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$PhI(OAc)_2$ Oxidative Dearomatization of *o*-Methoxy-phenols. A Facile Preparation of *ortho-endo* bicyclo[2.2.2]octenones

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Dedicated to the memory of Prof. Dr. Armin De Meijere

Abstract

Diels-Alder cycloadditions of 6-allyl-2,2-dimethoxycyclohexa-3,5-dienones with dienophiles furnished functionalized *ortho-endo* bicyclo[2.2.2]octenones with absolute regio-and stereoselectivity. The competition between self-dimerization and cycloaddition with an external dienophile exists, but the retro-Diels-Alder/Diels-Alder sequence favors the formation of the cycloadducts.

Keywords

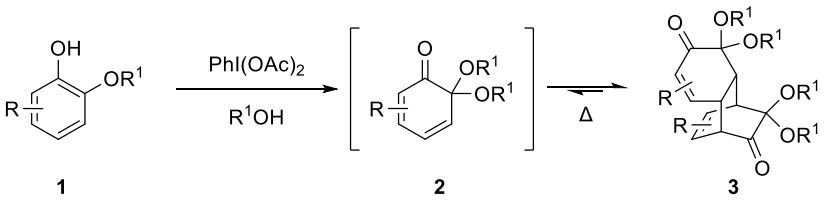
masked *o*-benzoquinones; Diels-Alder ; *o*-methoxyphenol ; (diacetoxy)iodobenzene oxidation

Introduction

It is widely recognized that Diels-Alder cycloadditions [1] are the most efficient pericyclic reactions for the construction of six-membered functionalized carbocyclic compounds in an atom-economical way. The reaction features the formation of two new *σ*-bonds at the expense of two *π*-bonds. A large variety of dienes and dienophiles, bearing various functional groups, can be used for the construction of many different types of ring structures. Although the reaction could yield several structural or stereoisomers, quite often one isomer is formed exclusively or at least in a preponderant amount.

Most Diels-Alder reactions involve a diene carrying electron-donating substituents and a dienophile bearing electron-withdrawing substituents. However, there is another

smaller group with inverse electron demand involving the reaction between an electron-deficient diene and an electron-rich dienophile. Masked *o*-benzoquinones (MOBs) [2-5], a synthetically useful class of cyclohexa-2,4-dienones, are a typical example of such reversed diene/dienophile reactivity. The main reason for this behavior is the presence of a 6-membered cyclic *s-cis* diene unit together with a conjugated carbonyl group at C-1 and a ketal group at C-6, forming a push-pull diene system. MOBs can be generated by *in situ* oxidation [6,7] of the readily available *o*-alkoxy phenols **1** using hypervalent iodine reagents in the presence of an alcohol (Scheme 1).

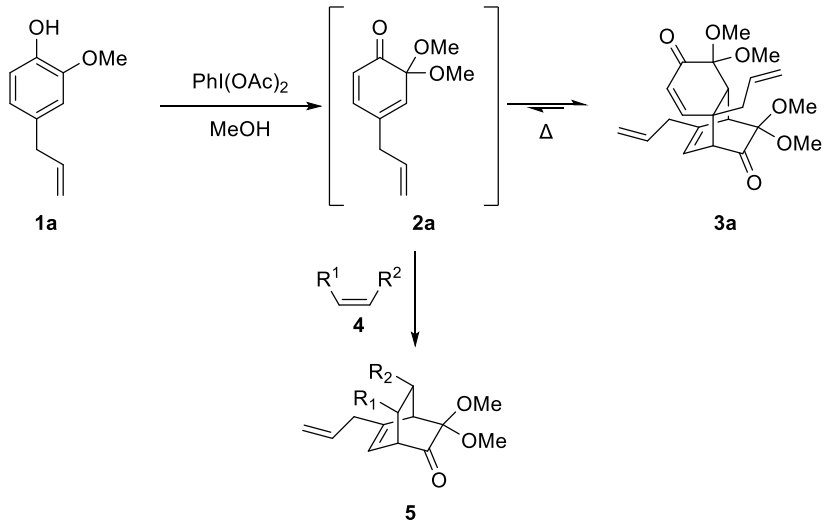


Scheme 1. Generation of 2,2-dialkoxycylohexa-3,5-dienones.

Alternatively, when the substituted 2,2-dialkoxycyclohexa-3,5-dienones **2** are too difficult to handle, due to their high propensity toward dimerization via self-cycloaddition, thermolysis [8,9] of dimer **3** might be a convenient source of MOBs **2**. Nevertheless, MOBs have been shown [10] to be efficient 4π components in inverse electron demand Diels-Alder reactions undergoing regio- and stereoselective cycloaddition with both electron-deficient and electron-rich dienophiles. The resulting bicyclo[2.2.2]octenone derivatives have been used as starting materials for the synthesis of different targets, including *cis*-decalins [11,12] and the triquinane ring system [13,14]. The same Diels-Alder processes were key steps in several complex natural product syntheses [5,15-17]. However, MOBs have been shown to also behave as dienophiles [11] in competitive Diels-Alder reactions with electron-rich dienes.

Results and Discussion

It is known that the oxidation of 4-allyl-2-methoxyphenol (**1a**) with (diacetoxy)iodobenzene in methanol (Scheme 2) affords 2,2-dimethoxycyclohexa-3,5-dienone **2a** [9] which dimerizes at room temperature to afford dimer **3a**, a natural product with interesting biological properties. However, performing this oxidation reaction in the presence of an excess of dienophile **4**, the desired cycloadduct **5** was isolated in moderate yields (Table 1). In all cases, the self-dimerization reaction of 2,2-dimethoxycyclohexa-3,5-dienone **2a** and the cycloaddition with the external dienophile are in competition with each other to a varying degree. The alternative approach, consisting of the retro-Diels-Alder reaction of dimer **3a** to generate dienone **2a** failed, since there is no substituent at C-1 carbon atom of the dimer. In contrast, the existence of a double bond adjacent to C-1 carbon atom permits this retro-Diels-Alder reaction to occur at much lower temperature.



Scheme 2. $PhI(OAc)_2$ oxidation of eugenol **1a**.

Cycloadduct **5a** was obtained as a single isomer, in 21% yield, when a solution of eugenol **1a** in methanol was slowly added to a solution of (diacetoxy)iodobenzene and styrene in methanol at room temperature; the resulting solution was refluxed for 24 h

(Table 1, entry 1). The reaction with *p*-methylstyrene was also considered. Dienone **2a**, generated by $PhI(OAc)_2$ oxidation of eugenol **1a**, reacts with *p*-methylstyrene under reflux to give cycloadduct **5b**, as a single diastereomer in 62% yield (Table 1, entry 2). Indene **4c**, with a *cis*-1,2-disubstituted double bond, is also suitable for this cycloaddition. Cycloadduct **5c** was obtained as a single diastereomer in 21% yield when a solution of eugenol **1a** in methanol was slowly added to a solution of (diacetoxy)iodobenzene and indene in methanol at room temperature; the resulting solution was stirred at room temperature for 72 h (Table 1, entry 3). 1-Buten-3-one (**4d**) was also considered for this cycloaddition. Quite surprising, cycloadduct **5d** was isolated as a single diastereomer in 77% yield, when a solution of eugenol **1a** in methanol was slowly added to a solution of (diacetoxy)iodobenzene and 1-buten-3-one (**4d**) in methanol at room temperature; the resulting solution was stirred at room temperature for 20 h (Table 1, entry 4). Similarly, methyl acrylate **4e** was reacted with *in situ* generated dienone **2a**. Cycloadduct **5e**, as a single diastereomer, was isolated in 50% yield after stirring the solution of dienone **2a** and methyl acrylate at room temperature for 22 h (Table 1, entry 5).

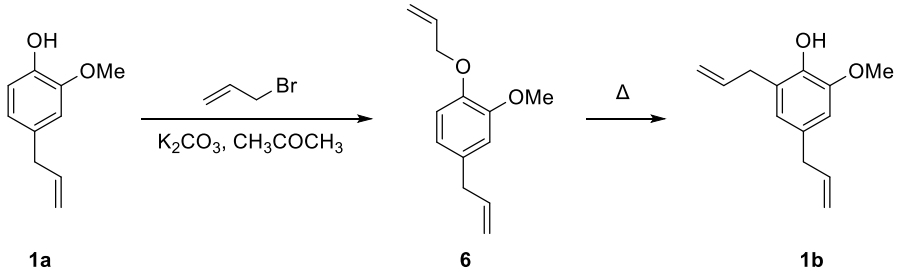
Table 1. $PhI(OAc)_2$ oxidation of eugenol.[a]

Entry	R^1	R^2	Method	Time (h)	Product	Yield (%)[b]
1	C_6H_5	H	B	24	**5a**	21
2	*p*-$CH_3C_6H_4$	H	B	20	**5b**	62
3		$C_6H_4CH_2$	A	72	**5c**	21

4	CH_3CO	H	A	20	**5d**	77
5	CH_3O_2C	H	A	22	**5e**	50

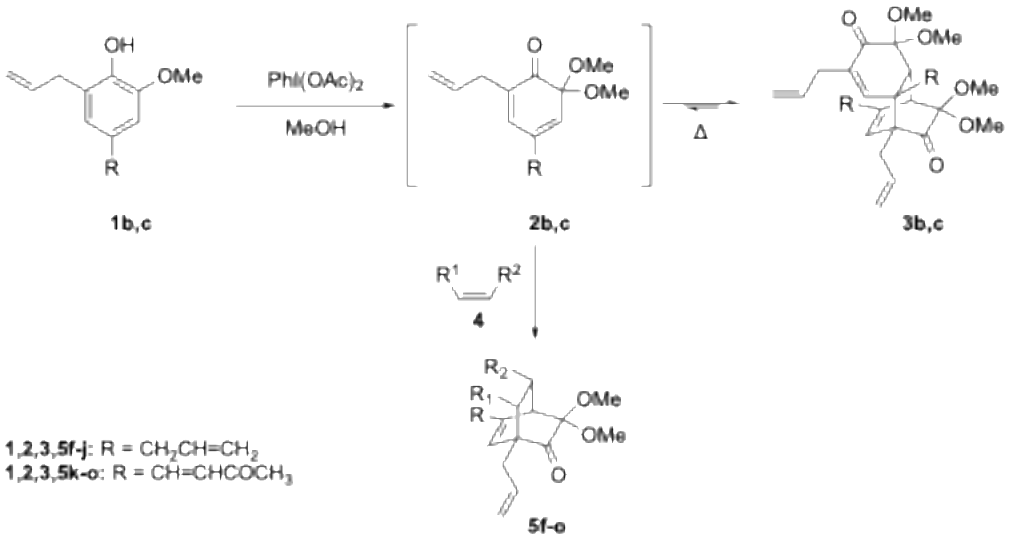
[a] All reactions were run via the slow addition of a solution of eugenol **1a** (1.52 – 2.07 mmol) in methanol (5 – 10 mL) to a solution of (diacetoxy)iodobenzene (1.80 – 2.67 mmol) and dienophile **4** (6.03 – 15.57 mmol) in methanol (10 mL) at room temperature and stirring the resulting mixture for the given time [Method A] or by the slow addition of a solution of eugenol **1a** (2.01 – 2.07 mmol) in methanol (10 mL) to a solution of (diacetoxy)iodobenzene (2.67 mmol) and dienophile **4** (14.22 – 15.57 mmol) in methanol (10 mL) at room temperature and refluxing the resulting mixture for the given time [Method B]. [b] Yield of isolated cycloadduct after flash column chromatography on silica gel.

Encouraged by the results obtained from the Diels-Alder reactions of dienone **2a** with olefinic dienophiles **4**, we became interested in introducing other appendages and functional groups at the C-6 position of the *o*-methoxy phenol core in order to generate highly functionalized bicyclo[2.2.2]oct-5-en-2-ones. Furthermore, the existence of an alkyl substituent at C-6 of eugenol could result in the isolation of the corresponding dimer bearing the alkyl group at C-1. In such a case, if this oxidative cycloaddition with an external dienophile is still sluggish, producing substantial amounts of the Diels-Alder dimer, the required dienone could be easily produced by the thermal retro-Diels-Alder reaction (~ 200 ºC) of the DA dimer. Eugenol was easily modified [18] upon reaction with allyl bromide and potassium carbonate resulting in ether **6**. Claisen rearrangement of ether **6** yields 2,4-diallyl-6-methoxyphenol (**1b**) (Scheme 3).



Scheme 3. Preparation of 2,4-diallyl-6-methoxyphenol (**1b**).

The oxidation of phenol **1b** with (diacetoxy)iodobenzene in methanol afforded dienone **2b** which dimerized at room temperature to afford dimer **3b** in 38% yield. Instead of isolating dienone **2b** in pure form, excess of an external dienophile was added, and the reaction was allowed to proceed at room temperature. The reaction was found to be sluggish, and it produced substantial amounts of the Diels-Alder dimer **3b** along with the desired cycloadduct **5** (Scheme 4).



Scheme 4. $PhI(OAc)_2$ oxidation of 2,4-diallyl-6-methoxyphenol (**1b**) and 6-allyl-dehydrozingerone **1c**.

To avoid such self-dimerization in the generation of dienone **2b**, the alternative retro-Diels-Alder/Diels-Alder sequence [8,9] was applied for the synthesis of cycloadducts. Thus, a mixture of *in situ* generated dimer **3b** with excess dienophile **4** in *o*-xylene was heated at 200 °C in a sealed test tube until the disappearance of the starting dimer (TLC monitoring). The bicyclo[2.2.2]octenones **5f-j** were isolated by flash column chromatography on silica gel in good yields (10-91%) (Table 2).

Table 2. $PhI(OAc)_2$ oxidation of 2,4-diallyl-6-methoxyphenol (**1b**).[a]

Entry	R^1	R^2	Method	Time (h)	Product	Yield (%)[b]

1	C_6H_5	H	A	18	**5f**	44
2	C_6H_5	H	B	20	**5f**	63
3	*p*-$CH_3C_6H_4$	H	A	18	**5g**	61
4	*p*-$CH_3C_6H_4$	H	B	18	**5g**	91
5	$C_6H_4CH_2$		A	18	**5h**	9
6	$C_6H_4CH_2$		B	18	**5h**	36
7	CH_3CO	H	A	18	**5i**	41
8	CH_3CO	H	B	17	**5i**	18
9	CH_3O_2C	H	A	18	**5j**	79
10	CH_3O_2C	H	B	18	**5j**	10

[a] All reactions were run via the slow addition of a solution of 2,4-diallyl-6-methoxyphenol (**1b**) (1.22 – 2.07 mmol) in methanol (5 – 10 mL) to a solution of (diacetoxy)iodobenzene (1.65 – 2.67 mmol) and dienophile **4** (11.73 – 15.27 mmol) in methanol (10 mL) at room temperature and stirring the resulting mixture for the given time [Method A] or by the slow addition of a solution of 2,4-diallyl-6-methoxyphenol (**1b**) (1.22 – 2.07 mmol) in methanol (10 mL) to a solution of (diacetoxy)iodobenzene (1.58 – 2.61 mmol). The solvent was evaporated under reduced pressure, a solution of dienophile **4** (7.85 – 11.62 mmol) in *o*-xylene (2 mL) was added and the resulting suspension was heated at 200 ^{o}C for the given time in a closed test tube with heavy walls [Method B]. [b] Yield of isolated cycloadduct after flash column chromatography on silica gel.

Cycloadduct **5f** was isolated, as a single diastereomer, in 44% yield when a solution of phenol **1b** in methanol was slowly added to a solution of (diacetoxy)iodobenzene and styrene in methanol at room temperature; the resulting solution was stirred at room

temperature for 18 h (Table 2, entry 1). An improved yield of 63% was observed when an *in situ* solution of dimer **3b** and excess styrene in *o*-xylene was heated, in a closed heavy-duty wall test tube, at 200 ^{o}C for 20 h (Table 2, entry 2). This improved yield could be easily explained by the fact that Diels-Alder reactions are accelerated by pressure [1], which was achieved by using the sealed tube. The reaction with *p*-methylstyrene, an electron-rich dienophile, was also considered. Cycloadduct **5g** was isolated in 61% yield when the reaction between phenol **1b** and (diacetoxy)iodobenzene in the presence of excess *p*-methylstyrene was run at room temperature for 18 h (Table 2, entry 3); however, a 91% yield of the same cycloadduct **5g**, as a single diastereomer, was obtained when a solution of dimer **3b** and excess of *p*-methylstyrene in *o*-xylene was heated at 200 ^{o}C for 18 h (Table 2, entry 4). This result is easily explained, since cycloadditions of masked *o*-benzoquinones are classified as inverse electron demand Diels-Alder reactions. Even if indene, a *cis* configurated dienophile, is expected to be less reactive due to steric hindrance from the two allyl groups, it reacts with dienone **2b** affording cycloadduct **5h** in only 9% yield (Table 2, entry 5). An improved yield of 36% of cycloadduct **5h** was attained when a solution of dimer **3b** and excess indene in *o*-xylene was heated at 200 ^{o}C for 18 h (Table 2, entry 6). Although methyl vinyl ketone is known as a good dienophile for a normal Diels-Alder cycloaddition, it leads to a 41% yield of cycloadduct **5i**, as a single diastereomer, when a solution of phenol **1b** in methanol was slowly added into a solution of (diacetoxy)iodobenzene and excess methyl vinyl ketone **4d** in methanol at room temperature; the resulting solution was stirred at room temperature for 18 h (Table 2, entry 7). Surprisingly, only a 18% yield of cycloadduct **5i** was isolated when a solution of dimer **3b** and excess methyl vinyl ketone **4d** in *o*-xylene was heated at 200 ^{o}C for 17 h (Table 2, entry 8). Similarly, methyl acrylate, a good dienophile for a normal Diels-Alder cycloaddition, afforded cycloadduct **5j** in 79% yield when the

reaction between phenol **1b** and (diacetoxy)iodobenzene in the presence of excess methyl acrylate was run at room temperature for 18 h (Table 2, entry 9); however, only a 10% yield of the same cycloadduct **5j**, as a single diastereomer, was isolated when a solution of dimer **3b** and excess methyl acrylate in *o*-xylene was heated at 200 ^{o}C for 18 h (Table 2, entry 10). Cycloadduct **5j** is stable under the reaction conditions, thus is not produced to a large extent under heating at 200 ^{o}C in a closed test tube with heavy walls. It seems that at this elevated temperature and pressure, the Diels-Alder cycloaddition of dienone **2b** behaves as expected for an inverse electron demand reaction while at room temperature the reactivity of dienone **2b** is so high that it reacts with electron-rich as well as electron-poor dienophiles.

Isoeugenol, a structural isomer of eugenol, is a vital precursor for flavours, and it is also prone to oxidation (Figure 1). Usually, isoeugenol oxidation refers to the oxidative cleavage of its propenyl double bond to produce vanillin, but it is also known to degrade into dimeric compounds (like oxyneolignans) and quinones, which are recognized as potent contact allergens. Dehydrozingerone (Figure 1), a structural analogue of isoeugenol, primarily functions through its potent antioxidant capacity, trapping radicals while undergoing oxidative dimerization to form symmetrical C–C linked dimers of significant scientific interest.

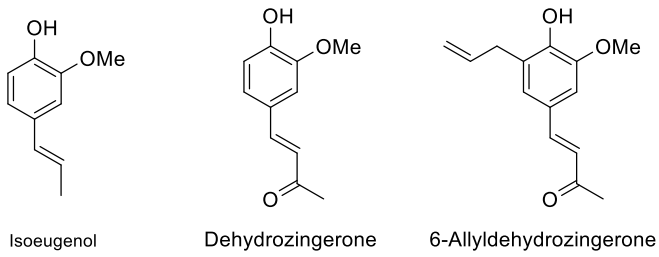
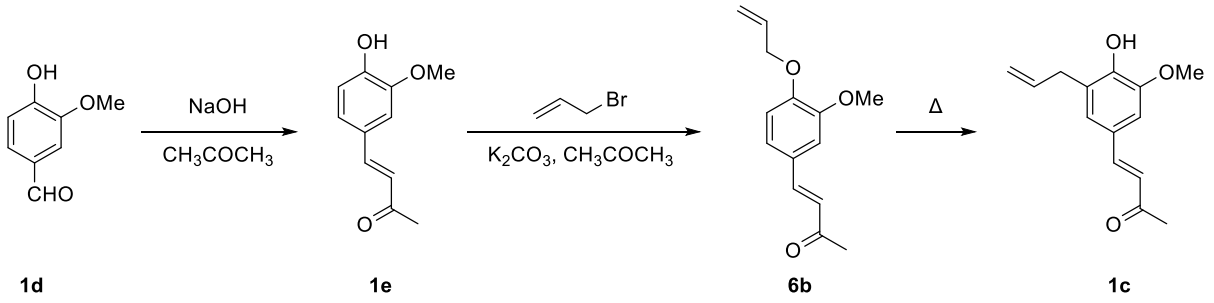


Figure 1. Structures of isoeugenol, dehydrozingerone, and 6-allyldehydrozingerone **1c**.

We initially examined the oxidation of isoeugenol with (diacetoxy)iodobenzene in methanol at room temperature in the presence of a large excess of an external dienophile. All attempts to detect the intermediary of a masked *o*-benzoquinone via the isolation of the corresponding dimer or the Diels-Alder cycloadduct failed. Presumably, a phenoxenium ion intermediate in its stabilized *p*-quinone methide form was generated [19]. To support this hypothesis, a shift to a less polar solvent, i.e. dichloromethane, led to the isolation of dehydrodiisoeugenol [20] from the (diacetoxy)iodobenzene oxidation of isoeugenol, presumably via the trapping of the phenoxenium ion intermediate by another isoeugenol molecule. On the other hand, the existence of a carbonyl group in the side chain, i.e. as in dehydrozingerone, permitted the isolation of the related masked *o*-benzoquinone [21] and its Diels-Alder cycloadditions with external dienophiles in moderate yields. Dehydrozingerone was easily prepared by the chemical modification of the aldehyde function of vanillin with acetone [22] and then converted into ether **6b** upon treatment with allyl bromide and potassium carbonate resulting in ether **6b** [18]. Claisen rearrangement of ether **6b** yields 6-allyl-dehydrozingerone **1c** (Scheme 5).



Scheme 5. Preparation of 6-allyl-dehydrozingerone (**1c**)

The oxidation of phenol **1c** with (diacetoxy)iodobenzene in methanol affords dienone **2c** which dimerized at room temperature to afford dimer **3c**. Instead of isolating dienone **2c** in pure form, an excess of an external dienophile was added, and the reaction was allowed to proceed at room temperature. The reaction was found to be

sluggish, and it produced substantial amounts of the Diels-Alder dimer **3c** along with the desired cycloadduct **5** (Scheme 4). To avoid such self-dimerization upon the generation of dienone **2c**, the alternative retro-Diels-Alder/Diels-Alder sequence [8,9] was applied for the synthesis of the desired cycloadducts. Thus, a mixture of *in situ* generated dimer **3c** with excess dienophile was heated at 200 ^{o}C in a sealed test tube until the disappearance of the starting dimer (TLC monitoring). The bicyclo[2.2.2]octenones **5k-o** were isolated by flash column chromatography on silica gel in moderate yields (up to 61%) (Table 3).

The reaction with styrene was first examined. Cycloadduct **5k** was isolated, as a single diastereomer, in 30% yield when a solution of phenol **1c** in methanol was slowly added to a solution of (diacetoxy)iodobenzene and styrene in methanol at room temperature; the resulting solution was stirred at room temperature for 18 h (Table 3, entry 1). A similar yield of 33% was isolated when an *in situ* solution of dimer **3c** and excess styrene was heated, in a closed heavy-duty wall test tube, at 200 ^{o}C for 0.5 h (Table 3, entry 2). The reaction with *p*-methylstyrene, an electron-rich dienophile, was examined next. A 50% yield of cycloadduct **5l** was observed when the reaction between phenol **1c** and (diacetoxy)iodobenzene in the presence of excess *p*-methylstyrene was run at room temperature for 18 h (Table 3, entry 3); however, the same cycloadduct **5l**, as a single diastereomer, was isolated in 61% yield when a solution of dimer **3c** and excess of *p*-methylstyrene in methanol was heated at 200 ^{o}C for 0.5 h (Table 3, entry 4). This result is easily explained since cycloadditions of masked *o*-benzoquinones are known as inverse electron demand Diels-Alder reactions. Even if indene, a *cis* configurated dienophile, is expected to be less reactive due to steric hindrance from the two substituents, it reacts with dienone **2c** affording cycloadduct **5m** in only 22% yield (Table 3, entry 5). An improved yield of 34% of cycloadduct **5m** was attained when a

solution of dimer **3c** and excess indene in methanol was heated at 200 ^{o}C for 0.33 h (Table 2, entry 6). Although methyl vinyl ketone is known as a good dienophile for a normal Diels-Alder cycloaddition, cycloadduct **5n** was not formed when a solution of phenol **1c** in methanol was slowly added to a solution of (diacetoxy)iodobenzene and excess methyl vinyl ketone **4d** in methanol at room temperature and the resulting solution was stirred at room temperature for 18 h (Table 3, entry 7). Cycloadduct **5n**, as a single diastereomer, was isolated in only 14% yield when a solution of dimer **3c** and excess methyl vinyl ketone **4d** in methanol was heated at 200 ^{o}C for 0.33 h (Table 3, entry 8). Similarly, methyl acrylate, a good dienophile for a normal Diels-Alder cycloaddition, afforded a 7% yield of cycloadduct **5o** when the reaction between phenol **1c** and (diacetoxy)iodobenzene in the presence of an excess of methyl acrylate was run at room temperature for 18 h (Table 3, entry 9); however, only a 29% yield of the same cycloadduct **5o**, as a single diastereomer, was obtained when a solution of dimer **3c** and excess methyl acrylate in methanol was heated at 200 ^{o}C for 0.5 h (Table 3, entry 10). In contrast to dienone **2b**, which reacts with electron-rich as well as electron-poor dienophiles, dienone **2c** reacts well only with electron-rich dienophiles as is expected for an inverse electron demand 4π component even at room temperature as well as at elevated temperature under pressure.

Table 3. PhI(OAc)$_2$ oxidation of 6-allyl-dehydrozingerone **1c**.[a]

Entry	R^1	R^2	Method	Time (h)	Product	Yield(%) [b]
1	C_6H_5	H	A	18	**5k**	30
2	C_6H_5	H	B	0.5	**5k**	33

3	*p*-$CH_3C_6H_4$	H	A	18	**5l**	50
4	*p*-$CH_3C_6H_4$	H	B	0.5	**5l**	61
5	$C_6H_4CH_2$		A	24	**5m**	22
6	$C_6H_4CH_2$		B	0.33	**5m**	34
7	CH_3CO	H	A	18	**5n**	0
8	CH_3CO	H	B	0.33	**5n**	14
9	CH_3O_2C	H	A	19	**5o**	7
10	CH_3O_2C	H	B	0.5	**5o**	29

[a] All reactions were run via the slow addition of a solution of 6-allyl-dehydrozingerone **1c** (0.90 – 1.55 mmol) in methanol (5 - 10 mL) to a solution of (diacetoxy)iodobenzene (1.30 – 2.08 mmol) and dienophile **4** (8.61 – 11.96 mmol) in methanol (10 mL) at room temperature and stirring the resulting mixture for the given time [Method A] or by the slow addition of a solution of 6-allyl-dehydrozingerone **1c** (1.08 – 1.85 mmol) in methanol (10 mL) to a solution of (diacetoxy)iodobenzene (1.37 – 2.39 mmol) and dienophile **4** (8.78 – 12.56 mmol) in methanol (10 mL), stirring the resulting mixture at room temperature for 18 h and then heating it at 200 ^oC for the given time [Method B]. [b] Yield of isolated cycloadduct after flash column chromatography on silica gel.

These Diels-Alder cycloadditions exhibit high regio- and stereoselectivity. There are four possible stereoisomers (Figure 2) as well as corresponding transition states but only one isomer is formed as the sole product. This extraordinary selectivity may be explained by invoking secondary orbital interactions. Competitive steric interactions developed at the *exo* transition state between the substituent of the dienophile and the dimethoxy acetal group on the ethano bridge of the masked *o*-benzoquinone can destabilize the *exo* approach (thermodynamic control), favoring the *endo* transition

state (kinetic control). The FMO model and *ab initio* calculations predict that the *ortho-endo* transition state (leading to isomer A) is more stable than the *meta-endo* transition state (leading to isomer C), where another steric interaction might develop between the substituent (X) of the dienophile and the 4-alkyl side chain (R) of the orthoquinone monoketal.

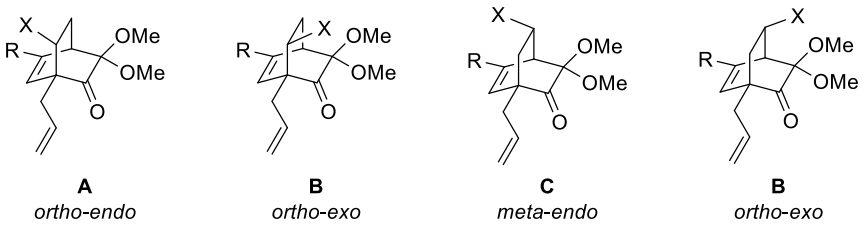


Figure 2. Structures of possible stereoisomers.

It is remarkable, that all these cycloaddition reactions proceed with absolute regio- and stereoselectivity, furnishing a single cycloadduct in most cases although a number of products are possible. While orthoquinone monoketals **2a,b** bear only one diene moiety that can act as a 4π Diels-Alder component, **2c** bears two distinct diene moieties (Figure 3).

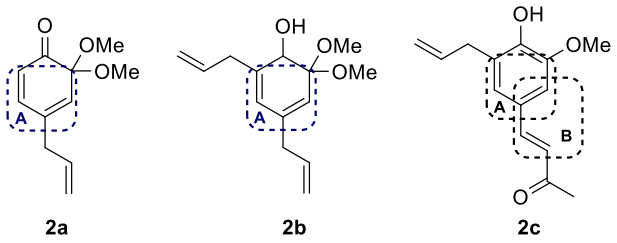


Figure 3. Possible *s-cis* diene moieties on orthoquinone monoketals **2**.

Nevertheless, in all cases examined where the orthoquinone monoketal behaved as a 4π Diels-Alder component, it always reacted via the internal diene subunit A. Apparently, the inner-ring *s-cis* diene subunit is more reactive than the inner-outer ring *s-cis* diene subunit since it leads to the more stable endocyclic olefinic cycloadducts.

Similarly, in all cases examined, when the orthoquinone monoketals behaved as a 2π Diels-Alder component, they always reacted as a dienophile with the C4–C5 double bond, despite the existence of the adjacent bulky dimethoxy acetal group. Apparently, the *cis* stereochemistry of the C4–C5 double bond permits the cycloadduct to take the *ortho-endo* configuration (kinetic control).

Conclusion

The Diels-Alder cycloadditions of 6-allyl substituted 2,2-dimethoxycyclohexa-3,5-dienones with various electron rich as well as electron-poor dienophiles have been studied. These reactions provide a facile entry to highly substituted bicyclo[2.2.2]oct-5-en-2-ones, albeit in competition to a varying degree with self-dimerization. It is remarkable that these Diels-Alder cycloadditions occur with absolute stereo- and regioselectivity. Further transformations of these products will bring diversity to highly substituted compounds of chemical and biological interest. It seems that the C-4 substituent on the phenol ring plays an important role on the reactivity. Clearly the inverse electron demand character of the dienone appears in the case of styrene dienophiles, introduction of an electron donating substituent such as a methyl group leads in an increase of the reaction yield. On the other hand, when the dienone bears a C-4 allyl substituent, the same Diels-Alder cycloaddition proceeds well at room temperature even if the dienophile bears electron accepting substituents. In contrast, when there is a C-4 but-3-en-2-one substituent, i.e. as in dehydrozingerone, the Diels-Alder cycloadditions with electron-poor dienophiles proceeds with moderate yields at higher temperatures.

In the absence of external dienophiles, the dienones usually undergo self-dimerization in an absolute regio- and stereoselective manner, with one dienone molecule acting as a diene the other as a dienophile. It may be concluded that the presence of an alkyl group, i.e. allyl, at the C-6 position of the dienone, permits the thermal retro-Diels-Alder of the corresponding dimer to occur (~ 200 ^{o}C), thus constituting an attractive alternative approach to the *in situ* generation of the dienone via direct oxidation of the *o*-methoxyphenol.

Supporting Information

Experimental procedures and spectroscopic data for all new compounds. Copies of 1H NMR and 13C NMR spectra for new compounds.

Supporting Information File 1: Experimental and analytical data

File Name: BJOC_Suppl_experimental

Supporting Information File 2: NMR Spectra

File Name: BJOC_Supporting_Spectra.

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Data Availability Statement

Data generated and analysed during this study are available from the corresponding author upon reasonable request.

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