Reaction of 1,2-Benzoquinones with Enamines

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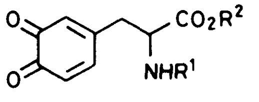
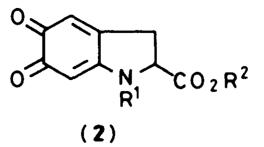
The reactions of 4-t-butyl-1,2-benzoquinone (**9a**), 4-methyl-1,2-benzoquinone (**9b**), and 1,2-benzoquinone (**9c**) with various enamines (**10**) and (**11**) are reported. Hydroxybenzodioxins (**13**) and (**14**) are isolated in most cases, and their conformational analyses are discussed. The reaction rates of 4-t-butyl-1,2-benzoquinone (**9a**) with the enamines (**10a**) and (**10b**) have been measured and an ionic mechanism is proposed.

Raper[1] and Harley-Mason[2] have suggested the intermediacy of three 1,2-benzoquinoid compounds, dopaquinone (**1**; $R^1 = R^2 = H$), dopachrome (**2**; $R^1 = R^2 = H$), and indole-5,6-quinone (**3**), during melanogenesis from dopa. These compounds which are very labile and easily polymerize into melanin have never been isolated or synthesized in spite of much work on 1,2-benzoquinones.[3]

Recently, we have reported that 2,3-disubstituted indoles such as tetrahydrocarbazole or 1,2,3,4-tetrahydrocyclopent[*b*]indole rapidly reacted with 1,2-benzoquinones to yield 1,4-benzodioxane derivatives.[4,5] Since these reactions were equivalent to the reaction of an enamine entity, it was of interest to study the trapping ability of enamines for 1,2-benzoquinones.

In the literature, Horspool *et al.*[6] reported that furans reacted at the enol ether functions with 1,2-benzoquinones such as *o*-chloranil to afford 1,4-benzodioxane derivatives (**4**), probably *via* a stepwise ionic [4 + 2] cycloaddition involving a zwitterionic intermediate such as (**5**). Recently, Dondoni *et al.* reported that whilst 2-(*N*-benzyl-*N*-methylamino)oxazole (**6a**) reacted with *o*-chloranil at the enol ether function to afford 1,4-benzodioxane derivatives (**7**), the corresponding de-amino derivative (**6b**) failed so to react even under forcing conditions; these results, they suggested, emphasized the importance of the electron-donating properties of dienophiles in the reaction of *o*-benzoquinones.[7] Enamines are aza analogues of enol ethers and, with an increased electron-donating capacity over furans, are expected to be a good trapping reagent for 1,2-benzoquinones. In spite of this, apart from the report by Reid and Torok who worked with stable 1,2-benzoquinones such as 9,10-phenanthrenequinone,[8] there are no literature reports of such reactions. We report here the reaction of labile 1,2-benzoquinones with enamines and the trapping ability of the latter.


(1)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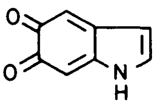
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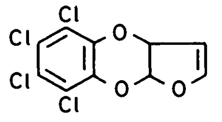
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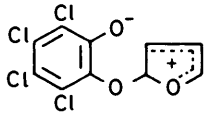
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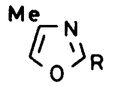
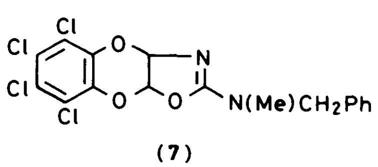
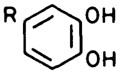
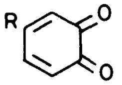

(6)
a; R = -N(Me)CH_2Ph
b; R = H


(7)

Results and Discussion

Reaction of 1,2-*Benzoquinones with Enamines*.—Pyrocatechols (**8**) were oxidized using cerium(IV) sulphate in a two-phase chloroform–sulphuric acid system to yield a red chloroform solution of the corresponding 1,2-benzoquinones (**9**). Since the labile nature of the latter necessitated rapid handling, the enamines (**10**) and (**11**) were added to the chloroform solution of


(8)
a; R = Bu^t
b; R = Me
c; R = H


(9)
a; R = Bu^t
b; R = Me
c; R = H


(10)
a; $R^1,R^2 = -NCH_2CH_2OCH_2CH_2$
b; $R^1,R^2 = -N[CH_2]_3CH_2$
c; $R^1,R^2 = -N[CH_2]_4CH_2$

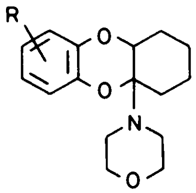

(11)
a; $R^1,R^2 = -NCH_2CH_2OCH_2CH_2$
b; $R^1,R^2 = -N[CH_2]_3CH_2$

Table 1. Reaction of the 1,2-benzoquinones (**9**) with the enamines (**10**) and (**11**)

1,2-Benzoquinones	Enamines	Products (yields %)[a]	M.p. (°C) [b.p. (°C)]	Solvent
(**9a**)	(**10a**)	(**12a**) (95)	138—139	Hexane
(**9a**)	(**10b**)	(**13a**) (52)	142—143	Hexane
(**9a**)	(**10c**)	(**13a**) (46)		
(**9a**)	(**11a**)	(**14**) (13)	58—59	Methanol
(**9a**)	(**11b**)	(**14**) (20)		
(**9b**)	(**10a**)	(**12b**) (33)	[122/10^{-4} Torr]	—
(**9b**)	(**10b**)	(**13b**) (17)	102—103	Methanol
(**9b**)	(**10c**)	(**13b**) (25)		
(**9c**)	(**10a**)	(**12c**) (11)	91—92	Hexane
(**9c**)	(**10b**)	(**13c**) (14)	47.5—49	Methanol
(**9c**)	(**10c**)	(**13c**) (12)		

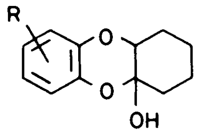
[a] The yields are those of the isolated products. [b] Bath temp.

1,2-benzoquinones without isolation; there was an immediate change in colour followed by gradual decolouration. As a result, 1,4-benzodioxane derivatives (**12**)—(**14**) were obtained in the yields summarized in Table 1. Although 2-amino-1,4-benzodioxane derivatives such as compound (**15**) were reported as the product from the reaction of phenanthrene-9,10-quinone with pyrrolidin-2-ylcyclohexene (**10b**),[8] 2-amino-1,4-benzodioxane derivatives (**12**) were obtained from the reaction only in the case of 1-morpholinocyclohexene (**10a**). In other cases, products were found to be 2-hydroxy derivatives (**13**). These 2-amino derivatives are very sensitive to acid. Actually, when the 2-amino derivative (**12a**) was treated with hydrochloric acid in methanol, the 2-hydroxy derivative (**13a**) was obtained quantitatively. Since the solutions of 1,2-benzoquinones were prepared without isolation from the oxidations in the chloroform–sulphuric acid two-phase system, some acidic impurities were unavoidable in the solvent during the reaction period with enamines. However, even if the crystalline 1,2-benzoquinone (**9a**) reacted with the enamine (**10b**) in dichloromethane, the product was the 2-hydroxy derivative (**13a**) in 55% yield, no 2-amino derivatives being obtained. Further, when the enamine (**10b**) was allowed to react with 1,2-benzoquinone (**9c**) prepared under 'dried' conditions, by an oxidation with Ag_2CO_3–Celite[9] in dichloromethane at 0 °C, the product was the 2-hydroxy derivative (**13c**) (18% yield); again no 2-amino derivatives were obtained. These 2-hydroxy derivatives were, therefore, thought to be formed by a hydrolysis of 2-amino derivatives during work-up (*e.g.* during extraction or chromatography on silica gel).



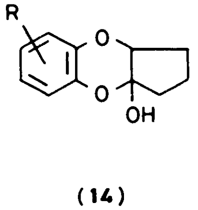
(**12**)

a ; R = Bu^t
b ; R = Me
c ; R = H

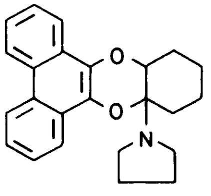


(**13**)

a ; R = Bu^t
b ; R = Me
c ; R = H



(**14**)



(**15**)

In contrast to 1,2-benzoquinone (**9c**) which gave the products (**12c**) and (**13c**) in low yield together with melanin-like black polymer, the benzoquinone (**9a**) and (**9b**) gave good yields of (**12c**) and (**13c**). Although at first this difference in behaviour was attributed to acidic impurities in the reaction media, since (**9c**) prepared under 'dry' conditions also gave a good yield of (**12c**) and (**13c**), it seemed likely that the low yields in the [4 + 2] cycloaddition were caused by the instability of 1,2-benzoquinone (**9c**) or an intermediate.

Structure Analyses and Isomerization of 2-Hydroxy Derivatives.—The structures of the products were deduced on the basis of spectral and microanalytical evidence. In the case of compound (**12a**), for example, analytical results suggested that the product was a 1:1 adduct of the 1,2-benzoquinone (**9a**) with the enamine (**10a**). Except for the aromatic carbon-carbon absorption band, no absorption bands characteristic of either the carbonyl group of 1,2-benzoquinone or carbon-carbon double bond of enamine were observed in the i.r. spectrum. In the ^1H n.m.r. spectrum, signals were observed for the morpholine methylene protons, the tetramethylene bridge, t-butyl protons, and aromatic protons; there was no olefinic proton signal characteristic of enamines present. In the ^{13}C n.m.r. spectrum, a doublet peak and a singlet peak were observed at δ 71.1 and 88.6, respectively, assignable to the sp^3 carbons adjacent to the oxygen atom.

From the n.m.r. spectra of the products the presence of isomers was observed. These were predictable for the following reasons: i, the possibility of the substituent being at either of two positions on the benzene ring, namely on the C-7 or C-8 carbon (regioisomer); ii, the possibility of a *cis* or a *trans* junction between the cyclohexane ring and the dioxane ring. Spectral results for the products showed the existence both of the regio- and the stereo-isomers. In the ^{13}C n.m.r. spectrum of compound (**14**), for example, a number of doublet signals characteristic of aromatic carbons were observed. Since a *cis*-conformation is preferred for the junction between a six- and a five-membered ring there are no stereoisomers of compound (**14**). The spectral observations must, therefore, arise as a result of regioisomers of (**14**). Further, in the ^{13}C n.m.r. spectrum of compound (**13c**), four pairs of the triplet peaks characteristic of the carbons of the tetramethylene bridge were observed. Since compound (**13c**) lacks an aromatic substituent no regioisomers are possible and the spectral observations must arise from the presence of stereoisomers.

Although 2-amino derivatives of compound (**12**) showed no spectroscopic (^1H n.m.r.) evidence for the presence of isomers, the 2-hydroxy compounds (**13**) did. In the ^1H n.m.r. spectrum of compound (**13c**), for example, the hydroxy proton gave rise to broad singlets at δ 3.16 and 3.26 whilst the 10a-methine proton gave double doublets at δ 3.77 and 4.02. In contrast, compound (**14**) showed none of the spectral characteristics exhibited by compound (**13c**). Since compound (**13c**) exists as stereoisomers and compound (**14**) as regioisomers, the ^1H n.m.r. spectral characteristics of the 2-hydroxy derivatives must be a result of the stereoisomers present.* To obtain information on the n.m.r.

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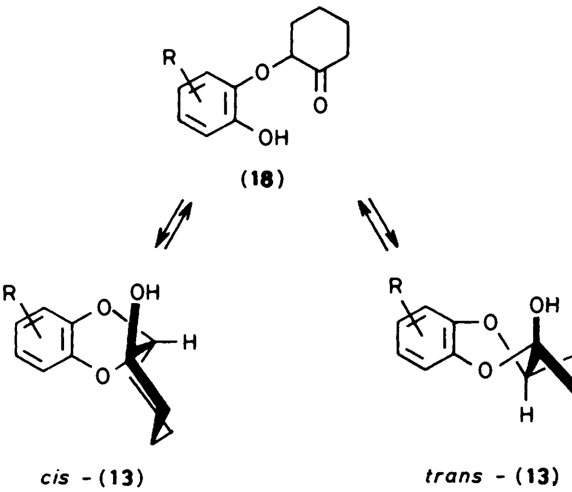
* In order to obtain evidence for the existence of regioisomers, the ^1H and ^{13}C n.m.r. spectra for compound (**13a**) were measured in C_6D_6 solution. There were no marked changes in the spectra, the peak of the t-butyl group being observed as a sharp singlet. Further, useful information was precluded by the poor solubility of (**13a**) although its ^1H n.m.r. spectrum was measured using an europium shift reagent [$Eu(fod)_3$].

characteristics of the regioisomers, the methoxy derivatives (**16a**), (**16b**), and (**17**) were synthesized by the treatment of the 2-hydroxy derivatives (**13a**), (**13c**), and (**14**), respectively with hydrochloric acid in methanol. Since a methoxy group is larger than a hydroxy group and, therefore, more susceptible to electromagnetic influence by the benzene ring, it was expected to be a good probe for the regioisomers; this proved to be the case. Thus, in the ^{1}H n.m.r. spectrum of the methoxy derivative (**16a**), four singlet peaks assignable to the methoxy group were observed while only one singlet peak assignable to the t-butyl group was observed. Also, two singlet peaks assignable to a methoxy group were observed in the ^{1}H n.m.r. spectra of the methoxy derivatives (**16b**) and (**17**).



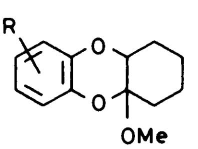
Scheme 1.

When compound (**13a**) was subjected to the ferric chloride test, a blue-black colouration was observed, which suggested the existence of a phenolic hydroxy group. These facts may be explained in the following way. The *cis*-isomer *cis*-(**13**) equilibrates with the *trans*-isomer *trans*-(**13**) *via* its opened-chain tautomer (**18**), which has a phenolic hydroxy group (Scheme 1). To investigate this equilibrium, the contribution of the opened-chain tautomer (**18**; R = H) was evaluated from the i.r. spectrum of compound (**13c**). When this was compared with that of the opened-chain derivative (**19**), the contribution of the opened-chain tautomer (**18**; R = H) in the equilibrium of (**13c**) was estimated to be < 7%. Hence, the equilibrium seemed to be largely in favour of the ring structure. To trap the opened-chain tautomer, acetylation of the 2-hydroxy compound was carried out. When compound (**13a**) was heated in acetic anhydride with sodium acetate, two products, (**20**) and (**21**), were obtained in 28 and 34% yield, respectively. The structure of (**21**) was assigned as a 2-(2-acetoxyphenoxy)cyclohexanone derivative on the basis of spectral evidence, *i.e.* phenolic ester and cyclohexanone carbonyl absorption. The former was observed at 1 755 cm^{-1} (i.r.) and δ 169.0 p.p.m. (^{13}C n.m.r.) and the latter at 1 720 cm^{-1} and δ 208.3 p.p.m. It was, therefore, concluded that the 2-hydroxy derivatives exist in a ring-chain isomerization equilibrium and thus consist of a mixture of thermodynamically stable isomers.

Calculation of the Heat of Formation of the 2-Hydroxy Derivatives.—It having been shown that compounds (**13**) exist as a mixture of ring-chain isomers as a result of the cyclohexane-dioxane ring-junctions, we wished to analyse the conformation and estimate the thermodynamical stability of the isomers. To this end, the heat of formation of *cis*-(**13c**) and *trans*-(**13c**), were calculated by means of the MINDO/3 method, and the results are summarized in Table 2.* From these results, it can be seen that the heat of formation of the isomers *cis*-(**13c**) and *trans*-(**13c**) are almost equivalent whilst lower than that of the chain tautomer (**18**). Such results indicate that, under equilibrium conditions, compound (**13c**) is a 1 : 1 mixture of *cis*-(**13c**) and *trans*-(**13c**) *via* the chain tautomer (**18**), with the equilibrium largely in favour of the ring structure, *cis*-(**13c**) and *trans*-(**13c**).

Table 2. The heat of formation of isomers of compounds (**13**) and (**14**) by the MINDO/3 method

Isomer	Heat of formation (kcal mol^{-1})
cis-(**13c**)	−72.7
trans-(**13c**)	−79.2
(**18**)	−68.8
cis-(**14**)	−79.2
trans-(**14**)	972.4



(**16**)
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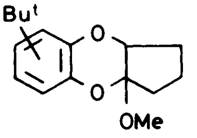
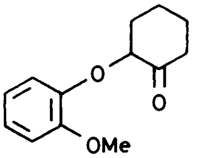
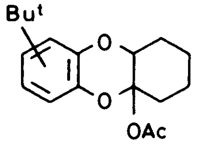
b ; R = H



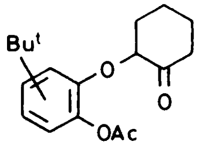
(**17**)



(**19**)

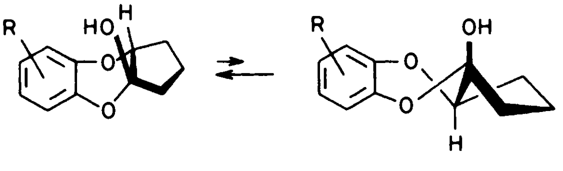


(**20**)



(**21**)

Similarly, a calculation of the heat of formation of the *cis*- and *trans*-(**14**) was carried out, and the results are summarized in Table 2. From the results, *cis*-(**14**) is seen to be more stable than *trans*-(**14**) the former predominating (Scheme 2). This calculated result agreed well with the fact that compound (**14**) was the sole product from the reaction of 1,2-benzoquinone (**9a**) and the enamine (**10a,b**).



Scheme 2.

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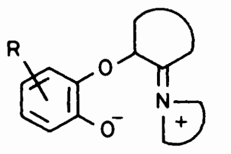
* Dreiding Model (Büchi) were used to obtain data for calculation.

Table 3. The reaction rate constants of 4-t-butyl-1,2-benzoquinone (**9a**) with 1-morpholinocyclohexene (**10a**), pyrrolidin-1-ylcyclohexene (**10b**), and cyclopentadiene

Substrates	k* (min^{-1} mol^{-1} l)	Relative rate	Solvents	Dielectric constants
(**10a**)	4.34	3.65	Hexane	1.88
(**10a**)	69.9	58.7	Chloroform	4.81
(**10a**)	107.3	90.2	Acetonitrile	37.5
(**10b**)	41.6	35.0	Chloroform	4.81
Cyclopentadiene	1.19	1	Chloroform	4.81

[a] At 25 °C.

Rate Constants for the Reaction of Enamines with 4-*t-Butyl*-1,2-*benzoquinones*.—The rate constants for the reaction were measured by the use of crystalline 4-t-butyl-1,2-benzoquinone (**9a**). Measurements were carried out under the pseudo-first-order condition using a large excess of enamines, the reactions being monitored by the u.v. absorbance of 1,2-benzoquinone (**9a**) at 386 nm. Cyclopentadiene, which is widely used as a trapping reagent for 1,2-benzoquinones, was used as a standard compound. From the results summarized in Table 3, it is apparent that the reaction of 1,2-benzoquinone with enamines proceeds at a rate almost 50 times faster than that with cyclopentadiene. Also, it was apparent that the reaction of 1,2-benzoquinone with enamines was accelerated in accord with the order of the polarity of the solvent. This suggested that the reaction proceeded not through a concerted process, such as the Diels-Alder reaction, but rather a stepwise ionic process. Tedder *et al.* proposed a zwitterionic species (**5**) for an intermediate in the reaction of 1,2-benzoquinones with furans.[6] Since a remarkable change in colour in the initial step of the reaction between 1,2-benzoquinones and enamines was observed, the reaction probably proceeds *via* a similar ionic mechanism including a zwitterionic intermediate such as (**22**) formed *via* a charge-transfer complex.



(**22**)

Experimental

M.p.s were measured on Yanagimoto Micro Melting Point Apparatus, and are uncorrected. I.r. spectra were measured on JASCO IRA-1 Infrared Spectrophotometer. ^1H and ^{13}C N.m.r. spectra were measured for $CDCl_3$ solutions on JEOL FX-100 (100 MHz) and JEOL FX-90Q (90 MHz) Spectrometer, respectively, with internal $SiMe_4$ as a standard. U.v. spectra were measured on Shimadzu UV-365 UV-VIS-NIR Recording Spectrophotometer. Pyrocatechols (**8**) were commercially available. The enamines (**10**) and (**11**) were synthesized from the corresponding ketones and amines in refluxing benzene under azeotropic conditions.

4a-*Morpholino*-7-(*or* 8)-*t-butyl*-1,2,3,4,4a,10a-*hexahydrodibenzo*-p-*dioxin* (**12a**): *General Procedure*.—To an ice–methanol cooled solution of 4-t-butylpyrocatechol (**8a**) (332 mg, 2 mmol) in chloroform (50 ml), a pre-cooled (in an ice–methanol bath) solution of cerium(IV) sulphate (1.82 g, 4.5 mmol) in 3M sulphuric acid, (25 ml) was added and the mixture stirred for 1 min.[10] The organic layer was separated, washed with 0.005M sulphuric acid, and dried ($MgSO_4$). To this solution, a solution of 1-morpholinocyclohexene (**10a**) (420 mg, 2.5 mmol) in chloroform (10 ml) was added dropwise. The mixture was stirred for 1 h at 0 °C and then evaporated under reduced pressure. Chromatography of the residue on silica gel with hexane–ethyl acetate (3:1) as eluant yielded (**12a**) (630 mg, 95%), m.p. 138—139 °C (Found: C, 72.4; H, 8.9; N, 4.15. $C_{20}H_{29}NO_3$ requires C, 72.25; H, 9.09; N, 4.21%); $\nu_{max.}$(KBr) 1 580 and 1 500 cm^{-1}; δ_H 1.27 (9 H, s, 7- or 8-Bu^t), 1.4—2.2 [8 H, m, $(CH_2)_4$], 2.7—2.9 (4 H, m, $NCH_2CH_2OCH_2CH_2$), 3.66 (4 H, t, J 4.6 Hz, $NCH_2CH_2OCH_2CH_2$), 4.2—4.3 (1 H, m, 10a-H), and 6.7—6.9 (3 H, m, ArH); δ_C 20.4 (t), 21.8 (t), 21.1 (t), 23.7 (t), 26.9 (t), 27.8 (t), 28.1 (t), 31.5 (q), 34.2 (s), 44.6 (t), 67.4 (t), 71.1 (d), 88.6 (s), 113.7 (d), 113.9 (d), 115.9 (d), 116.4 (d), 117.4 (d), 139.5 (s), 141.2 (s), 142.0 (s), and 144.6 p.p.m. (s).

7(*or* 8)-*Methyl*-4a-*morpholino*-1,2,3,4,4a,10a-*hexahydrodibenzo*-p-*dioxin* (**12b**) (33%), b.p. 122 °C/10^{-4} Torr (bath temp.) (Found: C, 70.55; H, 8.0; N, 4.8. $C_{17}H_{23}NO_3$ requires C, 70.56; H, 8.01; N, 4.84%); $\nu_{max.}$(film) 1 585 and 1 500 cm^{-1}; δ_H 1.2—2.0 [8 H, m, $(CH_2)_4$], 2.23 (3 H, s, 7- or 8-Me), 2.7—2.9 (4 H, m, $NCH_2CH_2OCH_2CH_2$), 3.5—3.7 (4 H, m, $NCH_2CH_2OCH_2CH_2$), 4.1—4.3 (1 H, m, 10a-H), and 6.5—6.8 (3 H, m, ArH); δ_C 20.6 (q), 21.8 (t), 26.8 (t), 27.7 (t), 44.6 (t), 67.3 (t), 71.0 (d), 88.4 (s), 116.2 (d), 116.5 (d), 116.9 (d), 117.2 (d), 121.1 (d), 121.6 (d), 130.7 (s), 139.7 (s), and 142.1 p.p.m. (s).

4a-*Morpholino*-1,2,3,4,4a,10a-*hexahydrodibenzo*-p-*dioxin* (**12c**) (11%), m.p. 91—92 °C (Found C, 69.75; H, 7.8; N, 4.95. $C_{16}H_{21}NO_3$ requires C, 69.79; H, 7.68; N, 5.08%); $\nu_{max.}$(KBr) 1 590 and 1 490 cm^{-1}; δ_H 1.3—2.1 [8 H, m, $(CH_2)_4$], 2.6—2.9 (4 H, m, $NCH_2CH_2OCH_2CH$), 3.4—3.7 (4 H, m, $NCH_2CH_2OCH_2CH_2$), 4.1—4.3 (1 H, m, 10a-H), and 6.81 (4 H, s, ArH); δ_C 20.8 (t), 21.8 (t), 27.0 (t), 27.9 (t), 44.7 (t), 67.3 (t), 71.2 (d), 88.4 (s), 116.7 (d), 117.0 (d), 120.7 (d), 121.2 (d), 142.1 (s), and 142.4 p.p.m. (s).

7(*or* 8)-*t-Butyl*-1,2,3,4,4a,10a-*hexahydrodibenzo*-p-*dioxin*-4a-*ol* (**13a**), m.p. 142—143 °C (Found: C, 73.35; H, 8.55. $C_{16}H_{22}O_3$ requires C, 73.25; H, 8.45%); $\nu_{max.}$(KBr) 3 300, 1 580, and 1 500 cm^{-1}; δ_H 1.27 (9 H, s, 7- or 8-Me), 1.4—2.1 [8 H, m, $(CH_2)_4$] 3.23 (1/2 H, s, D_2O exchangeable, OH), 3.33 (1/2 H, s, D_2O exchangeable, OH), 3.75 (1/2 H, dd, J 4.9 and 10.7 Hz, 10a-H), 4.00 (1/2 H, dd, J 4.9 and 9.7 Hz, 10a-H), and 6.7—6.9 (3 H, m, ArH); δ_C 22.1 (t), 22.3 (t), 23.0 (t), 23.7 (t), 28.0 (t), 28.1 (t), 31.5 (t), 34.6 (s), 35.6 (s), 77.0 (d), 94.0 (s), 94.3 (s), 116.4 (d), 118.5 (d), 118.8 (d), 138.0 (s), 139.6 (s), 140.5 (s), 144.7 (d), 144.9 (d), 145.2 (s), and 146.0 p.p.m. (s).

7(*or* 8)-*Methyl*-1,2,3,4,4a,10a-*hexahydrodibenzo*-p-*dioxin*-4a-*ol* (**13b**), m.p. 102—103 °C (Found: C, 70.9; H, 7.45. $C_{13}H_{16}O_3$ requires C, 70.9; H, 7.3%); $\nu_{max.}$(KBr) 3 400, 1 585, and 1 495 cm^{-1}; δ_H 1.3—2.2 [8 H, m, $(CH_2)_4$], 2.24 (3 H, s, 7- or 8-Me), 3.3 (1 H, br s, D_2O exchangeable, OH), 3.72 (2/3 dd, J 4.6 and 11.0 Hz, 10a-H), 3.98 (1/3 H, dd, J 4.2 and 9.5 Hz, 10a-H), and 6.6—6.8 (3 H, m, ArH); δ_C 20.7 (q), 22.1 (t), 22.2 (t), 22.8 (t), 23.6 (t), 27.8 (t), 28.0 (t), 34.6 (t), 35.5 (t), 75.6 (d), 94.0 (s), 94.2 (s), 116.7 (d), 117.9 (d), 118.2 (d), 122.1 (d), 122.3 (d), 131.4 (s), 132.2 (s), 138.2 (s), 140.7 (s), and 141.0 p.p.m. (s).

1,2,3,4,4a,10a-*Hexahydrodibenzo*-p-*dioxin*-4a-*ol* (**13c**), m.p. 47.5—49 °C (Found: C, 69.95; H, 6.95. $C_{12}H_{14}O_3$ requires C, 69.88; H, 6.84%); $\nu_{max.}$(KBr) 3 360, 1 590, and 1 485 cm^{-1}; δ_H 1.2—2.3 [8 H, m, $(CH_2)_4$], 3.16 (5/8 H, br s, D_2O exchangeable, OH), 3.26 (3/8 H, br s, D_2O exchangeable, OH), 3.77 (5/8 H, dd, J 4.9 and 11.2 Hz, 10a-H), 4.02 (3/8 H, dd, J 5.4 and 8.8 Hz, 10a-H), and 6.87 (4 H, s, ArH); δ_C 22.1 (t), 22.2 (t), 22.8 (t), 23.6 (t), 27.9 (t), 28.1 (t), 34.6 (t), 35.6 (t), 75.7 (d), 77.0 (d), 94.3 (s), 117.1 (d), 117.6 (d), 117.9 (d), 121.6 (d), 121.9 (d), 122.5 (d), 140.5 (s), and 141.5 p.p.m. (s).

6(*or* 7)-*t-Butyl*-2,3,3a,9a-*tetrahydro*-1H-*cyclopent*[b][1,4]-*benzodioxin*-3a-*ol* (**14**), m.p. 58—59 °C (Found: C, 72.35; H, 8.05. $C_{15}H_{20}O_3$ requires C, 72.55; H, 8.11%); $\nu_{max.}$ 3 240, 1 590, and 1 505 cm^{-1}; δ_H 1.27 (9 H, s, 6- or 7-Bu^t), 1.5—2.2 [6 H, m, $(CH_2)_3$] 3.4 (1 H, br s, D_2O exchangeable, OH), 4.0—4.2 (1 H, m, 9a-H), and 6.7—6.9 (3 H, m, ArH); δ_C 17.4 (t), 27.7 (t), 31.5 (q), 33.8 (t), 34.2 (s), 78.2 (d), 102.2 (s), 114.2 (d), 114.4 (d), 116.5 (d), 116.6 (d), 118.8 (d), 138.5 (s), 140.3 (s), 140.5 (s), and 145.2 p.p.m. (s).

Oxidation of Pyrocatechol (**8c**) *by Fétizon's Reagent and the Reaction with Pyrrolidin*-1-*ylcyclohexene* (**10b**).—A suspension of the pyrocatechol (**8c**) (447 mg, 4 mmol) and Fétizon's reagent (silver carbonate on Celite)[9] (5.9 g) in dichloromethane (100 ml) was stirred at 0 °C under an argon atmosphere for 2 h. The oxidant was then filtered off and the resulting solution of 1,2-benzoquinone (**9c**) was cooled in a solid CO_2–methanol bath. To this solution, a solution of pyrrolidin-1-ylcyclohexene (**10b**) (658 mg, 4.3 mmol) in dichloromethane (20 ml) was added dropwise under argon atmosphere. The mixture was stirred for 3 h after which, the solid CO_2–methanol bath was removed and the mixture stirred overnight. A similar work-up procedure to that described before yielded (**13c**) (150 mg, 18%).

Synthesis of 4-*t*-*Butyl*-1,2-*benzoquinone*.—4-t-Butylpyrocatechol (**8a**) (1.014 g, 6 mmol) was oxidized in a similar manner to that described before. Solvent was then removed from the reaction mixture and the residue chromatographed on silica gel with dichloromethane–acetone (30:1) as an eluant. Recrystallization of the product from hexane yielded (**9a**) (720 mg, 72%), m.p. 67—68 °C (lit.,[3b] 68 °C).

Reaction of 4-*t*-*Butyl*-1,2-*benzoquinone* (**9a**) *with Pyrrolidin*-1-*ylcyclohexene* (**10b**).—To a solid CO_2–methanol cooled solution of 4-t-butyl-1,2-benzoquinone (**9a**) (433 mg, 2.6 mmol) in dichloromethane (50 ml), a solution of pyrrolidin-1-ylcyclohexene (**10b**) (452 mg, 3 mmol) was added dropwise under an argon atmosphere. The mixture was stirred for 3 h after which the solid CO_2–methanol bath was removed, and stirring continued overnight. A similar work-up procedure to that described before yielded (**13a**) (355 mg, 55%).

4a-*Methoxy*-7(*or* 8)-*t*-*butyl*-1,2,3,4,4a,10a-*hexahydrodibenzo*-p-*dioxin* (**16a**).—The hydroxy compound (**13a**) (662 mg, 2.5 mmol) dissolved in methanol (20 ml) and concentrated hydrochloric acid (4 ml) was heated under reflux for 1 h. The solvent was then evaporated under reduced pressure and the residue chromatographed on silica gel with hexane–ethyl acetate (3:1) as eluant to yield unchanged starting material (**13a**) (109 mg, 17%) and the title compound (**16a**) (413 mg, 59%), m.p. 65—66 °C (Found: C, 73.9; H, 8.85. $C_{17}H_{24}O_3$ requires C, 73.88; H, 8.75%); $\nu_{max.}$($CHCl_3$) 1 595 and 1 500 cm^{-1}; δ_H 1.28 (9 H, s, 7- or 8-Bu^t), 1.3—2.1 [7 H, m, $(CH_2)_4$], 2.1—2.5 [1 H, m, $(CH_2)_4$], 3.26, 3.27, 3.31, and 3.33 (3 H, all s, 4a-OMe), 3.76 (1/2 H, dd, *J* 5.13 and 11.00 Hz, 10a-H), 4.03 (1/2 H, dd, *J* 4.65 and 9.04 Hz, 10a-H), and 6.8—6.9 (3 H, m, ArH); δ_C 21.9 (t), 22.3 (t), 22.7 (t), 23.8 (t), 28.1 (t), 28.4 (t), 29.7 (t), 31.6 (q), 34.2 (s), 48.1 (q), 48.6 (q), 74.7 (d), 77.0 (d), 96.2 (s), 96.5 (s), 114.2 (d), 116.3 (d), 118.6 (d), 139.1 (s), 139.7 (s), 140.5 (s), 144.5 (s), and 144.8 p.p.m. (s).

4a-*Methoxy*-1,2,3,4,4a,10a-*hexahydrodibenzo*-p-*dioxin* (**16b**) (71%), b.p. 40—42 °C/10^{-4} Torr (bath temp.) (Found: C, 71.3; H, 7.45. $C_{13}H_{16}O_3$ requires C, 70.88; H, 7.32%); $\nu_{max.}$($CHCl_3$) 1 595 and 1 495 cm^{-1}; δ_H 1.2—2.2 [7 H, m, $(CH_2)_4$], 2.2—2.5 [m, 1 H, $(CH_2)_4$], 3.24 and 3.29 (3 H, both s, 4a-OMe), 3.76 (1/2 H, dd, *J* 5.13 and 10.50 Hz, 10a-H), 4.04 (1/2 H, dd, *J* 4.39 and 9.77 Hz, 10a-H), and 6.85 (4 H, s, ArH); δ_C 21.9 (t), 22.3 (t), 22.8 (t), 23.8 (t), 28.1 (t), 28.4 (t), 29.6 (t), 31.2 (t), 48.1 (q), 48.5 (q), 74.9 (d), 77.0 (d), 96.1 (s), 96.4 (s), 117.1 (d), 117.3 (d), 117.5 (d), 121.2 (d), 121.5 (d), 121.8 (d), 122.0 (d), 140.5 (s), 141.3 (s), 141.8 (s), and 144.2 p.p.m. (s).

3a-*Methoxy*-6(*or*7)-t-*butyl*-2,3,3a,9a-*tetrahydro*-1H-*cyclopent*[b][1,4]*benzodioxin* (**17**) (40%), b.p. 45—47 °C/10^{-4} Torr (bath temp.) (Found C, 73.35; H, 8.7. $C_{16}H_{22}O_3$ requires C, 73.25; H, 8.45%); $\nu_{max.}$($CHCl_3$) 1 595 and 1 500 cm^{-1}; δ_H 1.28 (9 H, s, 6- or 7-Bu^t), 1.6—2.1 [6 H, m, $(CH_2)_3$], 3.37 and 3.39 (3 H, both s 3a-OMe), 4.3 (1 H, m, 9a-H), and 6.8—6.9 (3 H, m, ArH); δ_C 16.9 (t), 27.3 (t), 30.8 (t), 31.5 (q), 34.2 (s), 50.9 (q), 77.6 (d), 104.2 (s), 114.2 (d), 114.4 (d), 116.4 (d), 116.7 (d), 118.3 (d), 118.9 (d), 138.5 (s), 139.0 (s), 140.4 (s), 142.0 (s), and 144.8 p.p.m. (s).

2-(2-*Methoxyphenoxy*)*cyclohexanone* (**19**).—Guaiacol (1.260 g, 10 mmol) was dissolved in distilled ethanol (20 ml) and added dropwise to sodium (280 mg, 12 mmol) under an argon atmosphere at 0 °C. The mixture was stirred for 10 min at room temperature after which a solution of 2-chlorocyclohexanone (1.573 g, 12 mmol) in distilled ethanol (20 ml) was added dropwise to it at 0 °C; the mixture was then stirred overnight at room temperature. The white precipitate was filtered off and the solvent was evaporated under reduced pressure. The residue was extracted with dichloromethane and the extract washed with water, dried ($MgSO_4$) and evaporated. Chromatography of the residue on silica gel with hexane–ethyl acetate–chloroform (5:1:1) as eluant yielded the title compound (**19**) (394 mg, 18%), b.p. 120—123 °C/3 Torr (bath temp.) (Found C, 70.6; H, 7.35. $C_{13}H_{16}O_3$ requires C, 70.31; H, 7.35%); $\nu_{max.}$($CHCl_3$) 1 730, 1 595, and 1 495 cm^{-1}; δ_H($CDCl_3$) 1.6—2.7 [8 H, m, $(CH_2)_4$], 3.82 (3 H, s, OMe), 4.5—4.7 [1 H, m, C*H*(OAr)CO], and 6.7—6.9 (4 H, m, ArH); δ_C($CDCl_3$) 23.0 (t), 27.7 (t), 34.5 (t), 40.5 (t), 56.0 (q), 82.1 (d), 112.5 (d), 117.4 (d), 120.8 (d), 122.6 (d), 147.0 (s), 150.3 (s), and 207.9 p.p.m. (s).

Estimation of the Contribution of the Opened-chain Tautomer of (**13c**).—The relative peak intensity of the carbonyl absorption of both (**13c**) and (**19**) compared with the cyano absorption of benzonitrile was determined with a JASCO FT/IR-3 Spectrophotometer. The contribution of the opened-chain tautomer was calculated by comparing the relative intensity of (**13c**) with that of (**19**).

Acetylation of the Hydroxy Compound (**13a**).—The hydroxy compound (**13a**) (572 mg, 2.2 mmol) was dissolved in an acetic anhydride (10 ml) and sodium acetate (98 mg) mixture and heated at 80 °C for 2 h. The product was extracted with dichloromethane and the extract washed with aqueous sodium hydrogen carbonate, and then evaporated. Chromatography of the residue on silica gel with hexane–ethyl acetate (4:1) as eluant gave two products A and B along with the unchanged starting material (**13a**) (156 mg, 27%). Product A was compound (**20**) 134 mg, 28%), the 4a-hydroxy group which was acetylated. Product B was compound (**21**) (162 mg, 34%) the phenolic hydroxy group of which was acetylated.

4a-*Acetoxy*-7(*or* 8)-*t*-*butyl*-1,2,3,4,4a,10a-*hexahydrodibenzo*-p-*dioxin* (**20**), b.p. 60—65 °C/10^{-4} Torr (bath temp.) (Found C, 71.2; H, 8.0. $C_{18}H_{24}O_4$ requires C, 71.03; H, 7.95%); $\nu_{max.}$($CHCl_3$) 1 720, 1 595, and 1 500 cm^{-1}; δ_H 1.27 (9 H, s, 7- or 8-Bu^t), 1.5—2.1 [8 H, m, $(CH_2)_4$], 2.38 (3 H, s, OAc), 4.11 (1/2 H, dd, *J* 7.33 and 14.16 Hz, 10a-H), 4.64 (1/2 H, dd, *J* 4.88 and 10.25 Hz, 10a-H), and 6.8—7.0 (3 H, m, ArH); δ_C 20.8 (q), 22.0 (t), 22.2 (t), 23.0 (t), 25.8 (t), 28.1 (t), 28.2 (t), 30.0 (t), 31.5 (q), 32.2 (s), 72.6 (d), 72.8 (d), 100.4 (s), 100.6 (s), 114.0 (d), 114.4 (d), 118.4 (d), 137.2 (s), 138.3 (s), 138.9 (s), 140.0 (s), 146.0 (s), 146.3 (s), and 169.4 p.p.m. (s).

2-[2-*Acetoxy*-4(*or* 5)-*t*-*butyl*-1-*phenoxy*]*cyclohexanone* (**21**), b.p. 70—72 °C/10^{-4} Torr (bath temp.) (Found C, 71.05; H, 8.0. $C_{18}H_{24}O_4$ requires C, 71.02; H, 7.95%); $\nu_{max.}$ 1 755, 1 720, and 1 500 cm^{-1}; δ_H 1.26 (9 H, s, 4- or 5-Bu^t), 1.6—2.2 [7 H, m, $(CH_2)_4$], 2.30 (3 H, s, OAc), 2.5—2.7 [1 H, m, $(CH_2)_4$], 4.5 (1 H, m, 2-H), 6.77 (1 H, d, J 8.30 Hz), and 6.9—7.2 (2 H, m, ArH); δ_C 20.6 (q), 22.3 (t), 27.8 (t), 31.4 (q), 34.2 (s), 34.5 (t), 40.1 (t), 81.9 (d), 113.5 (d), 115.0 (d), 118.8 (d), 120.0 (d), 122.1 (d), 123.3 (d), 140.0 (s), 145.2 (s), 146.9 (s), 169.0 (s), and 208.3 p.p.m. (s).

Measurements of the Reaction Rate Constants.—A chloroform solution of crystalline 4-t-butyl-1,2-benzoquinone (**9a**) was prepared in a concentration of *ca.* 10^{-4} mol l^{-1}. Chloroform solutions of 1-morpholinocyclohexene (**10a**) and pyrrolidin-1-ylcyclohexene (**10b**), and cyclopentadiene were prepared in a concentration of *ca.* 10^{-2} mol l^{-1}. The solutions of the 1,2-benzoquinone (**9a**) (2 ml) and dienophile (2 ml) were mixed, and immediately placed in the u.v. cell (25 °C). The decrease of the u.v. absorption at 386 nm was measured with time. The reaction rate constants were calculated by means of the least-square method.

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