The Rearrangement of Oxonium Ylides through the 1,4-hydride abstraction

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Abstract

Oxonium ylides are a class of dipolar molecules that contain a negatively charged carbon atom connected to a positively charged oxygen atom. These molecules may undergo one of two well-known types of rearrangements: the [1,2]- Steven's and the [2,3]-sigmatropic rearrangements. Rh(II) catalyzed oxonium ylide generation of chromone diazoacetoacetate tetrahydro-4-pyranones affords methyl chromones in up to 70% yield. These results suggest a new pathway for the rearrangement of oxonium ylides. We believe this pathway is the [1,4]-hydride abstraction process.

Background

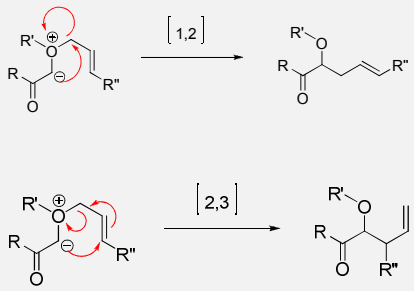


Figure 1. The [1,2]- Steven's and the [2,3] sigmatropic rearrangements.

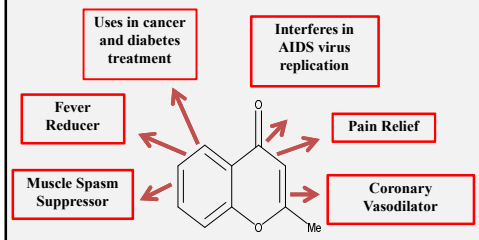


Figure 2. Biological applications of methyl chromone.

Results

The *Mukaiyama Michael Addition Reaction*

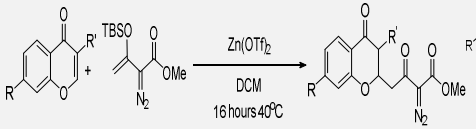
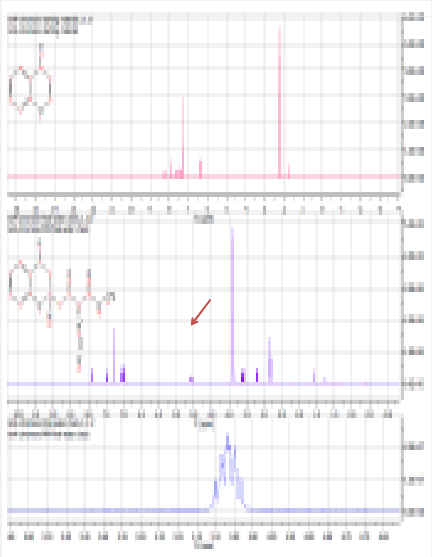


Table 1. Yields from the Mukaiyama Michael Addition Reaction.

Substrate	%Yield
chromone	96
6-bromochromone	99
3-bromo-4H-chromen-4-one	78.1



Scheme 1. ^1H-NMR of the MukaiyamaMichael Addition Reaction for the Chromone substrate.

The Decomposition Reaction

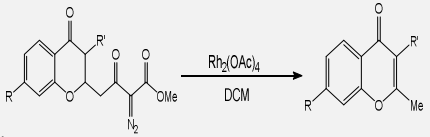
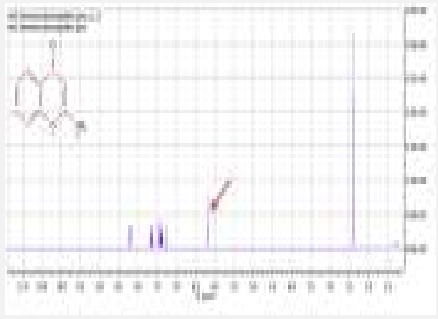


Table 2. Yields from the Decomposition Reaction.

Substrate	%Yield
Chromone diazoacetoacetate	70
6-bromochromone diazoacetoacetate	51.5



Scheme 2. ^1H-NMR of the Decomposition Reaction for the Chromone diazoacetoacetate substrate.

Figure 3. Images of the Mukaiyama Michael Reaction (left) and the Decomposition Reaction (right).

Conclusion/Future Plans

- The results show the methyl chromones form through the [1,4]-hydride abstraction.
- Yields must be improved for the substrates used in the decomposition reactions.
- The reaction scope will be expanded.

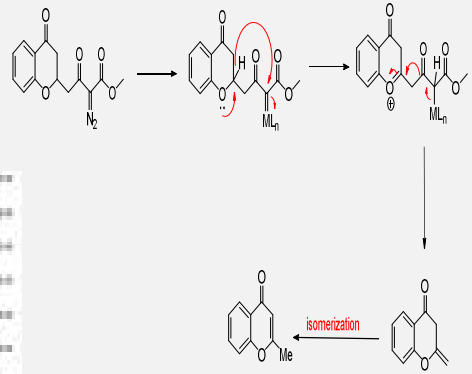


Figure 4. The [1,4]- hydride abstraction mechanism.

References

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Acknowledgements

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