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Mechanistic Study on Acid-Catalyzed Novel Rearrangement of Homobenzoquinone Epoxide

2010

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Preface

The studies presented in this thesis have been carried out under the guidance of Professor Takumi Oshima at Osaka University during 2004–2010.

This thesis deals with the acid- and photo-reaction of small-membered ring fused quinone derivatives were focused on the fundamental studies comprised of the following points, (1) remote $\pi$-aryl participation reaction of Homobenzoquinone epoxide, (2) a prominent role of oxirane Walsh orbital, (3) rearrangement reaction of cyclobutane-fused quinone. The author hopes that this basic work described in this thesis contributes to the further development of synthesis of novel carbon skeletons, which are difficult to produce by conventional methods.

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March, 2010
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**General Introduction**

Possessing both reactive carbonyl and olefinic bonds, quinones are powerful intermediate in organic synthesis. Consequently, quinones undergo various nucleophilic addition and cycloaddition such as Diels-Alder reaction, [2+2] photocycloaddition or addition of 1,3-dipoles (Scheme 1). Especially, the cycloaddition reaction of quinones has been the subject of extensive investigations largely,\(^1\) due to simple reaction mechanism and the potential offered by such reactions in natural products syntheses.\(^2\) Actually, product quinones having fused polycyclic ring systems are known as a structure component in important natural products that undergo a number of biochemical transformations\(^{1,3,4}\) and the studies of their synthesis and the reactivities of these compounds have interested many organic chemists.\(^5\)

![Scheme 1. Examples of the reaction of quinone](image)

In spite of their numerous kinds and complexities, the rearrangement reaction in organic chemistry can be broken down into relatively simple steps. The chemistry of small ring compounds is replete with examples of rearrangement. The relief of ring strain is a powerful driving force in assisting ring opening and ring expansions in three- or four-membered rings under conditions where large ring compounds or aliphatic analogs retain their original carbon skeletons intact. In fact, many potential applications of cyclopropane as useful building blocks have been predicted based on regio- and stereo-controlled ring-opening reactions.\(^6\)
other hand, the acid-catalyzed ring-opening reactions of epoxides have attracted a continuous interest from the synthetic and mechanistic viewpoints (Scheme 2). These reactions are generally proceed through the regio- and stereoselective ring cleavage via a $S_N$2-type anti nucleophilic displacements. These stereochemical features are much affected by the steric environments in the oxirane ring. Despite numerous investigations into the mechanistic aspects, a possible role of the characteristic oxirane Walsh orbital in the anti-nucleophilic ring cleavage of epoxides remains to be elucidated.

The many reviews devote only insignificant space to the interaction of small-membered ring and neighboring group. Even in the relatively well-documented field of keto-epoxides definite correlations have not been established between substrate structure, reagent, and the conditions and direction of reactions: several views are held on the mechanism which best describes such reactions. It may be said a priori that the direction of ring-opening will be determined by the concerted (or competing) influence of the nature of the small-membered ring, the neighboring group, and their relative arrangement (interaction). However, to determine the role of each of these factors in studying conformationally labile systems is an almost hopeless task. In fact, the nature of the electronic interactions between

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**Scheme 2. Examples of the reaction of epoxide**

Transformation Rearrangement

Nucleophilic Ring-Opening
three-membered ring (epoxy or cyclopropyl) and neighboring carbonyl group is usually described as conjugation resulting from orbital overlap of bent orbitals of the ring and a $p$-orbital of the carbonyl group.\textsuperscript{10} In these systems, the maximum overlap is achieved with the planes of carbonyl group and three-membered ring parallel and the keto-group on a bisector of the ring.\textsuperscript{11}

In the light of these situations, the author attempted to introduce the three- or four-membered rings and epoxide into the quinones and investigated the acid- and photo-induced reaction of them (Figure 1). It is expected that such conformationally rigid bi- or tricyclic compounds provide insights about orbital interaction on the rearrangement reactions of small-membered ring-fused polycyclic compounds and have potential of application for regio- or stereo-controlled reactions. Furthermore, it is also anticipated that these compounds give the knowledge of very rare remote neighboring group participation in the ring-opening due to the spatial proximity between the vacant bent orbitals of small-membered ring and $p$-orbitals of remote neighboring group.

The studies in the present thesis are concerted with the development of the rearrangement reaction of small-membered ring-fused quinone derivatives. In addition, pioneering works for the revealing the mechanism of the reaction and the role of orbital interaction between small-membered ring and neighboring groups, are described. This thesis consists of general introduction, four chapters and conclusion.
In Chapter 1, is described mechanism of \( \pi \)-aryl participated acid-catalyzed rearrangement reaction of Homobenzoquinone epoxide (HQ-Epoxide) and a prominent role of oxirane Walsh orbital. Especially, is focused on the kinetic solvent effects on the reaction, conformational effects of ethano-bridged compound and dual pathway reaction of disubstituted HQ-Epoxide.

In Chapter 2, is described kinetic evidence for remote \( \pi \)-aryl participation in the reaction and \( \eta^2 \)-type participated transition state. Kinetic substituents effects of the acid-catalyzed reaction of HQ-Epoxide were compared with those of the analogous reaction of cyclobutene-fused homobenzoquinone. And it was found that the reaction of HQ-Epoxide exhibit the \( \eta^2 \) \( \pi \)-aryl participation with more effective contribution at the ipso-position.

In Chapter 3, is described the consecutive reaction of HQ-Epoxide and the rearrangement reaction of cyclobutane-fused quinone epoxides. It was found that the subsequent ring-enlargement by 1,2-migration associated with the incorporated cyclopropane ring-opening, depending on the substituent pattern and cyclobutane-fused quinone epoxide underwent the novel skeletal rearrangement.

In Chapter 4, is described the intramolecular [2+2] photocycloaddition reaction of cyclobutane-fused quinones. Cyclobutane-fused quinone underwent the intramolecular [2+2] photocycloaddition to provide the novel cage compound which has very rare diagonal conjunction of two facing cyclobutane rings.

**Reference and Notes**


Chapter 1. Acid-Catalyzed Reaction of Homobenzoquinone Epoxide (HQ-Epoxide): A Prominent Role of Oxirane Walsh orbital

1-1. Introduction

The acid-catalyzed ring-opening reactions of epoxides have attracted a continuous interest from the synthetic and mechanistic viewpoints. These reactions are generally proceeded through the regio- and stereoselective ring cleavage via a $S_N2$-type anti nucleophilic displacements. These stereochemical features are much affected by the steric environments in the oxirane ring. Despite numerous investigations into the mechanistic aspects, a possible role of the characteristic oxirane Walsh orbital in the anti-nucleophilic ring cleavage of epoxides remains to be elucidated.

In order to clarify such an orbital interaction, the author has investigated the neighboring group participation which will affect the reactivity by way of the geometrically controlled through space electronic interactions with the incipient cation center (or the vacant orbital). In particular, $\pi$-aryl participation is commonly recognized in the organic reactions of compounds possessing the aromatic nucleus (or nuclei) adjacent to or in the topological neighborhood, promoting reaction via a rate-determining aryl-assisted transition state. In an aim of developing the new application of homobenzoquinones and revealing the the geometrical features of orbital interaction with the oxirane Walsh orbital in the transition state, the author synthesized the variously aryl-substituted homobenzoquinone epoxides $1a$-$g$ and investigated the acid-catalyzed reactions (Scheme 1).

In this chapter, the author wish to describe the following three points, (1) kinetic solvent effects on the reaction of HQ-Epoxide, (2) the conformational effects of reaction of 10,11-dihydro-5H-dibenzo[$a,d$]cycloheptene spiro-linked homobenzoquinone epoxide, (3) dual pathway acid-catalyzed rearrangement reactions of disubstituted HQ-Epoxides.
1-2. Results and Discussion

1-2-1. Conformers of Ethano-Bridged Homobenzoquinone Epoxide

Recently, 10,11-dihydro-5H-dibenzo[a,d]cycloheptene and its derivatives have received considerable pharmacological attention in view of a suitable subunit for drug-receptor concave-convex interaction. In our previous paper, the author has reported that the reaction of 5-diazo-10,11-dihydro-5H-dibenzo[a,d]cycloheptene and 2,5-dimethyl-1,4-benzoquinone gave the corresponding spirohomobenzoquinone (α-2a) via the conformationally locked nitrogen release of the primary adduct pyrazolines. The compound (α-2a) was found to turn out to be the more stable conformer (β-2a) at 100 °C by way of a complete one-way conformational inversion of the spiro-linked 10,11-dihydro-5H-dibenzo[a,d]cycloheptene moiety. The author also found that the epoxidation of conformers (α-2a) and (β-2a) proceeded without any conformational inversion to give the corresponding epoxides (α-1f) and (β-1f), respectively (Scheme 2), but that thermal equilibration was attained at 100 °C in CDCl₃ with a preference for (β-1f) (96%, by ¹H NMR).
As shown in Fig. 1(a), the dibenzo-fused cycloheptene ring in (α-1f) adopts a fairly twisted boat conformation, folding opposite to the cyclopropane Me-substituent in analogy with (α-2a), but the dihedral angle [θ = 33.1 (4)°] of the –CH2-CH2– bridge and the intramolecular bond angle (ω = 108.9°) centered at the spiro-carbon are slightly larger than those of the corresponding (α-2a) (27.3 and 107.8°) (Table 1). For comparison, the author also listed the reference crystalline values of θ and ω (57.9 and 114.6°) for the least strained pristine 10,11-dihydro-5H-dibenzo[a,d]cycloheptene8 (3) together with the differential dihedral angles (Δθ=θc – θx), in which θc and θx are the angles for (3) and the given conformer, respectively. On the other hand, as shown in Fig. 1(b), the conformationally inverted (β-1f) takes a more highly twisted boat conformation with θ = 63.6° and ω = 113° as compared with the corresponding (β-2) (55.5 and 111.3°). It was also found that the ω is well

![Diagram](image-url)
correlated with the \( \theta \) probably because of the constrained dibenzo-fusion; i.e., \( \omega = 0.133\theta + 104 \) \((n = 4, R = 0.99)\).

Table 1. Conformational parameters of the 10,11-dihydro-5\(H\)-dibenzo [a,d]cycloheptene rings of crystalline \((\alpha-2a), (\beta-2a), (\alpha-1f), (\beta-1f)\) as well as the reference \((3)\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \phi^a )</th>
<th>(( \Delta\phi^b ))</th>
<th>( \omega^c )</th>
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</thead>
<tbody>
<tr>
<td>( \alpha-2a )</td>
<td>27.3 (30.6)</td>
<td>107.8</td>
<td></td>
</tr>
<tr>
<td>( \beta-2a )</td>
<td>55.5 (2.4)</td>
<td>111.3</td>
<td></td>
</tr>
<tr>
<td>( \alpha-1f )</td>
<td>33.1 (24.8)</td>
<td>108.9</td>
<td></td>
</tr>
<tr>
<td>( \beta-1f )</td>
<td>63.6 (-5.7)</td>
<td>113.0</td>
<td></td>
</tr>
<tr>
<td>( 3 )</td>
<td>57.9 (0)</td>
<td>114.6</td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \) Dihedral angles (\( \phi \)) of –CH\(_2\)–CH\(_2\)–bridged. \( ^b \) Values in parentheses are the differential dihedral angles \( \Delta\phi = \phi_c - \phi_i \)

Assuming that the \( \Delta\theta \) is a measure of the strain energy of the spiro-linked seven-membered ring, it seems that the stability difference between the epoxides \((\alpha-1f)\) and \((\beta-1f)\) is smaller than that between \((\alpha-2a)\) and \((\beta-2a)\). This thermodynamical consideration is consistent with the observation that the conformers \((\alpha-1f)\) and \((\beta-1f)\) were equilibrated in preference of the latter (96%), though the parent \((\alpha-2a)\) exhibited the one-way isomerization to \((\beta-2a)\).

A perusal of the X-ray structure of \((\alpha-1f)\) indicates that the several atoms of the dibenzo-fused seven-membered ring occupy the crowded positions almost touching the underlying quinone component as represented by the very short spatial distances; i.e., C(8)···H(20) \((2.72 \text{ Å})\), O(1)···H(16) \((2.75)\), and O(1)···H(14) \((2.87)\). These unfavorable non-bonding interactions may be taken as a driving force for the conformational isomerization. However, such a van der Waals contact was also observed for the stable \((\beta-1f)\), in particular, between the ethano-bridge hydrogen atom H(14) and the facing carbonyl oxygen atom O(2) \([2.44 \text{ Å}]\), appreciably raising the strain energy of \((\beta-1f)\).

With respect to the structure of quinone frame, \((\beta-1f)\) is specially characterized by the almost planar plane as represented by the dihedral angles of 177.8 and -176.1\(^o\) for the bond linkages of O(2)-C(4)-C(3)-C(2) and O(1)-C(7)-C(2)-C(3), respectively, whereas the others conformers \((\alpha-2a), (\beta-2a)\) as well as \((\alpha-1f)\) adopt rather slightly folded \((12\sim22\text{o})\) boat conformations as indicated by the corresponding angles of 157.7 and -163.5\(^o\) for \((\alpha-2a)\), 164.0 and -168.2\(^o\) for \((\beta-2a)\), and 164.3 and -163.8\(^o\) for \((\beta-1f)\), respectively. Further interest is that the carbon atoms of oxirane rings of \((\alpha-1f)\) and \((\beta-1f)\) are almost planar as represented by the angles of 355\(^o\) or more when the author adds three angles made by the substituents of oxirane and another carbon center. Such a geometrical planarity of oxirane carbon is commonly known for the most of oxirane derivatives compiled in the Cambridge Structural Database.\(^9\)
1-2-2. Acid-Catalyzed Reaction of Homobenzoquinone Epoxides.

The acid-catalyzed reaction of diphenyl-substituted epoxides 1a and 1b in CDCl₃ at 30°C gave the tricyclic diketo-alcohols 4a and 4b, respectively, via the regioselective oxirane ring-opening at the Me-substituted C-O bond and the following transannular cyclization of endo-aromatic nucleus (Scheme 3). The structures of these compounds were deduced from the ¹H- and ¹³C-NMR as well as IR spectra.

The endo-Ph-substituted 1c also underwent the acid-catalyzed regioselective oxirane ring-cleavage to afford the similar tricyclic diketo-alcohol 2c (Scheme 3), whereas the exo-Ph-substituted 1d showed very slow complex decomposition (<5%) even on 6 h standing with 20 equiv excess of BF₃ (Scheme 4). This means that the endo-aromatic ring plays a crucial role in the present oxirane ring-opening as the π-electron nucleophile. As expected, the rigid compound 1e bearing the spiro-linked planar fluorenlydene moiety did not display the oxirane ring-opening even on one day standing with BF₃ because of the lack of anti assistance of π-donor aromatic ring for the C-O bond cleavage.
However, as shown in Scheme 5 and Table 2, the conformationally semirigid dibenzocycloheptene spiro-linked epoxides $\alpha$-$1f$ and $\alpha$-$1g$ were susceptible toward the acid-catalyzed regioselective oxirane ring-opening to produce the similar diketo-alcohol $4f$ for the former epoxide and the secondly transformed bicyclo[4.2.1]nonaene diketo-alcohol $5$ and its epimer $5'$ as well as the ring-contracted $6$ for the latter epoxide, respectively (further details will be described at Chapter 3). It is very noteworthy that the primary product $4g$ (not detected) underwent a facile acid-catalyzed acyl migration associated with the cyclopropane ring cleavage. It was found that the conformationally inverted $\beta$-$1f$ and $\beta$-$1g$ display the same regioselective oxirane ring-opening and the following degradation as the relevant $\alpha$-$1f$ and $\alpha$-$1g$, affording the same products. During the BF$_3$-catalyzed reactions at 30 $^\circ$C, conformational inversion of $\alpha$-conformers into $\beta$-conformers was not observed on $^1$H NMR measurement. However, the reactivity was much dependent on the conformational difference of the dibenzocycloheptene ring as experienced by the higher conversion (though shorter reaction time) of $\beta$-$1g$ compared to the conformational isomer $\alpha$-$1g$ (entries 2 and 4). The structures of $4f$, $5'$ and $6$ were confirmed by X-ray crystallographic analyses.

Table 2. Acid-catalysed rearrangement of $\omega/\beta$-$1f,g$ (30 mM) in CDCl$_3$ at 30 $^\circ$C

<table>
<thead>
<tr>
<th>entry</th>
<th>sub.</th>
<th>time (h)</th>
<th>conv. (%)</th>
<th>yield$^a$ (%)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>4</td>
<td>5</td>
<td>5'</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>$\alpha$-$1f$</td>
<td>24</td>
<td>90</td>
<td>100 0 0 0</td>
</tr>
<tr>
<td>2</td>
<td>$\alpha$-$1g$</td>
<td>16</td>
<td>12</td>
<td>0 28 42 30</td>
</tr>
<tr>
<td>3</td>
<td>$\beta$-$1f$</td>
<td>24</td>
<td>82</td>
<td>90 0 0 0</td>
</tr>
<tr>
<td>4</td>
<td>$\beta$-$1g$</td>
<td>2</td>
<td>85</td>
<td>0 74 21 2</td>
</tr>
</tbody>
</table>

$^a$ Based on consumed. $^b$ Determined by $^1$H NMR.

To clarify the reaction mechanisms, the kinetic solvent effects provide a useful mechanistic information on the transition state in such a way that the more polar the solvent is, the more stabilized the polar transition state is, with the rate being largely accelerated like in the S_N1 reactions. The author has measured the rate constants for the MeSO_3H-catalyzed oxirane ring-opening of the parent unsubstituted diphenylhomobenzoquinone epoxide 1a by monitoring its first-order decay in various less basic solvents (Figure. 2).

The rate constants in a wide range of solvents at 30°C are summarized along with the solvent polarity parameter $E_T(30)$ (Table 3). The total variation of $k_2$ amounts to only a factor of 3 over a wide range of solvent polarities investigated. The very poor kinetic solvent effects strongly support a concerted mechanism involving a less polar transition state in which the charge is highly dispersed on the π-aryl participated aromatic nucleus as well as on the breaking oxirane carbon atom. In such a S_N2-like transition state, it is conceived that the

![Figure 2](image-url)

**Figure 2.** A representative time course of the MeSO_3H ([30 mM])-catalyzed rearrangement of 1a into 4a in CDCl_3 (650 μl) at 30°C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E_T(30)$</th>
<th>$k_2^a$ (10^3 M^{-1}s^{-1})</th>
<th>$k_{rel}^b$</th>
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<tbody>
<tr>
<td>1,2-Dichloroethane</td>
<td>41.3</td>
<td>1.15</td>
<td>3.0</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>40.7</td>
<td>1.17</td>
<td>3.1</td>
</tr>
<tr>
<td>Chloroform-d</td>
<td>39.0</td>
<td>0.979</td>
<td>2.6</td>
</tr>
<tr>
<td>o-Dichlorobenzene</td>
<td>38.0</td>
<td>0.280</td>
<td>0.73</td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>37.0</td>
<td>0.380</td>
<td>0.99</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>36.8</td>
<td>0.297</td>
<td>0.77</td>
</tr>
<tr>
<td>Benzene</td>
<td>34.3</td>
<td>0.384</td>
<td>1.0</td>
</tr>
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</table>

*a The second-order rate constants $k_2$ were obtained by dividing the pseudo-first-order rate constants $k_{obs}$ by the catalyst concentration ([0.030 M])

*b Relative ratio of acid-catalyzed reaction of 1a in various solvents.
orbital interaction between the HOMO of the $\pi$-electron donating aromatic group and the
Walsh-type LUMO of oxirane ring$^{16}$ plays a crucial role in the cleavage of the relevant C-O
bond as depicted in Scheme 3. The aryl participation in the ring opening of oxiranes is
scarcely reported but has been put forwarded in order to explain the syn-stereochemistry in
the acid-induced ring opening of a particular case of oxiranes bearing aryl groups directly or
indirectly linked to the epoxide ring such as stilbene epoxides$^{17}$ and spiro-linked
2-phenyl-1,2-epoxid$^{18}$ or 1-benzyl-1,2-epoxides$^{11}$ in which the well-documented phenonium
ion intermediates are invoked.

1-2-4. Conformational Analysis in $\pi$-Aryl Participation.

As described above, acid-catalyzed reaction of these $\alpha$- and $\beta$-conformers of epoxides $1f$
and $1g$ resulted in the regioselective oxirane ring opening at the Me-substituted C-O bonds.
The following intramolecular nucleophilic attack (transannular cyclization) by the
endo-aromatic nucleus (Se2-Ar reaction) afforded the identical tricyclic diketoalcohols $4f,g$ as
the primary products (Scheme 5). Here, it is noted that the $\alpha$-$1f$ and $\beta$-$1g$ were subjected to
the whole inversion of the twist-boat form in these reactions, as represented by X-ray crystal
structure of $4f$. Due to the appreciable thermal stability, the $\alpha$- and $\beta$-conformers of epoxides
$1f$ and $1g$ take advantage of evaluating the conformational effects (i.e., stereoelectronic
effects) on the possible anti-$\pi$-aryl participation in the oxirane ring-cleavage. Therefore, the
author has made a kinetic investigation of acid-catalyzed rearrangement of each conformer of
$1f$ and $1g$ in comparison with the reference epoxides $1a-c$ (Scheme 1).

First, to assess the conformational stability of the less stable $\alpha$-conformers of $1f,g,2a,b$
the author carried out a kinetic study of the non-mediated thermal interconversion into the
corresponding $\beta$-isomers by $^1$H NMR in CDCl$_3$ at 80 °C in a sealed tube. Only the epoxide $3\alpha$
established the equilibration ($\alpha:\beta = 4:96$), whereas the other $\alpha$-conformers were completely
transformed into the corresponding $\beta$-isomers. The first-order rate constants $k_1/s^{-1}$ thus
obtained were given in Table 4. The estimated energy barriers from the $k_1$ values for $\alpha \rightarrow
\beta$ conversion are 108–109 and 117–125 kJ mol$^{-1}$ at 80 °C for $1f,g$ and $2a,b$, respectively.
These values are high enough to prevent the conformational interconversion at ordinary
temperature, although the epoxidation slightly reduced the energy barriers by $\sim 17$ kJ mol$^{-1}$.
Thus the thermal stability increases in the order of $\alpha$-$2b \succ \alpha$-$2a \succ \alpha$-$1f \succ \alpha$-$1g$. The
conformational locking for the intrinsically flexible parent dibenzocycloheptene ring$^{19}$ can be
ascribed to the repulsive van der Waals interaction between (A) the peri-hydrogen atom of
endo-aromatic ring and the quinone plane as well as (B) the peri-hydrogen atom of
exo-aromatic ring and the cyclopropane Me substituent.
Keeping this in mind, the author next investigated the kinetics of acid-catalyzed reactions of the α- and β- families of the conformationally locked 1f and 1g as well as the mobile 1a-c. The representative kinetic run was performed at 30 °C in a NMR tube containing epoxide (0.03 M) and BF3·OEt2 (0.30 M) in CDCl3 (0.65 mL) by following the decay of the diagnostic Me group of the relevant epoxide (TMS as an internal standard) over the second-half lives. During all kinetic runs, no indication of the conformational isomerization \( \alpha \rightarrow \beta \) was found by the NMR measurement, in accordance with the significant thermal stability of these α-conformers. The observed pseudo-first-order rate constants \( (k_{obs}/s^{-1}) \) were divided by the concentration of the acid to obtain the second-order rate constants \( k_2/s^{-1} M^{-1} \). The values of \( k_2 \) thus obtained are listed along with the relative rate constants \( k_2^{rel} \) (vs the reference 1a) in Table 4.

Table 4 indicates that the rates were accelerated or decelerated depending on the conformation (α or β) of the dibenzocycloheptene moiety and on the substitution pattern (p or m) of quinone dimethyl substituents. The most striking feature of the reactions of the 1f and 1g is a reversal of the relative reactivity of α and β-conformers. Thus, for 1f, the less stable α-conformer was ca 4 times more reactive than the stable β-one (entries 3 and 4), whereas for 1g the stable β-conformer was ca 25 times more reactive than the less stable α-one (entries 5 and 6). Additionally, the noticeable points are as follows; (1) the conformationally locked 1f and 1g (except β-1g) exhibited the reactivity comparable to that for the related 1a and b; (2) the m-dimethyl-substituted 1g and 1b tended to react faster than the p-dimethyl-substituted 1f and 1a (entries 3-8).

Table 4. Rate constants for the conformational inversion and BF3-catalyzed ring-opening of homobenzoquinone epoxides at 30°C in CDCl3.

<table>
<thead>
<tr>
<th>entry</th>
<th>compd.</th>
<th>inversion ( 10^5 k_1 / s^{-1} )</th>
<th>ring-opening of epoxide ( 10^3 k_2^{rel} / M^{-1}s^{-1} )</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>( \alpha-2a )</td>
<td>4.05^b</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>( \alpha-2b )</td>
<td>0.27^b</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>( \alpha-1f )</td>
<td>59.5^c</td>
<td>6.98</td>
</tr>
<tr>
<td>4</td>
<td>( \beta-1f )</td>
<td>2.72^d</td>
<td>1.84</td>
</tr>
<tr>
<td>5</td>
<td>( \alpha-1g )</td>
<td>89.3^b</td>
<td>3.99</td>
</tr>
<tr>
<td>6</td>
<td>( \beta-1g )</td>
<td>-</td>
<td>98.0</td>
</tr>
<tr>
<td>7</td>
<td>1a</td>
<td>-</td>
<td>5.16</td>
</tr>
<tr>
<td>8</td>
<td>1b</td>
<td>-</td>
<td>15.1</td>
</tr>
<tr>
<td>9</td>
<td>1c</td>
<td>-</td>
<td>4.64</td>
</tr>
</tbody>
</table>

^a The second-order rate constants were obtained by dividing the pseudo-first-order rate constants \( k_{obs} \) (at 30 °C in CDCl3) by the catalyst concentration ([0.30 M]). ^b Completely inverted into the corresponding \( \beta- \) isomer. ^c The \( k \) values at different temperature (60 and 70 °C) are 7.66 and 23.2 \( (x 10^{-5} s^{-1}) \), respectively, and give the extrapolated \( k \) values of 2.18 \( (x 10^{-5} s^{-1}) \) at 30 °C as well as the activation parameters \( (\Delta H^\ddagger = 97.9 \text{kJ/mol}, \Delta S^\ddagger = -35.3 \text{J/K.mol}, \Delta G^\ddagger = 108.6 \text{kJ/mol at 80 °C}) \). ^d Calculated from the equilibrium constant \( K = 2.1 \) at 80 °C.
These appreciable conformational effects can be explained by assuming that the present acid-catalyzed regioselective oxirane ring-opening occurs via an SN2-like concerted mechanism. Indeed, the concerted mechanism was strongly supported by the poor kinetic solvent effects in the MeSO₃H-mediated reaction of epoxide 1a as well as the appreciable kinetic substituent effects. Specifically, it can be envisaged that the reaction proceeds through the stereoelectronically controlled π-aryl participated rate-determining transition state with the aid of the vacant oxirane Walsh orbital (LUMO) as depicted in Figure 3. Here, the author can also imagine that the π-aryl participation would be significantly intensified in the conformers in which the approaching aromatic π-orbital (HOMO) performs the ideal head-to-head orbital overlapping with the oxirane Walsh orbital. Such a through space orbital interaction is favorably achieved for the conformers α-1f and β-1g (Figure 3a and d), overriding the high inversion energy cost (> 108 kJ mol⁻¹). This is a reason for the higher reactivity of α-1f and β-1g than the corresponding isomers β-1f and α-1g, respectively. By contrast, the corresponding orbital interaction for the less reactive conformers β-1f and α-1g is considerably reduced due to the rather insufficient orthogonal orbital interaction (Figure 3b and c), thus lowering the reactivity irrespective of requiring no conformational inversion.

Accordingly, the 25-fold higher reactivity of the stable β-1g compared with α-1g can be taken as a strong evidence for the occurrence of favored π-electron donating interaction with the oxirane vacant Walsh orbital as depicted in Figure 3d. As to α-1f, however, the rather diminished 3.5-fold higher lability than the β-isomer may be due to the additional steric interaction between the cyclopropane Me substituent and the exo-aromatic ring (B). As a result, the rates of epoxide ring-opening of 1f and 1g are governed by the critical balance between the attractive π-aryl participated orbital interaction and the repulsive van der Waals congestion associated with the conformational inversion of dibenzocycloheptene ring.

Incidentally, alternative SN1-like two-step mechanism may contradict the present kinetic results because the more reactive conformers α-1f and β-1g have the capturing aryl orbital

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**Figure 3.** Orbital interaction between HOMO (aromatic ring) and LUMO (Walsh orbital) in transition state.
unfavorably reacting across the ring system to engage the carbocation \( p \)-orbital (rehybridized from the Walsh orbital), whereas the less reactive \( \beta -1f \) and \( \alpha -1g \) enjoy the capture on the same side of the ring system. This would predict the result opposite to that deduced from the consideration of Walsh orbital.

1-2-5. Dual Pathway Acid-Catalyzed Reaction of Disubstituted HQ-Epoxide

Next, on the basis of the results described above, the author felt that an appropriately \( p \)-substituted diphenylhomobenzoquinone epoxide 1 might allow to provide a possible \( ipso \)-product from the \( \pi \)-aryl participated transition state. Herein, the author wishes to report the mechanistic evidence for the very rare \( \pi \)-aryl-assisted oxirane ring opening in the BF\(_3\)-catalyzed reaction of bis\((p\)-chlorophenyl\)homobenzoquinone epoxide 1i. The acid-induced reaction of \( p,p'\)-dimethyl-, unsubstituted, and \( p,p'\)-dichloro-substituted 1a, h, and i (0.02 mmol) was carried out in the presence of BF\(_3\) (0.40 mmol) in CDCl\(_3\) (0.62 ml) at ordinary temperature. The reaction proceeded in a regioselective oxirane ring-opening at the Me substituted C-O bond and on treatment with water gave the common \( o \)-phenylene bridged tricyclic diketo-alcohols 4a, h, and i (for 4i, as a mixture of small amount of its epimer 4'i) and 2,5-cyclohexadien-4-one spiro-linked tricyclic diketo-alcohol 7i (47%) for only the
chloro-substituted 1i in almost quantitative total yields based on the consumed 1 (Scheme 6).
Unfortunately, we could not isolate 4i and 4'i in pure form.

The structures of compounds 7i, 4h, i and 4'i were deduced from their 1H- and 13C-NMR spectra and the 7i was confirmed by the X-ray crystal analysis (Figure 4).

As shown in Scheme 6, the formation of 7i and 4a,h,i can be rationalized by the occurrence of the competitive ipso- and ortho- S$_2$2-Ar reaction via aryl bridged benzenonium ions, i.e., σ-complexes I and II, respectively. Although the intermediate II easily undergoes a rearomatization to afford 4a,h,i via a proton migration, the formation of compound 7i can be explained by the capture of the intermediate I with some water followed by the loss of HCl. Thus, the isolation of 7i and 4i is taken as a strong evidence for the appearance of both the σ-complexes, I and II. These schematic considerations prompted us to further examine the following mechanistic questions about the transition state leading to the above σ-complexes$^{22}$ as well as the marked substituent effects on the product distributions.

**Why does the p-chloro-substituted 1i provide the dual ipso/ortho conjunct products in contrast to the p,p’-dimethyl-substituted 1h and the unsubstituted 1a?**

This question can be easily solved by considering the characteristic electronic properties of p-Cl substituent as exhibiting the electron-donating resonance effect as well as the good leaving ability which would stabilize the adjoining positive center of I and then facilitate the release of HCl (Scheme 6). In view of the ipso-attack, the p-tolyl group would allow such a reaction more favorably than the p-chlorophenyl group due to the electron density at the ipso aromatic carbon. However, even if such an ipso σ-complex is formed for 1a and 1h and undergoes the attack of water at the p-position, the lack of the leaving ability of Me group (including H) will cause the transformation into the ortho σ-complex via a facile 1,2-shift on the aromatic ring.
1-3. Conclusion

In summary, the acid-catalyzed rearrangement of homobenzoquinone epoxides possessing endo-aromatic ring displayed a new synthesis of polycyclic compounds involving a regioselective oxirane ring-opening and a crucial transannular cyclization as well as the subsequent ring-enlargement by 1,2-acyl migration associated with the incorporated cyclopropane ring-opening, depending on the substitution pattern of the quinone methyl groups. These findings provide the useful information on the rearrangements of polycyclic epoxides and the design of more extended framework compounds. Additionally, based on the kinetics and conformational effects in acid-catalysed reactions of the present homobenzoquinone epoxides, the author has found that the π-aryl participated electron-donating interaction with the vacant oxirane Walsh orbital plays a prominent role in the epoxide ring-opening. Moreover, the dual pathway for 1i as well as the kinetic solvent effects is likely to prove that the acid-catalyzed ring-opening of diarylhomobenzoquinone epoxides 1 occurs via a concerted manner involving a very rare remote (δ-located) π-aryl participated transition state. The present findings will provide very useful insights into the mechanistic understanding of the acid-catalyzed ring-opening of epoxides.

1-4. Experimental Section

General procedures for the synthesis of homobenzoquinone epoxides. To a mixture of homobenzoquinone (0.5 mmol) and 30% H₂O₂ (0.75 mmol) in DMSO (1 mL) was added dropwisely (10 min) a solution of Bu₄NF (1M solution in THF, 0.5 mmol) at room temperature. After the addition of the reagent the reaction mixture was stirred for 2h. Then, the epoxide 1 was extracted with ethyl acetate (3 mL × 3). The organic layer was washed with water (3 mL × 3) and dried over magnesium sulfate. The solvent was evaporated in vacuo. The epoxide 1 was purified by column chromatography on silica gel (benzene as an eluent) and recrystallization from hexane-ether or hexane-benzene. The structures of all epoxides were deduced from the ¹H and ¹³C NMR, and IR spectra and the compounds α-1f, β-1f, α-1g were also confirmed by the X-ray crystallographic analyses.

General procedures for acid-catalyzed reaction of homobenzoquinone epoxides. To a CDCl₃ solution (670 µl) of 1 (0.02 mmol) in a NMR tube was added the requisite amount of BF₃·OEt₂ at room temperature by using a micro syringe. The progress of reaction was monitored by ¹H NMR. After a period of requisite time, the reaction solution was transferred into a separate funnel, diluted with chloroform (10 mL) and then washed with water (3 mL × 3). The aqueous layer was extracted with chloroform (5 mL × 2). The combined organic
layer was washed with water (3 mL × 3), then dried over calcium chloride. After the evaporation of the solvent in vacuo, the residue was submitted for a $^1$H NMR analysis to determine the product distribution. The column chromatographic treatment of the reaction mixtures on silica gel gave 5, 5', and 6 with a mixture of hexane-ethyl acetate as an eluant. The other compounds 4a-c, f and h were purified by recrystallization from hexane-ether. The structures of all products were deduced from the $^1$H and $^{13}$C NMR, and IR spectra. The structures of 4f, 5 and 5' were also confirmed by the X-ray crystallographic analyses.

1,5-Dimethyl-8,8-diphenyl-4-oxa-tricyclo[5.1.0.0$^{3,5}$]octane-2,6-dione (1a): mp. 123.5°C (from chloroform/n-hexane); $^1$H NMR(270 MHz, CDCl$_3$) δ 0.92 (s, 3H), 1.18 (s, 3H), 2.81 (s, 1H), 2.82 (s, 1H), 7.17-7.32 (m, 8H), 7.37-7.40 (m, 2H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ13.7, 16.9, 37.6, 39.7, 49.6, 60.1, 60.3, 127.5, 127.9, 128.2, 128.9, 129.1, 129.5, 138.1, 139.9, 198.1, 200.3; Anal Calcd for C$_{21}$H$_{18}$O$_3$ : C, 79.22; H, 5.70, Found : C, 79.10; H, 5.86.

1,3-Dimethyl-8,8-diphenyl-4-oxa-tricyclo[5.1.0.0$^{3,5}$]octane-2,6-dione (1b): mp. 229.4-229.8°C (from chloroform/n-hexane); $^1$H NMR(270 MHz, CDCl$_3$) δ 0.99 (s, 3H), 1.23 (s, 3H), 2.75 (d, 1H, $J$ = 1.15 Hz), 2.78 (d, 1H, $J$ = 1.15 Hz), 7.18-7.27 (m, 6H), 7.30-7.33 (m, 2H), 7.39 (m, 2H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 14.3, 17.4, 36.9, 40.0, 49.5, 60.0, 60.4, 127.6, 127.9, 128.3, 128.9, 129.1, 129.5, 138.1, 140.0, 198.2, 200.3; IR (KBr): 3378, 3082, 3056, 3031, 2999, 2938, 1958, 1897, 1698, 1597, 1580, 1493, 1447, 1372, 1344, 1294, 1278, 1235, 1198, 1159, 1083, 1060, 1026, 1011, 990, 974, 935, 906, 884, 863 cm$^{-1}$; Anal. Calcd for C$_{21}$H$_{18}$O$_3$ : C, 79.22; H, 5.70, Found : C, 79.52; H, 5.69.

endo-1,5,8-trimethyl-8-phenyl-4-oxa-tricyclo[5.1.0.0$^{3,5}$]octane-2,6-dione (1c): mp. 136.8-138.0°C (from chloroform/n-hexane); $^1$H NMR(270 MHz, CDCl$_3$) δ 0.94 (s, 3H), 1.54 (s, 6H), 2.16 (s, 1H), 2.62 (s, 1H), 7.11-7.15 (m, 2H), 7.22-7.33 (m, 3H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 13.7, 15.0, 26.4, 37.6, 41.7, 42.2, 59.6, 59.7, 127.8, 129.0, 139.1, 199.0, 200.6; IR (KBr): 3455, 2982, 2936, 1740, 1691, 1599, 1488, 1441, 1381, 1277, 1227, 1162, 1139, 1092, 1031, 940, 919, 836, 801 cm$^{-1}$; Anal Calcd for C$_{16}$H$_{16}$O$_3$ : C, 74.98; H, 6.29, Found : C, 74.71; H, 5.97.
exo-1,5,8-trimethyl-8-phenyl-4-oxa-tricyclo[5.1.0.0³⁵]octane-2,6-dione (1d): $^1$H NMR (270 MHz, CDCl$_3$) $\delta$ 1.01 (s, 3H), 1.27 (s, 3H), 1.55 (s, 3H), 2.26 (s, 1H), 3.49 (s, 1H), 7.26-7.37 (m, 5H); $^{13}$C NMR (67 MHz, CDCl$_3$) $\delta$ 14.0, 17.4, 20.6, 34.6, 35.7, 39.1, 63.3, 63.4, 127.3, 128.2, 128.6, 140.9, 199.6, 202.1; IR (KBr): 2964, 1695, 1496, 1445, 1387, 1332, 1262, 1165, 1068, 985, 865, 849 cm$^{-1}$; Anal Calcd for C$_{16}$H$_{16}$O$_3$: C, 74.98; H, 6.29, Found : C, 75.02; H, 6.42.

spiro-[9H-fluorene-9,8'-1,5-dimethyl-4-oxa-tricyclo[5.1.0.0³⁵]octane-2,6-dione] (1e): mp. 134.4-135.0 ˚C (from chloroform / n-hexane); $^1$H NMR (270 MHz, CDCl$_3$) $\delta$ 1.65 (s, 3H), 1.69 (s, 3H), 2.88 (s, 1H), 3.73 (s, 1H), 6.57 (d, 1H, $J$ = 7.91), 7.10 - 7.17 (m, 2H), 7.25 - 7.43 (m, 3H), 7.75 - 7.80 (m, 2H); $^{13}$C NMR (67 MHz, CDCl$_3$) $\delta$ 14.0, 15.9, 37.6, 38.5, 44.9, 63.9, 64.9, 120.3, 120.6, 121.6, 122.7, 126.5, 126.9, 127.5, 127.8, 139.5, 140.9, 141.2, 141.4, 198.2, 201.5; IR (KBr): 3394, 3053, 3006, 2973, 2933, 1705, 1482, 1449, 1396, 1378, 1310, 1204, 1198, 1144, 1112, 1101, 1084, 1064, 1003, 941, 901, 855, 830, 792, 783, 772, 760 cm$^{-1}$; Anal Calcd for C$_{21}$H$_{16}$O$_3$: C, 79.73; H, 5.10, Found : C, 79.48; H, 5.33.

exo-spiro-[10,11-Dihydro-dibenzo[a,d]cycloheptane-5,8'-1,5-dimethyl-4-oxatricyclo[5.1.0.0³⁵]octane-2,6-dione] ($\alpha$-1f): mp. 185.3-186.2°C (from chloroform/n-hexane); $^1$H NMR (270 MHz, CDCl$_3$) $\delta$ 0.78 (s, 3H), 1.60 (s, 3H), 2.44 (s, 1H), 2.81 - 2.96 (m, 2H), 3.00 (s, 1H), 3.30 - 3.41 (m, 1H), 4.08 - 4.17(m, 1H), 6.95 - 6.99(m, 2H), 7.00 - 7.26 (m,6H); $^{13}$C NMR (67 MHz, CDCl$_3$) $\delta$ 13.4, 18.5, 29.8, 31.6, 38.0, 44.9, 48.1, 59.7, 60.6, 125.8, 126.3, 126.5, 126.9, 128.1, 128.1, 130.2, 132.2, 134.9, 138.6, 139.2, 140.4, 197.4, 201.0; IR (KBr): 3385, 3051, 3034, 2967, 2940, 2896, 1933, 1700, 1601, 1486, 1460, 1445, 1373, 1330, 1261, 1229, 1206, 1177, 1153, 1099, 1084, 1073, 1053, 1019, 994, 958, 914, 874, 858, 806, 793, 779, 759 cm$^{-1}$; Anal Calcd for C$_{23}$H$_{20}$O$_3$: C, 80.21; H, 5.85, Found : C, 79.94; H, 5.88.
exo-spiro-[10,11-Dihydro-dibenzo[a,d]cycloheptane-5,8’-1,3-dimethyl-4-oxatricyclo[5.1.0.0^3,5]octane-2,6-dione] (α-1g): mp. 120.0-121.0°C (from hexane-chloroform); ¹H NMR (270 MHz, CDCl₃) δ 1.33 (s, 3H), 1.62 (s, 3H), 2.37 (d, 1H, J = 1.07), 2.81 (d, 1H, J = 1.07), 2.85-2.93 (m, 2H), 3.33-3.45 (m, 1H), 4.14-4.27 (m, 1H), 6.93-6.98 (t, 2H), 7.04-7.23 (m, 6H); ¹³C NMR (67 MHz, CDCl₃) δ 15.1, 19.4, 29.8, 31.6, 36.5, 44.1, 47.0, 60.3, 60.7, 125.5, 126.2, 126.4, 127.3, 128.0, 128.1, 130.2, 132.4, 134.6, 138.6, 139.4, 140.6, 197.3, 201.5; IR (KBr): 3061, 2992, 2938, 2895, 1693, 1601, 1487, 1460, 1375, 1279, 1195, 1089, 1058, 1038 cm⁻¹; Anal Calcd for C₂₃H₂₀O₃: C, 80.21; H, 8.5. Found: C, 79.95; H, 5.59.

endo-spiro-[10,11-Dihydro-dibenzo[a,d]cycloheptane-5,8’-1,5-dimethyl-4-oxatricyclo[5.1.0.0^3,5]octane-2,6-dione] (β-1f): mp. 117.2-118.5°C (from hexane-chloroform); ¹H NMR (270 MHz, CDCl₃) δ 1.21 (s, 3H), 1.34 (s, 3H), 2.70-2.95 (m, 2H), 2.73 (s, 1H), 2.97 (s, 1H), 3.43-3.66 (m, 2H), 7.02-7.20 (m, 7H), 7.34-7.37 (m, 1H); ¹³C NMR (67 MHz, CDCl₃) δ 14.6, 16.3, 30.3, 32.2, 37.9, 39.4, 48.8, 60.1, 61.0, 126.1, 126.2, 126.3, 126.8, 127.2, 128.1, 128.7, 130.2, 131.6, 135.5, 136.8, 138.4, 140.9, 199.0, 199.4; IR (KBr): 3389, 3047, 2983, 2969, 2917, 1956, 1707, 1690, 1488, 1445, 1426, 1384, 1358, 1327, 1252, 1210, 1158, 1110, 1085, 1064, 1020, 952, 930, 865, 837, 804, 795, 775, 762, 739 cm⁻¹; Anal Calcd for C₂₃H₂₀O₃: C, 80.21; H, 8.5. Found: C, 79.91; H, 5.83.

endo-spiro-[10,11-Dihydro-dibenzo[a,d]cycloheptane-5,8’-1,3-dimethyl-4-oxatricyclo[5.1.0.0^3,5]octane-2,6-dione] (β-1g): mp. 136-137°C (from hexane-chloroform); ¹H NMR (270 MHz, CDCl₃) δ 0.67 (s, 3H), 1.22 (s, 3H), 2.71-2.78 (m, 1H), 2.87-3.04 (m, 1H), 2.97 (d, 1H, J = 0.98), 3.03 (d, 1H, J = 0.98), 3.42-3.56 (m, 2H), 7.04-7.21 (m, 8H); ¹³C NMR (67 MHz, CDCl₃) δ 13.6, 16.2, 30.3, 32.2, 39.1, 40.0, 49.6, 59.6, 61.0, 126.3, 126.5, 127.3, 128.2, 128.6, 130.1, 131.7, 135.2, 137.2, 138.4, 141.1, 198.7, 198.9; IR (KBr): 3436, 3060, 3020, 2934, 194, 1487, 1444, 1338, 1315, 1281, 1197, 1112, 1059, 1019, 973, 905, 862, 826 cm⁻¹; Anal Calcd for C₂₃H₂₀O₃: C, 80.21; H, 5.85. Found: C, 80.00; H, 5.59.
exo-spiro[10,11-Dihydro-5H-dibenzo[a,d]cycloheptene-5,7'-1,3-dimethyl-bicyclo[4,1,0]hept-3-ene-2,5-dione] (α-2b): mp. 170-171 °C (from chloroform / n-hexane); \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.71 (s, 3H), 1.78 (d, 3H, \(J = 1.48\) Hz), 2.63 (s, 1H), 2.65-2.94 (m, 2H), 3.27-3.36 (m, 1H), 3.98-4.12 (m, 1H), 6.03 (q, 1H, \(J = 1.48\) Hz), 6.85-6.90 (m, 4H), 7.02-7.36 (m, 4H); \(^13\)C NMR (67.5 MHz, CDCl\(_3\)) \(\delta\) 16.7, 19.0, 30.0, 31.1, 39.5, 48.3, 50.5, 125.5, 126.1, 126.4, 127.5, 127.7, 127.9, 130.3, 131.9, 134.8, 136.2, 138.6, 138.6, 140.9, 149.9, 194.2, 198.1; IR (KBr): 3059, 3016, 2979, 2941, 2895, 1672, 1657, 1628, 1601, 1484, 1460, 1358, 1307, 1285, 1221, 1202, 1177 cm\(^{-1}\); HRMS: Calculated for C\(_{23}\)H\(_{20}\)O\(_2\), 328.1463, found 328.1461

endo-spiro[10,11-Dihydro-5H-dibenzo[a,d]cycloheptene-5,7'-1,3-dimethyl-bicyclo[4,1,0]hept-3-ene-2,5-dione] (β-2b): mp. 138-139 °C (from chloroform / n-hexane); \(^1\)H NMR(270 MHz, CDCl\(_3\)) \(\delta\) 1.28 (s, 3H), 1.50 (d, 3H, \(J = 1.48\) Hz), 2.64-2.71 (m, 1H), 2.91-2.96 (m, 1H), 3.21 (s, 1H), 3.41-3.49 (m, 2H), 6.23 (q, 1H, \(J = 1.48\)), 6.89-6.90 (m, 1H), 6.96-7.25 (m, 6H), 7.33-7.37 (m, 1H); \(^13\)C NMR (67.5 MHz, CDCl\(_3\)) \(\delta\) 16.0, 16.6, 29.9, 32.5, 41.5, 42.2, 51.4, 126.2, 126.3, 126.8, 127.9, 128.0, 128.6, 129.6, 131.8, 135.7, 136.1, 137.5, 138.4, 140.3, 149.2, 195.5, 196.6; IR (KBr): 3058, 3006, 2967, 2890, 1684, 1655, 1618, 1477, 1380, 1368, 1300, 1283, 1255, 1241, 1111 cm\(^{-1}\); HRMS : Calculated for C\(_{23}\)H\(_{20}\)O\(_2\), 328.1463, found 328.1461

(1R*,8R*,9S*,10R*,12S*)-12-Hydroxy-1,10-dimethyl-8-phenyl-tetracyclo-[6.4.1\(^1\)9.0\(^{27}\)0\(^{8,13}\)]trideca-2(7),3,5-triene-11,13-dione (4a): \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.27 (s, 3H), 1.64 (s, 3H), 2.73 (s, 1H), 3.02 (d, 1H, \(J = 4.59\), OH), 3.86 (d, 1H, \(J = 4.59\)), 6.82 (dd, 1H, \(J = 1.32, 7.91\)), 7.09 (ddd, 1H, \(J = 1.65, 7.25, 7.91\)), 7.20 (ddd, 1H, \(J = 1.32, 7.25, 7.58\)), 7.26-7.30 (m, 2H), 7.36-7.46 (m, 4H); \(^13\)C NMR (67 MHz, CDCl\(_3\)) \(\delta\) 14.5, 19.3, 41.8, 47.3, 52.6, 53.7, 85.5, 125.6, 127.8, 127.9, 128.1, 128.2, 128.5, 129.9, 130.1, 131.8, 136.1, 136.2, 136.5, 137.5, 140.3, 149.2, 205.0, 205.4; IR (KBr): 3457, 3008, 2935, 1744, 1685, 1488, 1442, 1378, 1307, 1235, 1151, 1054, 940, 912, 834, 793, 758 cm\(^{-1}\)
(1R*,8R*,9S*,10R*,12S*)-12-Hydroxy-1,9-dimethyl-8-phenyl-tetracyclo-[6.4.11.9.0².⁷.0⁸.¹³]trideca-2(7),3,5-triene-11,13-dione  (4b): mp. 74.8-75.2 °C (from hexane-chloroform); ¹H NMR (270 MHz, CDCl₃) δ 1.14 (s, 3H), 1.68 (s, 3H), 2.35 (s, 1H, OH), 3.05 (d, 1H, J=1.35 Hz, OH), 3.78 (d, 1H, J=1.35 Hz); ¹³C NMR (67 MHz, CDCl₃) δ 15.0, 15.3, 29.8, 37.9, 49.8, 52.6, 84.1, 125.3, 127.9, 128.1, 128.3, 128.9, 129.0, 129.2, 129.9, 131.0, 136.7, 136.9, 203.2, 206.3; IR (KBr): 3348, 3060, 3018, 2932, 2902, 2832, 1766, 1694, 1595, 1486, 1443, 1376, 1360, 1161, 1092, 1060, 1016, 973, 866 cm⁻¹

(1R*,8R*,9S*,10R*,12S*)-12-Hydroxy-1,8,10-trimethyl-tetracyclo-[6.4.11.9.0².⁷.0⁸.¹³]trideca-2(7),3,5-triene-11,13-dione  (4c): mp. 161.1-162.0 °C (from hexane-chloroform); ¹H NMR (270 MHz, CDCl₃) δ 1.52 (s, 3H), 1.57 (s, 3H), 1.73 (s, 3H), 2.26 (s, 1H), 2.76 (br, 1H, OH), 3.70 (br, 1H), 7.24-7.34 (m, 3H), 7.39-7.41 (m, 1H); ¹³C NMR (67 MHz, CDCl₃) δ 14.2, 16.2, 19.7, 42.6, 43.6, 47.1, 47.1, 53.6, 85.2, 125.3, 126.2, 127.8, 128.3, 136.7, 137.0, 205.2, 205.3; IR (KBr): 3464, 2925, 1715, 1698, 1559, 1541, 1508, 1489, 1457, 1387, 1204, 1034, cm⁻¹

(1R*,8R*,9S*,10R*,12S*)-12-Hydroxy-1,8,10-trimethyl-tetracyclo-[6.4.11.9.0².⁷.0⁸.¹³]trideca-2(7),3,5-triene-11,13-dione  (4f): mp. 164.5-165.0 °C (from hexane-chloroform); ¹H NMR (270 MHz, CDCl₃) δ 1.05 (s, 3H), 1.64 (s, 3H), 2.64 (d, 1H, J= 3.54, OH), 2.77-2.85 (m, 1H), 2.96 (s, 1H), 2.90-3.17 (m, 2H), 3.27-3.38 (m, 1H), 3.59 (d, 1H, J= 3.54), 6.95-6.99 (m, 1H), 7.10-7.11 (m, 2H), 7.13-7.31 (m, 4H); ¹³C NMR (67 MHz, CDCl₃) δ 14.3, 15.5, 31.2, 36.3, 40.4, 49.6, 50.5, 54.8, 86.3, 122.5, 126.5, 126.7, 129.1, 129.6, 131.9, 132.3, 135.7, 138.3, 140.6, 144.9, 204.5, 205.0; IR (KBr): 3380, 3037, 2928, 1708, 1598, 1542, 1482, 1446, 1381, 1325, 1278, 1156, 1040, 953, 930, 867, 836, cm⁻¹
(5): $^1$H NMR (270 MHz, CDCl$_3$) $\delta$ 1.62 (s, 3H), 1.80 (d, 3H, $J = 1.40$), 2.83-2.96 (m, 3H, OH), 3.14-3.30 (m, 2H), 4.15 (d, 1H, $J = 8.01$), 5.93 (q, 1H, $J = 1.40$), 7.02-7.05 (m, 1H), 7.13-7.30 (m, 5H) 7.74-7.78 (m, 1H); $^{13}$C NMR (67 MHz, CDCl$_3$) $\delta$ 17.1, 24.1, 32.3, 32.4, 32.5, 32.5, 57.7, 65.3, 90.1, 120.9, 126.4, 126.7, 127.4, 128.2, 129.0, 129.8, 131.0, 136.6, 137.0, 140.6, 140.7, 141.5, 154.4, 200.1, 210.3; IR (KBr): 3432, 2963, 1743, 1706, 1489, 1444, 1377, 1262, 1098, 1027, 867, cm$^{-1}$

(5'): mp. 112.2-112.6°C (from hexane-chloroform): $^1$H NMR (270 MHz, CDCl$_3$) $\delta$ 1.72 (s, 3H), 1.82 (d, 3H, $J = 1.32$), 2.82-2.92 (m, 2H), 3.13-3.24 (m, 2H), 3.94 (d, 1H, $J = 4.37$, OH), 4.40 (d, 1H, $J = 4.37$), 6.08 (q, 1H, $J = 1.32$), 6.96-6.99 (m, 1H), 7.11-7.28 (m, 5H) 7.83-7.87 (m, 1H); $^{13}$C NMR (67 MHz, CDCl$_3$) $\delta$ 16.6, 24.6, 31.8, 32.1, 63.5, 64.1, 86.3, 121.6, 126.0, 126.4, 127.3, 128.1, 128.2, 129.5, 130.9, 135.9, 137.2, 139.8, 140.6, 141.0, 157.1, 200.2, 207.3; IR (KBr): 3454, 2935, 1739, 1688, 1440, 1381, 1227, 1092, 1030, 918, 800, cm$^{-1}$

(6): mp. 238.3-238.8°C (from hexane-chloroform): $^1$H NMR (270 MHz, CDCl$_3$) $\delta$ 1.86 (s, 3H), 2.91-3.02 (m, 2H), 3.13-3.29 (m, 2H), 5.09 (s, 1H), 5.28 (s, 1H, OH), 6.75 (s, 1H), 7.03-7.08 (m, 1H), 7.18-7.33 (m, 5H), 7.76-7.79 (m, 1H) 9.43 (s, 1H); $^{13}$C NMR (67 MHz, CDCl$_3$) $\delta$ 11.7, 33.7, 36.0, 51.8, 64.9, 77.2, 118.7, 121.5, 125.5, 127.4, 128.0, 128.3, 130.9, 132.7, 140.4, 141.9, 143.0, 145.6, 146.2, 149.4, 190.1, 207.2; IR (KBr): 3568, 2925, 2851, 1772, 1684, 1571, 1542, 1386, 1185, 1117, 915, 857, cm$^{-1}$

1,3-Dimethyl-8,8-ditoly-4-oxa-tricyclo[5.1.0.0$^3$5]octane-2,6-dione (1h): mp 139.9-140.8 °C, colorless prisms (chloroform/pentane); $^1$H NMR(270 MHz, CDCl$_3$) $\delta$ 0.94 (s, 3H), 1.17 (s, 3H), 2.24 (s, 3H), 2.27 (s, 3H), 2.77 (s, 1H), 2.81 (s, 1H), 7.02-7.14 (m, 6H), 7.22-7.26 (m, 2H); $^{13}$C-NMR (67 MHz, CDCl$_3$) $\delta$ 13.8, 16.9, 21.1, 21.1, 37.7, 39.8, 49.3, 60.1, 60.4, 128.0, 129.2, 129.5, 129.7, 135.3, 137.3, 137.3, 137.6, 198.4, 200.5; IR (KBr) 1702 (C=O) cm$^{-1}$.

1,5-dimethyl-8,8-bis(4-chlorophenyl)-4-oxa-tricyclo[5.1.0.0^3,5]octane-2,6-dione (1i): mp 142.7-143.5 °C, colorless prisms (chloroform/pentane); \(^1^H\)-NMR(270 MHz, CDCl\(_3\)) δ 1.01 (s, 3H), 1.19 (s, 3H), 2.75 (s, 1H), 2.89 (s, 1H), 7.14-7.19 (m, 2H), 7.22-7.27 (m, 2H), 7.29 (s, 4H); \(^1^C\) NMR (67 MHz, CDCl\(_3\)) δ 13.8, 17.0, 37.2, 39.2, 47.4, 60.4, 129.3, 129.4, 129.6, 130.8, 133.9, 134.3, 136.1, 138.0, 197.8, 200.0; IR (KBr): 1702 (C=O) cm\(^{-1}\). HRMS: Calcd for C\(_{21}\)H\(_{16}\)Cl\(_2\)O\(_3\): 386.0476. Found: 386.0479.

\((1R^*,8R^*,9S^*,10R^*,12S^*)\)-12-Hydroxy-5-methyl-1,10-dimethyl-8-tolyl-tetracyclo-[6.4.1\(^9\).0\(^2\).7\(^8\).0\(^{13}\)]trideca-2(7),3,5-triene-11,13-dione (4h): mp. 237.5-238.4 °C (from chloroform/\(n\)-hexane); \(^1^H\) NMR(270 MHz, CDCl\(_3\)) δ 1.24 (s, 3H), 1.61 (s, 3H), 2.13 (s, 3H), 2.41 (s, 3H), 2.68 (s, 1H), 3.09 (d, 1H, \(J = 3.63\) Hz), 3.81 (d, 1H, \(J = 3.63\)) 6.64 (d, 1H, \(J = 1.65\) Hz), 6.97-7.00 (m, 1H), 7.13-7.16 (m, 2H), 7.22-7.33 (m, 3H); \(^1^C\) NMR (67 MHz, CDCl\(_3\)) δ 14.5, 19.3, 21.2, 21.3, 42.0, 47.4, 52.5, 53.3, 85.6, 125.5, 128.4, 128.6, 129.1, 129.9, 130.4, 131.6, 133.1, 133.4, 136.1, 137.9, 138.0, 205.5, 205.9; IR (KBr): 3357, 2921, 1707, 1493, 1458, 1393, 1327, 1069, 1041, 942 cm\(^{-1}\).

\(\text{Spiro[cyclohexa-2,5-dienone-4,8'-7-(4-chlorophenyl)-1,4-dimethyl-3-hydroxy-tricyclo[2.2.2.0^6,7]octane-2,5-dione]}\) (7i): mp 206.6-206.9 °C (from chloroform/\(n\)-hexane); \(^1^H\) NMR(270 MHz, CDCl\(_3\)) δ 1.00 (s, 3H), 1.08 (s, 3H), 2.75 (s, 1H), 2.93 (s, 1H), 4.00 (s,1H), 6.17 (dd, 1H, \(J = 1.81, 10.4\) Hz), 6.52 (dd, 1H, \(J = 1.81, 10.2\) Hz), 6.54 (dd, 1H, \(J = 3.13, 10.4\) Hz), 6.82 (dd, 1H, \(J = 3.13, 10.2\) Hz), 7.00-7.10 (m, 2H), 7.25-7.26 (m, 2H); \(^1^C\) NMR (67 MHz, CDCl\(_3\)) δ10.9, 14.8, 29.8, 43.1, 46.0, 52.8, 56.0, 75.4, 128.9, 129.7, 130.5, 131.3, 134.4, 135.3, 142.7, 147.5, 184.0, 203.0, 204.0; IR (KBr): 3417, 2925, 1745, 1664, 1261, 1091, 801 cm\(^{-1}\).
(1R*,8R*,9S*,10R*,12S*)-12-Hydroxy-5-chloro-1,10-dimethyl-8-(4-chlorophenyl)-tetracyclo-[6.4.1^1.9.0^2.7.0^8.13]trideca-2(7),3,5-triene-1,13-dione (4i):\(^{1}\)H NMR(270 MHz, CDCl\(_3\)) \(\delta\) 1.33 (s, 3H), 1.65 (s, 3H), 2.67 (s, 1H), 4.09 (s, 1H), 6.76 (d, 1H, \(J = 1.65\) Hz), 7.17-7.31 (m, 3H), 7.34-7.56 (m, 3H).

(1R*,8R*,9S*,10R*,12R*)-12-Hydroxy-5-chloro-1,10-dimethyl-8-(4-chlorophenyl)-tetracyclo-[6.4.1^1.9.0^2.7.0^8.13]trideca-2(7),3,5-triene-11,13-dione (4'i):\(^{1}\)H NMR(270 MHz, CDCl\(_3\)) \(\delta\) 1.70 (s, 3H), 1.83 (s, 3H), 3.15 (s, 1H), 6.40 (s, 1H), 6.93 (d, 1H, \(J = 1.81\) Hz), 6.93-7.34 (m, 4H), 7.55 (d, 2H, \(J = 8.74\) Hz).

**X-ray Crystal structure Determination of \(\alpha\)-1f:** C\(_{23}\)H\(_{20}\)O\(_3\), M = 344.41, monoclinic, space group P2\(_{1}\)/a with \(a = 12.517(1)\), \(b = 10.206(1)\), \(c = 14.704(2)\) Å, \(\beta = 11.747(7)\)\(^{\circ}\), \(V = 1744.7(4)\) Å\(^3\), \(Z = 4\), \(D_{calc} = 1.311\) g/cm\(^3\), \(R = 0.136\) and \(R_w = 0.188\) for 3922 reflections with \(I > 2.0\sigma(I)\).

**X-ray Crystal structure Determination of \(\beta\)-1f:** C\(_{23}\)H\(_{20}\)O\(_3\), M = 344.41, orthorhombic, space group Pbca with \(a = 9.4653(3)\), \(b = 14.6974(4)\), \(c = 25.3890(9)\) Å, \(V = 3532.0(2)\) Å\(^3\), \(Z = 8\), \(D_{calc} = 1.295\) g/cm\(^3\), \(R = 0.100\) and \(R_w = 0.176\) for 3955 reflections with \(I > 2.0\sigma(I)\).
X-ray Crystal structure Determination of 1d: C\textsubscript{17}H\textsubscript{17}O\textsubscript{2}, M = 253.32, orthorhombic, space group Pna\textsubscript{2}1 with \(a = 16.1082(4)\), \(b = 11.8925(4)\), \(c = 7.0686(2)\) Å, \(V = 1354.11(7)\) Å\(^3\), \(Z = 4\), \(D_{\text{calc}} = 1.242\) g/cm\(^3\), \(R = 0.127\) and \(R_w = 0.142\) for 13581 reflections with \(I > 2.0\sigma(I)\).

Figure 5. ORTEP drawing of 1d.

X-ray Crystal structure Determination of 4f: C\textsubscript{23}H\textsubscript{22}O\textsubscript{4}, M = 362.42, orthorhombic, space group P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1} with \(a = 7.7719(6)\), \(b = 12.712(1)\), \(c = 18.431(2)\) Å, \(V = 1821.0(3)\) Å\(^3\), \(Z = 4\), \(D_{\text{calc}} = 1.322\) g/cm\(^3\), \(R = 0.074\) and \(R_w = 0.155\) for 2263 reflections with \(I > 2.0\sigma(I)\).

Figure 6. ORTEP drawing of 4f.

X-ray Crystal structure Determination of 7i: C\textsubscript{21}H\textsubscript{17}O\textsubscript{4}Cl, M = 368.82, monoclinic, space group P2\textsubscript{1}/a with \(a = 11.4880(7)\), \(b = 12.525(1)\), \(c = 13.3085(6)\) Å, \(\beta = 114.312\), \(V = 1754.1(2)\) Å\(^3\), \(Z = 4\), \(D_{\text{calc}} = 1.404\) g/cm\(^3\), \(R = 0.141\) and \(R_w = 0.203\) for 2516 reflections with \(I > 2.0\sigma(I)\).
1-5. Reference and Notes


(12) We could not detect 2g by $^1$H NMR even for shorter reaction time (10 min, 30% conversion) under the same condition.
(13) Crystallographic data for the structure of 2f, 4 and 5 have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 650017, 650018 and 650209. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44-1233-336033. E-mail: deposit@ccdc.cam.ac.uk.


(20) A preliminary kinetic study indicated that the introduction of p,p'-dimethyl or p,p'-dichloro substituents results about 11-fold increase or 33-fold decrease in the rate of the parent epoxide 5; further details will be described at Chapter 2.

(21) The conversions of 1a, 1h, and 1i were >99% (for 4h), 100 (0.5h), and 82 (20h), respectively.

Chapter 2. Kinetic Evidence for $\eta^2$ π-Aryl Participation in Acid-Catalyzed Reaction of HQ-Epoxide

2-1. Introduction

π-Aryl participation is one of the most sophisticated physicochemical phenomena that control the reactivity of substrates and sometimes govern the reaction mechanism. These effects are generally derived from (ascribed to) the through-space electronic stabilization of the transition states by the direct π-electronic donation (not by resonance) from the contained aryl groups to the reaction center (usually, but not necessarily an incipient carbocation). A large number of studies have been made of the π-aryl assisted solvolyses of β-aryltosylates and brosylates from the kinetic and stereochemical point of view. In these adjacent β-aryl-substituted substrates, the kinetic substituent effects as well as the product analyses clearly indicated that the π-aryl participation occurs at the proximal ipso-carbon and hence the phenonium ion (σ-complex) can be formed as an intermediate. By contrast, little is known for the anchimeric assistance of the aryl group located in the γ-position or further away from the reaction site. However, the remote π-aryl participation is of continuous theoretical interest because a detailed understanding of the physical origin and scope of such interactions has become one of the major goals of physical organic chemistry. Compared to the more conventional π-aryl participation at the ipso-position, the elucidation of the steric and electronic factors controlling the remote electron-donation and knowing which positions of the aromatic ring are responsible for such phenomenon, are of prime importance.

Very recently, the author reported that the unsubstituted and $p$-substituted diphenylhomobenzoquinone epoxides 1 (X, Y = H, Me and Cl) show a remote π-aryl participated transannular $S_{E2}$-Ar cyclization of endo-phenyl group associated with the acid-catalyzed regioselective oxirane ring-cleavage to give the ortho-carbon bound tricyclic diketo-alcohols 2 and the ipso-carbon bound 2,5-cyclohexadien-4-one spiro-linked tricyclic diketo-alcohol 3 (only for the π-resonating $p$-Cl substituted entity) as shown in Scheme 1a. This observation raises a question as to which positions of the aromatic ring and how the aryl group interacts with the vacant oxirane Walsh orbital.

Herein, aiming at obtaining physicochemical information on the π-aryl participated transition state, the author has conducted kinetic studies of the BF$_3$-catalyzed transannular cyclization of variously endolexo $m$- and $p$-substituted diarylhomobenzoquinone epoxides 1a-k in CDCl$_3$ at 30 °C. Based on the kinetic substituent effects, the author has found that the dihapto ($\eta^2$)-type coordination (through ipso and ortho) of endo-aromatic ring occurs in the rate-determining oxirane ring-cleavage. A modified Hammett treatment indicated that the ipso/ortho contribution ratio (=1.6) is considerably higher than that (0.89) of the similar
S_{E2}-Ar transannular cyclization of cyclobutene-fused diarylhomobenzoquinones 4 into the ortho-carbon bound tetracyclic keto-alcohols 5 (Scheme 1b). These results were explained in terms of the stereoelectronic effects in the orbital interaction between the \( \pi \)-donor aromatic rings (HOMO) and the vacant anti-bonding orbitals of the cleaved oxirane and cyclobutene rings (LUMO).

Scheme 1.

2-2. Results and Discussion

2-2-1. Synthesis and Structural Characteristics of Epoxides

The \( \text{endo/exo} \)-substituted diarylhomobenzoquinone epoxides 1a-k were prepared by the epoxidation of diarylhomobenzoquinones\(^9\) derived from 1,3-dipolar cycloaddition of the corresponding \( m- \) and \( p- \)substituted diphenyldiazomethanes with 2,5-dimethyl-1,4-benzoquinone.\(^{10}\) For the mono-substituted diphenyldiazomethanes, a mixture of \( \text{endo/exo} \)-substituted isomers was formed and separated by careful column chromatography and recrystallization. The \( m- \)chloro-substituted 1i, however, could not be
isolated due to the very similar endolexo adsorbability on silicagel. The structures of 1a-k were deduced as the cis-transoid-cis tricyclic dione frame from the representative X-ray crystal structural analysis of bis(p-chlorophenyl)-substituted 1j (Figure 1). The original quinone frame was found to adopt an appreciable pseudo-boat conformation with a slight deformation opposite to the endo-aromatic ring. This deformation results in an overhang of endo-aryl ring above the quinone plane and a pseudoaxial flipping of the conjunct planar oxirane ring as noted by the average dihedral angle (95.4°) between the epoxide ring and the fused quinone plane. The very short spatial distance (3.21 Å) between the endo-aromatic ipso-carbon and the cleaved epoxide tertiary carbon seems to allow the π-electron donation to the underlying acid-activated oxirane ring. However, the corresponding distance (4.74 Å) with the outside exo-aromatic ipso-carbon is long enough to inhibit the through-space π-electron donation. Such π-electron participation becomes very important if the present epoxide ring-opening reaction proceeds through an SN2 type intramolecular transannular cyclization. As a result, the geometrical features of 1 can take advantage of π-anchimeric assistance in the present acid-catalyzed ring-opening.

2-2-2. Kinetic Substituent Effects

The observed pseudo-first-order rate constants $k_{obs}(1)$ were divided by the concentration of BF$_3$ to provide the second-order rate constants $k(1)$. The values for $k(1)$ and the relative rate constants $k_{rel}(1)$ (vs the unsubstituted 1g) are collected in Table 1. For comparison, Table 1 also includes the relative rate constants $k_{rel}(4)$ (vs the unsubstituted entity) for the previous BF$_3$-catalyzed reactions of similarly endolexo m- and p-substituted analogous cyclobutene-fused diarylhomobenzoquinones 4a-k.

A perusal survey of Table 1 indicated some noticeable differences between the epoxides 1a-k and the cyclobutene-fused 4a-k: (1) for the endo-substituted series, the rates were...
increased more effectively in 1 ($k^p_{-	ext{MeO}}/k^p_{-	ext{CF3}} = 8200$) than in 4 ($= 5600$)\(^2\); (2) by contrast, the same substituent change brought about only a small increase for the exo-substituted 1 (2-fold) and for 4 (11-fold); (3) of particular interest is that the endo-$p$-substituted 1 (X = MeO, Me, Cl) reacted faster than the endo-$m$-substituted isomer, whereas the endo-$m$-substituted 4 exhibited rather higher reactivity than the endo-$p$-substituted isomer; (4) on the other hand, exo-$m/p$-substituted couples showed the usual substituent effects for both the 1 and 4.

Since the endo-aromatic ring is located at the δ-position with respect to the epoxide carbon atom, the notable rate-acceleration by electron-donating $m$- and $p$-substituents can not be ascribed to the direct inductive or the resonance stabilization of a rate-determining transition state. Indeed, the exo-aromatic substituents lacked the drastic effects on the rates. Accordingly, the remarkable rate dependency on the endo-substituents must be explained by considering the through-space electron donation of the overhanging aromatic nucleus to the acid-activated oxirane ring. In order to evaluate the degree to which the present acid-catalyzed ring-opening reactions respond to the meta and para substituent changes of 1, the author

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<td>0.86</td>
</tr>
<tr>
<td>17</td>
<td>exo-$1\text{i}$</td>
<td>H</td>
<td>m-Cl</td>
<td>0.345</td>
<td>0.71</td>
</tr>
<tr>
<td>18</td>
<td>exo-$1\text{k}$</td>
<td>H</td>
<td>p-CF$_3$</td>
<td>0.278</td>
<td>0.57</td>
</tr>
</tbody>
</table>

$^a$The second-order rate constants $k$ were obtained by dividing the pseudo-first-order rate constant $k_{\text{obs}}$ by the concentration of BF$_3$. The $k$ values are the average of at least two measurements. Error limit of $k$ is ±2%.

$^b$The relative rate constant of cyclobutene ring-opening reaction of analogous homobenzoquinones 4.

$^c$The second-order rate constant $k(4\text{g}) = 1.25 \times 10^{-3}$ M$^{-1}$s$^{-1}$ (cf ref 8).
applied a linear free energy relationships analysis for $k_{rel}(1)$. As a consequence, it was found that the usual Hammett treatment for the endo-X substituted series by using $\sigma$ or $\sigma^+$ one parameter\textsuperscript{13} provided rather poor correlations; $\log k_{rel}^{endo}(1) = -4.5\sigma + 0.35$ ($r^2 = 0.89, n = 8$) and $-2.8\sigma^+ - 0.09$ ($r^2 = 0.77, n = 8$) respectively.\textsuperscript{14} These unsatisfactory correlations with the normal single parameter apparently indicate that the $\pi$-aryl participation of endo-aromatic ring must be performed not only at the ipso- but also at the ortho-carbon atom. This simultaneous binding seems to be responsible for the formation of the ortho- and the ipso-carbon bound products, $2j$ and $3j$, from the bis($p$-chlorophenyl)-substituted $1j$ (Scheme 1a).\textsuperscript{6}

Based on these findings, the author thought that the transannular $S_{E2}$-Ar cyclization of endo-aryl groups of $1$ involves a dihapto ($\eta^2$) $\pi$-aryl participated transition state through the ipso and the ortho carbon atom. Although the $m$-substituted aromatic nucleus has two different ortho-positions with respect to the ipso-carbon, the less congested ortho-position, that is to say para to the introduced $m$-substituent, is expected to participate in the product formation (vide infra). Accordingly, the author attempted to correlate the $\log k_{rel}^{endo}(1)$ with the combination of newly defined two site-dependent substituent parameters $\sigma^{ipso}$ and $\sigma^{ortho}$ which display the substituent effects on the ipso- and ortho-aromatic carbon atoms, respectively. Thus, the substituent constant $\sigma^{ipso}$ is related to the ipso-participation by using $\sigma^+_p$ for $p$-$X$ and $\sigma_m$ for $m$-$X$ substituent.\textsuperscript{13} On the other hand, the other $\sigma^{ortho}$ refers to the ortho-participation by using, specifically, $\sigma_m$ for $p$-$X$ and $\sigma^+_p$ for the $m$-$X$ substituent,

$$\log k_{rel}^{endo}(1) = -2.49\sigma^{ipso} - 1.62\sigma^{ortho} - 0.108 \quad (R^2 = 0.98, n = 8) \quad (1)$$

![Figure 2](image-url)

**Figure 2.** Plots of the observed $\log k_{rel}^{endo}(1)$(obs) vs the calculated $\log k_{rel}^{endo}(1)$(calc) according to eq. 1 for BF$_3$-catalyzed rearrangements of unsubstituted $1g$ and endo-substituted $1a$, $d$-$f$, $h$, $i$, and $k$ in CDCl$_3$ at 30 °C.
respectively. As expected, a very sufficient regression was obtained by considering such \( \eta^2 \)-type coordination of endo-aromatic ring through the ipso and ortho-positions (eq. 1 and Figure 2). Here, it is noteworthy that the \( \eta^2 \)-binding of aromatic ring is more effectively performed at the ipso-carbon than the ortho-one as indicated by the percent contribution of the parameter \( \sigma_{\text{ipso}} \) (61\%) and \( \sigma_{\text{ortho}} \) (39\%).

As to the exo-Y substituted series, the author observed only 2-fold rate-acceleration irrespective of the wide range of \( p\)-MeO/\( p\)-CF\(_3\) substituent variation. These exo-isomers provided a good linear free energy relationship when used Yukawa-Tsuno (Y-T) equation,\(^{15,3(d)}\) where \( \sigma^0 \) is the normal substituent constant and \( \Delta \sigma_R^+ \) is the resonance substituent constant defined by (\( \sigma^+ - \sigma^0 \)) (eq. 2). The present reaction yielded a small negative reaction constant (\( \rho = -0.912 \)) and a small resonance parameter (\( r = 0.237 \)). These very low values are certainly due to the reduced exo-substituent effects on the far more remote acid-activated oxirane-ring (\( \delta \)-position through the intervened cyclopropane and carbonyl function). Incidentally, the well-known acetoyses of \( \beta\)-aryltosylates and brosylates at 75-115 °C also displayed the Y-T equations with larger \( \rho \) values of \(-3.3 \) to \(-4.0 \) and \( r \) values of 0.54 \( \sim \) 0.63.\(^{16}\) The enhanced substituent effects of these reactions can be explained by the formation of phenonium ion intermediates via the \( \pi \)-aryl participation at the ipso-carbon.

In the later section, the author will discuss these kinetic substituent effects from the mechanistic viewpoints in comparison with those of the analogous S\(_{\text{E2-Ar}}\) transannular cyclization of 4a-k.

2-2-3. Mechanistic Considerations

(a) \( \pi \)-Aryl Participation in S\(_{\text{N2}}\) type Ring-Opening of Epoxide. The acid-catalyzed cleavage of the oxirane C-O bond preferentially occurs in such a way that the substituent of the oxirane ring further stabilizes the developing positive charge by both, electron donation and the conjugation.\(^{17}\) Accordingly, the reaction features are highly dependent on the substituents on the oxirane ring as well as the nucleophiles. Mechanistically, the nucleophilic displacement of epoxides can be rationalized by either concerted attack of a nucleophile on the acid activated oxirane ring (S\(_{\text{N2}}\) mechanism) or by stepwise attack of a nucleophile on a pre-formed carbocation intermediate (S\(_{\text{N1}}\) mechanism).\(^{17(b),(e),(f),18}\) Most of the reactions are generally known to proceed through the regio- and stereoselective ring cleavage under the S\(_{\text{N2}}\) anti nucleophilic assistance.\(^{19}\) However, the S\(_{\text{N1}}\) mechanism is reported for the reaction of epoxides bearing strongly electron-releasing and conjugated substituents in the high polar solvents.\(^{20}\)
Since the present epoxide ring is substituted by two electron-withdrawing quinone carbonyl groups, the acid-catalyzed ring-cleavage of 1 seems to obey the $S_N2$ process in the less polar $CDCl_3$. Under these conditions, the overhanging $endo$-aromatic ring is apt to behave as an effective internal $\pi$-nucleophile. Indeed, the author has obtained very poor kinetic solvent effects ($k_{\text{dichloroethane}}/k_{\text{benzene}} = 3.0$) regardless of the appreciable change of solvent polarity (as indicated by the polarity parameter; $E_T(30) = 41.3$ for 1,2-dichloroethane and 34.3 for benzene) for the same transannular cyclization of 1g by protic acid Me$\text{SO}_3$H. The negligible solvent effects can be taken as a conclusive mechanistic criterion for the concerted process involving the less polar transition state.

The mechanistic evidence for the concertedness was also obtained for the above mentioned dual $ipso/ortho$ transannular $S_{E2}$-Ar reactions of bis($p$-chlorophenyl)homobenzoquinone epoxide 1j. The common $\pi$-aryl participated transition state leads to the $ortho$-linked product 2 via $\sigma$-complex I and competetively to the $ipso$-linked product 3 via the $\pi$-resonating $\sigma$-complex II followed by the hydrolysis with residual water (Scheme 2). The present $p$-anisyl- and $p$-chloro-substituted $endo$-1a and $endo$-1h also provided 3a (~100 %) and 3h (80%) along with 2h (20%), respectively. Quantitative formation of 3a for the reaction of $endo$-1a may be explained in view of the reaction pathways on which the common transition state TS would prefer the very facile degradation into the $\pi$-resonating and water sensitive intermediate II rather than the less stabilized I. By contrast, other $para$-substituents (including H) brought about the exclusive formation of 2 via the $ortho$-linked $\sigma$-complex I. This is probably because the possible $ipso$-linked $\sigma$-complex II can not be transformed into the stable 3 via the nucleophilic...
displacement by residual water, but rather underwent the facile 1,2-shift to the ortho-linked I reading to 2. Thus, it is not surprising that the percent contribution of the $\sigma^{ipso}$ and $\sigma^{ortho}$ in the transition state stabilization cannot be directly reflected on the product distributions which are dependent on the following channels to the respective I and II as well as the contaminant water. The author also found that the transannular cyclization of endo m-X-substituted aromatic ring occurs exclusively at the less congested ortho-position (i.e., para-position with respect to the m-X) as confirmed by the representative reaction of endo m-MeO-substituted 1d. A significant steric hindrance of m-MeO with the oxirane Me group probably inhibits the alternative $\pi$-aryl participation at the adjacent ortho-position.

(b) Prominent Role of Oxirane Walsh Orbital. In the acid-catalyzed intramolecular $\text{S}_\text{E2}-\text{Ar}$ reactions of 1a-k, the vacant oxirane Walsh orbital seems to play a crucial role in the initial epoxide ring-opening with the aid of endo-aromatic ring. However, the aryl participation in the ring opening of epoxides is scarcely reported but has been put forward in the acid-induced ring opening of a particular case of epoxides bearing aryl groups directly or indirectly linked to the oxirane ring. For instance, the well-documented phenonium ion intermediates via the aryl participated transition states are invoked in the reactions of stilbene oxides and spiro-linked 2-phenyl-1,2-epoxide or 1-benzyl-1,2-epoxides. In our previous study using the ethano-bridged diphenylhomobenzoquinone epoxides, the author has found that the rate of the acid-catalyzed transannular cyclization is highly dependent on the rigid conformation of endo-aryl ring. The author rationalized the conformational effects on the basis of the $\pi$-aryl participated orbital interaction with the vacant oxirane Walsh orbital. Keeping this in mind, the author will later interpret the present kinetic substituent effects in terms of the geometrically restricted orbital interaction in the $\text{S}_\text{E2}$-type epoxide ring-opening.

The author has previously found that the analogous cyclobutene-fused endolexo m- and p-substituted diarylhomobenzoquinones 4 exhibited the similar $\pi$-aryl participated transannular $\text{S}_\text{E2}-\text{Ar}$ cyclization under BF$_3$ acid conditions (Scheme 1b). This cyclobutene ring-opening reaction involves the formal vinyl-anion migration to the adjacent acid-activated carbonyl carbon associated with the concerted $\text{S}_\text{N2}$ transannular cyclization of endo-aryl group. Accordingly, the vacant cyclobutene anti-bonding orbital activated by the adjoining BF$_3$-complexed carbonyl group will accept the $\pi$-electrons of the endo-aryl group and facilitate the $\sigma$-bond cleavage. Therefore, a comparison between the epoxide and the cyclobutene ring-opening reactions will provide a very useful insight into the stereoelectronic effects in the $\pi$-aryl participated orbital interaction.

2-2-4. Stereoelectronic Effects in Dihapto($\eta^3$) $\pi$-Aryl Participation

As previously reported, the author has obtained the excellent two parameter regression using the $\sigma^{ipso}$ and $\sigma^{ortho}$ parameters for the BF$_3$-catalyzed transannular cyclization of cyclobutene-fused endo m- and p-substituted diarylhomobenzoquinones 4 (eq. 3). This
equation also manifested the \( \eta^2 \)-coordination in the \( \pi \)-aryl participated transition state (Figure 3b). The percent contribution of \( \sigma^{ipso} \) (47\%) is slightly smaller than that of \( \sigma^{ortho} \) (53\%). This is in contrast to the reaction of epoxides 1, where the \( \sigma^{ipso} \) contributed 1.6 times more effectively than \( \sigma^{ortho} \) (eq. 1).

\[
\log k_{cel}^{endo}(4) = -2.07 \sigma^{ipso} - 2.33 \sigma^{ortho} - 0.172 \quad (R^2 = 0.99, n = 8) \quad (3)
\]

Why does the *endo*-4 undergo the slightly enhanced substituent effects on the ortho-carbon atom, but the *endo*-1 the more significant substituent effects on the ipso-carbon atom? To answer this question, the author must recall that the acid-catalyzed \( S_N2 \)-type nucleophilic displacement of 1 and 4 involves the \( \pi \)-aryl participated transition states. The \( \pi \)-electron donation should occur onto the vacant oxirane Walsh orbital of 1 and the cyclobutene anti-bonding \( \sigma^* \) orbital of 4, respectively. Since the lowest unoccupied Walsh orbital (LUMO) is trigonally bent, the geometrical orbital interaction with the *endo*-aromatic ring (HOMO) may be represented in Figure 3. Thus, the dihapto \( \pi \)-aryl participation of 1 can be more effectively performed at the ipso-carbon rather than the ortho-one (Figure 3a). By contrast, such a stereoelectronic preference for the ipso-position should be considerably reduced for 4 because the vector of the relevant four-membered cyclobutene \( \sigma^* \)-bond deviates from the vertical plane through the ipso- and para-position of the aromatic ring (Figure 3b). Indeed, a theoretical calculation by DFT B3LYP/6-31G* method\(^{27} \) apparently showed the similar geometrical characteristics for the relevant vacant orbitals of epoxide and cyclobutene

![Figure 3](image)

Figure 3. a) Representative lowest unoccupied Walsh orbital of epoxides 1 and b) the unoccupied orbital (in part) of cyclobutene ring of 4.

![Figure 4](image)

Figure 4. LUMO orbitals of (a) epoxide 1g and (b) cyclobutene-fused analogue 4g optimized by B3LYP/6-31G* method (exo-aromatic ring is omitted for clarity).
ring moieties (Figure 4). The vacant Walsh orbital of 1g at the carbon corner is conjugated with the carbonyl π*-orbital but is rather directed to the aromatic ipso-carbon (as yellow dotted arrow in Figure 4a). On the other hand, the vector of vacant cyclobutene orbital of 4g is essentially perpendicular (yellow dotted arrow) to the quinone plane and is expected to enjoy the ideal ipso-ortho η² coordination with the faced endo-aromatic nucleus (Figure 4b). This is because the epoxides 1g display more effective ipso-contribution in the η² π-aryl participation than the cyclobutene-cleaved 4g.

\[
\log k_{rel}^{exo} = -0.794(\sigma^0 + 0.904\Delta\sigma^+) \quad (R^2 = 0.96, n = 8) \quad (4)
\]

As to the exo-Y substituted 4, the author previously obtained the Y-T equation (eq. 4) with a larger \( r \) value of 0.904 than the similar equation for exo-1 (\( r = 0.237 \), eq. 2). The larger resonance parameter \( r \) means that the π-delocalization of exo-aryl substituents of 4 can appreciably stabilize the developing positive charge on the acid-activated γ-located carbonyl carbon atom. Such an activation of carbonyl π*-orbital results in the acceleration of the concerted vinyl anion migration responsible for the S_{E2}-Ar transannular cyclization of 4. By contrast, as seen in the Y-T equation 2, the reduced resonance stabilization by the exo-aryl substituents of 1 may be due to the change in the reaction mechanism. The epoxide ring-opening is substantially facilitated by the binding of BF₃ not at the carbonyl oxygen but at the epoxide oxygen atom. Even if the carbonyl function is activated by BF₃ like in 4, it would rather deactivate the ring-opening because of the destabilization of the developing positive charge on the epoxide carbon atom.

2-3. Conclusion

In summary, the author has performed a kinetic study of the BF₃-catalyzed ring-opening reactions of endo/exo m- and p-substituted diarylhomobenzoquinone epoxides 1. These reactions proceeded through two types of S_{E2}-Ar transannular cyclizations to give tricyclic diketo-alcohols and cyclohexadienone spiro-linked tricyclic diketo-alcohols, respectively. The rates were significantly accelerated by the through-space π-aryl participation of electron-donating endo-aromatic rings, but negligibly influenced by the through-bond electronic effects of exo-aromatic rings. The Hammett treatment using modified site-dependent substituent parameters \( \sigma^{ipso} \) and \( \sigma^{ortho} \) indicated that the ipso-ortho dihapto(\( \eta² \)) π-aryl participation occurs for the endo-aryl groups. Kinetics substituent effects of these reactions were compared with those of the analogous acid-catalyzed transannular cyclization of the cyclobutene-fused diarylhomobenzoquinones 4. It was found that the present epoxides 1 exhibit the η² π-aryl participation with the 1.6-times more effective contribution at the ipso-position, whereas the cyclobutene-fused homologues 4 with almost comparable ipso-ortho contribution. These results were interpreted in terms of the geometrical
features of the π-electron accepting vacant orbital of oxirane and cyclobutene ring. The physicochemical information obtained in the present study will provide a very important insight into the understanding of the π-aryl participation as well as the mechanistic aspects in the acid-catalyzed ring-opening reaction of epoxides.

2-4. Experimental Section

Materials. Deuterated Chloroform (CDCl₃) was purchased from Aldrich Chemicals Ltd. and used without further purification. All epoxides 1a-k were prepared according to the previous methods by the epoxidation of the corresponding diarylhomobenzoquinones.⁶ The endolexo isomeric mixtures were separated by a column chromatography on silica gel with a mixture of hexane/ethyl ether as an eluent and purified by recrystallization from chloroform/pentane. The analytical data are collected below. Unfortunately, we could not obtain the pure endo-1e, endolexo-1i because of the contamination of the respective isomers. The assignment of the endolexo stereochermy of 1a, d-f, h, and k failed because of the complexity in their ¹H-NMR spectra. Thus, the stereochemistry was tentatively deduced from their kinetic behaviors; i.e., the more reactive isomers of 1a and d-f are endo but the more reactive isomers of 1h, i, and k are exo.

Kinetic Measurements. The kinetic data were obtained by at least duplicate measurements according to the NMR spectroscopic methods. The solution of epoxide 1 (0.02 mmol, CDCl₃, 0.67 mL) for kinetic experiments was prepared in a stoppered NMR tube and preheated at 30°C (±0.1) in a thermostated bath. The reaction was initiated by the quick addition of the requisite volume of catalyst BF₃·OEt₂ (0.3 M) and submitted for the NMR measurements at 30°C (±0.1) in a thermostated tube holder. For the reactive 1a, the introduced amount of BF₃·OEt₂ was reduced to 1/10 and 1/5 (0.03 and 0.06 M). For the less or least reactive endo-1h, 1j and endo-1k, the NMR tube was sealed with a gas burner. The progress of reactions was followed by requisite interval monitoring the relative signal intensity of the diagnostic methy groups on cyclopropane (0.91 ~ 1.01 ppm) and oxirane ring (1.17 ~ 1.22) of 1 over 75% conversion with respect to the internal standard TMS. For the least reactive endo-1k, the measurements were performed at requisite time interval by taking the sealed NMR tube out of a thermostated bath (30°C (±0.1)). The natural logarithmic plots of the relative amounts of 1 with respect to the measurement starting point (t = 0) gave the correlation line against time. The obtained first-order rate constants (slope) were divided by the concentration of catalyst to provide the second-order rate constants. The first-order decay plots and the logarithmic plots for the most reactive endo-1a, the unsubstituted 1g, and the least reactive endo-1k are represented in SI.
Acid-Catalyzed Reaction of 1a-k. The acid-induced reactions of epoxides 1a-k (0.02 mmol) were carried out in the presence of BF₃·OEt₂ (0.30 M) in CDCl₃ (0.67 mL) at room temperature. After the completion of reactions, the reaction solution was transferred into a separate funnel, diluted with chloroform (10 mL) and then washed with water (3 mL × 3). The aqueous layer was extracted with chloroform (5 mL × 2). The combined organic layer was washed with water (3 mL × 3), then dried over calcium chloride. After the evaporation of the solvent in vacuo, the residue was submitted for the ¹H NMR analysis to determine the product distributions. The reactions were found to give the ortho-carbon bound tricyclic diketo-alcohols 2b-k together with the ipso-carbon bound 2,5-cyclohexadien-4-one spiro-linked tricyclic diketo-alcohol 3a (~100%), 3h (the same as 3a, 80), and 3j (81) for endo-1a, endo-1h, and 1j, respectively, in almost quantitative total yields based on the consumed 1. Except for the representative reactions of endo-1a, 1b, endo-1d, endo-1h, and 1j, no further detailed analyses of products were carried out. The analytical data of the products 2b, 2g, 2j, 3j have been already described elsewhere.⁶,²⁸ The new compounds 3a and endo-2d were isolated by column chromatography on silica gel with a mixture of hexane/ethyl acetate as an eluent.

Endo-1,5-dimethyl-8-phenyl-8-(4-anisyl)-4-oxa-tricyclo[5.1.0.⁰³⁵]octane-2,6-dione (endo-1a): mp 116.5-117.5 °C, colorless prisms (chloroform/pentane): ¹H-NMR (270 MHz, CDCl₃) δ 0.91 (s, 3H), 1.19 (s, 3H), 2.78 (s, 1H), 2.80 (s, 1H), 2.75 (s, 3H), 6.80-6.84 (m, 2H), 7.18-7.30 (m, 7H); ¹³C-NMR (67 MHz, CDCl₃) δ 13.6, 16.7, 37.9, 40.0, 49.2, 55.3, 60.1, 60.4, 114.4, 127.8, 129.2, 129.5, 129.6, 132.3, 138.7, 159.0, 195.8, 200.6; IR (KBr) 1705 (C=O) cm⁻¹. Anal Calcd for C₂₂H₂₀O₄: C, 75.84; H, 5.79; O, 18.37. Found: C, 75.69; H, 5.72; O, 18.59.

Exo-1,5-dimethyl-8-(4-anisyl)-8-phenyl-4-oxa-tricyclo[5.1.0.⁰³⁵]octane-2,6-dione (exo-1a): mp 105.8-106.8 °C, colorless prisms (chloroform/pentane): ¹H-NMR (270 MHz, CDCl₃) δ 0.99 (s, 3H), 1.17 (s, 3H), 2.79 (s, 1H), 2.86 (s, 1H), 3.73 (s, 3H), 6.76-6.79 (m, 2H), 7.16-7.37 (m, 7H); ¹³C-NMR (67 MHz, CDCl₃) δ 13.8, 16.8, 37.5, 39.5, 48.9, 55.3, 60.3, 60.5, 114.5, 127.5, 128.2, 129.0, 130.2, 130.8, 140.5, 159.1, 198.6, 200.8; IR (KBr) 1695 (C=O) cm⁻¹. Anal Calcd for C₂₂H₂₀O₄: C, 75.84; H, 5.79; O, 18.37. Found: C, 75.69; H, 5.72; O, 18.59.
1,5-dimethyl-8,8-bis(3-anisyl)-4-oxa-tricyclo[5.1.0.0³⁵]octane-2,6-dione (1c): mp 194.5-195.1 °C, colorless prisms (chloroform/pentane); 
\(^1\)H-NMR (270 MHz, CDCl\(_3\)) δ 0.97 (s, 3H), 1.20 (s, 3H), 2.78 (s, 1H), 2.84 (s, 1H), 3.74 (s, 3H), 3.78 (s, 3H), 6.71-7.36 (m, 8H); \(^{13}\)C-NMR (67 MHz, CDCl\(_3\)) δ 13.8, 16.7, 37.6, 49.5, 55.3, 60.1, 60.3, 112.7, 113.8, 114.6, 115.1, 120.7, 121.8, 130.0, 130.2, 139.5, 141.2, 159.8, 198.3, 200.5; IR (KBr) 1698 (C=O) cm\(^{-1}\). Anal Calcd for C\(_{23}\)H\(_{22}\)O\(_5\): C, 73.00; H, 5.86; O, 21.14. Found: C, 72.97; H, 5.85; O, 21.18.

**Endo-1,5-dimethyl-8-(3-anisyl)-8-phenyl-4-oxa-tricyclo[5.1.0.0³⁵]octane-2,6-dione (endo-1d):** mp 165.6-166.6 °C, colorless prisms (chloroform/pentane); 
\(^1\)H-NMR (270 MHz, CDCl\(_3\)) δ 0.98 (s, 3H), 1.18 (s, 3H), 2.80 (s, 1H), 2.85 (s, 1H), 3.74 (s, 3H), 6.72-6.86 (m, 3H), 7.14-7.41 (m, 6H); \(^{13}\)C-NMR (67 MHz, CDCl\(_3\)) δ 13.8, 16.8, 37.6, 39.7, 49.6, 55.3, 60.1, 60.3, 113.8, 115.1, 121.8, 127.7, 128.4, 128.9, 130.3, 139.6, 139.8, 198.4, 200.5; IR (KBr) 1699 (C=O) cm\(^{-1}\). Anal Calcd for C\(_{22}\)H\(_{20}\)O\(_4\): C, 75.84; H, 5.79; O, 18.37. Found: C, 75.72; H, 5.75; O, 18.53.

**Exo-1,5-dimethyl-8-(3-anisyl)-8-phenyl-4-oxa-tricyclo[5.1.0.0³⁵]octane-2,6-dione (exo-1d):** mp 168.8-169.8 °C, colorless prisms (chloroform/pentane); 
\(^1\)H-NMR (270 MHz, CDCl\(_3\)) δ 0.91 (s, 3H), 1.21 (s, 3H), 2.80 (s, 1H), 2.80 (s, 1H), 3.78 (s, 3H), 6.73-6.76 (m, 1H), 6.90-6.96 (m, 2H), 7.19-7.26 (m, 6H); \(^{13}\)C-NMR (67 MHz, CDCl\(_3\)) δ 13.6, 16.8, 37.6, 39.7, 49.5, 55.3, 60.1, 60.4, 112.6, 114.6, 120.6, 128.0, 129.2, 129.7, 130.0, 138.2, 141.5, 159.9, 198.3, 200.6; IR (KBr) 1699 (C=O) cm\(^{-1}\). Anal Calcd for C\(_{22}\)H\(_{20}\)O\(_4\): C, 75.84; H, 5.79; O, 18.37. Found: C, 75.72; H, 5.75; O, 18.53.

**Endo-1,5-dimethyl-8-phenyl-8-(4-tolyl)-4-oxa-tricyclo[5.1.0.0³⁵]octane-2,6-dione (endo-1e):** (This compound could not be obtained in pure form because of the contamination of small amount of exo-1e). 
\(^1\)H-NMR (270 MHz, CDCl\(_3\)) δ 0.95 (s, 3H), 1.18 (s, 3H), 2.25 (s, 3H), 2.80 (s, 1H), 2.83 (s, 1H), 7.39-6.86 (m, 3H), 7.14-7.39 (m, 9H); \(^{13}\)C-NMR (67 MHz, CDCl\(_3\)) δ 13.7, 16.8, 21.0, 37.5, 39.6, 49.4, 60.1, 60.4, 127.6, 128.3, 128.9, 129.4, 129.8, 135.2, 137.9, 140.3, 198.5, 200.7. Anal Calcd for C\(_{22}\)H\(_{20}\)O\(_3\): C, 79.50; H, 6.06; O, 14.44. Found: C, 79.50; H, 6.05; O, 14.45.
**Exo-1,5-dimethyl-8-(4-tolyl)-8-phenyl-4-oxa-tricyclo[5.1.0.0³⁵]octane-2,6-dione** (*exo-1e*): mp 143.9-144.9 °C, colorless prisms (chloroform/pentane); $^1$H-NMR (270 MHz, CDCl$_3$) δ 0.91 (s, 3H), 1.19 (s, 3H), 2.28 (s, 3H), 2.79 (s, 1H), 2.80 (s, 1H), 7.10-7.28 (m, 9H); $^{13}$C-NMR (67 MHz, CDCl$_3$) δ 13.6, 16.8, 21.0, 37.8, 39.8, 49.5, 60.1, 60.3, 127.9, 128.2, 129.2, 129.6, 129.7, 137.1, 137.5, 138.5, 198.5, 200.7; IR (KBr) 1708 (C=O) cm$^{-1}$. Anal Calcd for C$_{22}$H$_{20}$O$_3$: C, 79.50; H, 6.06; O, 14.44. Found: C, 79.50; H, 6.05; O, 14.45.

**Endo-1,5-dimethyl-8-phenyl-8-(3-tolyl)-4-oxa-tricyclo[5.1.0.0³⁵]octane-2,6-dione** (*endo-1f*): mp 137.1-138.1 °C, colorless prisms (chloroform/pentane); $^1$H-NMR (270 MHz, CDCl$_3$) δ 0.93 (s, 3H), 1.18 (s, 3H), 2.27 (s, 3H), 2.79 (s, 1H), 2.80 (s, 1H), 6.99-7.41 (m, 9H); $^{13}$C-NMR (67 MHz, CDCl$_3$) δ 13.6, 16.8, 21.2, 37.6, 39.8, 49.7, 60.0, 60.2, 126.6, 127.6, 128.4, 128.7, 129.0, 129.1, 130.2, 138.2, 139.1, 140.1, 198.4, 200.5; IR (KBr) 1700 (C=O) cm$^{-1}$. Anal Calcd for C$_{22}$H$_{20}$O$_3$: C, 79.50; H, 6.06; O, 14.44. Found: C, 79.33; H, 5.97; O, 14.70.

**Exo-1,5-dimethyl-8-(3-tolyl)-8-phenyl-4-oxa-tricyclo[5.1.0.0³⁵]octane-2,6-dione** (*exo-1f*): mp 116.2-117.2 °C, colorless prisms (chloroform/pentane); $^1$H-NMR (270 MHz, CDCl$_3$) δ 0.92 (s, 3H), 1.19 (s, 3H), 2.32 (s, 3H), 2.80 (s, 1H), 2.81 (s, 1H), 7.02-7.27 (m, 9H); $^{13}$C-NMR (67 MHz, CDCl$_3$) δ 13.6, 16.8, 21.4, 37.6, 39.7, 49.7, 60.1, 60.3, 125.4, 127.9, 128.5, 128.8, 128.9, 129.2, 129.6, 138.4, 138.8, 139.9, 198.5, 200.7; IR (KBr) 1703 (C=O) cm$^{-1}$. Anal Calcd for C$_{22}$H$_{20}$O$_3$: C, 79.50; H, 6.06; O, 14.44. Found: C, 79.33; H, 5.97; O, 14.70.

**Endo-1,5-dimethyl-8-phenyl-8-(4-chlorophenyl)-4-oxa-tricyclo[5.1.0.0³⁵]octane-2,6-dione** (*endo-1h*): mp 126.2-127.2 °C, colorless prisms (chloroform/pentane); $^1$H-NMR (270 MHz, CDCl$_3$) δ 1.01 (s, 3H), 1.19 (s, 3H), 2.81 (s, 1H), 2.89 (s, 1H), 7.18-7.38 (m, 9H); $^{13}$C-NMR (67 MHz, CDCl$_3$) δ 13.6, 16.8, 37.4, 39.3, 48.3, 60.3, 60.4, 127.9, 128.3, 129.1, 129.4, 131.0, 134.2, 136.8, 139.7, 198.2, 200.5; IR (KBr) 1695 (C=O) cm$^{-1}$. Anal Calcd for C$_{22}$H$_{17}$ClO$_3$: C, 71.49; H, 4.86; Cl, 10.05; O, 13.60. Found: C, 71.20; H, 4.87; Cl, 10.23; O, 13.70.
**Exo-1,5-dimethyl-8-(4-chlorophenyl)-8-phenyl-4-oxa-tricyclo[5.1.0.0^{3,5}]octane-2,6-dione (exo-1h):** mp 173.7-174.7 °C, colorless prisms (chloroform/pentane); $^1$H-NMR (270 MHz, CDCl$_3$) δ 0.92 (s, 3H), 1.19 (s, 3H), 2.77 (s, 1H), 2.82 (s, 1H), 7.21-7.34 (m, 9H); $^{13}$C-NMR (67 MHz, CDCl$_3$) δ 13.6, 16.8, 37.3, 39.5, 48.6, 60.2, 60.3, 128.2, 129.2, 129.3, 129.6, 129.7, 133.7, 137.8, 138.6, 198.1, 200.3; IR (KBr) 1705 (C=O) cm$^{-1}$. Anal Calcd for C$_{21}$H$_{17}$ClO$_3$: C, 71.49; H, 4.86; Cl, 10.05; O, 13.60. Found: C, 71.20; H, 4.87; Cl, 10.23; O, 13.70.

**Endo/exo-1,5-dimethyl-8-phenyl-8-(3-chlorophenyl)-4-oxa-tricyclo[5.1.0.0^{3,5}]octane-2,6-dione (endo/exo-1i):** (These compounds could not be separated); $^1$H-NMR (270 MHz, CDCl$_3$) δ 0.93 (s, 3H), 1.01 (s, 3H), 1.19 (s, 3H), 1.20 (s, 3H), 2.78 (s, 1H), 2.81 (s, 1H), 2.81 (s, 1H), 2.87 (s, 1H), 7.14-7.40 (m, 18H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 13.6, 13.6, 16.8, 16.8, 37.3, 37.5, 39.4, 39.5, 48.5, 48.7, 60.2, 60.2, 60.2, 60.3, 126.6, 127.8, 128.0, 128.0, 128.3, 128.3, 128.4, 128.5, 129.1, 129.3, 129.7, 129.7, 130.3, 130.5, 134.8, 135.0, 137.5, 139.3, 140.2, 141.9, 198.0, 198.0, 200.2, 200.2; IR (KBr): 1703 (C=O) cm$^{-1}$. Anal Calcd for C$_{21}$H$_{17}$ClO$_3$: C, 71.49; H, 4.86; Cl, 10.05; O, 13.60. Found: C, 71.43; H, 4.83; Cl, 10.00; O, 13.74.

**Endo-1,5-dimethyl-8-phenyl-8-(4-trifluoromethylphenyl)-4-oxa-tricyclo[5.1.0.0^{3,5}]octane-2,6-dione (endo-1k):** mp 158.8-159.8 °C, colorless prisms (chloroform/pentane); $^1$H-NMR (270 MHz, CDCl$_3$) δ 0.96 (s, 3H), 1.22 (s, 3H), 2.85 (s, 1H), 2.87 (s, 1H), 7.24-7.55 (m, 9H); $^{13}$C-NMR (67 MHz, CDCl$_3$) δ 13.5, 14.0, 16.9, 37.3, 39.3, 48.4, 60.2, 60.3, 123.6 (q, $J_{CF} = 272.1$ Hz), 126.1 (q, $J_{CF} = 3.91$ Hz), 128.1, 128.4, 129.2, 130.1, 130.3 (q, $J_{CF} = 33.0$ Hz), 139.1, 142.3, 198.1, 200.4; IR (KBr) 1704 (C=O) cm$^{-1}$. Anal Calcd for C$_{22}$H$_{17}$F$_3$O$_3$: C, 68.39; H, 4.43; F, 14.75; O, 12.42. Found: C, 68.27; H, 4.39; F, 14.84; O, 12.50.

**Exo-1,5-dimethyl-8-(4-trifluoromethylphenyl)-8-phenyl-4-oxa-tricyclo[5.1.0.0^{3,5}]octane-2,6-dione (exo-1k):** mp 157.8-158.8 °C, colorless prisms (chloroform/pentane); $^1$H-NMR (270 MHz, CDCl$_3$) δ 0.94 (s, 3H), 1.20 (s, 3H), 2.81 (s, 1H), 2.84 (s, 1H), 7.23-7.60 (m, 9H); $^{13}$C-NMR (67 MHz, CDCl$_3$) δ 13.6, 16.9, 37.1, 39.3, 48.6, 60.2, 60.3, 123.8 (q, $J_{CF} = 272.1$ Hz), 126.1 (q, $J_{CF} = 3.91$ Hz), 128.4, 128.9, 129.4, 129.5 (q, $J_{CF} = 33.0$Hz), 129.6, 137.3, 143.8, 197.9, 200.1; IR (KBr) 1701 (C=O) cm$^{-1}$. Anal Calcd for C$_{22}$H$_{17}$F$_3$O$_3$: C, 68.39; H, 4.43; F, 14.75; O, 12.42. Found: C, 68.27; H, 4.39; F, 14.84; O, 12.50.
(1R*,8R*,9S*,10R*,12S*)-12-Hydroxy-5-methoxy-1,10-dimethyl-8-phenyl-tetracyclo-[6.4.1,9.02,7.08,13]trideca-2(7),3,5-triene-11,13-dione (2d): mp 164.4-165.1 °C, colorless prisms (chloroform/pentane); $^1$H-NMR (270 MHz, CDCl$_3$) $\delta$ 1.14 (s, 3H), 1.24 (s, 3H), 2.63 (br, 1H), 3.05 (s, 1H), 3.58 (s, 3H), 3.65 (s, 1H), 6.06 (d, 1H, $J$ = 2.64 Hz), 6.68 (dd, 1H, $J$ = 2.64, 8.24 Hz), 6.97 (d, 1H, $J$ = 8.24 Hz), 7.14-7.16 (m, 1H), 7.38-7.42 (m, 2H), 7.48-7.50 (m, 2H); $^{13}$C-NMR (67 MHz, CDCl$_3$) $\delta$ 14.5, 21.1, 38.2, 49.7, 54.0, 55.1, 60.6, 81.3, 112.0, 115.8, 125.0, 128.5, 128.8, 129.3, 130.1, 131.1, 136.5, 138.3, 159.6, 203.2, 205.6; IR (KBr) 3330 (-OH), 1714, 1698 (C=O) cm$^{-1}$; HRMS: Calculated for C$_{22}$H$_{20}$O$_4$, 348.1362, Found: 348.1356

Spiro[cyclohexa-2,5-dienone-4,8'-7-phenyl-1,4-dimethyl-3-hydroxycyclo[2.2.2.0$^{6,7}$]octane-2,5-dione] 3a (same as 3h): mp 97.3-98.1 °C, colorless prisms (chloroform/pentane); $^1$H-NMR (270 MHz, CDCl$_3$) $\delta$ 1.00 (s, 3H), 1.07 (s, 3H), 2.79 (s, 1H), 3.06 (s, 1H), 4.01 (s, 1H), 6.13 (dd, $J$ = 1.98, 10.22 Hz), 6.51 (dd, $J$ = 1.98, 10.22 Hz), 6.58 (dd, $J$ = 3.30, 10.22 Hz), 6.86 (dd, $J$ = 3.30, 10.22 Hz), 7.07 (br, 2H), 7.29 (br, 3H); $^{13}$C-NMR (67 MHz, CDCl$_3$) $\delta$ 10.8, 14.7, 43.2, 46.2, 53.0, 53.6, 56.0, 75.5, 128.6, 129.0, 129.2, 129.4, 131.2, 131.2, 134.2, 143.2, 148.1, 184.4, 203.7, 204.6; IR (KBr) 3411 (-OH), 1747, 1712, 1664 (C=O) cm$^{-1}$; HRMS: Calculated for C$_{23}$H$_{22}$O$_3$, 334.1205, found 334.1197

6-(hydroxybis(4-methoxyphenyl)methyl)-2,5-dimethylcyclohex-2-en-1,4-dione (6): mp 173.4-174.1 °C; $^1$H-NMR (270 MHz, CDCl$_3$) $\delta$ 1.36 (s, 3H), 2.02 (d, 3H, $J$ = 1.89 Hz), 3.80 (s, 3H), 3.80 (s, 3H), 5.39 (s, 1H), 6.64 (q, 1H, $J$ = 1.62 Hz), 6.84-6.88 (m, 4H), 7.14-7.25 (m, 4H); $^{13}$C-NMR (67 MHz, CDCl$_3$) $\delta$ 14.4, 15.9, 55.3, 81.6, 113.7, 128.5, 133.0, 137.1, 143.4, 146.7, 147.1, 159.2, 187.7, 191.4; IR (KBr) 3447 (O - H) cm$^{-1}$; Anal Calcd for C$_{23}$H$_{22}$O$_3$: C, 73.00; H, 5.86; O, 21.14; found C, 72.83; H, 5.75; O, 21.42.
Figure 5. First-order decay plots of the relative ratio of 1g against time for the reaction at 30°C in CDCl₃ with various catalyst concentration [BF₃] (= 0.090 M for Run 1; 0.30 for Run 2; 0.60 for Run 3, respectively). The first-order rate constants $k_{\text{obs}}$ were calculated by natural logarithmic plots of the relative ratio of 1g vs time and the second-order rate constants $k$ were obtained by dividing the $k_{\text{obs}}$ by [BF₃]. Inset: a linear dependency of $k$ on [BF₃].
Figure 6. Logarithmic plots of the $[\text{endo-1a}] / [\text{endo-1a}]_0$ vs time for the reaction at $30^\circ C$ in CDCl$_3$ with various catalyst concentration ([BF$_3$] = 0.060 M for Run 1 and 0.030 for Run 2, respectively).

Figure 7. Logarithmic plots of the relative $[\text{endo-1k}] / [\text{endo-1k}]_0$ vs time for the duplicate reactions at $30^\circ C$ in CDCl$_3$ with catalyst concentration [BF$_3$] (= 0.90 M).
Calculation Procedure. All calculations were executed by PC SPARTAN’04 on a general Windows PC (Intel Celeron 2.8GHz, 2GB RAM). Geometries of 1g and 4g were optimized by density functional theory calculation (B3LYP/6-31G* level). The optimized energies were –650526.028 kcal/mol (1g) and –942075.871 kcal/mol (4g).

X-ray Crystal Structure Determination of 1j: C_{21}H_{16}Cl_{2}O_{3}, M = 387.26, monoclinic, space group P2_1/n with a = 13.6787(3), b = 15.7928(3), c = 17.9803(4) Å, \( \beta = 107.2044(1) ^o \), \( V = 3710.40(13) \) Å \(^3\), \( Z = 8 \), \( D_{calc} = 1.386 \) g/cm\(^3\), \( R = 0.0959 \) and \( R_w = 0.2478 \) for 7111 reflections with \( I > 2.0 \sigma(I) \).

X-ray Crystal Structure Determination of 6: C_{23}H_{22}O_{5}, M = 378.42, monoclinic, space group Pn with a = 8.9422(2), b = 10.7454(3), c = 10.7371(3) Å, \( \beta = 110.3428(14) ^o \), \( V = 967.35(4) \) Å \(^3\), \( Z = 2 \), \( D_{calc} = 1.299 \) g/cm\(^3\), \( R = 0.0487 \) and \( R_w = 0.1220 \) for 3310 reflections with \( I > 2.0 \sigma(I) \).

Figure 8. ORTEP drawing of 6.

2-5. Reference and Notes


(11) Crystallographic data for this compound have been deposited at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data-request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223336033. CCDC 749514.

(12) Our attempt to follow the rate of the reaction of di(p-anisyl)homobenzoquinone epoxide by NMR was failed because of the very fast degradation. Interestingly, this reaction gave neither 2 nor 3 type product, but yielded di(anisyl)methyl-substituted benzoquinone derivative 6 which seems to arise from the cyclopropane ring-cleavage as well as the loss of oxygen atom. The structure of 6 was determined by the X-ray crystal structural analysis. CCDC 750112.


(14) The author obtained rather worse correlations when the author assumed the π-aryl participation occurs only at the ortho carbon; log \( k_{rel}^{exo}(1) = -0.38\sigma -0.01 \) \( (R^2 = 0.96, n = 8) \) and \(-0.24\sigma^+ -0.05 \) \( (R^2 = 0.82, n = 8) \).


(26) Recently, Wang and Tantillo suggested a stepwise reaction pathway for the acid-catalyzed transannular cyclization of 4 based on DFT calculations, (Wang, S. C.; Tantillo, D. J. *J. Org. Chem.* 2007, 72, 8394–8401). However, the poor kinetic solvent effects for the reaction of 4 and especially for the present 1 explicitly rule out the intervention of the carbocation intermediate derived from the stepwise $S_N1$ mechanism.


Chapter 3. Consecutive Acid-Catalyzed Rearrangement

Reaction of HQ-Epoxides and Cyclobutane-Fused Quinone Epoxide

3-1. Introduction

Thermal and photochemical skeleton rearrangements of strained small rings with multiple bonds and functional groups have attracted much attention from both synthetic and mechanistic viewpoints. Especially, polycyclic ketones bearing high strain energy have great potential to induce a skeletal rearrangement in the presence of acid catalyst. An enormous variety of carbocyclic and heterocyclic medium ring compounds with a wide range of functional groups has been reported to undergo these fascinating processes for modern synthetic chemistry. Transannular cyclization requires a suitable conformation of substrates and prudent selection of functional groups. In this regard, comprehensive knowledge of factors governing reactivity will yield insight into widespread application of transannular reaction.

In Chapter 1 and 2, the author described that the acid-catalyzed rearrangements of polycyclic epoxides to afford the caged diketo alcohol product in quantitative yield.

In this Chapter, the author deals with the consecutive novel skeletal rearrangement to cyclopropane ring opening products and acid-catalyzed rearrangement reaction of cyclobutane-fused quinone epoxides (Scheme 1).
3-2. Results and Discussion

3-2-1. Acid-Catalyzed Reaction of Diketo-Alcohol

CF$_3$SO$_3$H catalyzed reactions of HQ-Epoxide 1a was carried out in CDCl$_3$ at room temperature under the same conditions as BF$_3$ or MeSO$_3$H reactions. This protic acid-catalyzed reaction of 1a gave the cyclopropane ring opened product 3a and unidentified product 3a’ (Scheme 2).

![Scheme 2](image)

Next, the author isolated the BF$_3$-catalyzed reaction product 2a and investigated the CF$_3$SO$_3$H catalyzed reaction (Scheme 3). It is interesting to note that the cyclopropane ring opened product 3a was isolated selectively. This result means that the compound 3a was obtained via transannular product 2a but unknown product 3a’ was formed directly from 1a.

![Scheme 3](image)

3-2-2. Acid-Catalyzed reaction of Ethano-Bridged HQ-Epoxide

As described in Chapter 1, ethano-bridged HQ-epoxide 1g underwent the novel consecutive skeltal rearragements. The involved major processes are 1) cyclopropane ring opening, 2) acyl migration reaction, 3) epimerization, 4) ring contraction reaction (Scheme 4).

![Scheme 4](image)
The reactivity was much dependent on the conformational difference of the dibenzocycloheptene ring as experienced by the higher conversion (though shorter reaction time) of $\beta-1g$ compared to the conformational isomer $\alpha-1g$ (Table 1). It is very noteworthy that the primary product $4g$ (not detected) underwent a facile acid-catalyzed acyl migration associated with the cyclopropane ring cleavage. The resulting product 5 was found to undergo the keto-enol tautomerization to be more stable epimer $5'$. The structures of $4f$, $5'$ and 6 were confirmed by X-ray crystallographic analyses (Figure 1). Unfortunately, at present, we have no satisfactory mechanistic explanation for the transformation $5' \rightarrow 6$, although the $5'$ is likely to undergo the initial 1,2-migration to the activated carbonyl group and formal loss of one carbon unit.

**Table 1.** Acid-catalysed rearrangement of $\alpha/\beta-1g$ (30 mM) in CDCl3 at 30 °C

<table>
<thead>
<tr>
<th>sub.</th>
<th>time (h)</th>
<th>conv. ($%$)</th>
<th>yield$^a$ ($%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha-1g$</td>
<td>16</td>
<td>12</td>
<td>42</td>
</tr>
<tr>
<td>$\beta-1g$</td>
<td>2</td>
<td>85</td>
<td>21</td>
</tr>
</tbody>
</table>

$^a$ Based on consumed 1. $^b$ Determined by $^1$H NMR.

![Figure 1](image)

**Figure 1.** ORTEP drawings of a) $4f$ and b) $5'$.

Here, the question is raised on why $4g$ undergoes the subsequent cyclopropane ring-opening as well as the acyl migration in contrast to the analogous $4f$ (Scheme 5). Only difference between $4f$ and $4g$ is the substitution pattern of the two quinone Me groups (ie., *para* for $4f$ and *meta* for $4g$). Furthermore, it is noted that the similarly *meta*-Me-substituted less strained tricyclic diketo-alchoh $4b$ do not exhibit such an acyl migration (See Scheme 3 in Chapter 1).
Based on the structural comparison of $4g$ with the persistent $4b$ and $4f$, we can imagine the several reasons; (1) the $4g$ has the less hindered carbonyl group (only substituted by $\alpha$–OH group) that is needed to be activated by BF$_3$ for the present cyclopropane ring opening, whereas the relevant carbonyl group of $4f$ is well blocked both by the $\alpha$-Me and $\alpha'$-OH substitutes, (2) for $4g$, the Me group on cyclopropane ring may accelerate the migration of acyl group by stabilizing the generating positive charge, but this is not the case for $4f$, (3) in contrast to $4f$, compound $4g$ forces the considerable coplanarity of ethano-bridged two aromatic nuclei capable of favorably resonating with the cleaved cyclopropane ring. All of these steric and electronic effects would be responsible for the lability of $4g$.

However, the possibility that the transformation of $4g$ into $5$ occurs through a concerted orbital controlled [\(\sigma^2s + \sigma^2a\)] process can not be thoroughly ruled out (Figure 2). In this mechanism, the disrotatory mode of ring-opening (C$_2$-C$_3$ $\sigma$-bond) involves charge transmittance to the antibonding C$_1$-C$_4$ bond. The partially developing positive charge at C$_1$-carbon atom can be favorably stabilized by the substituted Me group. The stable compound $4f$ lacks the corresponding Me group.

![Figure 2. A possible concerted [\(\sigma^2s + \sigma^2a\)] pathway for the transformation $4g \rightarrow 5$. For simplicity, the ethano-bridge is omitted.](image)

### 3-2-3. Acid-Catalyzed reaction of Cyclobutane-Fused Quinone Epoxide

Next, the author attempted the skeltal rearrangement of cyclobutane-fused quinone $7$. The reaction of $7$ (30 mM) with BF$_3$-Et$_2$O (3 equiv.) in chloroform at room temperature proceeded rapidly to give tricyclic compound $8$ and diphenylethene $9$ in yields of 57 and 23%, respectively (Scheme 6). Unlike the acid-catalyzed reaction of homobenzoquinone epoxide $1$, the phenylene-bridged product was not determined in this reaction. Although not presently understood the mechanistic details of this reaction, the author thought that this reaction
proceeded through the *endo*-Ar transannular reaction. Therefore as shown in Scheme 7, the acid-coordinated 7 would produce the bridged intermediate I and cyclobutane ring opened intermediate II, respectively depending on which oxygen atom (i.e., epoxyde or C=O oxygen atom) is bound by the Lewis acid. The resulting I can perform the cyclobutane ring opening reaction and Ph migration following dehydration to give the tricyclic product 8. The II will provide diphenylethene and quinoepoxide, but quinoepoxide is easily decomposed by acid.

3-3. Conclusion

The author found that the subsequent ring-enlargement by 1,2-acyl migration associated with the incorporated cyclopropane ring-opening, depending on the substitution pattern of the quinone methyl groups. In this Chapter, the author has also investigated the acid-catalyzed rearrangement of cyclobutane-fused quinone epoxide 7. The compound 7 underwent the novel consecutive skeletal rearrangements. These findings provide the useful information on the rearrangements of polycyclic epoxides and the design of more extended framework compounds.

3-4. Experimental Section

**General procedures for the synthesis of homobenzoquinone epoxides.** To a mixture of homobenzoquinone (0.5 mmol) and 30% H$_2$O$_2$ (0.75 mmol) in DMSO (1 mL) was added dropwisely (10 min) a solution of Bu$_4$NF (1M solution in THF, 0.5 mmol) at room temperature. After the addition of the reagent the reaction mixture was stirred for 2h. Then, the epoxide I was extracted with ethyl acetate (3 mL $\times$ 3). The organic layer was washed with water (3 mL $\times$ 3) and dried over magnesium sulfate. The solvent was evaporated *in vacuo*. The epoxide I was purified by column chromatography on silica gel (benzene as an eluent) and recrystalization from hexane-ether or hexane-benzene. The structures of all epoxides
were deduced from the $^1$H and $^{13}$C NMR, and IR spectra.

**General procedures for the synthesis of cyclobutane-fused quinone epoxide.**
Cyclobutane-fused quinones were synthesized by the [2+2] photocycloaddition of the 2,5-dimethyl $p$-benzoquinone (0.5 mmol) with 1,1-diphenylethene (0.7 mmol). To a mixture of cyclobutane-fused quinone (0.5 mmol) and 30% H$_2$O$_2$ (0.75 mmol) in DMSO (1 mL) was added dropwisely (10 min) a solution of Bu$_4$NF (1M solution in THF, 0.5 mmol) at room temperature. After the addition of the reagent the reaction mixture was stirred for 2h. Then, the epoxide 7 was extracted with ethyl acetate (3 mL $\times$ 3). The organic layer was washed with water (3 mL $\times$ 3) and dried over magnesium sulfate. The solvent was evaporated in vacuo. The epoxide 7 was purified by column chromatography on silica gel (benzene as an eluent) and recrystallization from hexane-ether or hexane-benzene. The structures of all epoxides were deduced from the $^1$H and $^{13}$C NMR, and IR spectra.

**General procedures for acid-catalyzed reactions.** To a CDCl$_3$ solution (670 µl) of 1 or 7 (0.02 mmol) in a NMR tube was added the requisite amount of acid at room temperature by using a micro syringe. The progress of reaction was monitored by $^1$H NMR. After a period of requisit time, the reaction solution was transferred into a separate funnel, diluted with chloroform (10 mL) and then washed with water (3 mL $\times$ 3). The aqueous layer was extracted with chloroform (5 mL $\times$ 2). The combined organic layer was washed with water (3 mL $\times$ 3), then dried over calcium chloride. After the evaporation of the solvent in vacuo, the residue was submitted for a $^1$H NMR analysis to determine the product distribution. The column chromatographic treatment of the reaction mixtures on silica gel gave 5, 5’, and 6 with a mixture of hexane-ethyl acetate as an eluent. The structures of all products were deduced from the $^1$H and $^{13}$C NMR, and IR spectra. The structures of 4f, 5 and 5’ were also confirmed by the X-ray crystallographic analyses.

**1,5-Dimethyl-8,8-diphenyl-4-oxa-tricyclo[5.2.0.0$^{3,5}$]nonane-2,6-dione**
(7) : yellow powder; $^1$H NMR(270 MHz, CDCl$_3$) $\delta$ 1.14 (s, 3H), 1.50 (s,3H), 2.50 (d, 1H, $J$ = 12.5), 3.30 (s, 1H), 3.80 (dd, 1H, $J$ =0.6, 12.5), 4.01(d, 1H, $J$ = 0.6), 6.98 - 7.02 (m, 2H), 7.06 - 7.25 (m, 4H), 7.32 - 7.35 (m, 2H); $^{13}$C NMR (67.5 MHz, CDCl$_3$) $\delta$ 13.7, 16.9, 37.6, 39.7, 49.6, 60.1, 60.3, 127.5, 127.9, 128.2, 128.9, 129.1, 129.5, 138.1, 139.9, 198.1, 200.3.
3,10a-Dimethyl-9-phenyl-4a,10a-dihydro-phenanthrene-1,4-dione (8):
white crystal; mp. 161.2 - 162.0 °C; 1H NMR (270 MHz, CDCl₃) δ
1.38 (s, 3H), 2.03 (d, 3H, J = 1.48), 3.89 (s, 1H), 5.76 (s, 1H), 6.61 (d, 1H, J = 1.48), 7.05 - 7.13 (m, 2H), 7.20 - 7.40 (m, 7H); 13C NMR (67.5 MHz, CDCl₃) δ
16.8, 21.4, 50.8, 58.5, 77.1, 126.4, 126.5, 127.8, 128.2, 128.6, 129.0, 129.2, 129.3, 131.3, 132.8, 136.7, 138.8, 140.7, 151.9, 198.1, 200.9.

3-5. Reference and Notes


(3) We could not detect 4g by 1H NMR, even for shorter reaction times (10 min, 30% conversion) of 1g under the same conditions. Another possibility that compound 1g undergoes a prior acyl migration coupled with cyclopropane ring cleavage to give an intermediary dioxocycloheptene epoxide is unlikely, because of its increased heat of formation (by 70.79 kJ/mol on DFT calculation with B3LYP/6-31G*). Incidentally, 4g and 5 are more stable than 1g by 76.94 and 80.35 kJ/mol, respectively.

(4) Crystallographic data for the structure of 4f, 5' and 6 have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 650017, 650018 and 650209. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44-1233-336033. E-mail: deposit@ccdc.cam.ac.uk.

(5) We confirmed that the treatment of isolated 5' with BF₃ for 12 h under the same conditions provided compound 6 in 96% yield on 52% conversion.

Chapter 4. Intramolecular [2+2] Photocycloaddition Reaction of Cyclobutane-Fused Quinone

4-1. Introduction

Intramolecular photochemical [2+2] cycloaddition is one of the most sophisticated methods for the synthesis of strained polycyclic cage compounds. Especially, intramolecular [2+2]-photocycloadditions involving cyclic enones is widely used in organic synthesis as they can lead to cyclobutanes, a precursor for the synthesis of natural molecules. The [2+2] photocycloaddition of cyclic enones with alkene has been widely investigated from the mechanistic point of view. A variety of starting molecules bearing the incorporated several π-bond functionaries have been reported to exhibit these fascinating processes. In these photocycloadditions, the geometrical and topological arrangements of the relevant two 2π-components play a crucial role in an efficient cycloaddition of the conformationally restricted substrates. In particular, quinones and their derivatives have attracted the continuous attention in view of the conjugated ring system as well as the suitable structural design of the reacting sites. Accordingly, a number of studies have been made on their intramolecular photocycloadditions.

The author now wishes to report that the photoreaction of variously methyl-substituted 1,4-benzoquinones with 1,1-diphenylethene resulted in the reversible intramolecular [2+2] cycloaddition of the primary 1:1 photoadducts to afford the pentacyclic diones only via the 1,2-addition of endo-phenyl ring (Scheme 1).

Scheme 1.
4-2. Results and Discussion

4-2-1. Substitution Patterns of Me-Groups

Irradiation of quinones 1a-d (30 mM) and 2 equiv. amount of 1,1-diphenylethene in benzene under the argon atmosphere with a high-pressure Hg lamp through a Pyrex filter ($\lambda > 300$ nm) provided the regioisomeric mixture of the primary 1:1 photoadducts 2 and 3 along with the respective secondary intramolecular [2+2] cycloaducts 4 and 5 in almost quantitative total yield (Scheme 1 and Table 1). The structures of these products were deduced from their $^1$H and $^{13}$C NMR spectra. The pentacyclic cage compound 5a was also confirmed by the X-ray crystal analysis (Figure 1). It is clearly demonstrated that the cage compound 5a includes the diagonal connection of the two cyclobutane rings.

In conformity with this distinctive structure, all cage compounds obtained exhibited no diagnostic NOE effects between the inwardly directed allyl proton (H_a) of fused cyclohexadiene and the inside methylene proton of the original cyclobutane ring.

The polycyclic products 4 and 5 are considered to be formed via a very rare intramolecular [2+2] photoreaction between the excited enedione C=C double bond with the facing

---

**Table 1.** Product Distributions in Photoreaction of Quinones 1a-d with 1,1-Diphenylethene.$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>compound</th>
<th>irradiation time (h)$^c$</th>
<th>yield (%)$^b$</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a$^d$</td>
<td>4</td>
<td>60</td>
<td>20</td>
<td>5</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1b$^d$</td>
<td>6</td>
<td>30</td>
<td>26</td>
<td>35</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1c</td>
<td>1</td>
<td>14</td>
<td>34</td>
<td>42</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1d</td>
<td>1</td>
<td>43</td>
<td>–</td>
<td>57</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Carried out in benzene-d$_6$ in a NMR tube through a Pyrex filter. $^b$ Based on quinone used. $^c$ Irradiation time for complete consumption of quinones. $^d$ Trace amount of unidentified products were detected in the $^1$H NMR spectra of the reaction mixture.

**Figure 1.** ORTEP drawing of 5a. For clarity, hydrogen atoms are omitted.

In conformity with this distinctive structure, all cage compounds obtained exhibited no diagnostic NOE effects between the inwardly directed allyl proton (H_a) of fused cyclohexadiene and the inside methylene proton of the original cyclobutane ring.

The polycyclic products 4 and 5 are considered to be formed via a very rare intramolecular [2+2] photoreaction between the excited enedione C=C double bond with the facing
endo-phenyl ring at the 1,2-position.\textsuperscript{11} Mechanistically, as in the case of usual [2+2] photocycloaddition of enones,\textsuperscript{12} these reactions seem to involve a triplet 1,4-biradical intermediate derived from the spin-inverted excited triplet state of the primary 1:1 adducts, \textit{2} and \textit{3}.

Interestingly, the prolonged irradiation established the photochemical equilibration between the primary and the secondary photoadducts under the complete consumption of the starting quinones as represented for the case of quinone \textit{1d} (Figure 2). This finding apparently indicates the occurrence of [2+2] cycloreversion of the cage compounds (Scheme 1).

![Figure 2](image-url)

**Figure 2.** Time-dependent product ratios (%) of \textit{2d} and \textit{4d} in photochemical reaction of quinone \textit{1d} with 1,1-diphenylethene (2 equiv) in benzene-\textit{d}_6 irradiated in a NMR tube through a Pyrex filter.

To more explicitly know the Me-substituent effects on the photostationary product ratios of cage compounds / bicyclic diones, we have performed the photoequilibration by using the isolated bicyclic diones. As expected, NMR monitoring of the reactions showed the apparent equilibration within 100 min at the photostationary state for all cases tested (Table 2). We also noted that the irradiation of cage compound led to the identical photoequilibrium as exemplified for \textit{5a} (entry 2). A perusal of Table 2 indicates that the relative ratios (%) of cage

<table>
<thead>
<tr>
<th>entry</th>
<th>compound</th>
<th>irradiation time (min)\textsuperscript{a}</th>
<th>yield (%)\textsuperscript{b}</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>\textit{2a}</td>
<td>100</td>
<td>10</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>\textit{3a}</td>
<td>60</td>
<td>–</td>
<td>43(44)\textsuperscript{b}</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>\textit{2b}</td>
<td>60</td>
<td>67</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>\textit{3b}</td>
<td>60</td>
<td>–</td>
<td>31</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>\textit{2c}</td>
<td>60</td>
<td>90</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>\textit{2d}(=\textit{3d})</td>
<td>100</td>
<td>70(&gt;99)\textsuperscript{c}</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\textsuperscript{a} irradiation in a NMR tube in benzene-\textit{d}_6 through a Pyrex filter. \textsuperscript{b} Value in parenthesis was obtained in the photocycloreversion of \textit{5a}. \textsuperscript{c} Value in parenthesis was attained by irradiation of \textit{2c} through a filter (>350 nm).
compounds tended to increase for the bicyclic diones in which the ipso-carbon of endo-phenyl ring combines to the unsubstituted alkenoic carbon atom (entries 2, 3 and 5), but decrease for the bicyclic diones in which the ipso-carbon needs to bind to the Me-substituted alkenoic carbon (entries 1 and 4). However, the tetramethyl-substituted 2d(=3d) provided an unexpected intrinsically large amount of cage compound probably because of rather enhanced steric congestion around original cyclobutane ring (entry 6). Thus, the lower ratios of cage compounds can be explained in terms of the more enhanced steric congestion between the ipso-carbon of phenyl ring and the substituted Me group.

Why does the present intramolecular photoreaction bring about the diagonal [2+2] cycloaddition of endo-phenyl ring? To answer the question, we first made of the conformational analysis of the representative 2d on the basis of its X-ray crystal structure (Figure 3a). The whole structure of 2d\(^{13}\) was found to be considerably twisted in such a way that the endo-phenyl ring is inwardly located over the quinone plane. Namely, the cyclobutane ring of 2d adopts a packed conformation and the endo-phenyl ring considerably overhangs the quinone frame (Figure 3b). The spatial distances (broken lines) between the relevant carbon atoms are 3.45 (C(19)-C(26)) and 3.46Å (C(9)-C(8)), respectively. These values are sufficient for the effective photochemical [2+2] cycloaddition.\(^{14}\)

![Figure 3.](image)

**Figure 3.** a) ORTEP drawing of 2d. For clarity, hydrogen atoms are omitted, b) Schematic conformational representation of 2d showing the favorable topological overlapping of endo-phenyl ring and quinone plane for [2+2] photocycloaddition.

Furthermore, the p-orbital axis of the aromatic ipso-carbon is allowed to favorably overlap with that of the underlying alkenoic carbon atom. These conformational preference would lead to the diagonal conjunction of two cyclobutane rings.

### 4-2-2. Selective Synthesis of Cage Compound 4

To obtain some information on the photoreversibility in the present intramolecular [2+2] cycloaddition of bicyclic diones, we have measured the absorption spectra of 2d and 4d in benzene (Figure 4). It was found that both the 2d and 4d have the comparable absorptions in the range of 300–340 nm which are responsible for cycloaddition and cycloreversion.
However, 2d apparently showed the larger absorption band over 340 nm as compared with 4d, thus resulting in almost one-way transformation of 2d to 4d on longer-wavelength irradiation (>350 nm) (Table 2, entry 6).

As to the photochemical cycloreversion of cyclobutane ring, the conformations of the adjoining π-bond substituents play a role in the efficient bond cleavage.15 In the case of 4 and 5, it is likely that the fused cyclohexadiene ring and the two vicinal carbonyl groups are responsible for the regioselective bond fission on account of the favorable excited π-electron donating conjugation with the anti-bonding orbital (σ*) of the cleaved cyclobutane ring.

An attempt was done to determine the triplet energies of cyclobutane-fused quinones 2 and cage compounds 4 by the procedure of Hammond and Saltiel,16 since 2 and 4 did not emit phosphorescence in rigid glasses. Thus, the photostationary state isomer ratios of 2d/4d were measured in the presence of various sensitizers with triplet energies covering 177-353 kJ/mol in benzene (Table 3). Figure 5 plots the ratio against the triplet energy of the sensitizer. This plot allows us to estimate the triplet energy of 2d and 4d as ca. 230 and ca. 200 kJ/mol, respectively. By using triplet sensitizer (9-fluoreneone or benzile), cyclobutane-fused quinone 2 was selectively formed.

Now, the selective synthesis of each compound 2 and 4 has been achieved successfully.
Table 3. Photostationary state isomer ratios in triplet sensitizer irradiation of 2d.

<table>
<thead>
<tr>
<th>sensitizer</th>
<th>triplet energy(^a) (kJ/mol)</th>
<th>isomer ratio(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2d</td>
</tr>
<tr>
<td>anthracene</td>
<td>177</td>
<td>57.8</td>
</tr>
<tr>
<td>acridine</td>
<td>190</td>
<td>66.7</td>
</tr>
<tr>
<td>9-fluorenone</td>
<td>210</td>
<td>100</td>
</tr>
<tr>
<td>benzilé</td>
<td>223</td>
<td>100</td>
</tr>
<tr>
<td>p-nitroaniliné</td>
<td>231</td>
<td>91.0</td>
</tr>
<tr>
<td>2-acetonapththone</td>
<td>247</td>
<td>66.7</td>
</tr>
<tr>
<td>naphthalene</td>
<td>253</td>
<td>25.6</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>260</td>
<td>19.8</td>
</tr>
<tr>
<td>fluorene</td>
<td>282</td>
<td>20.1</td>
</tr>
<tr>
<td>4'-methylacetophenone</td>
<td>305</td>
<td>26.6</td>
</tr>
<tr>
<td>acetophenone</td>
<td>311</td>
<td>30.0</td>
</tr>
<tr>
<td>acetone</td>
<td>332</td>
<td>30.1</td>
</tr>
<tr>
<td>benzene</td>
<td>353</td>
<td>30.0</td>
</tr>
</tbody>
</table>

\(^a\) S. L. Murov, “Handbook of Photochemistry,” Marcel Dekker, New York (1973). \(^b\) Determined by \(^1\)H NMR.

Figure 3. Hammpmd-Saltiel plot of triplet sensitized isomerization of 1d.

To gain further information on the mechanistic property of intramolecular [2+2] photocycloaddition reaction, the author investigated the aromatic ring substituents effect on the photoreaction of variously \( m \) - and \( p \)-substituted diarylcyclobutane-fused quinone \( 1d-m \) (Scheme 2).

The quantum yield for the photocycloaddition reaction of variously substituted cyclobutane-fused quinone \( 2d-m \) to cage compound \( 4d-m \) were determined in benzene at their low conversion (<10%). Here, it should be noted that the quantum yields increased with increasing electron-donating power of the substituent on phenyl ring (except \( endo-p\text{-OMe} \) entry 8). Although not presently understood the mechanistic explanation for such substituents effect, now it is under consideration.

### Table 4. Photostationary equilibrated product ratios (2 : 4) in reversible photocycloaddition of 2.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compd.</th>
<th>X</th>
<th>Y</th>
<th>Irradiation time (min)</th>
<th>Ratio(^a) 2 : 4</th>
<th>( \Phi ) (2 : 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2d</td>
<td>H</td>
<td>H</td>
<td>100</td>
<td>30 : 70</td>
<td>0.043</td>
</tr>
<tr>
<td>2</td>
<td>2e</td>
<td>( p\text{-CF}_3 )</td>
<td>H</td>
<td>240</td>
<td>18 : 82</td>
<td>0.029</td>
</tr>
<tr>
<td>3</td>
<td>2f</td>
<td>H</td>
<td>( p\text{-CF}_3 )</td>
<td>180</td>
<td>29 : 71</td>
<td>0.032</td>
</tr>
<tr>
<td>4</td>
<td>2g</td>
<td>( p\text{-F} )</td>
<td>( p\text{-F} )</td>
<td>300</td>
<td>23 : 77</td>
<td>0.032</td>
</tr>
<tr>
<td>5</td>
<td>2h</td>
<td>( p\text{-Cl} )</td>
<td>( p\text{-Cl} )</td>
<td>100</td>
<td>50 : 50</td>
<td>0.030</td>
</tr>
<tr>
<td>6</td>
<td>2i</td>
<td>( p\text{-Me} )</td>
<td>( p\text{-Me} )</td>
<td>100</td>
<td>20 : 80</td>
<td>0.049</td>
</tr>
<tr>
<td>7</td>
<td>2j</td>
<td>( p\text{-OMe} )</td>
<td>( p\text{-OMe} )</td>
<td>120</td>
<td>13 : 87</td>
<td>0.103</td>
</tr>
<tr>
<td>8</td>
<td>2k</td>
<td>( p\text{-OMe} )</td>
<td>H</td>
<td>300</td>
<td>9 : 91</td>
<td>0.037</td>
</tr>
<tr>
<td>9</td>
<td>2l(^b)</td>
<td>H</td>
<td>( p\text{-OMe} )</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>2m(^b)</td>
<td>( m\text{-OMe} )</td>
<td>H</td>
<td>100</td>
<td>17 : 83</td>
<td>0.15</td>
</tr>
</tbody>
</table>

\(^a\) Irradiated in a NMR tube in benzene-\( d_6 \) through a Pyrex filter.\(^b\) Unfortunately, it was not isolated in pure.
4-3. Conclusion

In summary, the primary [2+2] photocycloadducts of variously Me-substituted 1,4-benzoquinones with 1,1-diphenylethene underwent the reversible intramolecular [2+2] photocycloaddition to provide pentacyclotetradeca-10,12-diene-2,7-diones. The cage skeleton was characterized by very rare diagonal conjunction of two facing cyclobutane rings. The geometrical features of these reactions were interpreted in terms of the conformational preference which allowed the proximity of the relevant $2\pi$ components.

4-4. Experimental Section

Preparative Photoreaction of Quinones with 1,1-diphenylethene. Typical experimental procedure is described for the case of $p$-xyloquinone (1a). A solution of $p$-xyloquinone 1a (1.0 g, 7.4 mmol) and 1,1-diphenylethene (2.58 ml, 14.8 mmol) in benzene (20 mL) was irradiated in a Pyrex tube with a filtered light (> 300 nm) at room temperature under an argon atmosphere for 40 h. After removal of solvent in vacuo, the reaction mixture was submitted for $^1$H NMR to determine the product distributions. Column chromatographic treatment of the reaction mixture on silica gel successively gave recovered 1,1-diphenylethene, 2a (1.78 g, 76 %), 3a (0.33 g, 14 %), 4a (trace) and 5a (trace) with a mixture of ethyl acetate (5−20 % by volume) and hexane as eluent. The compounds 4 and 5 were separately prepared by irradiation (>300 nm) of a solution of 2 and 3 in a NMR tube (benzene-$d_6$) (vide infra). The structures of compounds 2-5 were deduced from the $^1$H-NMR, $^{13}$C-NMR, IR spectra as well as elemental analysis as shown below.

Reversible Photoisomerization of 2 and 3 into 4 and 5. General procedure is described for the case of 2. A solution of 2 (0.02 mmol) in benzene-$d_6$ (670 µl) was irradiated in a NMR tube with a filtered light (> 300 nm). The $^1$H-NMR monitoring of the reaction revealed the photoequilibration within 100 min for all the primary [2+2] photocycloadducts 2 and 3.

1,4-Dimethyl-8,8-diphenyl-bicyclo[4.2.0]oct-3-ene-2,5-dione(2a) : mp 80.9-82.5 °C (from hexane-chloroform); $^1$H NMR (270 MHz, CDCl$_3$) $\delta$ 1.51 (s, 3H), 1.72 (d, 3H, $J$= 1.48), 2.84 (dd, 1H, $J$= 2.14, 10.4), 3.21 (dd, 1H, $J$= 10.4, 12.5), 3.56 (dd, 1H, $J$= 1.48, 12.5), 6.21 (q, 1H, $J$= 1.48), 7.04-7.19 (m, 6H), 7.24-7.36 (m, 4H); $^{13}$C NMR (270MHz, CDCl$_3$) $\delta$ 16.6, 22.8, 33.4, 47.1, 56.2, 59.2, 126.1, 126.5, 127.0, 127.5, 128.1, 128.2, 128.5, 139.2, 141.5, 145.3, 150.7, 200.3, 200.5; IR (KBr): 1669, 1616, 1495, 1439, 1375, 1360, 1325, 1294, 1225 cm$^{-1}$. Anal. Calcd for C$_{22}$H$_{20}$O$_2$: C, 83.51; H, 6.37%. Found: C, 83.51; H, 6.29%.
1,4-Dimethyl-7,7-diphenyl-bicyclo[4.2.0]oct-3-ene-2,5-dione (3a):
mp 126.5-127.3 °C (from hexane-chloroform); \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.37 (s, 3H), 1.62 (d, 3H, \(J = 1.32\)), 2.55 (d, 1H, \(J = 12.5\)), 3.71 (d, 1H, \(J = 12.5\)), 4.10 (s, 1H), 6.27 (q, 1H, \(J = 1.32\)), 7.05-7.20 (m, 6H), 7.29-7.40 (m, 4H); \(^1^3\)C NMR (270MHz, CDCl\(_3\)) \(\delta\) 16.1, 26.3, 42.45, 45.6, 53.8, 61.0, 126.2, 127.5, 128.3, 138.0, 149.9, 151.8, 198.2, 202.7; IR (KBr): 1669, 1616, 1495, 1439, 1375, 1360, 1325, 1294, 1225 cm\(^{-1}\). Anal. Calcd for C\(_{22}\)H\(_{20}\)O\(_2\): C, 83.51; H, 6.37%. Found: C, 83.39; H, 6.40%.

1,3-Dimethyl-8,8-diphenyl-bicyclo[4.2.0]oct-3-ene-2,5-dione (2b):
mp 106.7-107.4 °C (from hexane-chloroform); \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.55 (s, 3H), 1.67 (d, 3H, \(J = 1.40\)), 2.85 (dd, 1H, \(J = 1.98, 10.7\)), 3.19 (dd, 1H, \(J = 10.7, 12.5\)), 3.55 (dd, 1H, \(J = 1.98, 12.5\)), 6.28(q, 1H, \(J = 1.40\)), 7.01-7.18 (m, 6H), 7.23-7.35 (m, 4H); \(^1^3\)C NMR (270MHz, CDCl\(_3\)) \(\delta\) 16.6, 23.0, 33.0, 47.7, 55.2, 59.4, 126.1, 126.5, 126.8, 127.6, 128.1, 128.3, 138.7, 141.7, 145.6, 151.4, 199.7, 201.1; IR (KBr): 1661, 1618, 1579, 1493, 1464, 1446, 1376, 1315, 1267 cm\(^{-1}\).

1,3-Dimethyl-7,7-diphenyl-bicyclo[4.2.0]oct-3-ene-2,5-dione (3b):
mp 127.1-128.0 °C (from hexane-chloroform); \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.37 (s, 3H), 1.74 (d, 3H, \(J = 1.48\)), 2.56 (d, 1H, \(J = 12.5\)), 3.75 (d, 1H, \(J = 12.5\)), 4.05 (s, 1H), 6.20(q, 1H, \(J = 1.48\)), 7.03-7.21 (m, 6H), 7.26-7.39 (m, 4H); \(^1^3\)C NMR (270MHz, CDCl\(_3\)) \(\delta\) 16.7, 26.6, 42.8, 45.0, 54.0, 61.6, 126.0, 126.1, 126.6, 127.8, 127.6, 128.5, 139.3, 140.3, 150.0, 150.4, 197.1, 203.2; IR (KBr): 1679, 1659, 1609, 1578, 1492, 1454, 1444, 1375, 1314, 1296, 1274 cm\(^{-1}\).

1,3,6-Trimethyl-8,8-diphenyl-bicyclo[4.2.0]oct-3-ene-2,5-dione (2c):
mp 118.7-119.9 °C (from hexane-chloroform); \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.21 (s, 3H), 1.41 (s, 3H), 1.65 (d, 3H, \(J = 1.48\)), 2.72 (d, 1H, \(J = 12.0\)), 3.76 (d, 1H, \(J = 12.0\)), 6.25(q, 1H, \(J = 1.48\)), 7.01-7.15 (m, 6H), 7.22-7.32 (m, 4H); \(^1^3\)C NMR (270MHz, CDCl\(_3\)) \(\delta\) 16.5, 18.1, 21.6, 39.5, 49.0, 58.4, 58.5, 126.0, 126.4, 126.9, 127.6, 128.0, 128.2, 137.5, 141.6, 145.8, 150.9, 201.6, 203.4; IR (KBr): 1663, 1626, 1597, 1579, 1493, 1463, 1446, 1375, 1349, 1298, 1251, 1221 cm\(^{-1}\). Anal. Calcd for C\(_{22}\)H\(_{20}\)O\(_2\): C, 83.60; H, 6.71%. Found: C,83.46; H,6.56%.
1,3,4,6-Tetramethyl-7,7-diphenyl-bicyclo[4.2.0]oct-3-ene-2,5-dione (2d=3d): mp 116.1-117.0 °C (from hexane-chloroform); "H NMR (270 MHz, CDCl3) δ 1.20 (s, 3H), 1.43 (s, 3H), 1.64 (d, 3H, J = 1.07), 1.72 (d, 3H, J = 1.07), 2.71 (d, 1H, J = 12.0), 3.73 (d, 1H, J = 12.0), 6.98-7.15 (m, 4H), 7.20-7.34 (m, 6H); 13C NMR (270MHz, CDCl3) δ 13.0, 13.0, 18.3, 21.8, 39.9, 47.9, 58.3, 58.4, 125.9, 126.2, 126.9, 127.5, 128.0, 141.8, 145.7, 145.9, 146.8, 200.2, 203.1; IR (KBr): 1655, 1618, 1598, 1580, 1492, 1463, 1446, 1373, 1331, 1271, 1236 cm⁻¹.

9,13-dimethyl-12-phenyl-pentacyclo[8.2.2.0^1,6.0^7,13.0^9,12]tetradeca-2,4-diene-8,14-dione (4a): "H NMR (270 MHz, CDCl3) δ 1.34 (s, 3H), 1.79 (s, 3H), 2.44 (d, 1H, J = 11.0), 2.84 (d, 1H, J = 7.58), 3.08 (dd, 1H, J = 7.58, 11.0), 3.15 (m, 1H), 3.29 (m, 1H), 5.32 (m, 1H), 5.71-5.78 (m, 2H), 5.81-5.87 (m, 1H), 6.94-6.97 (m, 2H), 7.23-7.29 (m, 1H), 7.32-7.38 (m, 2H).

7,10-dimethyl-12-phenyl-pentacyclo[8.2.2.0^1,6.0^7,13.0^9,12]tetradeca-2,4-diene-8,14-dione (5a): "H NMR (270 MHz, CDCl3) δ 1.27 (s, 3H), 1.30 (s, 3H), 2.56 (d, 1H, J = 10.7), 2.66 (d, 1H, J = 10.7), 3.04 (m, 1H), 3.31 (s, 1H), 3.63 (s, 1H), 5.56-5.61 (m, 1H), 5.72-5.76 (m, 1H), 5.82-5.88 (m, 1H), 5.84-5.98 (m, 1H), 6.25-6.45 (m, 1H), 7.05-7.09 (m, 2H), 7.22-7.29 (m, 1H), 7.33-7.38 (m, 1H); 13C NMR (270MHz, CDCl3) δ 12.6, 18.3, 41.2, 44.6, 46.4, 47.3, 53.1, 57.6, 57.8, 64.6, 122.8, 123.3, 124.6, 125.4, 126.3, 126.6, 128.4, 142.4, 207.5, 208.9.

7,9-dimethyl-12-phenyl-pentacyclo[8.2.2.0^1,6.0^7,13.0^9,12]tetradeca-2,4-diene-8,14-dione (4b): "H NMR (270 MHz, CDCl3) δ 1.32 (s, 3H), 1.35 (s, 3H), 2.57 (dd, 1H, J = 1.90, 11.0), 2.76 (dd, 1H, J = 1.90, 7.58), 3.12 (dd, 1H, J = 7.58, 11.0), 3.22 (m, 1H), 3.63 (s, 1H), 5.55-5.63 (m, 2H), 5.73-5.79 (m, 1H), 5.90-5.97 (m, 1H), 6.91-6.95 (m, 2H), 7.23-7.29 (m, 1H), 7.31-7.37 (m, 2H); 13C NMR (270MHz, CDCl3) δ 12.9, 14.2, 22.4, 33.6, 45.6, 52.1, 53.8, 57.0, 63.3, 123.5, 124.4, 125.0, 125.4, 127.0, 127.3, 128.2, 139.9, 206.5, 210.6.
10,13-dimethyl-12-phenyl-pentacyclo[8.2.2.0^1,6.0^7,13.0^9,12]tetradeca-2,4-diene-8,14-dione (5b): \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.29 (s, 3H), 1.78 (s, 3H), 2.53 (s, 1H), 2.53 (s, 1H), 3.05 (d, 1H), 3.11 (dd, 1H), 3.27 (dd, 1H), 5.49 (m, 1H), 5.73-5.79 (m, 1H), 5.72-5.73 (m, 2H), 5.92-5.98 (m, 1H), 7.07-7.12 (m, 2H), 7.23-7.29 (m, 1H), 7.34-7.39 (m, 2H); \(^{13}\)C NMR (270MHz, CDCl\(_3\)) \(\delta\) 14.1, 18.5, 41.0, 41.2, 48.7, 52.5, 52.7, 54.7, 56.8, 64.5, 120.5, 124.8, 126.7, 126.9, 127.0, 127.4, 128.4, 142.9, 207.2, 208.0.

7,9,10-trimethyl-12-phenyl-pentacyclo[8.2.2.0^1,6.0^7,13.0^9,12]tetradeca-2,4-diene-8,14-dione (4c): \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.08 (s, 3H), 1.20 (s, 3H), 1.32 (s, 3H), 2.61 (d, 1H, \(J = 10.9\)), 2.69 (d, 1H, \(J = 10.9\)), 3.27 (m, 1H), 3.65 (s, 1H), 5.52 (dd, 1H, \(J = 0.82, 9.73\)), 5.61 (dd, 1H, \(J = 3.38, 9.73\)), 5.74 (dd, 1H, \(J = 5.44, 9.73\)), 5.89-5.96 (m, 1H), 6.90-7.09 (m, 3H); \(^{13}\)C NMR (270MHz, CDCl\(_3\)) \(\delta\) 11.7, 12.8, 13.4, 39.8, 45.1, 47.0, 50.7, 54.4, 54.8, 56.7, 63.1, 123.6, 124.4, 125.4, 126.9, 127.7, 128.1, 140.0, 207.6, 211.1.

7,9,10,13-tetramethyl-12-phenyl-pentacyclo[8.2.2.0^1,6.0^7,13.0^9,12]tetradeca-2,4-diene-8,14-dione (4d): \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 0.99 (s, 3H), 1.14 (s, 3H), 1.15 (s, 3H), 1.76 (s, 3H), 1.94 (d, 1H, \(J = 10.9\)), 2.09 (d, 1H, \(J = 10.9\)), 3.07 (m, 1H), 5.17-5.24 (m, 1H), 5.26-5.34 (m, 1H), 5.38-5.45 (m, 1H), 6.64-6.67 (m, 2H), 6.90-7.09 (m, 3H); \(^{13}\)C NMR (270MHz, CDCl\(_3\)) \(\delta\) 7.74, 11.4, 11.9, 13.5, 38.8, 43.5, 50.9, 51.7, 53.4, 54.0, 56.3, 63.0, 120.6, 120.9, 125.3, 125.7, 126.3, 126.9, 128.0, 140.6, 208.7, 210.7; IR (KBr): 1655, 1618, 1598, 1580, 1492, 1463, 1446, 1373, 1331, 1271, 1236 cm\(^{-1}\).
1,3,4,6-tetramethyl-7,7-dip-tolylbicyclo[4.2.0]oct-3-ene-2,5-dione (2i); \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.18 (s, 3H), 1.40 (s, 3H), 1.65 (q, 3H, \(J = 0.99\) Hz), 1.74 (q, 3H, \(J = 0.99\) Hz), 2.14 (s, 3H), 2.25 (s, 3H), 2.67 (d, 1H, \(J = 11.9\) Hz), 3.66 (d, 1H, \(J = 11.9\) Hz), 6.85 (d, 2H, \(J = 8.24\) Hz), 7.05 (d, 2H, \(J = 5.94\) Hz), 7.08 (d, 2H, \(J = 5.94\) Hz), 7.18 (d, 2H, \(J = 8.24\) Hz); \(^{13}\)C NMR (67.5 MHz, CDCl\(_3\)) \(\delta\) 13.0, 13.1, 18.2, 20.8, 21.0, 21.7, 39.8, 47.9, 57.8, 58.1, 126.7, 127.3, 128.6, 128.6, 135.3, 135.6, 139.1, 143.2, 145.6, 146.7, 200.4, 203.2; IR (KBr): 3317, 3020, 2987, 2959, 2922, 2872, 2731, 2361, 1905, 1795, 1655, 1618, 1510, 1468, 1447, 1377, 1335, 1324, 1279, 1251, 1237, 1197, 1162, 1142, 1114 cm\(^{-1}\); Anal Calcd for C\(_{26}\)H\(_{28}\)O\(_2\): C, 83.83; H, 7.58, Found: C, 83.59; H, 7.61.

7,7-bis(4-methoxyphenyl)-1,3,4,6-tetramethylbicyclo[4.2.0]oct-3-ene-2,5-dione (2j); mp. 96.4-97.2 °C (from chloroform / n-hexane); \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.18 (s, 3H), 1.39 (s, 3H), 1.69 (q, 3H, \(J = 0.99\) Hz), 1.75 (q, 3H, \(J = 0.99\) Hz), 2.65 (d, 1H, \(J = 12.4\) Hz), 3.64 (d, 1H, \(J = 12.4\) Hz), 3.66 (s, 3H), 3.74 (s, 3H), 6.60 (d, 2H, \(J = 8.90\) Hz), 6.80 (d, 2H, \(J = 8.90\) Hz), 7.10 (d, 2H, \(J = 8.90\) Hz), 7.21 (d, 2H, \(J = 8.90\) Hz); \(^{13}\)C NMR (67.5 MHz, CDCl\(_3\)) \(\delta\) 13.0, 13.2, 18.2, 21.6, 21.8, 39.8, 47.8, 55.2, 57.2, 58.1, 113.1, 113.3, 127.8, 128.6, 134.2, 138.6, 145.8, 146.6, 157.4, 157.5, 200.5, 203.2; IR (KBr): 3433, 2997, 2981, 2958, 2958, 2830, 2044, 1672, 1654, 1606, 1578, 1512, 1463, 1378, 1335, 1296, 1248, 1190, 1179, 1112 cm\(^{-1}\); Anal Calcd for C\(_{26}\)H\(_{28}\)O\(_4\): C, 77.20; H, 6.98, Found: C, 77.13; H, 6.98.

7,7-bis(4-chlorophenyl)-1,3,4,6-tetramethylbicyclo[4.2.0]oct-3-ene-2,5-dione (2h); \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.17 (s, 3H), 1.37 (s, 3H), 1.70 (q, 3H, \(J = 1.15\) Hz), 1.75 (q, 3H, \(J = 1.15\) Hz), 2.63 (d, 1H, \(J = 12.0\) Hz), 3.64 (d, 1H, \(J = 12.0\) Hz), 7.02 (d, 2H, \(J = 6.76\) Hz), 7.10 (d, 2H, \(J = 9.07\) Hz), 7.20-7.23 (m, 4H); \(^{13}\)C NMR (67.5 MHz, CDCl\(_3\)) \(\delta\) 13.0, 13.3, 18.4, 21.6, 39.4, 47.9, 57.4, 57.9, 128.1, 128.2, 128.3, 128.9, 132.1, 132.5, 139.8, 143.9, 146.3, 146.7, 199.8, 202.7; IR (KBr): 3423, 2989, 2966, 2873, 2361, 1658, 1615, 1492, 1467, 1404, 1374, 1334, 1281, 1235, 1094, 1065 cm\(^{-1}\); Anal Calcd for C\(_{24}\)H\(_{22}\)Cl\(_2\)O\(_2\): C, 69.74; H, 5.25; Cl, 17.15, Found: C, 69.45; H, 5.25; Cl, 17.31.
7,7-bis(4-fluorophenyl)-1,3,4,6-tetramethylbicyclo[4.2.0]oct-3-ene-2,5-dione (2g); \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.20 (s, 3H), 1.40 (s, 3H), 1.71 (q, 3H, \(J = 1.32\) Hz), 1.76 (q, 3H, \(J = 1.32\) Hz), 2.67 (d, 1H, \(J = 12.2\) Hz), 3.68 (d, 1H, \(J = 12.2\) Hz), 6.73-6.80 (m, 2H), 6.93-7.00 (m, 2H), 7.13-7.20 (m, 2H), 7.23-7.30 (m, 2H); \(^1^3\)C NMR (67.5 MHz, CDCl\(_3\)) \(\delta\) 12.7, 13.1, 18.3, 21.5, 39.7, 47.7, 57.2, 57.9, 114.8 \((J = 21.2)\), 115.0 \((J = 21.2)\), 128.5 \((J = 7.82)\), 129.4 \((J = 7.82)\), 139.6 \((J = 289.4)\), 139.6 \((J = 289.9)\), 146.3, 146.7, 159.3, 162.9, 200.1, 202.9; IR (KBr): 3423, 2989, 2966, 2873, 2361, 1658, 1615, 1492, 1467, 1404, 1374, 1334, 1281, 1235, 1094, 1065 cm\(^{-1}\).

**endo-** (1R,6S,7S)-1,3,4,6-tetramethyl-7-phenyl-7-(4-(trifluoromethyl)phenyl)bicyclo[4.2.0]oct-3-ene-2,5-dione (2e); \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.21 (s, 3H), 1.44 (s, 3H), 1.66 (q, 3H, \(J = 0.98\) Hz), 1.74 (q, 3H, \(J = 0.98\) Hz), 2.76 (d, 1H, \(J = 12.2\) Hz), 3.74 (d, 1H, \(J = 12.2\) Hz), 7.13-7.18 (m, 1H), 7.26-7.39 (m, 8H); \(^1^3\)C NMR (67.5 MHz, CDCl\(_3\)) \(\delta\) 12.8, 13.0, 18.3, 21.5, 39.6, 48.0, 58.3, 58.3, 124.8, 124.9, 126.4, 127.0, 128.1, 128.3, 128.8, 145.1, 146.2, 146.3, 146.9, 199.9, 203.1; IR (KBr): 3317, 3057, 2987, 2987, 2973, 1933, 1672, 1656, 1617, 1600, 1494, 1469, 1445, 1410, 1380, 1333, 1272, 1237, 1208, 1173, 1109 cm\(^{-1}\); Anal Calcd for C\(_{25}\)H\(_{23}\)F\(_3\)O\(_2\): C, 72.8; H, 5.62; F, 13.82; Found: C, 72.62; H, 5.61; F, 13.99.

**exo-** (1R,6S,7S)-1,3,4,6-tetramethyl-7-phenyl-7-(4-(trifluoromethyl)phenyl)bicyclo[4.2.0]oct-3-ene-2,5-dione (2f); \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.13 (s, 3H), 1.34 (s, 3H), 1.58 (q, 3H, \(J = 0.99\) Hz), 1.66 (q, 3H, \(J = 0.99\) Hz), 2.62 (d, 1H, \(J = 11.9\) Hz), 3.69 (d, 1H, \(J = 11.9\) Hz), 6.91-7.05 (m, 3H), 7.10-7.15 (m, 2H), 7.36 (d, 2H, \(J = 8.24\) Hz), 7.45 (d, 2H, \(J = 8.24\) Hz); \(^1^3\)C NMR (67.5 MHz, CDCl\(_3\)) \(\delta\) 12.8, 13.0, 18.2, 21.6, 39.6, 47.8, 58.1, 58.1, 125.1, 125.1, 126.7, 127.4, 127.6, 128.2, 140.8, 146.1, 146.1, 149.9, 200.0, 202.8; IR (KBr): 3317, 3057, 2987, 2959, 2873, 1933, 1672, 1656, 1617, 1600, 1494, 1469, 1445, 1410, 1380, 1333, 1272, 1237, 1208, 1173, 1109 cm\(^{-1}\); Anal Calcd for C\(_{25}\)H\(_{23}\)F\(_3\)O\(_2\): C, 72.8; H, 5.62; F, 13.82; Found: C, 72.53; H, 5.56; F, 14.00.
endo-(1R,6S,7S)-1,3,4,6-tetramethyl-7-phenyl-7-(3-methoxyphenyl)bicyclo[4.2.0]oct-3-ene-2,5-dione (2m); \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta \) 1.19 (s, 3H), 1.42 (s, 3H), 1.67 (q, 3H, \(J = 4.09\) Hz), 1.74 (q, 3H, \(J = 0.99\) Hz), 2.71 (d, 1H, \(J = 12.0\) Hz), 3.68 (d, 1H, \(J = 12.0\) Hz), 3.69 (s, 3H), 6.51-6.55 (m, 1H), 6.74-6.81 (m, 2H), 6.95-6.98 (m, 1H), 7.01-7.16 (m, 1H), 7.23-7.33 (m, 4H); \(^1\)C NMR (67.5 MHz, CDCl\(_3\)) \(\delta \) 13.0, 13.0, 18.2, 21.8, 40.1, 47.9, 55.0, 58.2, 58.3, 112.2, 113.3, 120.0, 125.9, 126.9, 127.9, 129.0, 143.4, 145.4, 145.7, 146.6, 159.0, 200.1, 203.0; IR (KBr): 3317, 3057, 2987, 2959, 2873, 2871, 2150, 1672, 1656, 1617, 1494, 1469, 1445, 1410, 1380, 1333, 1272, 1237, 1208, 1173, 1109 cm\(^{-1}\).

3,7,9,10,13-pentamethyl-12-tolyl-pentacyclo[8.2.2.0\(^1,6\).0\(^7\).0\(^13\).0\(^9\).0\(^12\)]tetradeca-2,4-diene-8,14-dione (4i); \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta \) 1.06 (s, 3H), 1.11 (s, 3H), 1.21 (s, 3H), 1.56 (s, 3H), 1.62 (dd, 3H, \(J = 2.47, 1.48\) Hz), 2.32 (s, 3H), 2.47 (d, 1H, \(J = 10.8\) Hz), 2.60 (d, 1H, \(J = 10.8\) Hz), 3.22 (m, 1H), 5.24-5.28 (m, 2H), 5.63 (d, 1H, \(J = 9.89\) Hz), 6.88 (d, 2H, \(J = 7.90\) Hz), 7.13 (d, 2H, \(J = 7.90\) Hz).

3-methoxy-7,9,10,13-tetramethyl-12-ansyl-pentacyclo[8.2.2.0\(^1,6\).0\(^7\).0\(^13\).0\(^9\).0\(^12\)]tetradeca-2,4-diene-8,14-dione (4j); \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta \) 1.07 (s, 3H), 1.12 (s, 3H), 1.22 (s, 3H), 1.59 (s, 3H), 2.46 (d, 1H, \(J = 10.9\) Hz), 2.61 (d, 1H, \(J = 10.9\) Hz), 3.36 (d, 1H, \(J = 3.63\) Hz), 3.50 (s, 3H), 3.79 (s, 3H), 4.40 (dd, 1H, \(J = 3.63, 1.98\) Hz), 5.36 (d, 1H, \(J = 10.2\) Hz), 5.63 (dd, 1H, \(J = 1.98, 10.2\) Hz), 6.86 (d, 2H, \(J = 8.90\) Hz), 6.93 (d, 2H, \(J = 8.90\) Hz); \(^1\)C NMR (67.5 MHz, CDCl\(_3\)) \(\delta \) 7.48, 11.5, 11.7, 13.4, 38.9, 43.1, 51.0, 53.6, 53.8, 54.3, 55.2, 55.5, 61.7, 113.6, 123.9, 127.1, 129.1, 132.7, 153.7, 158.3, 209.2, 211.3;
3-chloro-7,9,10,13-tetramethyl-12-(4-chlorophenyl)-pentacyclo[8.2.0^{1,6}.0^{7,13}.0^{8,12}]tetradeca-2,4-diene-8,14-dione (4h); ¹H NMR (270 MHz, CDCl₃) δ 1.08 (s, 3H), 1.13 (s, 3H), 1.22 (s, 3H), 1.61 (s, 3H), 2.48 (d, 1H, J = 11.0 Hz), 2.62 (d, 1H, J = 11.0 Hz), 3.27 (d, 1H, J = 3.80 Hz), 5.34 (d, 1H, J = 10.1 Hz), 5.66 (dd, 1H, J = 3.80, 1.48 Hz), 5.72 (dd, 1H, J = 10.1, 1.48 Hz), 6.91 (d, 2H, J = 8.57 Hz), 7.33 (d, 2H, J = 8.57 Hz); ¹³C NMR (67.5 MHz, CDCl₃) δ 7.84, 11.3, 11.8, 13.5, 38.6, 44.6, 50.1, 51.1, 53.4, 54.0, 56.2, 62.9, 120.1, 123.9, 128.2, 128.8, 129.0, 129.8, 133.1, 138.6, 207.6, 209.5.

3-fluoro-7,9,10,13-tetramethyl-12-(4-fluorophenyl)-pentacyclo[8.2.0^{1,6}.0^{7,13}.0^{8,12}]tetradeca-2,4-diene-8,14-dione (4h); ¹H NMR (270 MHz, CDCl₃) δ 1.08 (s, 3H), 1.13 (s, 3H), 1.22 (s, 3H), 1.61 (s, 3H), 2.48 (d, 1H, J = 11.0 Hz), 2.62 (d, 1H, J = 11.0 Hz), 3.27 (d, 1H, J = 3.80 Hz), 5.34 (d, 1H, J = 10.1 Hz), 5.66 (dd, 1H, J = 3.80, 1.48 Hz), 5.72 (dd, 1H, J = 10.1, 1.48 Hz), 6.91 (d, 2H, J = 8.57 Hz), 7.33 (d, 2H, J = 8.57 Hz); ¹³C NMR (67.5 MHz, CDCl₃) δ 7.84, 11.3, 11.8, 13.5, 38.6, 44.6, 50.1, 51.1, 53.4, 54.0, 56.2, 62.9, 120.1, 123.9, 128.2, 128.8, 129.0, 129.8, 133.1, 138.6, 207.6, 209.5.

7,9,10,13-tetramethyl-3-trifluoromethyl-12-phenyl-pentacyclo[8.2.0^{1,6}.0^{7,13}.0^{8,12}]tetradeca-2,4-diene-8,14-dione (4e); ¹H NMR (270 MHz, CDCl₃) δ 1.09 (s, 3H), 1.17 (s, 3H), 1.25 (s, 3H), 1.55 (s, 3H), 2.53 (d, 1H, J = 10.9 Hz), 2.68 (d, 1H, J = 10.9 Hz), 3.32-3.35 (m, 1H), 5.50 (dd, 1H, J = 9.89, 0.99 Hz), 5.87 (d, 1H, J = 0.99 Hz), 6.17-6.19 (m, 1H), 6.96-6.99 (m, 2H), 7.25-7.39 (m, 3H); ¹³C NMR (67.5 MHz, CDCl₃) δ 7.74, 11.1, 11.7, 13.4, 38.7, 42.6, 50.9, 51.4, 53.5, 54.2, 56.5, 63.3, 121.6, 124.0, 124.6, 127.1, 127.2, 127.8, 128.4, 140.1, 207.8, 209.7.
7,9,10,13-tetramethyl-12-(4-trifluoromethylphenyl)-pentacyclo[8.2.2.0^{1,6}.0^{7,13}.0^{9,12}]tetradeca-2,4-diene-8,14-dione (4f); \[^{1}H\] NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.09 (s, 3H), 1.15 (s, 3H), 1.23 (s, 3H), 1.66 (s, 3H), 2.53 (d, 1H, \(J = 10.9\) Hz), 2.63 (d, 1H, \(J = 10.9\) Hz), 3.23 (m, 1H), 5.22 (m, 1H), 5.62-5.67 (m, 1H), 5.72-5.83 (m, 2H), 7.12 (d, 2H, \(J = 8.24\) Hz), 7.60 (d, 2H, \(J = 8.24\) Hz).

2-methoxy-7,9,10,13-tetramethyl-12-phenyl-pentacyclo[8.2.2.0^{1,6}.0^{7,13}.0^{9,12}]tetradeca-2,4-diene-8,14-dione (4m); \[^{1}H\] NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.07 (s, 3H), 1.11 (s, 3H), 1.14 (s, 3H), 1.61 (s, 3H), 2.51 (d, 1H, \(J = 10.9\) Hz), 2.63 (d, 1H, \(J = 10.9\) Hz), 3.29 (m, 1H), 3.53 (s, 3H), 4.76 (d, 1H, \(J = 6.59\) Hz), 4.98 (d, 1H, \(J = 9.56\) Hz), 5.81 (dd, 1H, \(J = 6.59, 9.56\) Hz), 7.01 (d, 2H, \(J = 6.92\) Hz), 7.24-7.34 (m, 3H); \(^{13}C\) NMR (67.5 MHz, CDCl\(_3\)) \(\delta\) 10.4, 11.1, 11.8, 13.4, 39.0, 44.4, 51.5, 53.4, 54.1, 54.2, 54.7, 56.1, 62.3, 94.5, 113.5, 126.8, 127.2, 128.1, 128.1, 140.7, 157.3, 209.1, 210.7.

**X-ray Crystal Structure Determination of 2d:** C\(_{24}\)H\(_{24}\)O\(_2\), \(M = 344.45\), monoclinic, space group P2\(_1\)/c with \(a = 9.0060(4)\), \(b = 15.4309(6)\), \(c = 14.1258(6)\) Å, \(\beta = 103.187(1)^{\circ}\), \(V = 1911.3(1)\) Å\(^3\), \(Z = 4\), \(D_{calc} = 1.197\) g/cm\(^3\), \(R = 0.090\) and \(R_w = 0.180\) for 4362 reflections with \(I > 2.0\sigma(I)\).

**X-ray Crystal Structure Determination of 2i:** C\(_{26}\)H\(_{28}\)O\(_2\), \(M = 372.51\), monoclinic, space group P2\(_1\)/c with \(a = 8.7765(4)\), \(b = 19.7514(8)\), \(c = 12.5870(6)\) Å, \(\beta = 101.484(1)^{\circ}\), \(V = 2138.2(2)\) Å\(^3\), \(Z = 4\), \(D_{calc} = 1.157\) g/cm\(^3\), \(R = 0.129\) and \(R_w = 0.187\) for 4904 reflections with \(I > 2.0\sigma(I)\).
X-ray Crystal Structure Determination of 4d: C_{24}H_{24}O_{2}, M = 344.45, monoclinic, space group P2_1/a with \(a = 9.1018(2), b = 16.3061(3), c = 12.8443(2) \text{ Å}, \beta = 104.4717(8)^{\circ}, V = 1845.81(6) \text{ Å}^3, Z = 4, \text{Dcalc} = 1.157 \text{ g/cm}^3, R = 0.198 \text{ and } Rw = 0.214 \text{ for } 1886 \text{ reflections with } I > 2.0\sigma(I).

X-ray Crystal Structure Determination of 2f: C_{25}H_{23}O_{2}, M = 412.45, orthorhombic, space group P2_12_12_1 with \(a = 16.8434(3), b = 8.5049(2), c = 14.6979(3) \text{ Å}, V = 2105.5(1) \text{ Å}^3, Z = 4, \text{Dcalc} = 1.301 \text{ g/cm}^3, R = 0.169 \text{ and } Rw = 0.160 \text{ for } 2303 \text{ reflections with } I > 2.0\sigma(I).

Figure 5. ORTEP drawing of 2f.

X-ray Crystal Structure Determination of 2g: C_{24}H_{22}F_{2}O_{2}, M = 380.43, monoclinic, space group P2_1/n with \(a = 14.2181(3), b = 8.3439(2), c = 17.9660(3) \text{ Å}, \beta = 111.8375(7)^{\circ}, V = 1978.44(6) \text{ Å}^3, Z = 4, \text{Dcalc} = 1.277 \text{ g/cm}^3, R = 0.065 \text{ and } Rw = 0.1402 \text{ for } 3831 \text{ reflections with } I > 2.0\sigma(I).

Figure 6. ORTEP drawing of 2g.
X-ray Crystal Structure Determination of 2k: C_{25}H_{26}O_{3}, M = 380.43, monoclinic, space group P-1 with \(a = 8.2764(2)\), \(b = 21.2146(5)\), \(c = 10.8897(3)\) Å, \(\beta = 96.284(2)^\circ\), \(V = 1900.54(8)\) Å³, \(Z = 4\), \(D_{calc} = 1.329\) g/cm³, \(R = 0.0603\) and \(R_w = 0.1404\) for 3762 reflections with \(I > 2.0\sigma(I)\).

![Figure 7. ORTEP drawing of 2k.](image)

X-ray Crystal Structure Determination of 2j: C_{26}H_{28}O_{4}, M = 404.50, monoclinic, space group P2_{1}/a with \(a = 9.9518(3)\), \(b = 13.4718(4)\), \(c = 17.0032(5)\) Å, \(\beta = 104.4754(14)^\circ\), \(V = 2207.24(11)\) Å³, \(Z = 4\), \(D_{calc} = 1.217\) g/cm³, \(R = 0.0717\) and \(R_w = 0.2299\) for 4228 reflections with \(I > 2.0\sigma(I)\).

![Figure 8. ORTEP drawing of 2j.](image)
X-ray Crystal Structure Determination of 4g: \( \text{C}_{26}\text{H}_{28}\text{O}_{4}, M = 404.50 \), monoclinic, space group \( \text{P2}_1/\text{a} \) with \( a = 9.9518(3), b = 13.4718(4), c = 17.0032(5) \, \text{Å}, \beta = 104.4754(14)^\circ \), \( V = 2207.24(11) \, \text{Å}^3 \), \( Z = 4 \), \( D_{\text{calc}} = 1.217 \, \text{g/cm}^3 \), \( R = 0.0717 \) and \( R_w = 0.2299 \) for 4228 reflections with \( I > 2.0\sigma(I) \).

![Figure 9. ORTEP drawing of 4g.](image)

X-ray Crystal Structure Determination of \( \alpha\text{-2m} \): \( \text{C}_{25}\text{H}_{26}\text{O}_{3}, M = 374.48 \), monoclinic, space group \( \text{P2}_1/\text{a} \) with \( a = 13.4860(3), b = 10.2260(4), c = 14.9480(5) \, \text{Å}, \beta = 90.3660(14)^\circ \), \( V = 2061.4(11) \, \text{Å}^3 \), \( Z = 4 \), \( D_{\text{calc}} = 1.207 \, \text{g/cm}^3 \), \( R = 0.1227 \) and \( R_w = 0.4403 \) for 3938 reflections with \( I > 2.0\sigma(I) \).

![Figure 10. ORTEP drawing of \( \alpha\text{-2m} \).](image)
X-ray Crystal Structure Determination of $\beta$-2m: C$_{25}$H$_{26}$O$_3$, M = 374.48, monoclinic, space group P2$_1$/a with $a$ = 13.4664(3), $b$ = 10.2169(2), $c$ = 14.998(3) Å, $\beta$ = 90.7449(13)$^\circ$, $V$ = 2059.44(11) Å$^3$, $Z$ = 4, $D_{\text{calc}}$ = 1.208 g/cm$^3$, $R$ = 0.0491 and $R_w$ = 0.1720 for 3675 reflections with $I$ > 2.0$\sigma$(I).

4-5. Reference and Notes


(8) We could not find any appreciable CT absorption due to the quinone-ethene complexation over practical 330 nm in view of the essential superimposition of UV spectrum of 1a (10 mM in benzene; \( \lambda_{\text{shol}} = 350 \) nm (\( \varepsilon = 134 \)), \( \lambda_{\text{max}} = 427 (25.3) \) and \( 443 (25.7) \), and \( \lambda_{\text{shol}} = 470 (15.6) \)) in the absence and the presence of 10 equivalent of ethene. This implies that the possible CT complex plays a less important role in the present [2+2] photocycloaddition.

(9) Crystallographic data for the compound 5a have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 615010. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

(10) Recently, Xu et al. reported that the irradiation of chloranil with variously p-substituted 1,1-diphenylethene gave the pentacyclic cage compounds with orthogonally connected two cyclobutane rings in markedly contrast to our pentacyclic cage compounds; see J. Org. Chem. 2000, 65, 30–40.


(13) Crystallographic data for the compound 2d have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 615011. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).


Conclusions

This thesis deals with the acid- and photo-reaction of small-membered ring fused quinone derivatives comprised of the following points, (1) remote $\pi$-Aryl participation reaction of Homobenzoquinone epoxide, (2) a prominent role of oxirane Walsh orbital, (3) rearrangement reaction of cyclobutane-fused quinone. The author hopes that this basic work described in this thesis contributes to the further development of synthesis of novel carbon skeletons, which are difficult to produce by conventional methods.

In chapter 1, the acid-catalyzed rearrangement of homobenzoquinone epoxides possessing endo-aromatic ring displayed a new synthesis of polycyclic compounds involving a regioselective oxirane ring-opening and a crucial transannular cyclization. Additionally, based on the kinetics and conformational effects in acid-catalysed reactions of the present homobenzoquinone epoxides, the author has found that the $\pi$-aryl participated electron-donating interaction with the vacant oxirane Walsh orbital plays a prominent role in the epoxide ring-opening. Moreover, the dual pathway for $p,p'$-dichloro substituted homobenzoquinone epoxide is likely to prove that the acid-catalyzed ring-opening of diarylhomobenzoquinone epoxides occurs via a concerted manner involving a very rare remote ($\delta$-located) $\pi$-aryl participated transition state. These findings will provide very useful insights into the mechanistic understanding of the acid-catalyzed ring-opening of epoxides.

In chapter 2, the author has performed a kinetic study of the BF$_3$-catalyzed ring-opening reactions of endo/exo $m$- and $p$-substituted diarylhomobenzoquinone epoxides. These reactions proceeded through two types of $S_{E2}$-Ar transannular cyclizations to give tricyclic diketo-alcohols and cyclohexadienone spiro-linked tricyclic diketo-alcohols, respectively. The rates were significantly accelerated by the through-space $\pi$-aryl participation of electron-donating endo-aromatic rings, but negligibly influenced by the through-bond
electronic effects of exo-aromatic rings. The Hammett treatment using modified site-dependent substituent parameters $\sigma^{ipso}$ and $\sigma^{ortho}$ indicated that the $ipso$/$ortho$ dihapto($\eta^2$) $\pi$-aryl participation occurs for the $endo$-aryl groups. Kinetics substituent effects of these reactions were compared with those of the analogous acid-catalyzed transannular cyclization of the cyclobutene-fused diarylhomobenzoquinones. It was found that the present epoxides exhibit the $\eta^2$ $\pi$-aryl participation with the 1.6-times more effective contribution at the $ipso$-position, whereas the cyclobutene-fused homologues with almost comparable $ipso$/$ortho$ contribution. These results were interpreted in terms of the geometrical features of the $\pi$-electron accepting vacant orbital of oxirane and cyclobutene ring. The physicochemical information obtained in the present study will provide a very important insight into the understanding of the $\pi$-aryl participation as well as the mechanistic aspects in the acid-catalyzed ring-opening reaction of epoxides.

In chapter 3, the author found that the subsequent ring-enlargement by 1,2-acyl migration associated with the incorporated cyclopropane ring-opening reaction, depending on the substitution pattern of the quinone methyl groups. The author has also investigated the acid-catalyzed rearrangement of cyclobutane-fused quinone epoxide. This compound underwent the novel consecutive skeletal rearrangements. These findings provide the useful information on the rearrangements of polycyclic epoxides and the design of more extended framework compounds.

In chapter 4, the primary [2+2] photocycloadducts of variously Me-substituted 1,4-benzoquinones with 1,1-diphenylethene underwent the reversible intramolecular [2+2] photocycloaddition to provide pentacyclotetradeca-10,12-diene-2,7-diones. The cage skeleton was characterized by very rare diagonal conjunction of two facing cyclobutane rings. The geometrical features of these reactions were interpreted in terms of the conformational preference which allowed the proximity of the relevant $2\pi$ components.
List of Publications

1. “Two Conformers of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene spiro-linked with homobenzoquinone epoxide”
   Haruyasu Asahara, Takuya Koizumi, Eiko Mochizuki, and Takumi Oshima

   Haruyasu Asahara, Eiko Mochizuki and Takumi Oshima

3. “Acid-Catalyzed Rearrangement of Aryl-Substituted Homobenzoquinone Epoxides”
   Haruyasu Asahara, Emi Kubo, Kyoko Togaya, Takuya Koizumi, Eiko Mochizuki, and Takumi Oshima

4. “Mechanistic evidence for the remote π-aryl participation in acid-catalyzed ring opening of homobenzoquinone epoxides”
   Takumi Oshima, Haruyasu Asahara, Takuya Koizumi, and Saki Miyamoto

5. “Conformational Effects in Acid-Mediated Ring Opening of Epoxides: A Prominent Role of the Oxirane Walsh Orbital”
   Takumi Oshima, Haruyasu Asahara, Emi Kubo, Saki Miyamoto, and Kyoko Togaya

6. “Kinetic Evidence for Dihapto (η²) π-Aryl Participation in Acid-Catalyzed Ring-Opening of Diarylhomobenzoquinone Epoxides”
   Haruyasu Asahara, Kohta Saito, Naohiko Ikuma, and Takumi Oshima

7. “Substituent Effect on Intramolecular [2+2] Photocycloaddition of Cyclobutane-Fused Quinone”
   Haruyasu Asahara, Naohiko Ikuma, Kei Ohkubo, Shunichi Fukuzumi, and Takumi Oshima
   in preparation

(List of Supplementary Publications)

   Takuya Koizumi, Kenji Harada, Haruyasu Asahara, Eiko Mochizuki, Ken Kokubo and Takumi Oshima
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Haruyasu Asahara