The Diels-Alder reactions of carbomethoxy-*p*-benzoquinones with simple dienes

Maria Carolina Donatoni, Timothy John Brocksom*, Marciana P. Uliana and Kleber T. de Oliveira

Universidade Federal de São Carlos, Chemistry Department, São Carlos-SP, 13565-905, Brazil.

**brocksom@terra.com.br*

Keywords: Diels-Alder, carbomethoxy-p-benzoquinones, microwaves

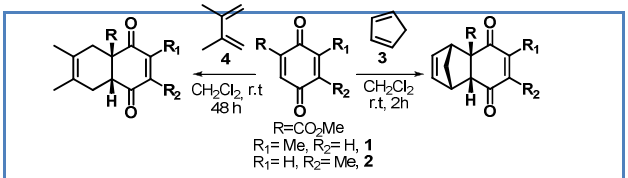
INTRODUCTION

The Diels-Alder reactions of *p*-benzoquinones and derivatives with simple dienes provide functionalized cycloadducts that can be employed in the synthesis of bioactive terpenes.[1-3] We now present our results on the Diels-Alder reactions of carbomethoxy-*p*-benzoquinones with simple dienes, performed at room temperature, with Lewis acid catalysis, and with microwave irradiation.

RESULTS AND DISCUSSION

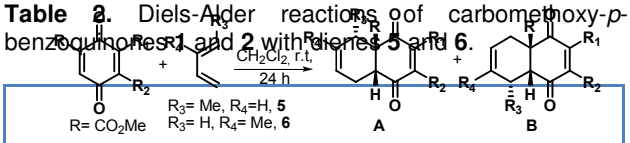
We have studied the Diels-Alder reactions of 2-carbomethoxy-6- and -5-methyl-*p*-benzoquinones (**1** and **2** respectively) with cyclopentadiene (**3**) and 2,3-dimethyl-1,3-butadiene (**4**) (Table 1), and with *trans*-piperylene (**5**) and isoprene (**6**) (Table 2).

Table 1. Diels-Alder reactions of carbomethoxy-*p*-benzoquinones **1** and **2** with dienes **3** and **4**.



Entry	R_1	R_2	diene	Yield (%)
1	Me	H	**3**	92
2	Me	H	**4**	71
3	H	Me	**3**	89
4	H	Me	**4**	70

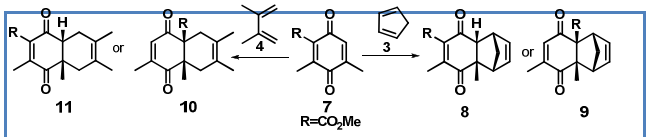
Table 2. Diels-Alder reactions of carbomethoxy-*p*-benzoquinones **1** and **2** with dienes **5** and **6**.



Entry	R_1	R_2	R_3	R_4	A: B ratio	Yield (%)
1	Me	H	Me	H	14:1	75
2	Me	H	H	Me	B	76
3	H	Me	Me	H	2:1	70
4	H	Me	H	Me	5:1	79

We have also studied the Diels-Alder reactions of 2-carbomethoxy-3,5-dimethyl-*p*-benzoquinone (**7**) with dienes **3** and **4** (Table 3).

Table 3. Diels-Alder reactions of carbomethoxy-*p*-benzoquinone **7** with dienes **3** and **4**.



Entry	Conditions	diene	product	Yield (%)
1	A	**3**	**8**	80
3	B	**3**	**9**	22
4	A	**4**	NR	NR
5	B	**4**	**10**	64
6	C	**4**	**11**	12
7	D	**4**	**11**	31

A: CH_2Cl_2, r.t, 96 h; **B**: CH_2Cl_2, $SnCl_4$ (10 mol%), -90ºC to r.t,1h; **C**: CH_2Cl_2, Microwave, 2 h, 140 ºC; **D**: CH_2Cl_2, Microwave, 2h, 160 ºC. NR= No reaction.

CONCLUSION

The Diels-Alder reactions of dienophiles **1** and **2** show high chemoselectivity for the carbomethoxy substituted double bond. The Diels-Alder reactions of *p*-benzoquinone **7** with dienes **3** and **4** show variable chemoselectivity, depending upon the reaction conditions. We suggest a methyl group non-bonded interaction with the carbomethoxy group to explain this chemoselectivity difference.

ACKNOWLEDGEMENTS

The authors thank FAPESP, CNPq and CAPES for financial support and fellowship.

REFERENCES

[1] Brocksom, T. J.; et. al. "Diels-Alder Reactions in the Synthesis of Higher Terpenes," in *Organic Synthesis: Theory and Applications*, T. Hudlicky (ed). JAI/Elsevier, Vol. 5, 39-87, 2001.

[2] Brocksom, T. J.; Brocksom, U.; Nakamura, J.; Ferreira, M. L. *J. Braz. Chem. Soc.* **2001**, *12*, 597.

[3] Brocksom, T. J.; Donatoni, M. C.; Uliana, M. P.; Vieira, Y. W.; *Quim. Nova*, **2010**, *33*, 2211.