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SHORT COMMUNICATION

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Versatile Domino Rearrangement of Diphenylhomobenzoquinone Epoxides Induced by CF_3SO_3H

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CF_3SO_3H-catalyzed reaction of 5-alkyl-(*R*)-substituted diphenylhomobenzoquinone epoxides (R = Me, *i*Pr, *t*Bu) provided indenoquinones, a cyclopenta[*b*]chromene-2-carbaldehyde, and furan-3(2*H*)-ones through novel cationic domino rearrangements depending on the R substituents. The mechanisms of these reactions were described by a combination of various key steps involving (i) transannular cyclization of the *endo*-phenyl group, (ii) epoxide and cyclopropane ring opening, (iii) ring contraction of the original quinone frame, (iv) dehydration and intramolecular S_E2/S_N2-Ar cyclization, as well as (v) possible pseudopericyclic cheletropic decarbonylation.

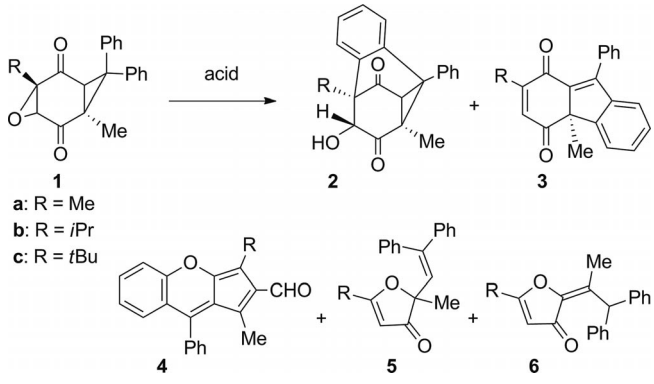
Introduction

The use of domino reactions in synthetic organic chemistry is fascinating, especially with regard to the preparation of structurally defined highly complex molecules and the construction of biologically important natural substances.[1] In view of the ability to form several bonds in one sequence without isolating any intermediates, changing the reaction conditions, or adding new reagents, such reactions can be economically and environmentally favorable because they reduce reagent/solvent and human resources. In addition, the strategic design of the starting compounds and the mechanistic elucidation of the sequential process provide useful information to the development of synthetic organic chemistry.

In this connection, we have previously synthesized highly strained tricyclic diones as molecular building blocks for the construction of various polycyclic compounds in acid-catalyzed systems.[2] The designed tricyclic diones containing both a cyclopropane and a cyclobutene ring were synthesized from the [2+2] photocycloaddition of alkynes to diphenylhomobenzoquinones.[2] The BF_3-catalyzed reactions were found to give several bicyclic and tricyclic compounds through domino rearrangements involving sequential opening of the cyclobutene and cyclopropane rings.[3]

Very recently, we found that the BF_3-catalyzed reaction of newly prepared diphenylhomobenzoquinone epoxide **1a** (R = Me) undergoes π-aryl participated epoxide ring opening to provide quantitatively tricyclic diketo alcohol **2a** (Table 1, Entry 1).[4] In this paper, we wish to report that CF_3SO_3H (TfOH) brought about the intriguing multipath domino rearrangements of **1a** leading to new products **3a**–

Table 1. Product distribution in the acid-catalyzed domino rearrangements of **1a**–**c** and **2a** in $CDCl_3$ at 30 °C.



Entry	Compd.	Acid (equiv.)[b]	Time [h][c]	Yield [%][a] 2	3	4	5	6
1	**1a**	BF_3 (3)[d]	24	100	0	0	0	0
2	**1a**	MsOH (3)	2	99	0	0	0	0
3	**1a**	TfOH (1)	1.5	90	2	0	7	0
4	**1a**	TfOH (3)	1.5	10	52	3	23	11
5	**1a**	TfOH (10)	1.5	0	53	0	0	46
6	**1b**	TfOH (3)	1.5	0	45	0	50	4
7	**1c**[e]	TfOH (3)	1.5	0	0	0	99	0
8	**2a**	TfOH (3)	1.5	–	53	47	0	0
9	**2a**	TfOH (10)	1	–	78	21	0	0
10	**2a**	TfOH (20)	1	–	98	1	0	0

[a] Based on the amount of **1** or **2a** used, and calculated by ^1H NMR spectroscopy. [b] MsOH = $MeSO_3H$, TfOH = CF_3SO_3H. [c] Reactions were complete except for BF_3 catalyst (Entry 1; 65% conversion). [d] See ref.[4a] [e] CO gas evolution was analytically confirmed (GASTEC GV-100S).

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6a (Table 1, Entry 4). We also extended the reaction to more congested **1b** (R = *i*Pr) and **1c** (R = *t*Bu) to estimate their steric effects on these reaction features.

Results and Discussion

The reactions of **1a**–**c** and **2a** with the requisite number of equivalents of TfOH were carried out in $CDCl_3$ at 30 °C according to a previous report.[4] The reaction conditions and the product distributions are collected in Table 1. The structures of **3**–**6** were deduced from their ^1H NMR, ^{13}C NMR, HSQC, HMBC, ^1H–^1H COSY, and IR spectra, in addition to HRMS (see the Supporting Information). The structure of **5c** was also confirmed by X-ray crystal structural analysis (Figure 1). It is noteworthy that the MS data of these compounds suggested a loss of water for **3** and **4** and a loss of carbon monoxide for **5** and **6**.

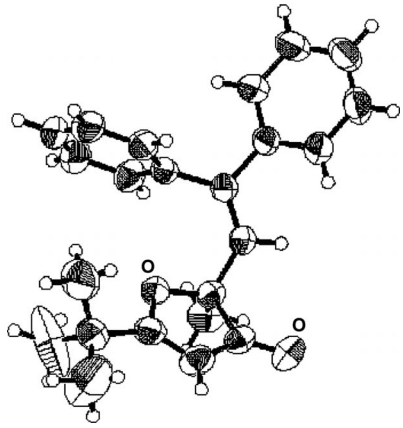
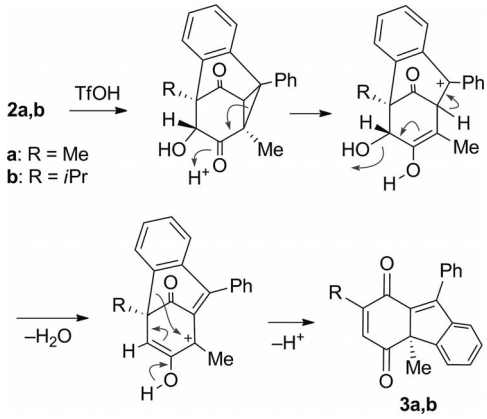


Figure 1. ORTEP drawing of compound **5c**.

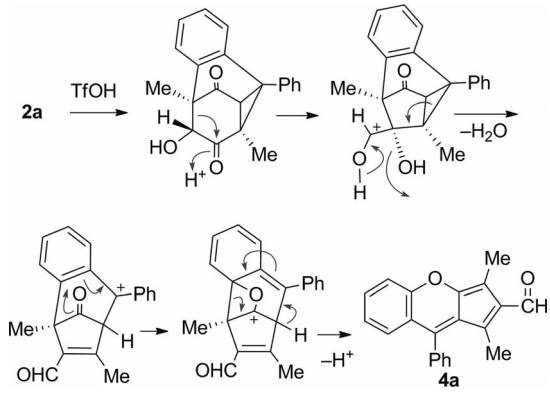
Some noticeable points can be extracted from Table 1: (1) BF_3- or $MeSO_3H$-catalyzed reaction of **1a** gave only tricyclic diketo-alcohol **2a** through ring opening of the epoxide and transannular cyclization of the *endo*-phenyl ring (Table 1, Entries 1 and 2). (2) CF_3SO_3H catalysis brought about further rearrangement to afford new products **3a**–**6a**,[5] and the distributions were dependent upon the amount of acid (Table 1, Entries 3–5). (3) *i*Pr-Substituted **1b** provided **3b** and **5b** without the formation of **2b** (Table 1, Entry 6), and moreover, *t*Bu-substituted **1c** yielded **5c** as the sole product (Table 1, Entry 7). (4) The reaction of **2a** did not produce **5a** or **6a**, but **3a**/**4a** instead, and the amount of **3a** formed increased with an increase in the amount of acid added (Table 1, Entries 8–10).

On the basis of these notions, the mechanisms of these versatile domino rearrangements leading to compounds **3**–**6** is clearer. The formation of indenoquinones **3** can be explained by considering the transformation of **2** by several processes: acid-induced cyclopropane ring opening, dehydration followed by double bond migration, and transannular *ipso*-S_E2-Ar electrophilic aromatic substitution (Scheme 1).



Scheme 1. TfOH-catalyzed rearrangement of **2a**,**b** into **3a**,**b**.

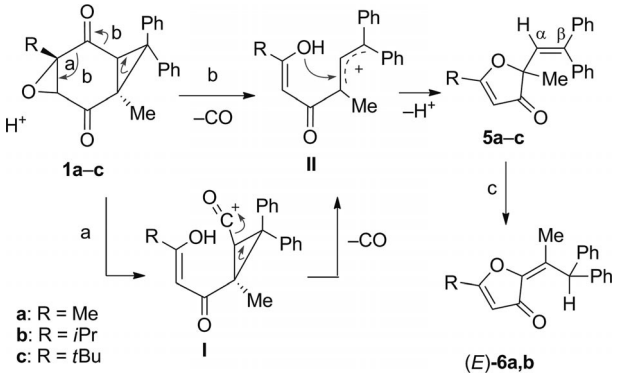
By contrast, the formation of **4a** was only observed for the Me-substituted homologue. It was also found that the original quinone framework was completely degraded during the transformation into **4a**. This rearrangement seems to proceed through a reaction sequence involving initial ring-contraction of **2a** by 1,2-shift of the *o*-phenylene-bridged carbon atom onto the acid-activated carbonyl carbon atom[6] with simultaneous formylation and dehydration associated with cyclopropane ring cleavage and intramolecular *ipso*-S_N2-Ar displacement by the carbonyl oxygen atom followed by deprotonation and electron reorganization into **4a** (Scheme 2). The inability to form **4b** (R = *i*Pr) may be attributable to the steric hindrance of the *i*Pr group, which would inhibit the initial ring contracted 1,2-shift. Moreover, the large excess amount of TfOH dramatically suppressed the formation of **4a** probably because of the additional protonation of the intervening OH group, which reduces the 1,2-shift (Table 1, Entries 8–10).



Scheme 2. TfOH-catalyzed rearrangement of **2a** into **4a**.

As seen in Table 1 (Entries 1–3), the product ratios of **5a** and **6a** on varying the amount of TfOH imply that **6a** is derived from **5a** through 1,2-Me shift (Scheme 3, path c) promoted by protonation at the alkenyl β-carbon atom. Indeed, preliminary treatment of **5a** with an excess amount of TfOH in $CDCl_3$ for 8 h brought about its complete transformation into **6a**.[7] Obtained **6a** is assigned as the *E*-isomer, which is more stable than the *Z*-isomer by 1.76 kcal/mol on the basis of the optimized geometries calculated at

the B3LYP/6-311+G** level. Regarding the mechanism for the formation of **5**, it is very informative that carbon monoxide was expelled in the reaction of **1c** but not in the reaction of **2a**, as confirmed by a CO gas analyzer (GASTEC GV-100S).



Scheme 3. TfOH-catalyzed rearrangement of **1** to **5** by two possible decarbonylation pathways.

What is the mechanism of acid-induced decarbonylation from epoxides **1**? Two possibilities are outlined in Scheme 3 (paths a and b), although the later stage leading to **5** can be interpreted by the favorable *5-endo-trig* cyclization[8] of intermediate allyl cation II. Path a involves stepwise heterolytic bond cleavage to generate acyl cation I, which will undergo CO evolution and cyclopropane ring cleavage to afford II. On the other hand, path b is a concerted pericyclic reaction such as cheletropic decarbonylation.[9] However, epoxides **1** do not satisfy the cyclic loop of interacting π-orbitals predicted by the Woodward and Hoffman rule.[10] This contradiction may be resolved by relying on pseudopericyclic reactions.[11] Since the original definition by Lemal et al.,[12] pseudopericyclic reactions were developed by Birney et al.[13] to include pericyclic reactions in which the cyclic array of overlapping orbitals is fulfilled by considering the orbital disconnections. The general characteristics of the thermal pseudopericyclic reactions can be summarized as follows: (1) A pseudopericyclic reaction may be orbital symmetry allowed regardless of the number of electrons involved. (2) Pseudopericyclic reactions will have planar transition states. (3) Energy barriers to pseudopericyclic reactions can be very low. Satisfying points (1) and (2), epoxides **1** will attain a pseudopericyclic orbital topology with two orbital disconnections at the departing CO bonded two carbon atoms (Figure 2). Of interest is that both the epoxide and the cyclopropane ring of **1** can offer *p* character Walsh orbitals[14] for the construction of the out-of-plane π orbital array in the quinone fragment.

In Figure 2, the departing CO is drawn hybridized as carbon monoxide and therefore the carbon lone pair *n* (HO) and CO π* (LU) orbitals can interact nucleophilically and electrophilically with epoxide σ* (LU) and cyclopropane σ (HO) orbitals, respectively. These in-plane sets of orbitals have orthogonal orbital interactions with the above out-of-plane π-orbital array (arbitrary phases), having a planar transition state. Recently, on the basis of molecular orbital

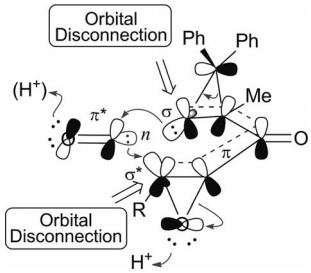


Figure 2. Schematic orbital interactions having two orbital disconnections in a plausible pseudopericyclic decarbonylation of **1**. The epoxide and cyclopropane rings offer *p* character Walsh orbitals for the out-of-plane π-orbital array. There are two orbital disconnections where the out-of-plane (arbitrary phases) and in-plane sets of orbitals meet at the carbon atoms of the epoxide and cyclopropane rings.

calculations, pseudopericyclic decarbonylation reactions have been invoked for several cyclic carbonyl compounds such as 2,3-furanone and 2,3-pyrroledione.[13,15]

Conclusions

In summary, we have found that TfOH-catalyzed reactions of diphenylhomobenzoquinone epoxides **1a**–**c** with 5-Me, *i*Pr, and *t*Bu substituents brought about domino rearrangements to give indenoquinones **3a** and **3b**, cyclopenta[*b*]chromene-2-carbaldehyde **4a**, and furanones **5a**–**c**, respectively, depending on the 5-alkyl substituents. The mechanistic investigations of these reactions show a variety of fundamental features of organic reactions involving a possible pseudopericyclic cheletropic decarbonylation and offer a very fascinating methodology in synthetic organic chemistry. As one of the general criteria of pseudopericyclic reactions (point 3), molecular orbital analysis is underway to estimate the possible low energy barrier to the decarbonylation process.

Experimental Section

General Procedure for the Synthesis of Homobenzoquinone Epoxides 1b and 1c: To a mixture of homobenzoquinone (0.5 mmol) and 30% H_2O_2 (0.75 mmol) in DMSO (1 mL) was added dropwise (10 min) a solution of Bu_4NF (1 M in THF, 0.5 mmol) at room temperature. After the addition of the reagent, the reaction mixture was stirred for 2 h. Then, epoxide **1** was extracted with ethyl acetate (3 × 3 mL). The organic layer was washed with water (3 × 3 mL) and dried with magnesium sulfate. The solvent was evaporated in vacuo. Epoxide **1** was purified by column chromatography on silica gel (benzene) and recrystallized (hexane/diethyl ether). The structures of all epoxides were deduced by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy.

General Procedure for the BF_3-Catalyzed Reaction of Homobenzoquinone Epoxides: To a $CDCl_3$ solution (600 μL) of **1** (0.02 mmol) in an NMR tube was added the requisite amount of acid at room temperature under an atmosphere of N_2 by using a microsyringe. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. After the requisite time, the reaction solution was transferred into a separatory funnel, diluted with chloroform (10 mL), and then washed with water (3 × 3 mL). The aqueous layer was

extracted with chloroform (2 × 5 mL). The combined organic layer was washed with water (3 × 3 mL) and then dried with calcium chloride. After evaporation of the solvent in vacuo, the residue was submitted to ^{1}H NMR spectroscopic analysis to determine the product distribution. The products were separated by column chromatography on silica gel (hexane/ethyl acetate). The structures of all products were deduced from ^{1}H NMR, ^{13}C NMR, and IR spectroscopy and HRMS.

General Procedure for the TfOH-Catalyzed Transformation of 5a Into 6a: To a $CDCl_3$ solution (600 μL) of **5a** (5.8 mg, 0.02 mmol) in an NMR tube was added the requisite amount of TfOH at room temperature under an atmosphere of N_2 by using a microsyringe. The progress of reaction was monitored by ^{1}H NMR spectroscopy. After the requisite time, the reaction solution was transferred into a separatory funnel, diluted with chloroform (10 mL), and then washed with aq. NaCl solution (3 × 3 mL). The combined organic layer was then dried with $MgSO_4$. After evaporation of the solvent in vacuo, the residue was submitted to ^{1}H NMR spectroscopic analysis to determine the product distribution. The products were separated by column chromatography on silica gel (hexane/ethyl acetate). The structure of the product was deduced from ^{1}H NMR, ^{13}C NMR, and IR spectroscopy and HRMS.

Supporting Information (see footnote on the first page of this article): Compound data and NMR spectra for **1b** and **1c** and products **3**–**6**.

Acknowledgments

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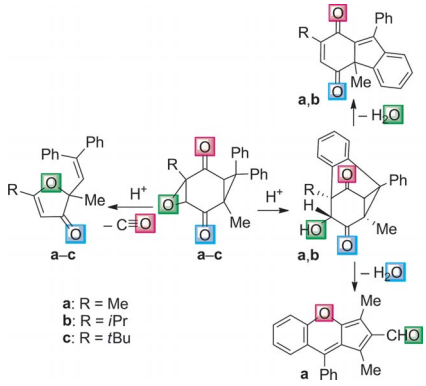
Domino Reaction

Acid-catalyzed reaction of various 5-alkyl-substituted diphenylhomobenzoquinone epoxides provided various products through novel cationic domino rearrangements and decarbonylation depending on the acid (BF_3/$MeSO_3H$/$TfSO_3H$) and the alkyl substituents (R = Me/*i*Pr/*t*Bu).



H. Asahara, S. Matsui, Y. Masuda, N. Ikuma, T. Oshima* 1–5

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Keywords: Domino reactions / Rearrangement / Epoxides / Decarbonylation / Pseudopericyclic reaction

