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Acid-Catalyzed Transannular Cyclization of 3a*H*-Cyclopentene[8]annulene-1,4-(5*H*,9a*H*)-diones and Some Proposed Mechanisms

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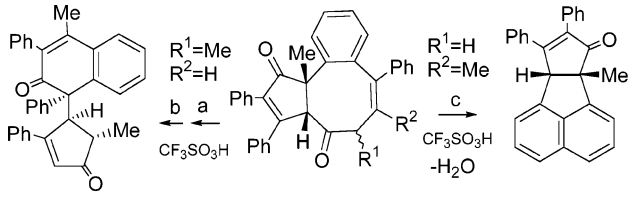

a: [3+2] Cycloaddition, b: [2+2] Cycloreversion, c: Friedel-Crafts

Bicyclic 3a*H*-cyclopentene[8]annulene-1,4-(5*H*,9a*H*)-diones underwent three types of acid-induced transannular reactions, Michael cyclization, [3 + 2] cycloaddition, and Friedel−Crafts *ipso*-alkylation, depending on the cyclopentenone ring substituent (Me or Ph) and the position of [8]-annulenone substituent as well as the nature of acids (BF_3, $MeSO_3H$, CF_3SO_3H). The Me-substituent permitted the Michael reaction for all acids used to give tricyclic diones by the activation of cyclopentenone carbonyl group. However, the Ph-substituent inhibited the Michael reaction for BF_3 and $MeSO_3H$ but allowed the [3 + 2] cycloaddition and Friedel−Crafts reaction for CF_3SO_3H depending on the position of annulenone substituent. These CF_3SO_3H reactions exhibited the following novel rearrangements, affording 2-naphthalenone and 7-acenaphthylene derivatives, respectively. The factors that control the reaction mode of these transannular cyclizations were discussed in view of the constraint twist-boat conformation of [8]annulenone ring as well as the ring substituent effects on the intramolecular cyclization. In addition, these [8]annulenone rings were found to easily undergo the intramolecular [2 + 2] photocyclization to provide the tetracyclic cage compounds which exhibited the facile cycloreversion under the influence of acid.

Introduction

Transannular cyclization is a sophisticated method for construction of polycyclic natural products and molecules of theoretical and structural interest.[1] 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.[1] Such an intramolecular cyclization is largely dependent on the nature of the reaction (e.g., ionic,[2] radical,[3] or pericyclic reaction[4]), reactivity of the two end groups, and geometrical features of the reacting ring molecules. Transannular cyclization requires a suitable conformation of substrates and prudent selection of functional groups. In this regard, comprehensive knowledge of factors governing reactivity

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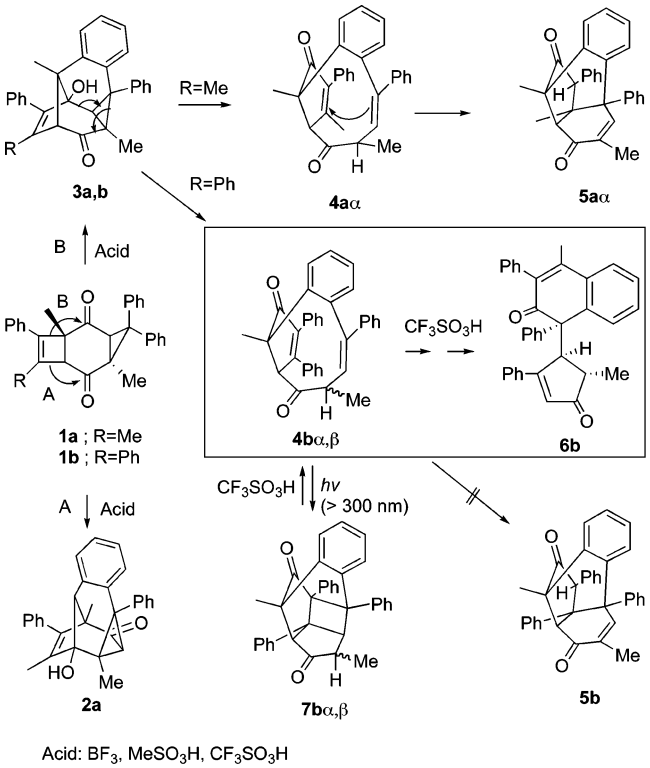
SCHEME 1

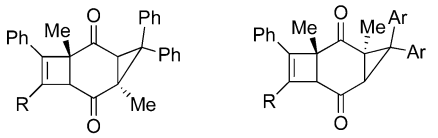


will yield insight into widespread application of transannular reactions.

Recently, we have found that the [2 + 2] photocycloadducts **1a**,**b** of 1,5-dimethyl-4,4-diphenylhomobenzoquinone with 1-phenyl-1-propyne and diphenylacetylene[5] undergo Lewis acid-catalyzed consecutive cleavage of the incorporated cyclobutene and cyclopropane rings. The primary Wagner−Meerwein migration of vinyl group was accelerated by the *endo*-phenyl π-participation.[6] These reactions gave, stereoselectively, 3a*H*-cyclopentene[8]-annulene-1,4-(5*H*,9a*H*)-diones **4a**α, **4b**α,β via the transient tetracyclic keto-alcohols **3a**,**b** (path B) along with the inert keto-alcohol **2a** (path A, only for **1a**), as outlined in Scheme 1.[7] Notably, the R = Me substituted **4a**α immediately underwent a subsequent Lewis acid-induced transannular Michael cyclization to provide the tricyclic dione **5a**α, whereas the R = Ph substituted epimeric mixture **4b**α,β (α/β = 2 for BF_3 catalyst) remained intact on the prolonged reaction (70 h).[7] The suffix "α(or β)" for **4a** and **4b** refers the epimer in which the stereogenic methyl group is located in the annulenone ring with *trans* (or *cis*) position with respect to the fused cyclopentenone ring. For **5a** (and also **5c**), "α(or β)" is used to denote the epimer in which the stereogenic cyclopentanone phenyl group is located in the *endo* (or *exo*) position (see Schemes 1 and 4). The reasons for these stereochemical results were described in our previous paper.[7]

Here, we report that the potent protic acid CF_3SO_3H brought about not the expected Michael cyclization to **5b** but the transannular [3 + 2] cycloaddition of the less labile **4b** and the following anomalous skeletal rearrangement to **6b** (Scheme 1). Our interest in the factors which govern the transannular cyclization prompted us to extend these acid-catalyzed reactions into the analogous [2 + 2] photoadducts **1c**−**e** of 1,3-dimethyl-4,4-diarylhomobenzoquinones in order to gain further mechanistic insight into the understanding of these intramolecular cyclizations.

CHART 1



1a; R = Me
1b; R = Ph

1c; R = Me, Ar = Ph
1d; R = Ph, Ar = Ph
1e; R = Ph, Ar = *p*-tolyl

TABLE 1. Acid-Catalyzed Rearrangement of 1a,b (30 mM) in $CDCl_3$ at 25 °C

					yield[a,b]/%					
					path A[c]	path B[c]				
entry	sub.	acid[d]	time (h)	conv[b] (%)	**2**	**3**	**4**α	**4**β	**5**α	**6**
1	**1a**	B	2	100[e]	42				58	
2	**1a**	M	15	100	21		20		59	
3	**1a**	M	60	100	19		5		75	
4	**1a**	F	0.1	100	22				78	
5	**1a**	F	24	100	21				79	
6	**1b**	B	20	87[e]		21	51	25		
7	**1b**	M	5	51		8	75	17		
8	**1b**	M	48	100		3	75	22		
9	**1b**	F	0.1	100			73	17		10
10	**1b**	F	24	100						∼100

[a] Based on consumed **1a**,**b**. [b] Determined by ^{1}H NMR. [c] Products via path A and B, respectively; see Scheme 1. [d] 3 equiv of acid was used with respect to **1a**,**b**. B = BF_3, M = $MeSO_3H$, F = CF_3SO_3H. [e] Taken from ref 7.

Results and Discussion

Acid-Catalyzed Reaction of 1a and 1b. The protic acid-catalyzed reactions of **1a** and **1b** (Chart 1) were carried out with 3 equiv of excess of $MeSO_3H$ (M) and CF_3SO_3H (F) in $CDCl_3$ at 25 °C under the same conditions as the previous BF_3 (B) reactions.[7] These reactions of **1a** (R = Me) also gave **4a**α (via labile tetracyclic keto-alcohol **3a**) and Michael adduct **5a**α along with the very stable **2a** as shown in Scheme 1, but the percentage amount of the path A route was reduced ca. 1/2 as compared with the BF_3 reaction (entries 1−5 in Table 1). As for the path B/path A ratios, it must be considered that the branching product ratios are determined by the balance of both the acid-binding constant (*K*) of each carbonyl function and

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(7) Koizumi, T.; Mochizuki, E.; Kokubo, K.; Oshima, T. *J. Org. Chem*. **2004**, *69*, 4577. According to the comment of one reviewer, we have carried out the conformational analysis by PM3 calculation for **4b**α. In contrast to the X-ray crystal structure, the calculation represented a slightly stable flipped conformation (by 2.5 kcal mol^{-1}) in which the double bond of [8]annulenone frame is far away from the fused cyclopentenone ring. Therefore, the present transannular reactions seem to proceed through the less abundant folded conformers (68.9 kcal mol^{-1}).

the actual rate constant (k) for the cyclobutene ring cleavage of the acid activated complex.[7] The compound **1a** is expected to have the higher binding affinity at the less hindered path A carbonyl function ($K_A > K_B$), but exhibit the increased rate constant for the path B ring cleavage because of the more stable tertiary carbocation-like transition state as compared with the secondary carbocation-like path A route ($k_A < k_B$).[8] Compared to BF_3, the present sulfonic acids would experience the reduced steric congestion even in the activation of path B carbonyl group and hence show the relatively increased path B ratio. However, we cannot rule out the possibility that the protic acid more stabilize the path B transition state than BF_3. Apparently, CF_3SO_3H was far more effective than $MeSO_3H$, as indicated by the complete transformation **4a**α → **5a**α within 0.1 h (entry 4). However, **2a** and **5a**α remained unchanged even after 24 h standing with CF_3SO_3H (entry 5). The inhibition of the possible epimerization (via keto−enol tautomerization) of **5a**α will be discussed in a later section in comparison with the facile transformation of the corresponding tricyclic dione **5c**α.

In remarkable contrast to **1a**, acid-catalyzed reactions of **1b** (R = Ph) proceeded exclusively via path B, although the reaction features were much dependent on the acids used. Thus, $MeSO_3H$ and BF_3 provided **3b** and its rearranged epimeric mixture of **4b**α,β with 2−4 times larger α-isomer (entries 6−8), whereas CF_3SO_3H engendered an unexpected transformation of **4b**α,β to afford quantitatively 2-naphthalenone derivative **6b** instead of giving the possible Michael product **5b** (entry 10). The exclusive path B from compound **1b** can be ascribed to the increased steric congestion at the path A carbonyl group (by R = Ph group). This will far more raise the kinetically favorable path B ring cleavage, as previously described.[7] This is also the case for the **1d** (R = Ph) which also yielded only path B product (vide infra, Table 2). As to the stereochemical result for **4b**, unfortunately, we have no sophisticated explanation for the acid dependency of preferential formation of α-isomer. The structure of **6b** was deduced from ^1H and ^{13}C NMR spectra. It was also confirmed unambiguously using X-ray crystal analysis (Supporting Information). Distinctive configurations of the three continuous stereogenic centers of **6b** are described in a later mechanistic consideration.

Before addressing the detailed mechanism for the respective transformation of **4a** → **5a** and **4b** → **6b**, we have undertaken a representative conformational analysis of **4b**α isomer based on its X-ray crystal structure (Figure 1).[7]

The eight-membered annulenone ring skeleton (C1−C8) was found to adopt a twist-boat conformation due to the fusion of cyclopentenone and benzene ring as well as the presence of the extra C3−C4 double bond. In such a folded conformation with three torsional constrains, the incorporated C3−C4 double bond can come close to the faced α,β-unsaturated cyclopentenone C1′−C2′−C3′ linkage. The spatial carbon−carbon distances between both the ends of C4 and C1′ (2.90 Å) and the C3 and C3′ (3.04)

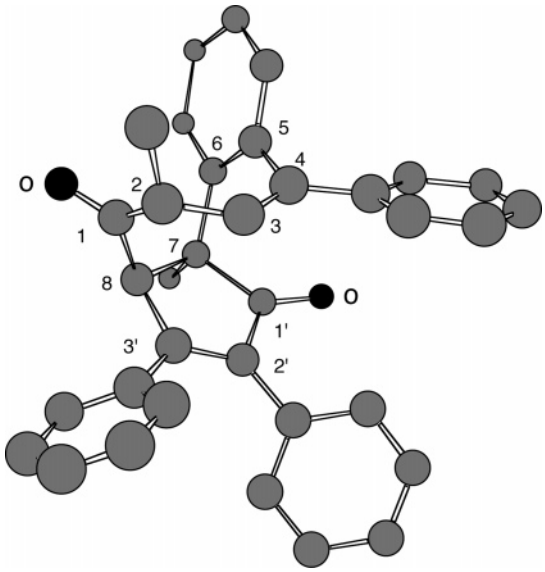
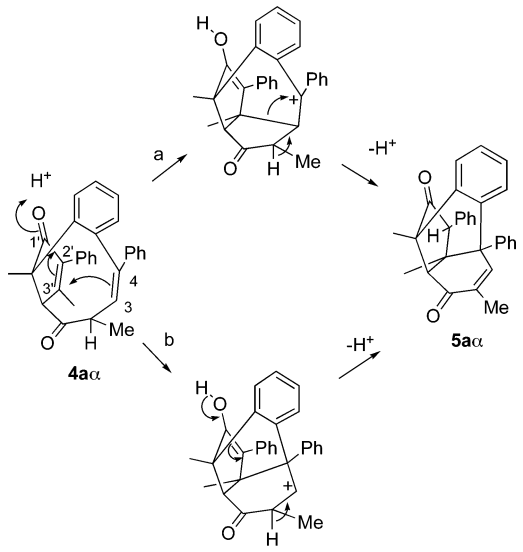


FIGURE 1. Chem 3D drawing of **4b**α (hydrogen atoms were ommitted). Selected distances: C4−C1′ (2.90 Å), C3−C3′ (3.04), C4−C3′ (3.67), C4−C2′ (3.28), and C1−C5 (2.88).

SCHEME 2



are favorably reduced for the transannular interaction. Thus, as seen for **4a** in Scheme 2, the intramolecular electrophilic cyclization of the acid-activated β-carbon (C3′) (i.e., hydroxyl-stabilized allyl cation terminus) to the olefin C3 (route a) and the following facile Wagner−Meerwein shift seems to be more feasible than the previously proposed direct bonding (route b) between the more remote C4 and the C3′ (3.67 Å). The route a and b are favorable 5- and 6-*exo-trig* ring-closure,[9] respectively. The former gives rise to the more stable biphenyl-stabilized carbocation intermediate. Such a preceding 5-*exo-trig* cyclization is also argued for the initial step of the CF_3SO_3H-catalyzed reaction of **4b** as described below.

(8) Very recently, we have found that the path B/A ratios for the BF_3-catalyzed reaction of **1a** and **1c** were much dependent on the acid concentrations because the increased amount of acid becomes to form the 2:1 complex with **1a** and **1c**, consequently raising the more labile path B ratio. See *J. Org. Chem.* **2005**, *70*, 7776−7779.

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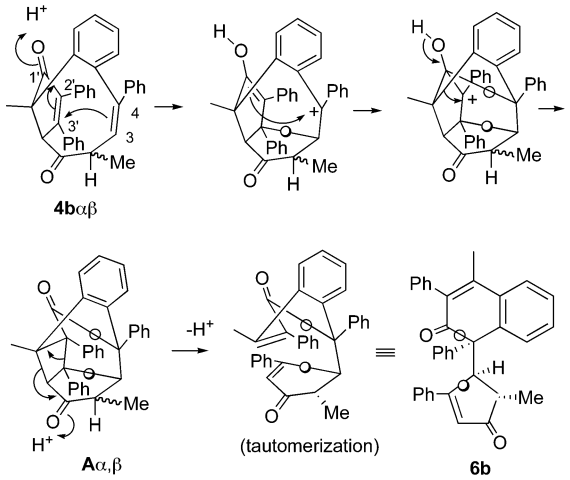
SCHEME 3



CF_3SO_3H-Catalyzed Novel Rearrangement 4b → 6b. On the other hand, the intricate transformation of **4b** → **6b** (Scheme 3) requires quite different transannular cyclization. A cautious structural comparison of **4b** with **6b** indicates that the cyclopentenone ring of **6b** is not identical to that of the precursor **4b**. It is newly constructed by transannular bonding between C3 and C3′ (depicted as a filled circle). In addition, the second transannular bonding between C4 and the faced C1′ (depicted as an open circle) is essential for the 2-naphthalenone ring of final product **6b** (Scheme 3). Thus, CF_3SO_3H-catalyzed rearrangement of **4b** can be speculated via the transannular [3 + 2] cycloaddition of the hydroxyl-stabilized allyl cation generated by the activation of cyclopentenone carbonyl group. Such a [3 + 2] cycloaddition mode of so-called allyl cation to the multiple bonds has been reported as a new methodology for construction of five-membered natural products and strained polycyclic compounds.[10]

Scheme 3 shows the initial transannular bonding between C3 and C3′ is the same as the Michael cyclization of **4a**α. However, the following 1,2-shift (of the formed new bond) may be inhibited by the apparent steric congestion of the adjoining three phenyl rings. Indeed, PM3 calculation revealed that the possible **5b** ($\Delta H_f = 74.2$ kcal mol^{-1}) is less stable than the precursor **4b**α by 5 kcal mol^{-1}, even though the obtained Michael product **5a**α is 3 kcal mol^{-1} more stable than the corresponding precursor **4a**α (ref 7, Table 2). Instead, the remaining diphenyl-stabilized cation center C4 suffers the reverse nucleophilic attack by the faced cyclopentene π-electrons, forming another transannular bond. The direct bonding between the C4 and C1′ coupled with the following 1,2-shift of the adjacent bond engenders transient tetracyclic dione **A** after proton release. Furthermore, in Scheme 3, the stepwise [3 + 2] cycloaddition of hydroxy-stabilized allyl cation may take advantage of the intervention of some tertiary benzyl cation intermediates. However, an alternative [3 + 2] pathway in which the positive C1′ first connects to C4 then C3 to C3′ cannot be thoroughly excluded because of the poor electrophilicity of the β-phenylenone functionality (C3′). The **A** would exhibit the [2 + 2] cycloreversion of the constructed four-membered ring to provide **6b**. Although the thermal [2 + 2] cycloreversion is a symmetry forbidden process,[11] the present reaction may be promoted by ionic ring cleavage under the influence of CF_3SO_3H (vide infra). The obtained stereochemistry of **6b** can be easily rationalized by tracing the mechanistic course of the reaction and by assuming the more stable *trans* arrangement of the cyclopentenone substituents via the acid-catalyzed tautomerization. Consistent with the sequential progress of these transformations, the calculated ΔH_f decreased in the order of **4b**α (68.9 kcal mol^{-1}) > **A**α (66.5) > **6b** (65.2).

TABLE 2. Products in Acid-Catalyzed Rearrangement of 1c−e (30 mM) in $CDCl_3$ at 25 °C

					yield[a,b]/%				
					path A[c]	path B[c]			
entry	sub.	acid[d]	time (h)	conv[b] (%)	**2**	**3**	**4**	**5**α,β	**7**
11	**1c**	B (3)	10	100	70	30			
12	**1c**	B (20)	40	100	37	26		37 (α)	
13	**1c**	M (3)	2	100	36	64			
14	**1c**	F (3)	1	100		12		88 (β)	
15	**1d**	B (3)	70	83		100			
16	**1d**	M (3)	24	65		100			
17	**1d**	M (10)	24	100		56	44		
18	**1d**	F (2)	0.1	100		87	13		
19	**1d**	F (2)	6	100		13	87		
20	**1d**	F (10)	18	100					100
21	**1e**	F (10)	18	100					100

[a] Based on consumed **1**. [b] Determined by ^{1}H NMR. [c] Products via path A and B, respectively; see Scheme 4. [d] Values in parentheses are equivalence of added acid with respect to **1c**−**e**. B = BF_3, M = $MeSO_3H$, F = CF_3SO_3H.

Mechanistic Evidence for the Rearrangement 4b → 6b. As shown in Figure 1, the twist-boat conformation of the [8]annulenone ring of **4b**α is very suited for the [2 + 2] photocycloaddition between the topologically faced two double bonds of C3−C4 and C2′−C3′. The distances between the relevant double bond termini are 3.04 and 3.42 Å, respectively. Indeed, irradiation of a benzene solution of a mixture of **4b**α,β (α/β = 3.5) in Pyrex tube (>300 nm) easily provided the [2 + 2] adducts **7b**α,β without any change of the α/β isomer ratio (Scheme 1). Of special interest is the rapid cycloreversion (<5 min) to the starting **4b**α,β by addition of CF_3SO_3H (90 mM). As expected, the further monitoring of the reaction by NMR showed the gradual transformation into **6b** (k_2 = 1.54 × 10^{-3} M^{-1} s^{-1} for major isomer **4b**α at 25 °C in $CDCl_3$) (Figure 2). These findings strongly support the intervention of the acid-sensitive transient intermediate **A** and its [2 + 2] cycloreversion to **6b** in view of the close structural resemblance between **A**α,β and **7b**α,β. Consequently, R = Ph substituted **4b** demonstrated [3 + 2] cycloaddition in contrast to the normal Michael cyclization of R = Me substituted **4a**.

Acid-Catalyzed Reaction of 1c−e. To know the effects of the substitution position of annulenone ring,

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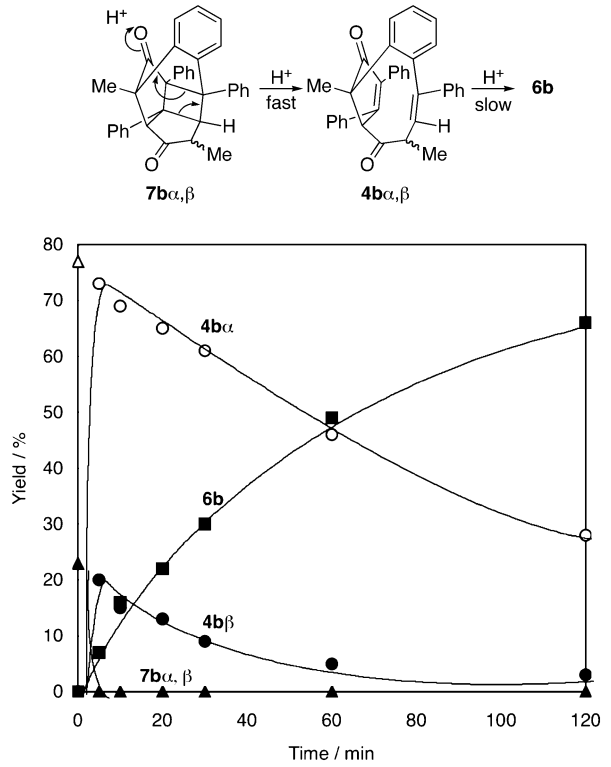
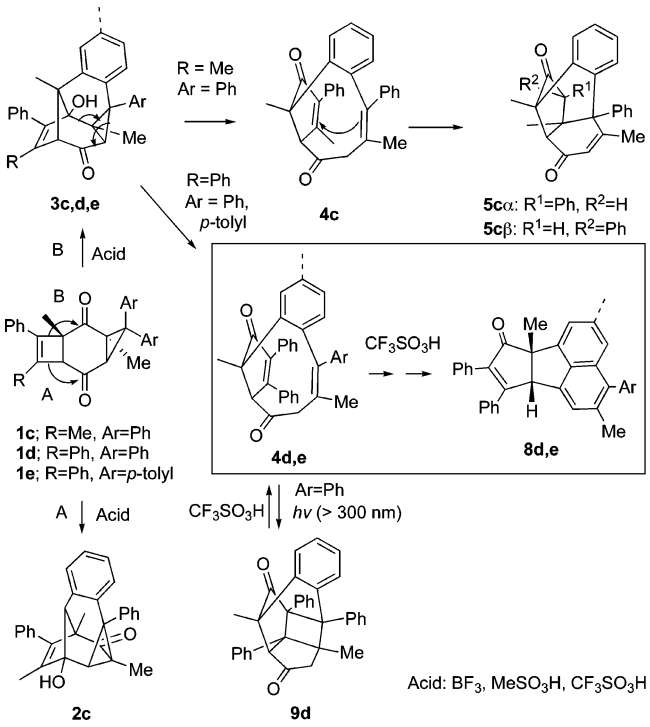


FIGURE 2. Time course for the rearrangement of **7b**α,*β* (△, ▲) to **4b**α,*β* (○, ●) and **6b** (■) with 3 equiv of CF_3SO_3H (90 mM) in $CDCl_3$ at 25 °C.

we have synthesized the analogous [2 + 2] photoadducts **1c**−**e** of 1,3-dimethyl-4,4-diarylhomobenzoquinones with 1-phenyl-1-propyne and diphenylacetylene. Like **1a**, the BF_3- and $MeSO_3H$-catalyzed reaction of **1c** proceeded via both path A/B to give tetracyclic keto-alcohols **2c** and **3c** along with tricyclic diones **5c**α,*β* (Scheme 4). Interestingly, in contrast to the case of **1a**, the tetracyclic keto-alcohol **3c** was isolated in this path B process (Table 2, entries 11−14). Furthermore, the transformation of **3c** into **5c** (via possible annulenone **4c**) was only attained by addition of a large excess of BF_3 or by strong CF_3SO_3H (entries 12 and 14). The higher stability of **3c** (and also **3d**) compared to **3a** (and **3b**) may be due to the conformational effect of the phenyl group on the cyclopropane ring. The phenyl ring of **3c** cannot adopt a favorable twisted conformation for the *π*-conjugation with the breakable *σ*-bond of cyclopropane because of the steric repulsion with the adjacent methyl substituent. By contrast, the **3a** bearing the differently substituted cyclopropane methyl group would allow the relevant phenyl ring to take an ideal conformation for such conjugation. Similar argument is also applied for the incredible stability of cyclopropane ring of **2a** (and **2c**) as compared with that of **3a** (and **3c**).[7]

It is also noted that BF_3 did not bring about the epimerization of **5c**α but did CF_3SO_3H completely. This is somewhat different from the case of **5a**α in which even potent CF_3SO_3H did not cause the epimerization (Scheme 1, Table 1). The only difference between **5a**α and **5c**α is the position of methyl group which is located at the unsaturated α-carbon (for **5a**) and *β*-one (for **5c**), respectively. The *β*-substituted methyl group would somewhat constrain the conformational rotation of adjacent phenyl

SCHEME 4

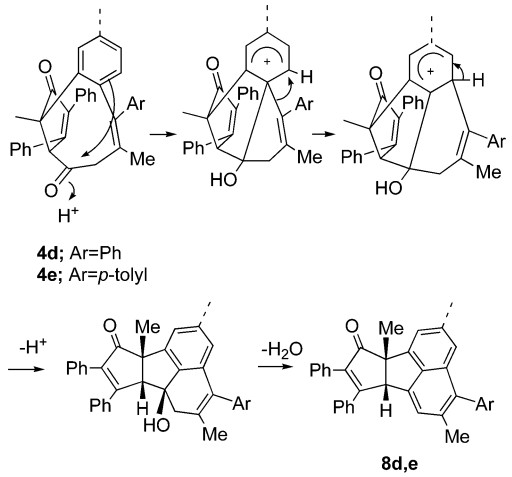


group and then restrict the orientation of the faced Ph (= R^1) ring. In fact, **5c**α provided ^{13}C NMR spectrum exhibiting the rotational restriction of one phenyl group in contrast to the *β*-isomer (see the Experimental Section). Since the acid-catalyzed keto−enol tautomerization is much more dependent on the electronic and steric effects of the α-phenyl substituent, we can imagine that the relevant methyl group of **5c**α exerts such a steric effect on the remotely substituted Ph (= R^1) group by way of the adjoining Ph group, thus enhancing the tautomerization. In addition, the slightly larger heat of formation for **5c**α (ΔH_f = 32.6 kcal mol^{-1}) as compared to **5a**α (30.2) seems to support the above argument and also become one reason for the facile epimerization of **5c**α. Inconformity with the complete transformation into *β*-isomer, PM3 calculation indicates that α epimer is less stable than the *β*-isomer by 8 kcal mol^{-1} for **5a** and 8.6 for **5c**, respectively.

As to **1d**, the BF_3 and the present protic acids caused only the path B rearrangement like **1b** and afforded **3d** (entries 15−16) and a mixture with annulenone **4d** (for 10 equiv excess of $MeSO_3H$, entry 17). As expected, CF_3SO_3H accelerated the conversion **3d** → **4d** as compared with BF_3 and $MeSO_3H$ (entries 18 and 19). Moreover, CF_3SO_3H induced further acid-catalyzed rearrangement of **4d** to afford 6b,9a-dihydro-7*H*-cyclopent[a]acenaphthylene-7-one **8d** in drastically contrast to the case of **4b**α,*β*. The structure of **8d** was deduced from the X-ray structural analysis of the similarly synthesized di-tolyl homologue **8e** (Table 2). The acenaphthylene ring system adopts the *cis*-fusion with the cyclopentenone ring (Supporting Information).

Considering that **4d** possesses the two-carbonyl groups, the formation of **8d** can be ascribed to the acid activation of annulenone carbonyl function rather than the cyclopentenone carbonyl group. In addition, as mentioned above, the twist-boat conformation of the annulenone ring

SCHEME 5



forces the C1 carbonyl carbon to come close to the opposite *o*-phenylene *ipso*-carbon (C5) with the distance of 2.88 Å (Figure 1). The hydroxy-stabilized carbocation center C1 thus formed will electrophilically attack at the faced phenylene carbon atom C5, forming the two new five-membered rings (Scheme 5). The resulting arenium ion can rearomatize by the 1,2-migration of the old phenylene-bond, followed by the proton release, and then by loss of water. To the best of our knowledge, the transannular *ipso*-Friedel Crafts alkylation is a very rare case.[12]

Why does the **4d** show the different type of transannular cyclization from that of **4b**α,*β*? We can explain the reason by resorting on the crucial steric effects of differently substituted methyl group of **4b** and **4d**. The methyl group of **4b** is located at the stereogenic α-carbon with respect to the annulenone carbonyl group and that of **4d** at the adjacent *β*-carbon (Schemes 1 and 4). As seen in Scheme 3, **4b** will allow the 5-*exo-trig* cyclization, which is essential for the [3 + 2] cyclization, whereas the methyl group of **4d** would impede such reaction due to the steric congestion with the opposite phenyl group. Accordingly, **4d** is considered to necessarily exhibit the unusual intramolecular Friedel−Crafts reaction. Indeed, the **4d** needed a longer reaction time and the more larger amount of CF_3SO_3H for the practical transformation as compared with **4b** (entries 9−10 and 19−20). As a result, the acid-catalyzed transannular cyclizations of 3a*H*-cyclopentene[8]annulene-1,4-(5*H*,9a*H*)-diones depend on which carbonyl function is responsible for the acid-activation and how largely the steric effects between the relevant two end groups contribute to the bonding interaction.

It is also noted that the irradiation of a benzene solution of **4d** in Pyrex tube (>300 nm) quantitatively gave the [2 + 2] photoadduct **9d** as in the case of **4b** (Scheme 4). This result suggests that the eight-membered annulenone ring of **4d** also adopts a twist-boat conformation likewise **4b** (Figure 1). As expected, when treated with CF_3SO_3H (90 mM), the **9d** rapidly exhibited the cycloreversion into **4d** (<5 min), and then slowly changed into **8d** with 2× diminished rate constant ($k_2 = 7.68 \times 10^{-4}$ M^{-1} s^{-1} at 25 °C in $CDCl_3$) than that of **4b**.

(12) For the well-known *ipso*-attack by NO_2^+, see: (a) Moodie, R. B.; Schofield, K. *Acc. Chem. Res*. **1976**, *9*, 287. (b) Fischer, A.; Henderson, G. N.; RayMahasay, S. *Can. J. Chem*. **1978**, *65*, 1233.

In conclusion, acid-catalyzed reactions of bicyclic 3a*H*-cyclopentene[8]annulene-1,4-(5*H*,9a*H*)-diones **4** exhibited three types of different transannular cyclizations: (1) the Michael addition (5-*exo-trig* or 6-*exo-trig*) leading to the tetracyclic diones, (2) the [3 + 2] cycloaddition followed by a novel sequential skeletal rearrangement to 2-naphthalenone derivatives, (3) the *ipso*-Friedel−Crafts alkylation accompanied by the rearomatization and the loss of water. These reactions were much dependent on the cyclopentenone ring substituent (Me or Ph) and the position of [8]annulenone methyl group as well as the nature of acids (BF_3, $MeSO_3H$, and CF_3SO_3H). It was found that the twist-boat conformation of the [8]annulenone rings and the substituent effects play a decisive role in these product differentiating transannular cyclizations. Such a restricted conformation also resulted in the facile transannular [2 + 2] photocyclization to afford tetracyclic cage compounds capable of undergoing the acid-catalyzed rapid cycloreversion. Consequently, the useful mechanistic information obtained in the present investigations will provide a beneficial insight into the understanding of the acid-catalyzed transannular reactions.

Experimental Section

Melting points were measured with a melting-point apparatus and were uncorrected. The ^1H NMR (270.05 MHz) and ^{13}C NMR (67.80 MHz) spectra were recorded on a spectrometer using trimethylsilane(TMS) as an internal standard. IR spectra were obtained with a spectrometer. Photoreactions were carried out under an argon atmosphere in a Pyrex tube with a high-pressure 300 W mercury lamp. The acid-catalyzed rearrangement products were isolated using a HPLC equipped with a chromato-integrator, UV detector, and pump.

Materials. All acids were used as purchased. Cyclobutene-fused homobenzoquinones **1c**−**e** were synthesized by the [2 + 2] photocycloaddition of the corresponding homobenzoquinones with alkynes as previously described.[5] The compounds **1a**,**b** were described elsewhere.[5] The structures of new compounds **1c**−**e** were deduced form the ^1H and ^{13}C NMR spectra, IR spectra, and elemental analysis as described below. The structure of **1d** was also confirmed by the X-ray crystal analysis.

General Procedure for the Acid-Catalyzed Reactions of 1. The acid-catalyzed reactions of **1** and the following workup procedures were carried out according to the previous manner.[7] The structures of the new compounds (**1c**, **1d**, **1e**, **2c**, **3c**, **3d**, **4d**, **5c**α, **5c***β*, **6b**, **8d**, and **8e**) were deduced from the ^1H and ^{13}C NMR and IR spectra. The structures of **1d**, **3c**, **3d**, **5c**α, **6b**, and **8e** were also confirmed by the X-ray structural analyses. The crystal structure of **4b**α is described elsewhere.[7]

Intramolecular [2 + 2] Photocyclization of 4bα,*β* **and 4d.** Irradiation of a solution of **4b**α,*β* (($\alpha/\beta = 3.5$), 30 mg, 0.063 mmol) in benzene (2 mL) through a Pyrex filter under an argon atmosphere at room temperature (>300 nm, 0.5 h, with a 300 W high-pressure mercury lamp) gave **7b**α,*β* ($\alpha/\beta = 3.5$) in a quantitative yield. The fractional crystallization from hexane-benzene solution provided the colorless prisms of minor **7b***β*. The major α-isomer was separated by a preparative HPLC. Similar photoreaction of **4d** also yielded a quantitative amount of **9d**. The structures of new compounds **7b**α,*β* and **9d** were investigated by the ^1H and ^{13}C NMR and IR spectra. The structure of **7b***β* was also confirmed by the X-ray crystal analysis (Supporting Information).

(1*R,3*R**,5*R**,7*R**)-1,3,8-Trimethyl-4,4,9-triphenyltricyclo[5.2.0.0^{3,5}]non-8-ene-2,6-dione (1c):** 68% isolated yield; mp 162−163 °C; colorless prisms (from hexane−benzene); ^1H

NMR ($CDCl_3$) δ 0.75 (s, 3H), 1.16 (s, 3H), 2.02 (d, 3H, J = 1.6 Hz), 2.54 (d, 1H, J = 1.6 Hz), 2.73 (s, 1H), 7.17−7.51 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 14.2, 18.8, 19.5, 40.1, 42.8, 47.1, 56.0, 61.3, 126.6, 127.2, 127.7, 127.7, 128.3, 128.7, 128.7, 128.9, 130.3, 132.6, 138.3, 138.4, 141.0, 143.7, 204.1, 208.1; IR (KBr) 1672 cm^{-1} (C=O). Anal. Calcd for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26. Found: C, 86.28; H, 6.41.

(1*R,3*R**,5*R**,7*R**)-1,3-Dimethyl-4,4,8,9-tetraphenyltricyclo[5.2.0.0^{3,5}]non-8-ene-2,6-dione (1d):** 73% isolated yield; mp 219−220 °C; colorless prisms (from hexane-benzene); ^{1}H NMR ($CDCl_3$) δ 0.73 (s, 3H), 1.26 (s, 3H), 2.76 (s, 1H), 3.18 (s, 1H), 7.15−7.56 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 18.7, 19.0, 39.3, 42.5, 46.3, 56.6, 59.1, 127.0, 127.2, 127.3, 127.5, 128.0, 128.3, 128.4, 128.5, 128.6, 128.6, 128.8, 130.4, 132.1, 132.5, 138.2, 138.7, 140.9, 144.3, 203.8, 207.2; IR (KBr) 1681 cm^{-1} (C=O). Anal. Calcd for $C_{35}H_{28}O_2$: C, 87.47; H, 5.87. Found: C, 87.65; H, 6.06.

(1*R,3*R**,5*R**,7*R**)-1,3-Dimethyl-4,4-bis(*p*-tolyl)-8,9-diphenyltricyclo[5.2.0.0^{3,5}]non-8-ene-2,6-dione (1e):** 77% isolated yield; mp 180−181 °C; colorless prisms (from hexane−benzene); ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 3H), 1.25 (s, 3H), 2.24 (s, 3H), 2.25 (s, 3H), 2.72 (s, 1H), 3.19 (s, 1H), 7.04−7.09 (m, 5H), 7.26−7.56 (m, 13H); HRMS *m/z* (M^+) found 508.2409, calcd for $C_{37}H_{32}O_2$ 508.2402.

(1*S,2*S**,9*S**,10*R**,13*S**,14*R**)-13-Hydroxy-1,10,12-trimethyl-2,11-diphenylpentacyclo[8.4.1.0^{2,14}.0^{3,8}.0^{9,13}]-pentadeca-3(8),4,6,11-tetraen-15-one (2c):** colorless crystal; ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 3H), 1.12 (s, 3 H), 1.93 (s, 1H), 2.01 (s, 3H), 2.52 (d, 1H, J = 2.6 Hz), 3.53 (d, 1H, J = 2.6 Hz), 6.89 (dd, 1H, J = 6.9, 2.0 Hz), 7.06−7.52 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 11.5, 15.1, 20.0, 38.9, 43.6, 48.1, 63.1, 68.6, 75.9, 126.0, 127.1, 127.5, 127.6, 127.7, 128.0, 128.1, 128.3, 129.4, 130.0, 130.3, 131.3, 132.3, 135.3, 137.1, 138.3, 139.2, 147.2, 205.0. The number (28) of ^{13}C NMR peaks may be due to the rotational restriction of one phenyl group.

(1*S,2*R**,9*R**,10*S**,13*S**,14*S**)-13-Hydroxy-9,11,14-trimethyl-2,12-diphenylpentacyclo[8.4.1.0^{2,14}.0^{3,8}.0^{9,13}]-pentadeca-3(8),4,6,11-tetraen-15-one (3c):** mp 286−287 °C; colorless prisms (from hexane−benzene); ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 3H), 1.80 (s, 1H), 1.83 (s, 3H), 1.87 (s, 3H), 2.47 (s, 1H), 2.89 (s, 1H), 6.56 (dd, 1H, J = 8.2, 1.0 Hz), 7.04−7.56 (m, 13 H); ^{13}C NMR ($CDCl_3$) δ 14.7, 16.3, 19.1, 42.3, 43.3, 51.7, 54.0, 82.8, 126.3, 126.8, 126.9, 127.3, 127.4, 128.2, 128.4, 128.54, 128.8, 129.1, 130.6, 131.1, 135.7, 135.9, 137.7, 139.1, 146.3, 200.7; IR (KBr) 3480 (br, OH), 1668 cm^{-1} (C=O).

(1*S,2*R**,9*R**,10*S**,13*S**,14*S**)-13-Hydroxy-9,14-dimethyl-2,11,12-triphenylpentacyclo[8.4.1.0^{2,14}.0^{3,8}.0^{9,13}]-pentadeca-3(8),4,6,11-tetraen-15-one (3d):** mp 289−290 °C; colorless prisms (from hexane-benzene); ^{1}H NMR ($CDCl_3$) δ 0.82 (s, 3H), 1.90 (s, 3H), 1.93 (s, 1H), 2.63 (d, 1H, J = 1.0 Hz), 3.34 (d, 1H, J = 1.0 Hz), 6.61 (dd, 1H, J = 7.9, 1.3 Hz), 7.06−7.57 (m, 18H); ^{13}C NMR ($CDCl_3$) δ 16.3, 19.3, 41.0, 43.1, 50.9, 55.1, 74.6, 82.7, 126.4, 126.95, 126.98, 127.3, 127.8, 127.96, 128.00, 128.2, 128.4, 128.5, 128.7, 128.9, 129.5, 130.6, 131.1, 135.5, 136.1, 136.2, 137.5, 137.7, 138.9, 147.2, 201.8; IR (KBr) 3439 (br, OH), 1674 cm^{-1} (C=O). The number (31) of ^{13}C NMR peaks may be due to the rotational restriction of one phenyl group.

(2*S,6*R**)-2,9-Dimethyl-4,5,10-triphenyltricyclo[9.4.0.0^{2,6}]-pentadeca-1(15),4,9,11,13-pentaene-3,7-dione (4d):** mp 217−218 °C; colorless prisms (from hexane−benzene); ^{1}H NMR ($CDCl_3$) δ 1.85 (s, 3H), 1.94 (s, 3H), 2.44 (d, 1H, J = 18.1 Hz), 2.89 (d, 1H, J = 18.1 Hz), 4.26 (s, 1H), 6.75 (dd, 1H, J = 7.7, 1.5 Hz), 6.74−7.44 (m, 17 H), 7.64 (d, 1H, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$) δ 24.8, 28.4, 51.4, 54.0, 69.3, 127.0, 127.6, 127.9, 128.0, 128.2, 128.3, 128.5, 128.7, 128.8, 129.0, 129.7, 130.4, 131.0, 131.2, 132.0, 133.1, 138.3, 140.7, 141.07, 141.13, 141.3, 155.9, 205.7, 206.5; IR (KBr) 1710 cm^{-1} (C=O).

(2*S,4*R**,5*R**,6*R**,10*R**)-2,5,9-Trimethyl-4,10-diphenyltetracyclo[9.4.0.0^{2,6}.0^{5,10}]pentadeca-1(15),8,11,13-tetraene-3,7-dione (5cα):** colorless crystal; ^{1}H NMR ($CDCl_3$) δ 1.66 (s, 3H), 1.75 (s, 3H), 1.80 (d, 3H, J = 1.0 Hz), 2.77 (s, 1H), 3.65 (s, 1H), 6.13(q, 1H, J = 1.0 Hz), 6.13−6.34 (m, 4H), 6.88−7.46 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 17.0, 21.9, 27.2, 49.9, 56.9, 59.0, 63.4, 66.2, 125.4, 125.5, 125.9, 126.7, 127.1, 127.9, 127.9, 128.4, 128.7, 129.7, 129.9, 130.9, 132.6, 132.8, 134.2, 134.8, 138.2, 168.9, 194.1, 206.7. The number (28) of ^{13}C NMR peaks may be due to the rotational restriction of one phenyl group.

(2*S,4*S**,5*R**,6*R**,10*R**)-2,5,9-Trimethyl-4,10-diphenyltetracyclo[9.4.0.0^{2,6}.0^{5,10}]pentadeca-1(15),8,11,13-tetraene-3,7-dione (5cβ):** colorless crystal; ^{1}H NMR ($CDCl_3$) δ 0.70 (s, 3H), 1.75 (s, 3H), 2.12 (d, 3H, J = 1.3 Hz), 2.95 (s, 1H), 4.29 (s, 1H), 6.13(q, 1H, J = 1.3 Hz), 7.09−7.46 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 16.9, 22.1, 22.4, 48.8, 56.8, 57.7, 62.0, 62.2, 126.9, 127.0, 127.2, 127.6, 127.7, 128.2, 128.2, 129.4, 130.7, 130.9, 133.3, 135.0, 136.1, 137.1, 138.9, 167.2, 194.8, 211.3; IR (KBr) 1749 and 1651 cm^{-1} (C=O).

(*R)-4-Methyl-1-((1*R**,5*R**)-5-methyl-4-oxo-2-phenylcyclopent-2-enyl)-1,3-diphenylnaphthalene-2(1*H*)-one (6b):** colorless crystal; ^{1}H NMR ($CDCl_3$) δ 1.36 (d, 3H, J = 7.3 Hz), 1.85 (s, 3 H), 2.59−2.67 (qd, 1H, J = 7.3, 1.0 Hz), 5.11−5.12 (dd, 1H, J = 1.3, 1.0 Hz), 5.89 (d, 1H, J = 1.3 Hz), 6.58−6.62 (m, 2H), 6.75 (dd, 2H, J = 6.9, 1.7 Hz), 7.08−7.31 (m, 12H), 7.37−7.44 (m, 2H), 7.50−7.53 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 18.1, 20.2, 47.3, 59.4, 61.8, 126.2, 127.1, 127.4, 127.58, 127.61, 127.7, 128.0, 128.2, 128.6, 128.8, 129.3, 129.4, 131.2, 132.8, 134.8, 135.1, 136.0, 140.1, 140.9, 146.9, 177.9, 197.1, 211.0; IR (KBr) 1702 and 1648 cm^{-1} (C=O). The number (28) of ^{13}C NMR peaks may be due to the unresolvable overlapping of two peaks.

(2*S,4*R**,5*R**,6*R**,8*R**,9*S**,10*R**)-2,8-Dimethyl-4,5,10-triphenylpentacyclo[9.4.0.0^{2,6}.0^{4,10}.0^{5,9}]pentadeca-1(15),-11,13-trien-3,7-dione (7bα):** colorless crystal; ^{1}H NMR ($CDCl_3$) δ 0.72 (d, 3H, J = 6.9 Hz), 1.87 (s, 3 H), 2.92−2.98 (qd, 1H, J = 6.9, 1.6 Hz), 3.10 (s, 1H), 4.89 (d, 1H, J = 1.6 Hz), 6.23 (d, 1H, J = 6.9 Hz), 6.39 (d, 1H, J = 7.9 Hz), 6.77−6.87 (m, 4H), 6.91−7.25 (m, 9H), 7.27−7.36 (m, 3H), 7.49 (d, 1H, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$) δ 9.8, 18.3, 49.5, 50.0, 51.6, 55.5, 61.1, 64.6, 67.5, 124.3, 125.72, 125.74, 126.1, 126.5, 126.6, 126.7, 127.1, 127.2, 127.6, 128.61, 128.63, 130.7, 130.8, 131.4, 134.2, 139.6, 142.4, 142.5, 142.7, 214.8, 217.4; IR (KBr) 1734 cm^{-1} (C=O).

(2*S,4*R**,5*R**,6*R**,8*S**,9*S**,10*R**)-2,8-Dimethyl-4,5,10-triphenylpentacyclo[9.4.0.0^{2,6}.0^{4,10}.0^{5,9}]pentadeca-1(15),-11,13-trien-3,7-dione (7bβ):** colorless crystal; ^{1}H NMR ($CDCl_3$) δ 1.37 (d, 3H, J = 7.9 Hz), 1.81−1.87 (m, 4 H), 3.10 (s, 1H), 4.57(s, 1H), 6.17−6.21 (dd, 1H, J = 7.9 Hz, 1.0 Hz), 6.38 (d, 1H, J = 7.9 Hz), 6.75−6.84 (m, 4H), 6.91−7.24 (m, 9H), 7.26−7.47 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 16.0, 18.2, 47.0, 51.5, 54.2, 56.7, 61.2, 64.8, 69.8, 124.6, 125.6, 126.2, 126.4, 126.5, 126.6, 127.2, 127.7, 128.3, 128.4, 129.8, 130.8, 131.2, 134.3, 141.0, 141.5, 141.8, 142.4, 214.8, 219.2; IR (KBr) 1734 cm^{-1} (C=O). The number (29) of the ^{13}C peaks may be due to the rotational restriction of one phenyl group.

(6b*S,9a*R**)-2,6b-Dimethyl-3,8,9-triphenyl-6b*H*-cyclopenta[*a*]acenaphthylen-7(9a*H*)-one (8d):** mp 210−211 °C; colorless prisms (from hexane−benzene); ^{1}H NMR ($CDCl_3$) δ 1.87 (s, 3H), 2.04 (s, 3H), 5.06 (s, 1H), 6.62 (s, 1H), 6.64−7.48 (m, 17H), 7.61 (d, 1H, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ 21.3, 23.4, 31.03, 60.5, 60.7, 119.2, 122.8, 123.7, 126.9, 127.7, 128.0, 128.2, 128.2, 128.4, 129.1, 129.7, 130.0, 131.0, 131.4, 134.6, 134.9, 135.1, 135.6, 136.4, 138.7, 139.7, 143.8, 167.3, 206.1; IR (KBr) 1699 cm^{-1} (C=O).

(6b*S,9a*R**)-2,5,6b-Trimethyl-3-(*p*-tolyl)-8,9-diphenyl-6b*H*-cyclopenta[*a*]acenaphthylen-7(9a*H*)-one (8e):** mp 207−208 °C; colorless prisms (from hexane−benzene); ^{1}H NMR ($CDCl_3$) δ 1.85 (s, 3H), 2.02 (s, 3H), 2.44 (s, 3H), 2.46 (s, 3H), 5.02 (s, 1H), 6.54 (s, 1H), 6.58−6.62 (m, 2H), 6.75 (dd, 2H, J = 6.9, 1.7 Hz), 7.08−7.31 (m, 9 H), 7.37−7.44 (m, 2H), 7.50−7.53 (m, 1H).

(2*S,4*R**,5*R**,6*R**,9*S**,10*R**)-2,9-Dimethyl-4,5,10-triphenylpentacyclo[9.4.0.0.^{2,6}.0^{4,10}.0.^{5,9}]pentadeca-1(15),-11,13-triene-3,7-dione (9d):** mp 212−214 °C; colorless prisms (from hexane-benzene); ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 3H), 2.15

(s, 3H), 2.36 (d, 1H, J = 18.7 Hz), 2.51 (d, 1H, J = 18.7 Hz), 2.89 (s, 1H), 6.27 (d, 1H, J = 8.3 Hz), 6.66−7.35 (m, 17H), 7.45 (d, 1H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 18.1, 23.4, 31.1, 54.1, 55.7, 56.8, 62.0, 68.7, 72.7, 124.1, 125.9, 126.0, 126.6, 127.1, 127.4, 127.6, 128.1, 128.2, 129.3, 130.4, 132.9, 133.2, 134.2, 140.96, 141.04, 141.9, 142.3, 214.4, 217.1; IR (KBr): 1733 cm^{-1} (C=O). Anal. Calcd for $C_{35}H_{28}O_2$: C, 87.47; H, 5.87. Found: C, 87.52; H, 6.03.

X-ray crystal structural determination of 1d: $C_{35}H_{28}O_2$, M = 480.61, monoclinic, space group $C2/c$ with a = 27.38(5) Å, b = 8.847(12) Å, c = 22.82(4) Å, β = 102.98(3)°, V = 5386.9-(13) Å^3, Z = 8, D_c = 1.185 g/cm^3, R = 0.095 and R_w = 0.104 for 4649 reflections with $I > 0.50\sigma(I)$.

X-ray crystal structural determination of 3c: $C_{30}H_{26}O_2$, M = 418.53, monoclinic, space group $P2_{1/c}$ with a = 12.752(7) Å, b = 13.44(1) Å, c = 14.274(4) Å, β= 115.22(3)°, V = 2213.46-(13) Å^3, Z = 4, D_c = 1.256 g/cm^3, R = 0.079 and R_W = 0.079 for 3380 reflections with $I > 3.00\sigma(I)$.

X-ray crystal structural determination of 3d: $C_{35}H_{28}O_2$, M = 480.61, monoclinic, space group $P2_{1/n}$ with a = 11.850(1) Å, b = 17.988(2) Å, c = 12.921(2) Å, β = 113.523(3)°, V = 2525.3(5) Å^3, Z = 4, D_c = 1.26 g/cm^3, R = 0.192 and R_W = 0.187 for 4400 reflections with $I > 0.00\sigma(I)$.

X-ray crystal structural determination of 5cα: $C_{30}H_{26}O_2$, M = 418.53, monoclinic, space group $P2_{1/c}$ with a = 15.503(5) Å, b = 8.505(2) Å, c = 16.954(3) Å, β = 100.37(2)°, V = 2199.0-(9) Å^3, Z = 4, D_c = 1.264 g/cm^3, R = 0.070 and R_w = 0.054 for 2657 reflections with $I > 0.3.00\sigma(I)$.

X-ray crystal structural determination of 6b: $C_{35}H_{28}O_2$, M = 480.61, monoclinic, space group $P2_{1/c}$ with a = 11.4670-(5) Å, b = 14.7091(7) Å, c = 15.4076(7) Å, β = 91.6973(8)°, V = 2597.7(2) Å^3, Z = 4, D_c = 1.229 g/cm^3, R = 0.094 and R_w = 0.131 for 5920 reflections with $I > 2.0\sigma(I)$.

X-ray crystal structural determination of 7bβ: $C_{35}H_{28}O_2$, M = 480.61, monoclinic, space group $P2_{1/c}$ with a = 9.0873(3) Å, b = 35.735(1) Å, c = 9.6538(3) Å, β = 105.671(1)°, V = 3018.4(2) Å^3, Z = 4, D_c = 1.229 g/cm^3, R = 0.141 and R_w = 0.234 for 6260 reflections with $I > 2.0\sigma(I)$.

X-ray crystal structural determination of 8e: $C_{37}H_{30}O_2$, M = 490.64, triclinic, space group P-1 with a = 9.7136(7) Å, b = 12.0508(2) Å, c = 12.8856(2) Å, α = 107.365(2)°, β = 104.062-(2)°, γ = 97.428(2)°, V = 1362.9(1) Å^3, Z = 2, D_c = 1.196 g/cm^3, R = 0.131 and R_w = 0.234 for 5377 reflections with $I > 0.00\sigma$-(I).

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Supporting Information Available: CIF files and ORTEP drawings of **1d**, **3c**, **3d**, **5c**α, **6b**, **7b**β, and **8e** and two tables for the time course of product distributions in the CF_3SO_3H-catalyzed rearrangements of **7b**α,β and **9d** into **4b**α,β and **4d**, and then **6b** and **8d**, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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