



# An experimental and theoretical study of the cycloaddition reactions of carbomethoxy-*para*-benzoquinones with 6,6-dimethyl-fulvene

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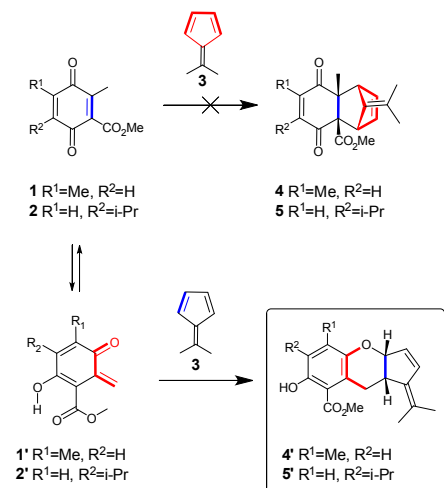
## INTRODUCTION

The Diels-Alder reactions of non-symmetric *para*-benzoquinones with simple dienes can furnish promising intermediates for the synthesis of bioactive natural products<sup>1</sup>. We now present our results on the Diels-Alder reactions of 6,6-dimethyl-fulvene and carbomethoxy-substituted *para*-benzoquinones. DFT calculations were also performed for the reactions reported herein.

## RESULTS AND DISCUSSION

Our study began with the reactions between the carbomethoxy-*para*-benzoquinones (**1** and **2**) and 6,6-dimethyl-fulvene (**3**), in DCM at room temperature, for 24 hours (Table 1). Surprisingly, we have observed, for both reactions, the formation of single cycloadducts, which arise from the hetero Diels-Alder reaction of the *para*-benzoquinone tautomers (**1'** and **2'**) with **3**. We do not observe the formation of cycloadducts **4** and **5**, which could have been formed by the direct Diels-Alder reaction (Scheme 1).

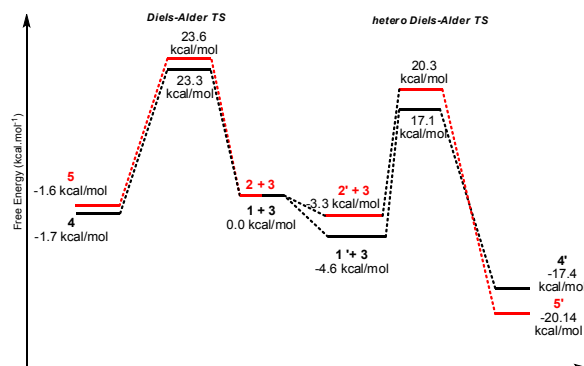
**Scheme 1.** Cycloaddition reactions of 6,6-dimethyl-fulvene (**3**) with carbomethoxy-*para*-benzoquinones (**1** and **2**).



**Table 1.** Diels-Alder reactions of dienophiles **1'** and **2'** with **3**

Entry	Dienophile	Product	Yield (%)
1	<b>1'</b>	<b>4'</b>	80
2	<b>2'</b>	<b>5'</b>	72

Gas-phase DFT calculations at the M062x/cc-pvdz level of theory were employed in order to compare the energetics of both pathways shown above. The activation energies and relative stabilities of the cycloadducts were evaluated (Figure 1).



**Figure 1.** Reaction profiles for the cycloaddition reactions. Free energies in kcal.mol<sup>-1</sup>.

## CONCLUSION

The observed experimental outcome for these reactions is in good agreement with our theoretical calculations, as the hetero Diels-Alder pathway involving the *para*-benzoquinone tautomers (**1'** and **2'**, with internal hydrogen bonding) shows lower activation energy barriers, and the more stable cycloadducts.

## ACKNOWLEDGEMENTS

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## REFERENCES

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