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Reaction of masked *o*-benzoquinones towards dienophiles with inverse electronic demand. Enol and thioenol ethers as dienophiles

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Abstract

The Diels–Alder reaction of masked *o*-benzoquinones and electron-rich dienophiles such as enol ethers and thioenol ethers is described.

Keywords: Diels–Alder; *o*-benzoquinones; enol ethers; thioenol ethers; bicyclo[2.2.2]octenones.

Recently, Liao et al. have reported a facile Diels–Alder reaction of furans and masked *o*-benzoquinones in which the heterocyclic nucleus acts as a dienophile.[1] Therefore, in this case the furan nucleus acts as an enol ether in a Diels–Alder process with inverse electronic demand. In a series of interesting papers, Liao et al. showed that this kind of masked benzoquinone, easily prepared from the related catechols with (diacetoxy)iodobenzene,[2] reacts with several electron deficient dienophiles such as cyclopentadiene,[3] vinylketones,[4] acrylates[5] and also in intramolecular Diels–Alder processes.[6] The results have been recently rationalised in terms of the FMO theory[7] and the synthetic utility of the resulted bicyclo[2.2.2]octenones has also been demonstrated.[8]

However, the behaviour of these quinones in a Diels–Alder reaction with inverse electronic demand, as expected from the behaviour of the furan derivatives, has not been considered with the relative exception of the isolated case of the reaction of vinylacetate and quinone **1a** (Fig. 1).[2]

In our hands, quinones **1** react with enol and thioenol ethers giving the cycloadducts as single diastereoisomers in acceptable yields (Table 1). In several cases the dimeric structure **2** has also been isolated.

The stereochemistry of the cycloaddition was established according to the observed NOE effect (4%) between the vinylic hydrogen H-6 and the methylenic hydrogen H-9 in the carbon not directly attached to the oxygen.

The regiochemistry of the cycloaddition is the same as that previously observed in the case of the reaction of **1a** and vinylacetate[2] and was determined by ^1H–^1H decoupling NMR experiments. This assignment was corroborated by catalytic hydrogenation (H_2/Pd–C 10%, MeOH, 30 psi, 100%) of the

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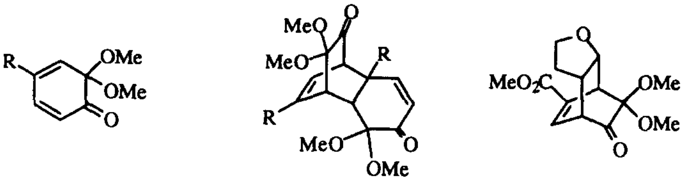


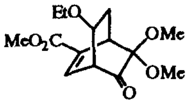
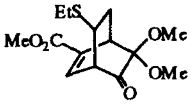
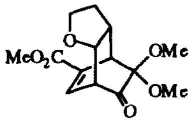
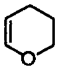
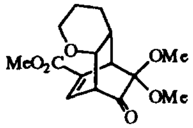
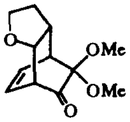
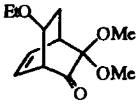
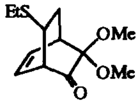
1a, R= CO$_2$Me
1b, R= H

2

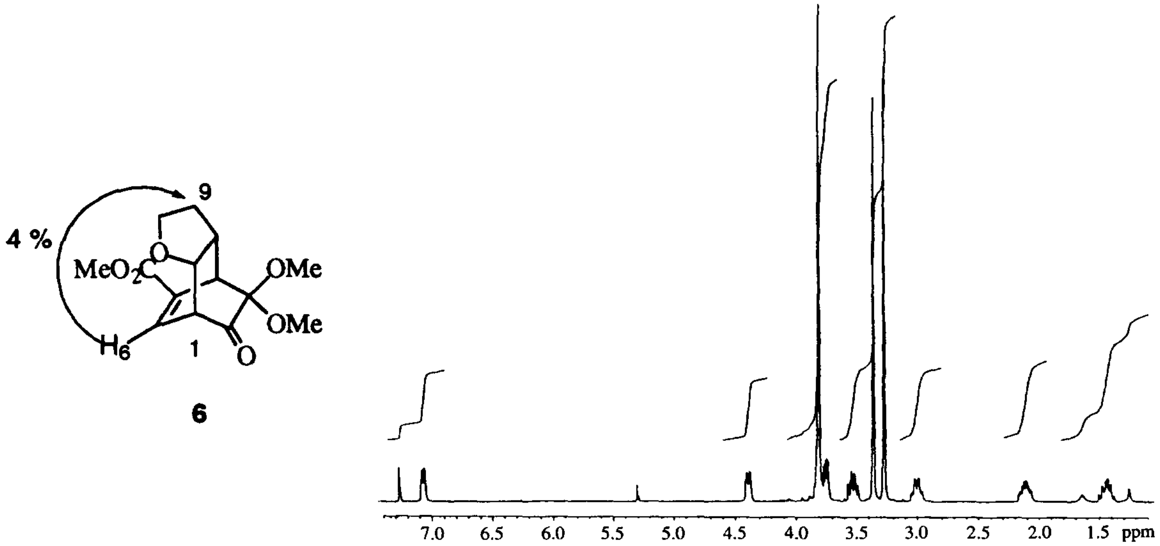
3

Figure 1.

Table 1
Reaction of masked *o*-benzoquinones **1** with enol and thioenolethers

Entry	Quinone	Dienophile	Adduct	Isolated yield
1	**1a**	CH$_2$=CHOEt		67 %[a] (**4**)
2	**1a**	CH$_2$=CHSEt		74 % (**5**)
3	**1a**			70 %[b] (**6**)
4	**1a**			53 % (**7**)
5	**1b**			21 %[c] (**8**)
6	**1b**	CH$_2$=CHOEt		48 %[d] (**9**)
7	**1b**	CH$_2$=CHSEt		82 %[e] (**10**)

[a] Recovered 18% starting catechol;
[b] Recovered 18% starting catechol;
[c] 52% dimeric **2b** has been isolated;
[d] 50% dimeric **2b** has been isolated;
[e] 12% dimeric **2b** has been isolated.



6

Figure 2.

cycloadduct of furan and **1a**, previously obtained by Liao et al.,[1a] and correlation of the spectroscopic data of the so-afforded compound **3** with its regioisomeric compound **6** (Fig. 2). It should be pointed out that compound **3** has the opposite regiochemistry to compound **6**.

In a typical experimental procedure, a mixture of 0.4 mmol of the starting catechol and 10 mmol of dienophile in 1.2 ml of MeOH was warmed to 50°C. When this temperature was reached, 1.2 mmol of (diacetoxy)iodobenzene in 3.6 ml of MeOH was added via a syringe pump over 1.5 h. The reaction mixture was stirred for 10 min and then the solvent was eliminated in vacuo. The crude product was chromatographed on SiO_2 using a mixture of hexane:EtOAc (10:1) as eluant.

In summary, in this paper we have shown that masked *o*-quinones react as diene components in Diels–Alder reactions with inverse electronic demand. The process constitutes an extension of this useful reaction from a synthetic point of view.

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