Ring-opening of oxabicyclic alkenes with hydride: a new approach to 1,2-dihydronaphthalenes and its ring contraction by iodine(III)

Aline Utaka (PG), Juliana L. L. F. Regueira (PG) and Luiz F. Silva Jr.* (PQ)

Instituto de Química, Universidade de São Paulo, CP 26077, CEP 05513-970, São Paulo

**luizfsjr@iq.usp.br*

Keywords: *ring-opening, oxabicyclic alkenes, hydride, indanes*

Abstract

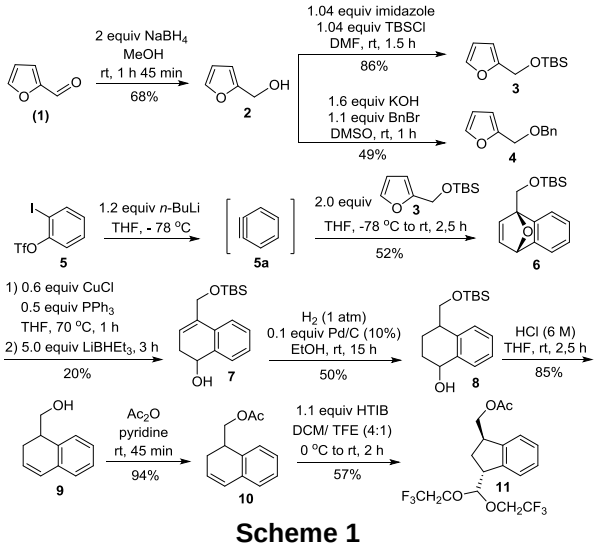
The hydride-mediated ring-opening of oxabicyclic alkenes is described to obtain dihydronaphthalenes, that was transformed into indanes.

Introduction

The transition metal-catalyzed ring-opening of heterobicyclic alkenes are important strategies to provide hydronaphthalenes. The protocols involve the use of carbon[1,2] and heteroatom[3,4] nucleophiles leading to substituted hydroxyl-compounds. However, the use of nucleophilic hydride reagents has never been described. Herein, we report our initial efforts for the copper-catalyzed ring-opening reaction of oxabicyclic alkenes using hydride as nucleophile. Additionally, this new methodology is useful to obtain 1,2-dihydronaphthalenes, which can be used in ring contraction with iodine(III) to access a variety of functionalized indanes.[5]

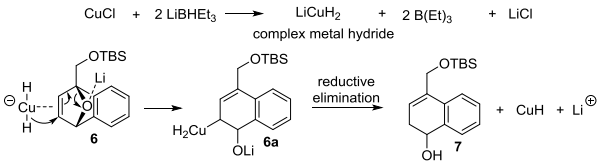
Results and Discussion

The model oxabicyclic alkene **6** was prepared employing a Diels Alder reaction between the benzyne **5a** and the furan derivative **3**, which was prepared in two steps from furfuraldehyde **(1)** (**Scheme 1**).



Scheme 1

We initiated our study based on protocol described for ring-opening reaction with Grignard reagents[2] using $LiAlH_4$ as nucleophilic source. Unfortunately, only starting material was recovered (**Table 1, entry 1**). Increasing the temperature and using $LiBHEt_3$ we obtained **7** in 16% yield (**entry 2**). Replacing the toluene by THF the yield was very similar in a much shorter reaction time (**entry 3**). Performing the reaction without PPh_3 the product was obtained in 11% yield and in the absence of both PPh_3 and copper salt only starting material was recovered (**entries 4** and **5**). These results indicate that copper plays an important role for the ring-opening reaction. The proposed mechanism is shown in **Scheme 2**. The first step is a copper catalyzed S_N2' reaction in which the *in situ* formed complex metal hydride reacts with the alkene **6**. Finally, **6a** undergoes a reductive elimination affording the product **7**.



Scheme 2

Using the hydroxyl-compound **7**, the double bond was reduced using catalytic hydrogenation, affording the tetralin **8** in 50% yield. Under acidic conditions, **8** was deprotected and dehydrated, giving **9** in 85% yield. After the protection of the hydroxyl group with Ac_2O the 1,2-dihydronaphthalene **10** was obtained in 94% yield. Finally, the treatment with iodine(III) gave the *trans*-indane **11** in 57% yield (**Scheme 1**).[5]

Table 1. Ring-opening reaction with hydride

Entry	Hydride	CuCl	PPh_3	Solvent	Time	Yield (%)
1	1.5 equiv $LiAlH_4$	0.2 equiv	0.2 equiv	Toluene	5 h	0[a][b]
2	3.0 equiv $LiBHEt_3$	0.25 equiv	0.25 equiv	Toluene	24 h	16[a]
3	5.0 equiv $LiBHEt_3$	0.6 equiv	0.6 equiv	THF	3 h	20[a]
4	5.0 equiv $LiBHEt_3$	0.6 equiv	-	THF	24 h	11[a]
5	5.0 equiv $LiBHEt_3$	-	-	THF	2 h30	0[a]

[a] starting material recovered. [b] rt.

Conclusion

Although great optimization is still required, we have developed the first example of ring-opening reaction of an oxabicyclic alkene with hydride. The methodology was useful to access 1,2-dihydronaphthalene and its ring contraction by iodine(III) gave an indane.

Acknowledgements

FAPESP, CNPq and CAPES for financial support.

[1] Lautens, M.; Renaud, J.; Hiebert, S. *J. Am. Chem. Soc.* **2000**, *122*, 1804. [2] Arrayás, R. G.; Cabrera, S.; Carretero, J. C. *Synthesis* **2006**, 1205. [3] Lu, Z.; Wang, J.; Han, B.; Li, S.; Zhou, Y.; Fan, B.; *Adv. Synth. Catal*. **2015**, *357*, 3121. [4] Lautens, M.; Fagnou, K.; Taylor, M. *Org. Lett*. **2000**, *2*, 1677. [5] Siqueira, F. A. et al. *J. Braz. Chem. Soc*. **2011**, *22*, 1795.