific Grignard reagents could undergo nucleophilic attack to THF and other cyclic ethers to open the ring. For

Table 1. Optimization of reaction conditions[a]

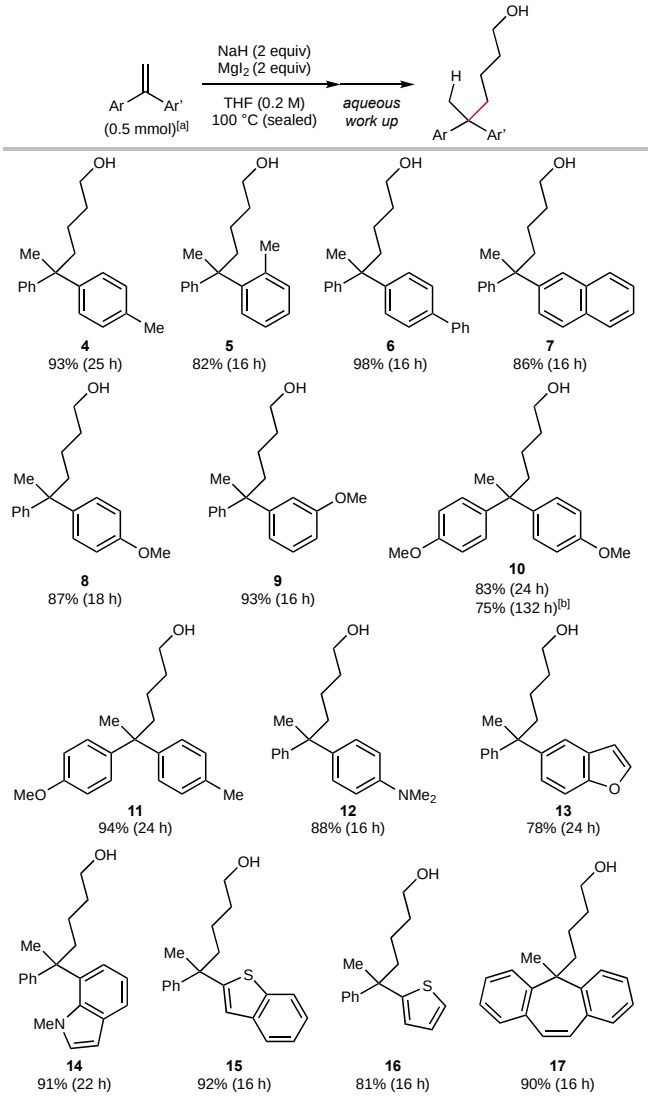


Entry	NaH (equiv)	Additive (equiv)	Temp (°C)	Time (h)	Conv. (%)	2 (%)[b]	3 (%)[b]
1	1.5	MgI_2 (1.5)	85	21	99	93	4
2	2	MgI_2 (2)	85	21	99	95	2
3	2	MgI_2 (2)	100	4	>99	99 (97)[c]	<1
4	2	NaI (2)	100	23	>99	7 (6)[c]	87 (72)[c]
5	2	LiI (2)	100	23	>99	72	25
6	2	CaI_2 (2)	100	23	6	<1	5

[a] The reactions were conducted using 0.5 mmol of **1** in THF (2.5 mL, 0.2 M) in sealed tube. [b] ^{1}H NMR yields based on the internal standard. [c] Isolated yields.

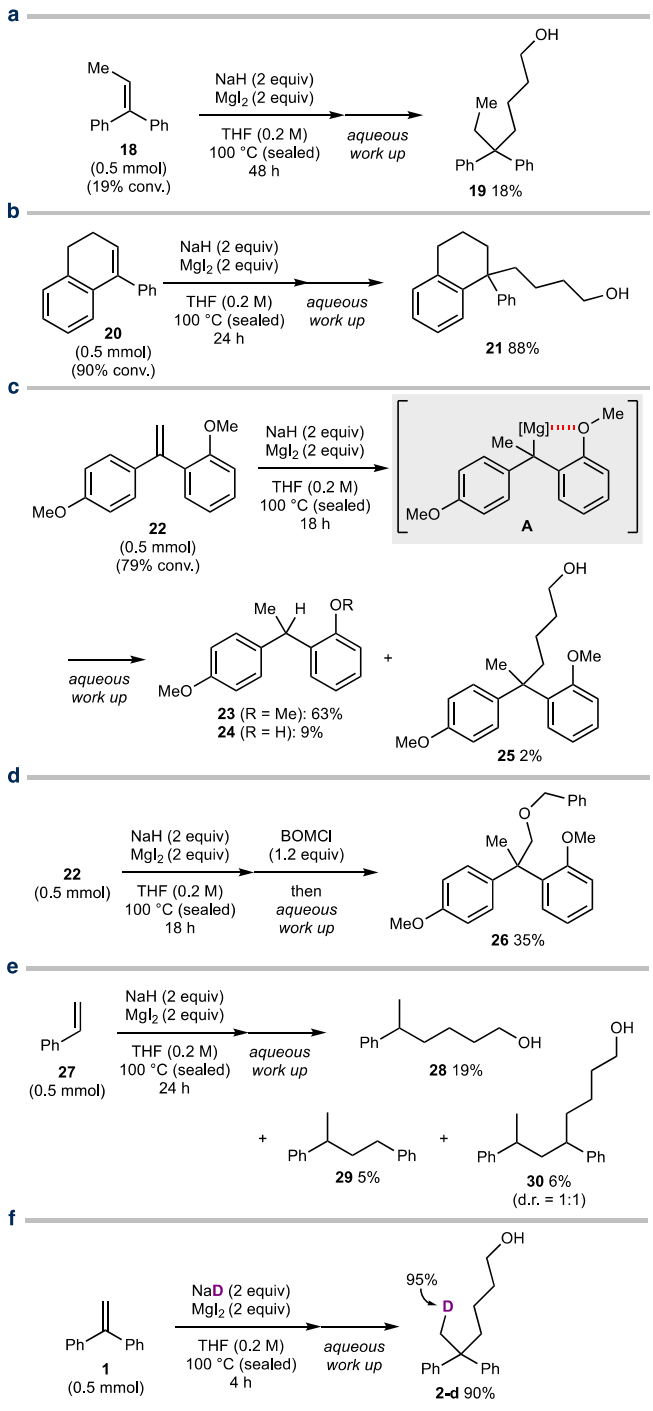
example, Jensen and Bedard discovered in 1958 that tritylmagnesium bromide could cleave THF to form 5,5,5-triphenyl-1-pentanol even at room temperature.[16] More recently, Madsen reported that benzyl and allyl Grignard reagents could cleave 4- and 5-membered ring cyclic ethers under harsh reaction conditions; either at >150 °C for long reaction time (>60 h) or at >180 °C under microwave irradiation.[17] Given the operational simplicity of our process starting from bench-stable 1,1-diphenylethylene (**1**), we further optimized the reaction conditions. The increase of the amounts of NaH and MgI_2 to 2 equivalents slightly improved the yield of **2** (entry 2). We found that the reaction at 100 °C proceeds rapidly to complete the process within 4 h, providing **2** in almost quantitative (97% isolated) yield (entry 3). The effect of the countercations was found impactful to the hydroalkylation process. Namely, the combination of NaH and NaI, which could be used for the generation of activated NaH *in situ* to promote various hydride transfer processes,[18-22] resulted in the formation of hydrogenated product, 1,1-diphenylethane (**3**), as the major product (72% isolated yield) along with the hydroalkylation product **2** in 6% isolated yield, after stirring the reaction mixture at 100 °C for 23 h (entry 4). On the other hand, the employment of LiI as an additive switched the selectivity, providing **2** and **3** in 72% and 25% NMR yields, respectively (entry 5). This remarkable reactivity difference originated from the countercation effect (Na^+ vs. Li^+) is in agreement with the previous reports by Wittig[23] and Evans[24] that trityllithium can open the ring of THF nucleophilically, likely due to more oxophilic nature of the lithium cation, whereas tritylsodium needs the aid of triphenylborane as a Lewis acid additive.[25] On the other hand, the attempt to utilize calcium iodide (CaI_2) was unsuccessful (entry 6).

Given that diarylmethanes are identified as a core unit of various active pharmaceutical ingredients[26,27] and functional materials,[28] we next turned our attention to investigating the substrate scope on the hydroalkylation of 1,1-diarylethylenes with THF using the optimized reaction conditions (Table 1, entry 3). With respect to the aryl substituents, the method was compatible with tolyl (for **4** and **5**), biphenyl (for **6**), 2-naphthyl (for **7**), methoxyphenyl (for **8**-**11**) and dimethylaminophenyl (for **12**) groups (Scheme 2). The present protocol is scalable up to 10 mmol scale despite longer reaction time required to complete the process (for **10**). Various electron-rich heteroarenes such as benzofuran (for **13**), indole (for **14**), benzothiophene (for **15**), and thiophene (for **16**) could also be installed. The hydroalkylation protocol allowed for the efficient construction of a C5-quaternary carbon center on the 5*H*-dibenzo[*a*,*d*][7]annulene scaffold **17**.



Scheme 2. Scope of 1,1-diarylethylenes. [a] The reaction conditions: 1,1-diarylethylenes (0.5 mmol), NaH (2 equiv), MgI_2 (2 equiv), THF (2.5 mL, 0.2 M), 100 °C

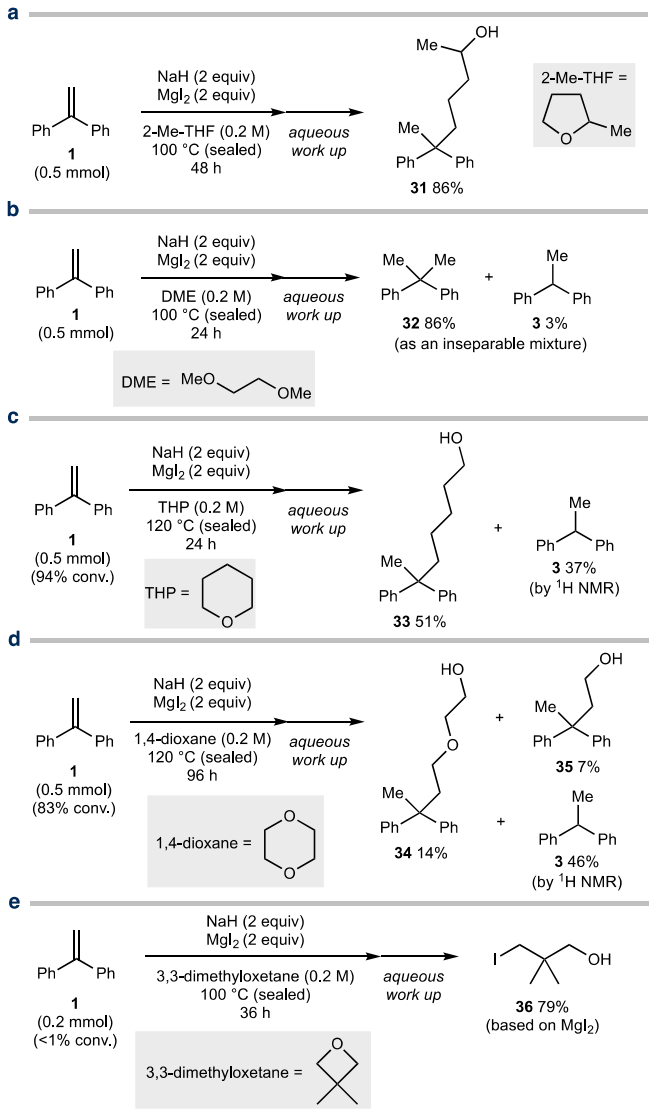
(sealed). Isolated yields were provided. The reaction times were given in the parentheses. [b] The reaction in 10 mmol scale.



Scheme 3. a. The reaction with 1,1-diphenylpropene (**18**). **b**. The reaction with 4-phenyl-1,2-dihydronaphthalene (**20**). **c**. The reaction with **22** having an *ortho*-methoxyphenyl group. **d**. Trap of organomagnesium intermediate **A** with BOMCl. **e**. The reaction with styrene (**27**) **f**. Deuterium labeling experiment with sodium deuteride (NaD).

We observed that the reaction of sterically more hindered 1,1-diphenylpropene (**18**) became sluggish, providing hydroalkylation product **19** only in 18% yield with 19% conversion of **18** even after heating for 48 h (Scheme 3a). On the other hand, hydroalkylation of 4-phenyl-1,2-dihydronaphthalene (**20**) proceeded smoothly to afford tetrahydronaphthalene **21** in 88% yield (Scheme 3b). Interestingly, the reaction of 1,1-diarylethylene **22** having a 2-methoxyphenyl group afforded protonated product **23** in 63% yield upon aqueous workup (Scheme 3c). We also isolated demethylated product **24** and hydroalkylated product **25** in 9% and 2% yields, respectively (Scheme 3c). This suggested that organomagnesium intermediate **A** formed via the hydromagnesiation of **22** could be stabilized by the coordination from the *ortho*-methoxy group, circumventing the successive nucleophilic functionalization with THF. Indeed, we could trap organomagnesium **A** through downstream treatment with benzyloxymethyl chloride (BOMCl) to obtain **26** having a new quaternary carbon center in 35% yield (Scheme 3d). Although the reaction of styrene (**27**) resulted in the full conversion, the hydroalkylation product **28** was isolated only in 19% yield, probably because of uncontrollable oligomerization/polymerization of **27** under the present reaction conditions (Scheme 3e). Indeed, we detected (1-methyl-3-phenylpropyl)benzene (**29**) and 5,7-diphenyloctan-1-ol (**30**) in 5% and 6% yield, respectively, which are derived from anionic dimerization of styrene (**27**). We also observed the precipitation of polystyrene from the product mixture through the treatment with methanol (see the Supporting Information for more details). The use of sodium deuteride (NaD) unambiguously confirmed that the process could be initiated by the hydromagnesiation of alkene **1** (Scheme 3f).

Finally, we tested other ethereal solvents[29] as the electrophile for hydroalkylation of 1,1-diphenylethylne (**1**) (Scheme 4). The reaction in 2-methyltetrahydrofuran (2-Me-THF) needed 48 h to complete the process, resulting in the ring-opening at the sterically less hindered C5 position to afford **31** in 86% yield (Scheme 4a). Interestingly, we observed that dimethoxyethane (DME) delivers a methyl group to provide 2,2-diphenylpropane (**32**) in 86% yield along with the formation of **3** in 3% yield (Scheme 4b). The reaction in a 6-membered ring ether, tetrahydropyran (THP) needed higher temperature (120 °C) to facilitate the reaction, providing the corresponding hydroalkylated product **33** in 51% yield along with hydrogenated product **3** in 37% yield (based on ^{1}H NMR) (Scheme 4c). However, the reaction in 1,4-dioxane became sluggish, resulting in incomplete conversion (83%) of **1** even after hearing at 120 °C for 96 h (Scheme 4d). In this case, we isolated hydroalkylation products **34** and **35** in 14% and 7% yields, respectively, along with substantial amounts of hydrogenated product **3** (46% yield based on ^{1}H NMR). The reaction in highly strained 3,3-dimethyloxetane resulted in nucleophilic ring-opening by an iodide ion, providing 3-iodo-2,2-dimethylpropan-1-ol (**36**) with full recovery of **1** (Scheme 4e).



Scheme 4. Scope of ether solvents. **a**. With 2-methyltetrahydrofuran (2-Me-THF). **b**. With dimethoxyethane (DME). **c**. With tetrahydropyran (THP). **d**. With 1,4-dioxane. **e**. With 3,3-dimethyloxetane.

Conclusions

We demonstrated the unique reactivity of 1,1-diarylethylmagnesium species, generated via the hydromagnesiation of 1,1-diarylalkenes, toward the alkylation with ethereal solvents such as THF, 2-Me-THF, DME, and THP. The present process offers direct access to diarylmethanes having a quaternary carbon center in a concise manner. Further efforts are currently underway to explore other types of alkenes for the hydromagnesiation and subsequent downstream functionalization with various electrophiles.

Experimental Section

A typical procedure: hydroalkylation of 1,1-diphenylethylene (**1**) in THF (Table 1, entry 3).

To a mixture of NaH (60% dispersion in mineral oil; 40.0 mg, 1.00 mmol, 2 equiv) and MgI_2 (278 mg, 1.00 mmol, 2 equiv) in 25 mL sealed tube was added a solution of 1,1-diphenylethylene (**1**) (90.8 mg, 0.504 mmol, 1 equiv) in THF (2.5 mL, 0.2 M). The reaction mixture was stirred at 100 ºC (sealed, an oil bath) for 4 h, before being quenched with saturated aqueous NH_4Cl solution (2 mL) and diluted with water (20 mL). The organic materials were extracted three times with CH_2Cl_2 (20 mL x 3). The combined organic layers were dried over Na_2SO_4 anhydrous, filtered and concentrated *in vacuo*. The NMR yields of 5,5-diphenylhexan-1-ol (**2**) (99% yield) and 1,1-diphenylethane (**3**) (<1% yield) were determined using 1,1,2,2-tetrachloroethane (20 µL, 0.189 mmol) as an internal standard. The crude residue was purified by flash column chromatography on silica gel (hexane:EtOAc = 80:20) to give 5,5-diphenylhexan-1-ol (**2**) in 97% yield (125 mg, 0.489 mmol) as a pale yellow oil.

Supporting Information

The authors have cited additional references within the Supporting Information.[30-52]

Acknowledgements

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Author Contribution Statement

S.C. designed the studies. *N.C.* and *E.Y.K.T.* performed the experiments. *S.C., N.C.* and *E.Y.K.T.* wrote the manuscript.

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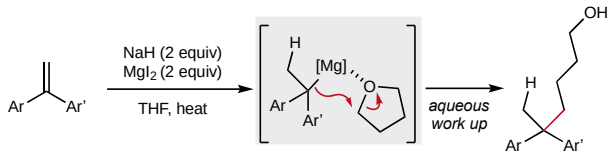

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