Zn-Catalyzed Direct Synthesis of 3-Iodo-1,3-dienes from α-Allenols

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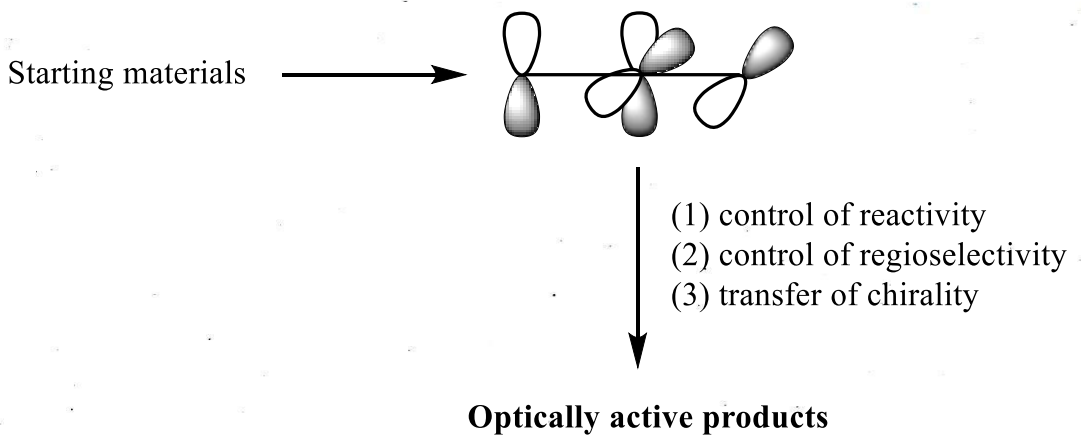
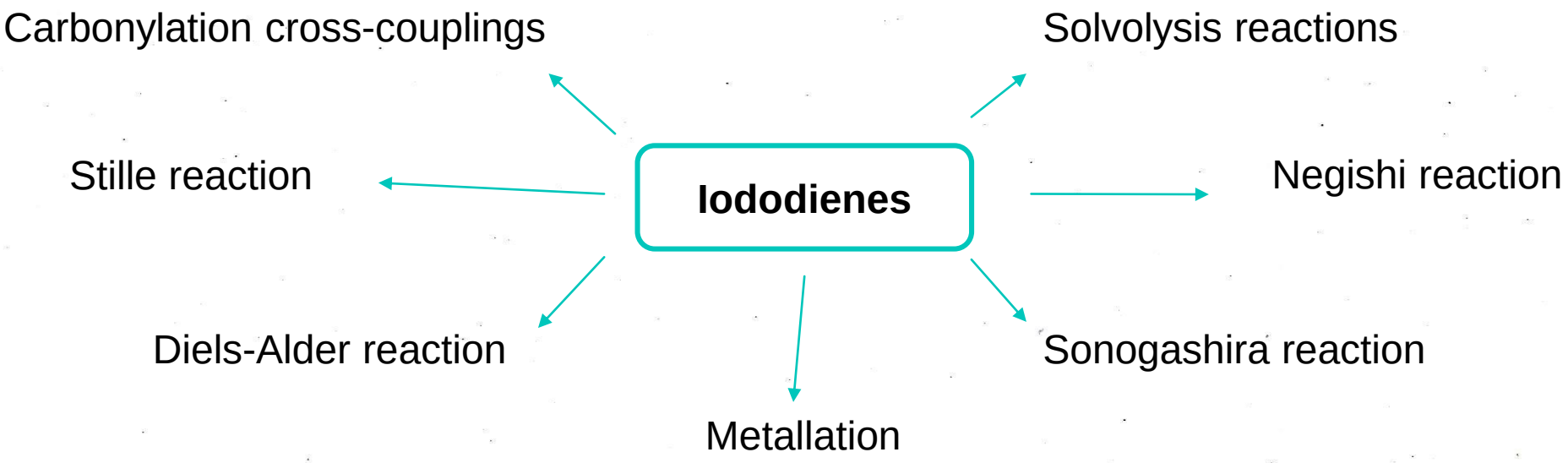
Introduction

In recent years, chemistry of these compounds has attracted the attention of many chemists giving rise to many studies due to the presence of a cumulated diene in the structure of the compound.
Among most important properties of the allenes include:



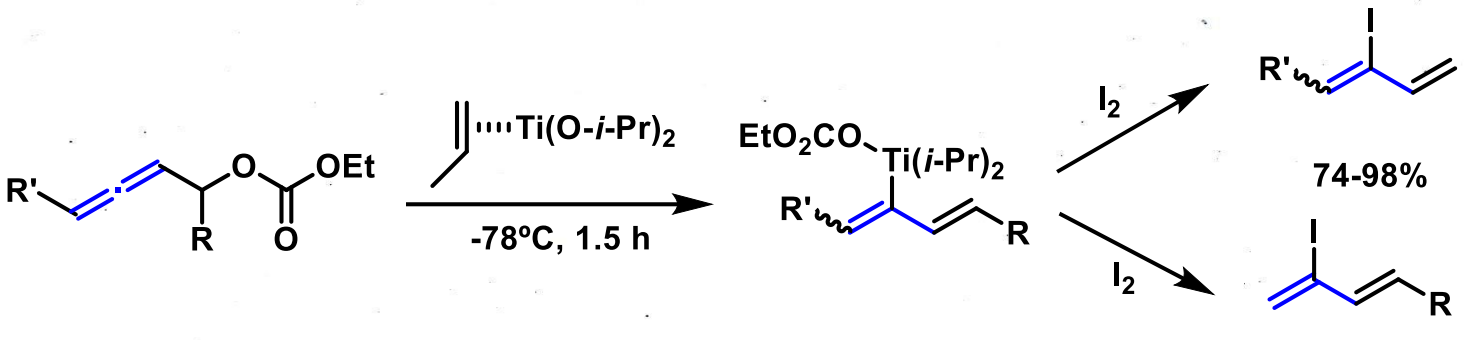
Introduction

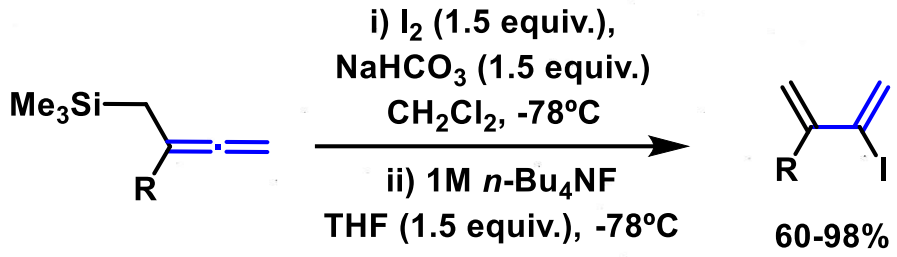
Iododienes are interesting species for the organic chemistry because of their wide reactivity applications. These compounds are intermediates of many reactions as Diels-Alder reactions, palladium-catalyzed reactions such as Stille, Negishi, and Sonogashira and carbonylation cross-couplings, and solvolysis reactions and metalation.



Introduction

Previous reports on the synthesis of iododienes from allenes





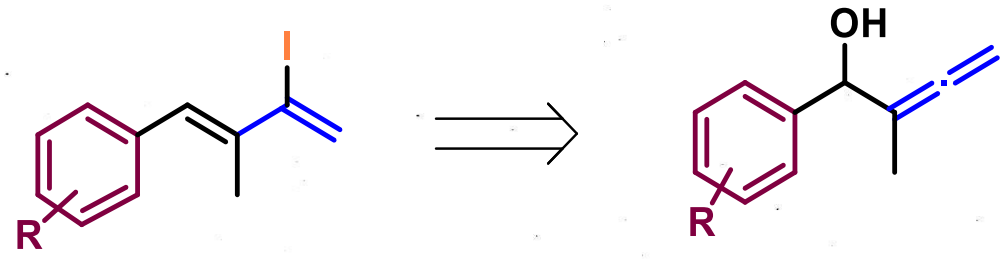
Okamoto et al. described the oxidant addition of (η^2-propene)Ti(O-i-Pr)$_2$ to α-allenyl carbonates to form titanium compounds that by reacting them with molecular iodine they obtained 2-iodo-1,3-dienes.

Nishimaya et al. observed the obtaining of 2-iodo-1,3-butadiene by treatment of 1-trimethylsilyl-2,3-butadiene with I_2 and tetra-n-butylammonium fluoride (TBAF).

Okamoto, S.; Sato, H.; Sato, F. *Tetrahedrom Lett.*, **1996**, *37*, 8865. Nishiyama, T.; Esumi, T.; Iwabuchi, Y.; Irie, H.; Hatakeyama, S. *Tetrahedrom lett.*, **1998**, *39*, 43.

Objetive

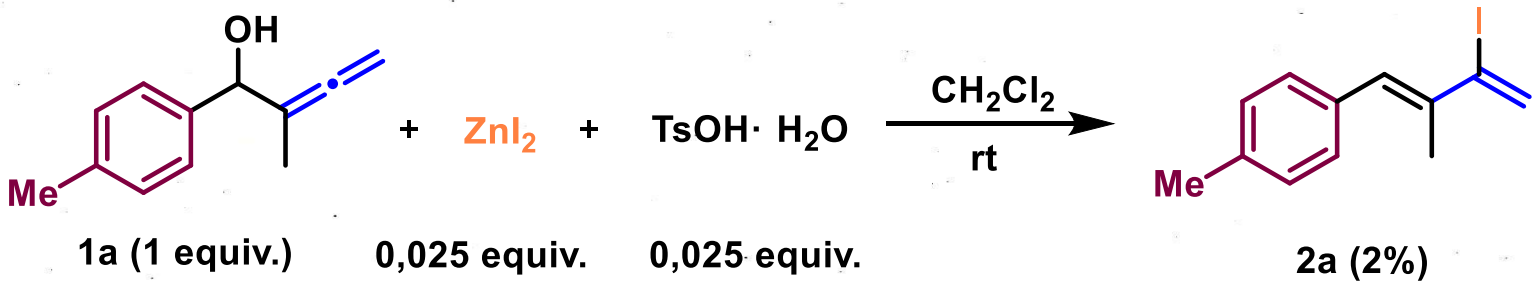
The main aim of this project is the development of a new synthetic method that allows to obtain 3-iodo-1,3-dienes directly from α-allenols through a sustainable process.



3-iodo-1,3-diene **α-allenol**

Results and Discussion

Allenol **1a** was selected as model substrate. Initial experiments were performed though the reaction of **1a** with ZnI_2 and *p*-toluenesulfonic acid monohydrate in dichloromethane which provided the 3-iodo-1,3-diene **2a** as the only reaction product.

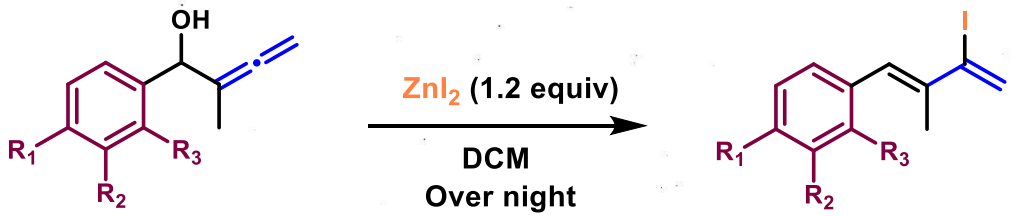


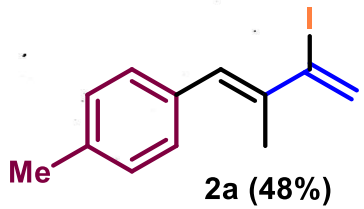
Entry	ZnI_2 (equiv.)	TsOH H_2O (equiv.)	Yield (%)
1	0.025	0.025	2
2	0.1	0.1	33
3	1.2	0.1	37
4	**1.2**	**-**	**48**

The yield was very low and the reaction was optimized conditions were optimized (see Table) . The highest yield of the product was achieved by employing 1.2 equiv. of ZnI_2 at room temperature in dichloromethane wihtout the presence of *p*-toluenesulfonic acid.

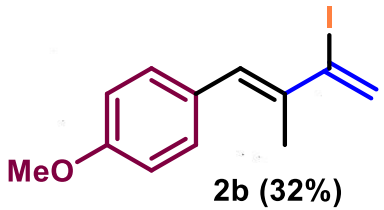
Results and Discussion

The scope of the reaction was explored in different α-allenols giving rise to the corresponding 3-iodo-1,3-dienes **2a-h** in reasonable yields (22−69%) and good (*E*)-diastereoselectivity.

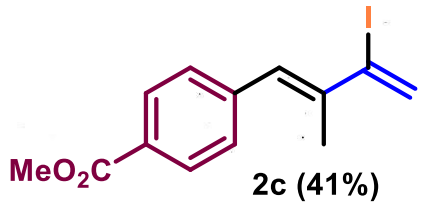




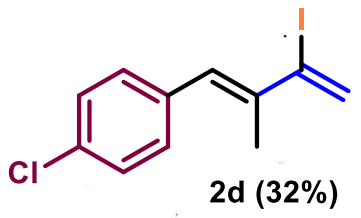
2a (48%)



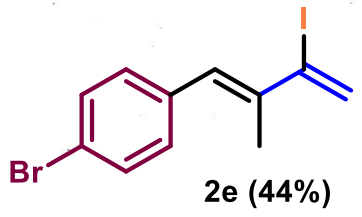
2b (32%)



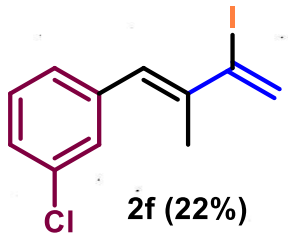
2c (41%)



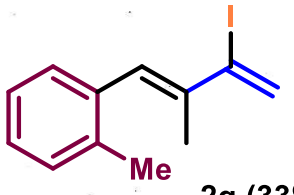
2d (32%)



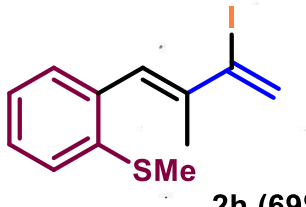
2e (44%)



2f (22%)



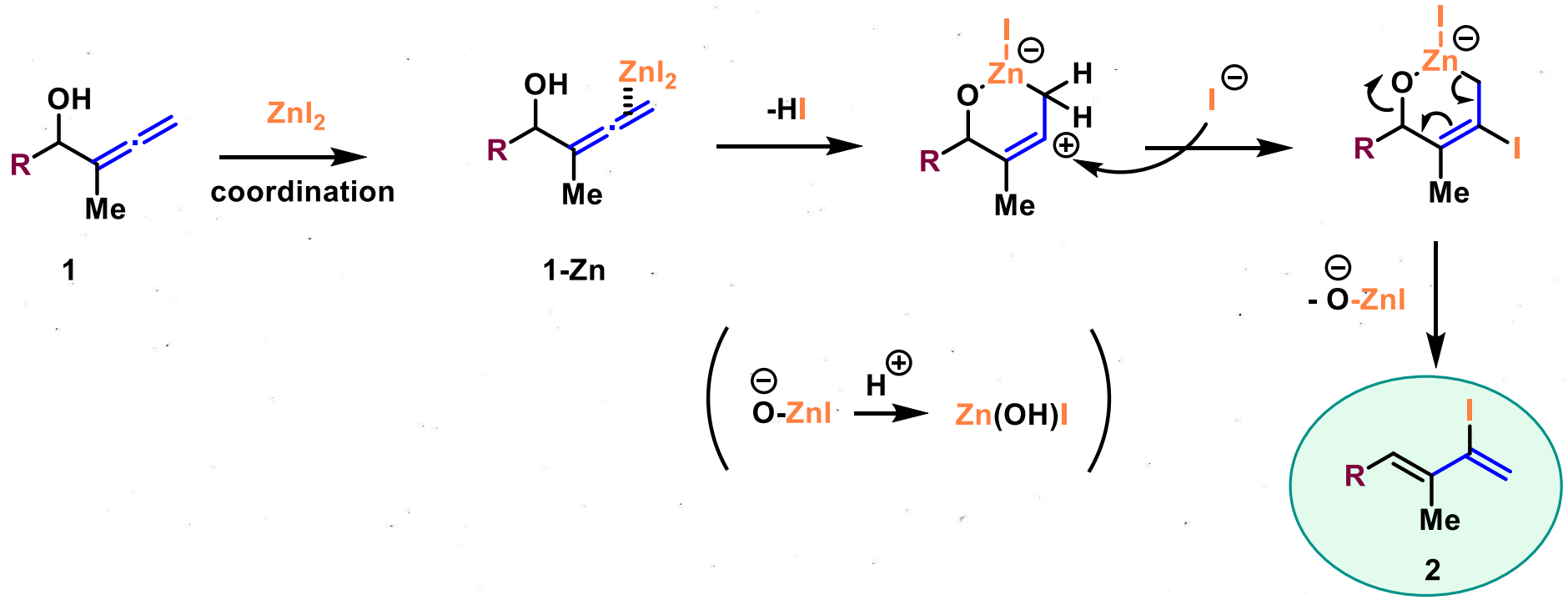
2g (33%)



2h (69%)

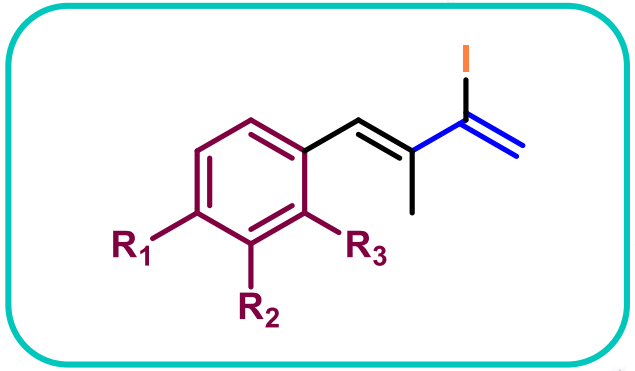
Results and Discussion

Possible pathway for the generation of 3-iodo-1,3-dienes **2** from α-allenols **1**.



Conclusions

In conclusion, we present here the regiocontrolled synthesis of 3-iodo-1,3-dienes, directly from α-allenols through a sustainable process using zinc (II) derivatives as metallic promoter.



Acknowledgements:

Members of the research group:

Beatriz Peñín
Prof. Teresa Martínez del Campo
Prof. Pedro Almendros

Support for this work by AEI (MICIU) and FEDER (Project PGC2018-095025-B-I00).