

## Synthesis of Epoxy Derivatives Via Diels-Alder Reaction

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### Abstract

Isobenzofuran is used as a cyclic diene in Diels-Alder reaction with benzoquinone and substituted benzoquinones as dienophile to afford several epoxy derivatives.

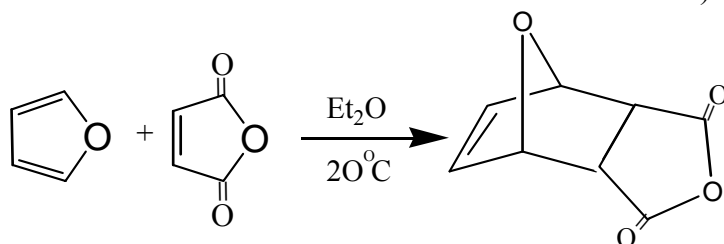
In the present paper the establishment of the structures of the new products is based on the physical properties and spectral data (IR, and  $^1\text{H-NMR}$ ).

### Introduction

Furan is less aromatic than pyrrole, hence, undergoes [4+2] cycloaddition reactions much more readily. It combines as a diene with

electron-poor <sup>(1)</sup>dienophiles to yield Diels-Alder-type adducts.

It reacts, for example, with maleic anhydride, at room temperature, and the only isolated adduct is the exo isomer (the more thermodynamically favored adduct):



Exo adduct

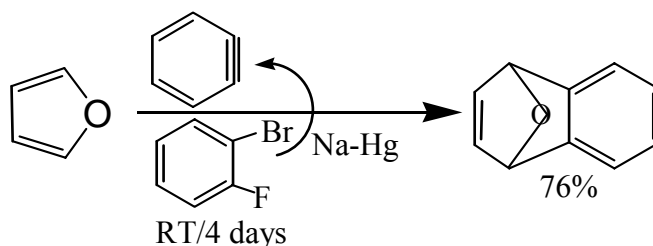
For many pairs of adducts, formed between dienophiles and cyclic dienes, the exo product has fewer steric interactions and is the more stable. In some cases, however, secondary electronic effects may overcome steric preferences so that the endo (kinetic

product) is favoured.  $\alpha,\beta$ -Unsaturated ketones (including quinones), aldehydes, and sulfones can be epoxidized with alkaline <sup>(2)</sup> $\text{H}_2\text{O}_2$ , but this is a nucleophilic addition, by a Michael-type mechanism, involving attack by  $\text{HOO}^-$  <sup>(3)</sup>.

Epoxides can also be prepared by treating olefins with oxygen or with an alkyl epoxide<sup>(4)</sup>, catalyzed by a complex of V or Mo. The reaction with oxygen, can also be carried out with a catalyst, is probably a free-radical process<sup>(5)</sup>.

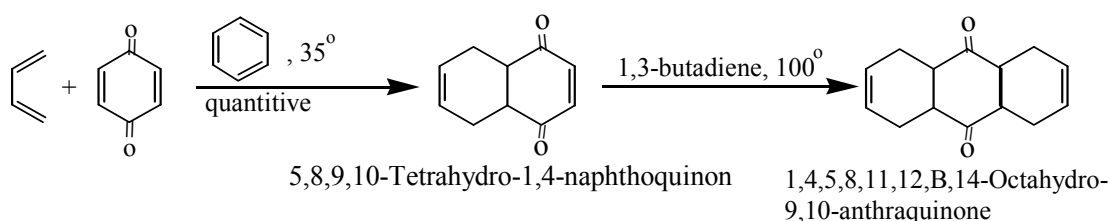
Benzo[b]furan<sup>(6)</sup> possess aromaticity of the hetrocycle which is weaker than that for indole.

Furan reacts with powerful dienophiles<sup>(7)</sup> like benzyne, to give Diels-Alder adducts. No reaction occurs, however, with slightly less reactive dienophiles like acrolein or methyl acrylate unless the furan in question is further activated, e.g. by the presence of a methoxyl group.



*p*-Benzoquinone is used extensively<sup>(8)</sup> in Diels-Alder reactions; two moles of diene can be used. The initial cycloaddition needs no more

energy and occurs readily, but the second mole needs heating as shown below:



Epoxy compounds play an important role in the industrial field, through its' uses in plastic, artificial rubber, adhesives and industrial fibers industries and a basic material in the preparation of anti-freeze materials<sup>(6)</sup>.

### Experimental

Instrumentation:

- 1- Melting points are measured on a kofler hot stage apparatus and are uncorrected
- 2- The IR spectra are recorded on a Pye-Unicam SP 1100 Infrared spectrophotometer.
- 3- The <sup>1</sup>H-NMR Spectra are registered at 60 MHz

Hitachi Perkin-Elmer Spectrometer using tetra methylsilane (TMS) as an internal standard and CDCl<sub>3</sub> as a solvent.

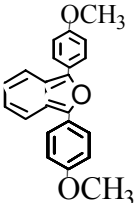
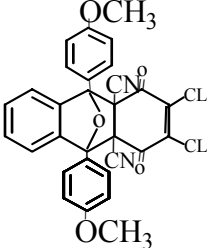
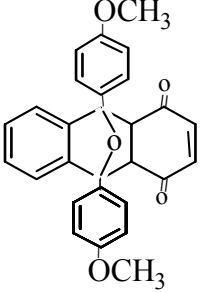
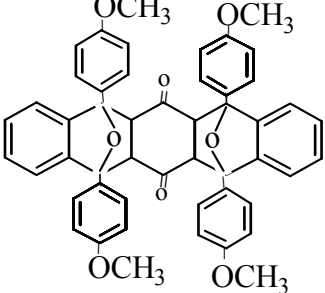
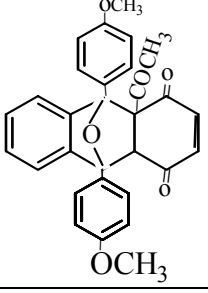
### Preparation of Substituted Isobenzofuran<sup>(9)</sup> (1)

In a 250 ml round- bottomed flask (0.0066 mole, 0.72ml) of orthophthldehydic acid (o.formyl benzoic acid) is stirred magnetically with (20) ml of 60% dilute sulfuric acid until the solution becomes clear. The reaction mixture is then cooled by ice- cold water to about 4°C, and (0.0066mole, 0.72ml) of anisole is added with continuous stirring (the end

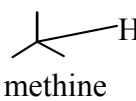
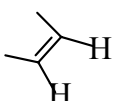
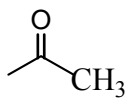
of the reaction is followed by TLC). After two hours about (200) ml ice-cold water is added and the mixture is stirred for five minutes, the precipitate is filtered and washed with water then by saturated solution of sodium

bicarbonate, the white precipitate is recrystallised from ethanol to produce the 1,3-Di-(4-methoxy phenyl) isobenzofuran (1), m.p.116-118°C (see Table-1).

**Table -1 Structure, names, and Some Physical Properties of Products (1, 2, 3, 4 and 5)**

Compd. NO.	Structure	Name	M.P. (°C)	Yield (%)	Recryst. from
1		1,3-Di-(p-methoxy phenyl) isobenzofuran	116-118	83	Ethanol
2		2,3-Dichloro-9,10-di-(p-methoxyphenyl)-13,14-dicyano-9,10-epoxy-1,4-anthraquinone	151-152	70	Petroleum ether(60-80)
3		9,10-Di-(p-methoxyphenyl)-13,14-dihydro-9,10-epoxy-1,4-anthraquinone	217-219	78	Petroleum ether(60-80)
4		Dibenzo[b-i]-5,7,12,14-(tetra-p-methoxyphenyl)-5,14,7,12-diepoxy-5a,6a,12a,13a-tetrahydro-6,13-naphthaquinone	194-195	60	Petroleum ether(60-80)
5		9,10-Di-(p-methoxyphenyl)-13-aceto-9,10-epoxy-1,4-(14H) naphthaquinone	126-128	85	Petroleum ether(60-80)

**Table-2 Spectral data of compounds (1, 2, 3, 4 and 5)**

Cpd. No.	IR(KBr), $\nu$ $\text{cm}^{-1}$			$^1\text{H-NMR}(\text{CDCl}_3)$ , $\delta$ ppm					
	C=O	C=C	C-O-C	 methine			OCH <sub>3</sub>	Ar-H and olefinic C-H	-OH Enol
1	---	1610	1040	---	---	---	---	---	---
2	1670	1600	1160 C $\equiv$ N 2260	---	---	---	3.8 6H,s	6.8-7.8 ,m	---
3	1720	1620	1120	1.4 2H,d	Seened with aromatic protons in case of keto form	---	3.8-3.9 6H,s	6.7-7.8 12H+2H,m	11.9 2H,d
4	1720	1620	1260 Epoxide - o-c str.	2.5 4H,d	---	---	3.2-4.2 12H,s	6.5-7.9 24H,m	---
5	1650	1590	1110	1.6 1H,s	Seened with aromatic protons in case of keto form	2.25 3H,s	3.85 6H,s	6.7-7.8 12H+2H,m	11.9 2H,d

**Diels-Alder reaction of compound (1) with benzoquinone and substituted benzoquinone:**

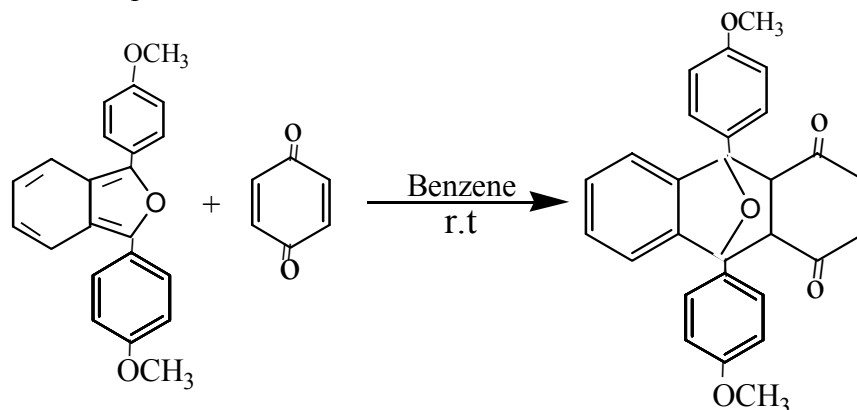
**General procedure<sup>(10)</sup>:**

By using equimolars of the reactants, one equivalent of 1, 4-benzoquinone or substituted 1, 4-benzoquinone is dissolved in dry ether and one equivalent of substituted isobenzofuran is added. The reaction mixture is left in the dark for (24) hours at room temperature. The solvent (ether) is evaporated under vacuum at about (40) °C. The product is recrystallised from petroleum ether (60-80) to get the pure precipitates (Table-1). The spectral methods (IR,  $^1\text{H-NMR}$ ) are used to confirm the structures of the afforded compounds (2, 3, 4 and 5) see Table -2.

**Note:**

In the case of compound number (4), two equivalents of substituted isobenzofuran (1) are used and the solvent used is refluxed acetone.

## General equation

**Preparation of 2-Acetyl-1,4-benzoquinone<sup>(10)</sup>**

Two grams of 2,5-dihydroxy acetophenone are stirred with (10)g of anhydrous sodium sulfate in addition to (5)g of silver oxide Ag<sub>2</sub>O (activated in oven for (1) hour at 100°C). stirring continued for (2-3) hours at room temperature after adding (50) ml of dry ether. The residues are filtered and the filtrate is evaporated to get a yellow orange solid, recrystallised from cyclohexane (m.p 56-57°C, yield 90 %.)

**Results and Discussion**

In agreement with the several published new researches it is decided to use cyclic diene such as substituted isobenzofuran which was prepared as mentioned<sup>(9)</sup> and 1,4-benzoquinone and substituted analogues as dienophiles via Diels-Alder reaction<sup>(10)</sup>

The structure of synthesized reactant (isobenzofuran) has been confirmed by spectral data (Table -2). The IR spectrum shows a strong band at (1610) cm<sup>-1</sup> related to the stretching vibration of the carbon- carbon double bond (ν C=C), whereas the ethereal C-O band appears<sup>(11)</sup> at (1040) cm<sup>-1</sup>

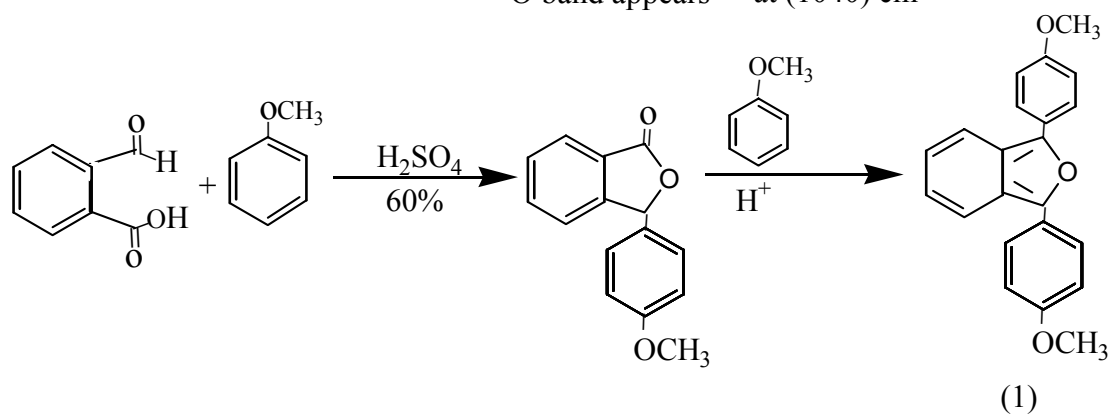
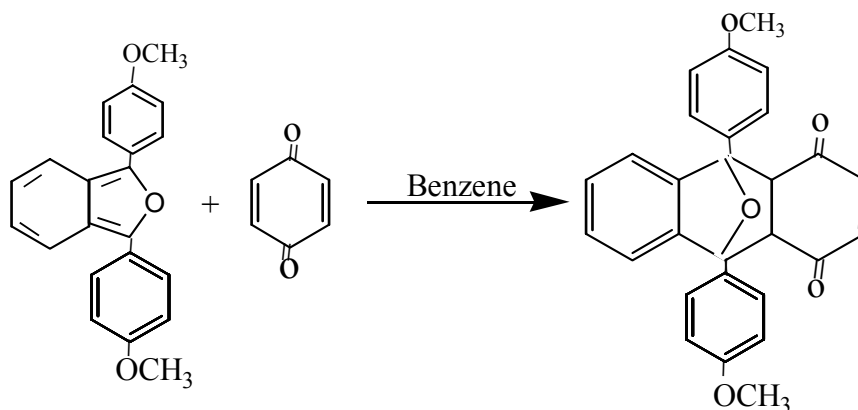


Table -1 illustrates some physical properties of substituted isobenzofuran as well as its structure and name.

The Diels-Alder adduct structures (2-5) are established according to spectroscopic evidence (Table-2).



The IR spectra of epoxy derivatives show a range<sup>(11)</sup> of (1720-1650)  $\text{cm}^{-1}$  which relates to both  $\alpha$ ,  $\beta$ -unsaturated and saturated carbonyl stretching vibration, while the stretching vibration of  $\text{C}=\text{C}$  seems in the range of (1620-1590)  $\text{cm}^{-1}$  which fits the range of conjugated olefins<sup>(11)</sup>, finally, the epoxide  $\text{C}-\text{O}$  stretching vibration lies in the range of (1260-1110)  $\text{cm}^{-1}$  which is in agreement with published values<sup>(11)</sup>.

For methine protons (Table-2) the  $^1\text{H-NMR}$  spectra<sup>(11,15)</sup> show a doublet signal at  $\delta(1.4)$  ppm for two protons and another doublet at  $\delta(2.5)$  ppm for two protons while the singlet signal at  $\delta(1.6)$  ppm for one proton relates to compounds 3, 4 and 5 respectively.

The olefinic protons in 3 and 5 are overlapped with the aromatic protons in the case of keto form but it seems clearly that the enol form is predominated due to the appearance of the two singlet at  $\delta(11.9)$  ppm for the two hydroxyl protons of each compound of 3 and 5.

The singlet signal at  $\delta(2.25)$  ppm is related to the three protons of the acetyl group of compound number 5.

The protons of methoxy groups in all products appear as a singlet signal and resonate at  $\delta(3.8-4.2)$  ppm, but the aromatic protons resonate at multiplet signals at the range of  $\delta(6.5-7.9)$  ppm for numbers 2, 3, 4 and 5 (Table-2).

Table-1 illustrates the melting points, structures and names of the new epoxy derivatives.

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