Superacid-Catalyzed Electrocyclization of 1-Phenyl-2-propen-1-ones to 1-Indanones. Kinetic and Theoretical Studies of Electrocyclization of Oxonium−Carbenium Dications

Takayoshi Suzuki, Tomohiko Ohwada,* and Koichi Shudo

Contribution from the Faculty of Pharmaceutical Sciences, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

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Abstract: Strongly acidic conditions are required to induce the Nazarov-type cyclization of aryl vinyl ketones, although chemical analogy with the Nazarov reaction would superficially imply a straightforward electrocyclization reaction of the *O*-protonated monocation. In this paper we describe the superacid-catalyzed prototype cyclization of 1-phenyl-2-propen-1-ones. The acidity dependence of these cyclization reactions as revealed by kinetic measurements strongly suggests the involvement of the *O*,*O*-diprotonated dication rather than the *O*-protonated monocation. That is, the cyclization of 1-phenyl-2-propen-1-ones represents an electrocyclization of the oxonium−carbenium dication. We also describe the effect of substituents at the 2-position of 1-phenyl-2-propen-1-ones. *Ab initio* calculations, based on the density functional theory, support the idea that electrocyclization of the dication is energetically more favarable than that of the monocation.

It is well known that cyclization reactions of divinyl ketones (1,4-pentadien-3-ones) to 2-cyclopentenones, i.e., Nazarov and related reactions, are catalyzed by acids.[1,2] These reactions are relevant to the prototype electrocyclization of the pentadienyl cation to the cyclopentyl cation.[3] In this context, the intermediacy of *O*-protonated divinyl ketones, i.e., the 3-hydroxy-1,4-pentadienium cation, has been established in the Nazarov and related reactions.[1,2] However, the analogous cyclization reaction of benzophenone did not proceed even on heating in a strong acid such as trifluoromethanesulfonic acid (TFSA). As judged from the basicity of benzophenone,[4] *O*-protonated benzophenone, which may have a 3-hydroxy-1,4-pentadienium character, should be formed in TFSA. Phenyl vinyl ketones, wherein one of the phenyl groups of benzophenone is replaced with an olefin, are thus of interest as potential substrates for cyclization. Some previous studies of relevant cyclization reactions have been reported.[5−9] Acid-catalyzed cyclization reaction of naphthalenyl vinyl ketones to give benzoindanone derivatives was described as early as 1927:[5] the reaction required drastic conditions, such as heating on a steam bath in concentrated sulfuric acid. Related cyclizations of 1-benzoyl-1-cyclohexene[6] and 1-benzoyl-1-cycloheptene[7] were also reported, and also required strongly acidic conditions, such as a mixture of phosphoric acid and phosphorus pentoxide (equivalent to polyphosphoric acid) with heating on a steam bath or a mixture of phosphoric acid and formic acid at 90 °C. The prototype cyclization of 1-phenyl-2-propen-1-ones, in particular of 2-methyl- (**1g**) and 2-ethyl-1-phenyl-2-propen-1-ones (**1h**) was previously investigated,[8] and was found to be catalyzed by concentrated sulfuric acid. Cyclization of 1,2-diaryl-2-propen-1-ones with multiple substituents on the aromatic rings was also reported to be catalyzed by concentrated sulfuric acid.[9] Although the cyclization reactions of aromatic vinyl ketones have been reported, they have not been well-characterized, particularly in the following respects: (1) The observation that strongly acidic conditions are required to induce the Nazarov-type cyclization of these compounds has not been rationalized. The reaction intermediates in the cyclization of 1-phenyl-2-propen-1-ones and related aromatic systems have been little discussed, though a superficial chemical analogy with the Nazarov reactions led to the suggestion that the electrocyclization reaction involves the *O*-protonated phenyl vinyl ketones.[6] (2) Although the parent 1-phenyl-2-propen-1-one is known,[8,10] it has not been established whether or not the prototype electrocyclization of this compound takes place. A substituent at the 2-position of 1-phenyl-2-propen-1-ones seems to be relevant to the cyclization, because the reported examples of the cyclization are limited to 2-substituted 1-phenyl-2-propen-1-one derivatives such as 1-benzoyl-1-cyclohexene.

In this paper we will focus on the prototype cyclization of 1-phenyl-2-propen-1-ones as aromatic precursors (Scheme 1) and show that the acidity dependence of these cyclization reactions strongly suggests the involvement of the *O*,*O*-diprotonated dication rather than the *O*-protonated monocation.

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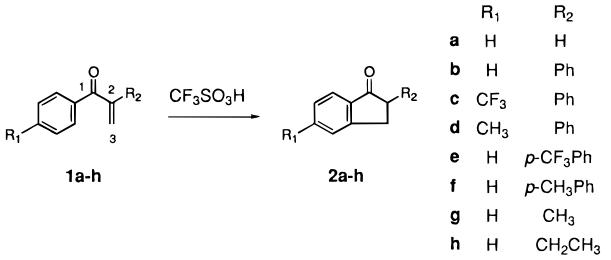
Table 1. Acid-Catalyzed Cyclizations of 1-Phenyl-2-propen-1-ones and Their Acidity Dependence

enone	acid	$\sim -H_0$[a]	time (h)	temp (°C)	recovery (%)	yield (%)
1a	TFSA	12.7	120	25	6	63
	6% TFSA−94% TFA	8.7	120	25	24	51
1b	TFA	2.7	5	0	98	0
	6% TFSA−94% TFA	8.7	5	0	40	59
	TFSA	12.7	5	0	0	98
1c	30% TFSA−70% TFA	10.6	5	0	37	61
	TFSA	12.7	5	0	3	93
1d	6% TFSA−94% TFA	8.7	5	0	52	48
	TFSA	12.7	5	0	6	91
1e	6% TFSA−94% TFA	8.7	5	0	57	43
	TFSA	12.7	5	0	0	99
1f	6% TFSA−94% TFA	8.7	5	0	22	78
	TFSA	12.7	5	0	0	100
1g	7% TFSA−93% TFA	8.9	2	25	45	49
	TFSA	12.7	2	25	0	97
1h	7% TFSA−93% TFA	8.9	3	25	39	54
	TFSA	12.7	3	25	0	97

[a] Corrected values of the acidity function of the reaction media (see Table 2 and ref 14).

Scheme 1



That is, the cyclization of 1-phenyl-2-propen-1-ones represents an electrocyclization of the oxonium−carbenium dication.

Results and Discussion

Acid-Catalyzed Electrocyclization of 1-Phenyl-2-propen-1-one and Its 2-Substituted Derivatives. We found that the cyclization reaction of the parent 1-phenyl-2-propen-1-one (**1a**) is catalyzed by TFSA at 25 °C to give 1-indanone (**2a**) in 63% yield, together with 6% recovery of **1a** after 120 h (Table 1). The 1-indanone derivative is considered to be formed by 4π-electrocyclization between the benzene ring and the enone moiety.[11] The reaction was slow even at 25 °C. The corresponding cyclizations of 2-substituted 1-phenyl-2-propen-1-ones were much faster in TFSA. 1,2-Diphenyl-2-propen-1-one (**1b**) readily gave a cyclized product, 2-phenyl-1-indanone (**2b**), in 98% yield in TFSA at 0 °C after 5 h (Scheme 1). Therefore, the 2-substituent of 1-phenyl-2-propene-1-ones is not essential for the cyclization, but does facilitate the reaction. This facile reaction is in contrast with that of the isomeric enone, chalcone (1,3-diphenyl-2-propen-1-one), which did not give cyclized products even on heating at 80 °C in TFSA.[12]

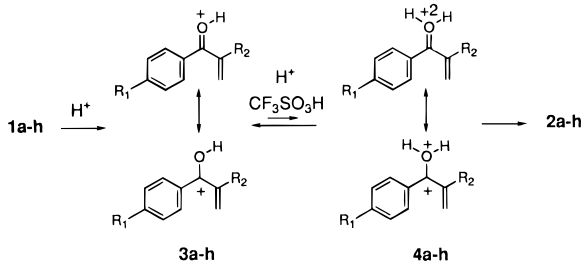
This cyclization depends on the acidity of the reaction medium, as judged from the yields of the product (Tables 1 and 2).[13,14] The pK_{BH^+} values of α,β-unsaturated ketones and indanones for *O*-monoprotonation are expected to be around −4 to −6 (e.g., chalcone, −5.2; 2-cyclopenten-1-one, −3.6; 2-cyclohexen-1-one, −3.6; acetophenone, −6.15).[4,15] In 6% TFSA−94% TFA ($H_0 \approx -8.7$),[14] the reaction of the parent **1a** slowed further than in TFSA. In TFA ($H_0 \approx -2.7$) the cyclization of **1b** did not take place at 0 °C after 5 h. As the acidity was increased to $H_0 \approx -8.7$ by the addition of TFSA to TFA (6% TFSA−94% TFA), the cyclization of **1b** to give indanone **2b** began to start, though slowly (**2b**, 59% yield together with 40% recovery of **1b**). The reaction in TFSA is rapid and quantitative. Even at $H_0 \approx -8.7$ (6% TFSA−94% TFA), where the medium is sufficiently acidic to *O*-monoprotonate the ketone to a large extent to give the monocation **3b** (Scheme 2), the electrocyclization reaction is incomplete. Thus, these results indicate that the electrocyclization of 1,2-diphenyl-2-propen-1-one (**1b**), and presumably also **1a**, requires a strong acid catalyst, which is compatible with previous observations, and excludes the intervention of the *O*-protonated enone **3b** as a reactive intermediate.

Table 2. Corrected Values of the Acidity Function of the Acid Media in the Presence of Cyclopentanone

acid[a]	acid/cyclopentanone[b] (equiv)	uncorrected H_0[c]	corrected H_0[d]
100% TFSA	96	−14.1	−12.72
86% TFSA−14% TFA	90	−13.0	−12.39
61% TFSA−39% TFA	99	−12.2	−11.56
27% TFSA−73% TFA	95	−10.9	−10.62
16% TFSA− 84% TFA	97	−10.2	−9.98
7% TFSA−93% TFA	102	−9.1	−8.85

[a] Weight percent of the composite acids. [b] Mole ratios of acid and cyclopentanone. [c] Reference 13. [d] Reference 14.

Scheme 2



Similar cyclization reactions take place with 1,2-diaryl-2-propen-1-ones **1c**−**1f** (Table 1). The presence of a single methyl or trifluoromethyl group on one of the two benzene rings did not significantly modify the reaction. These reactions also exhibited acidity dependence; in 6% TFSA−94% TFA ($H_0 \approx -8.7$) for **1d**−**1f** (30% TFSA−70% TFA ($H_0 \approx -11$) for **1c**) the reactions are slow. In TFSA all the substrates gave substituted 1-indanones quantitatively.

A related cyclization of 2-methyl- (**1g**) and 2-ethyl-1-phenyl-2-propen-1-ones (**1h**) was previously studied,[8] the reaction being catalyzed by concentrated sulfuric acid (88% yield of **2g**; 49% yield of **2h**). TFSA catalyzes these cyclization reactions of **1g** and **1h** more efficiently than sulfuric acid to give indanones

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(14) Because the enone substrate **1** and the formed indanone **2** can undergo *O*-protonation, i.e., they are oxygen-bases, the acidity of the reaction medium would be decreased, particularly in the range of high acidity. We therefore estimated the lowering of the acidity of the reaction medium by measuring the protonation of cyclopropanone in 100 (95 ± 5) equiv of TFSA−TFA mixtures, which have an acidity stronger than $H_0 \approx -9$ (Table 2). We chose cyclopropanone in place of the reaction substrates **1** because of the comparable pK_{BH^+} value of cyclopropanone (−7.5) to those of the enones and indanones (refs 4 and 15), its inert reactivity, and the absence of strong UV absorption.

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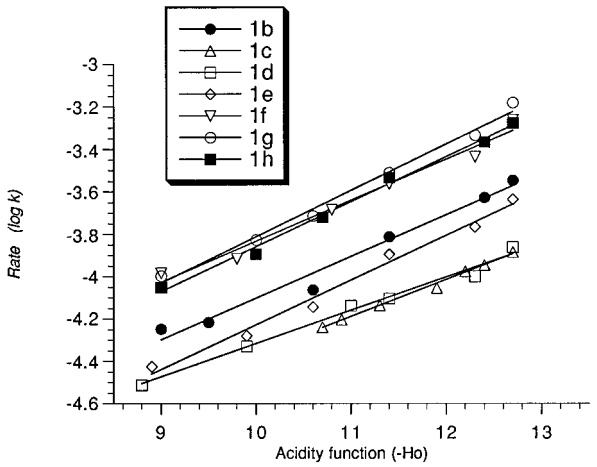
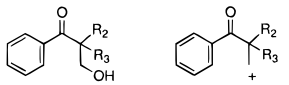


Figure 1. Acidity−rate relationships in the cyclization of **1b**−**1h**.

(both in 97% yield at 25 °C for 2 h). A similar acidity dependence of these reactions was observed: in 7% TFSA−93% TFA ($H_0 \approx -8.9$)[14] for **1g** and **1h** the reactions are not complete. In TFSA the reactions are fast and quantitative. These observations confirm the requirement of a strong acid catalyst.

Another related cyclization of 3-hydroxy-2-methyl-1-phenylpropan-1-one **5** ($R_2 = H$, $R_3 = CH_3$) to give 3-methylindanone (**2g**), catalyzed by concentrated sulfuric acid, was also reported.[8] This cyclization reaction was considered to proceed through the enone intermediate **1g**, formed by the dehydration of **5** in the acid, because a quaternary precursor, 3-hydroxy-2,2-dimethyl-1-phenylpropan-1-one **5** ($R_2 = R_3 = CH_3$) failed to cyclize in the presence of sulfuric acid or phosphoric acid, instead being degraded to isobutyrophenone. A similar intervention of the enone intermediate was proposed in the cyclization of the related precursor 1-(3-chloro-1-propionyl)naphthalene to give 4,5-benzo-3-indanone.[5] These previous observations are consistent with a mechanism involving electrocyclization of the protonated enones **1** rather than an intramolecular Friedel−Crafts-type reaction involving the primary carbenium ion **6** which can be formed by *C*-protonation of the enones **1**.



5 **6**

Kinetic Evidence for Dicationic Intermediates. In order to elucidate the acidity dependence of the reaction quantitatively, we carried out rate measurements in the TFSA−TFA system. Rate constants of the cyclization of the diaryl cases **1b**−**1f** were measured at 0 °C, and those of the alkyl-substituted compounds **1g** and **1h** were measured at 25 °C. The cyclization reactions of all the substrates **1b**−**1h** were conducted in the presence of a large excess (100 equiv) of acids. These reactions showed the first-order kinetics, giving excellent linear relationships ($r \geq 0.99$ in all cases) between the corrected[14] (and uncorrected) acidity values and rates, with slopes of 0.16−0.22 (Figure 1 and Tables 2 and 3). The slopes are comparable to those obtained in the superacid-catalyzed cyclodehydration of 1,3-diphenyl-1-propanones, which involves *O*,*O*-diprotonated ketones.[17] The reaction is accelerated in strong acid (H_0 more than −8.9), showing no plateau of the rate up to the acidity of TFSA solution (−12.7). According to the Zucker−Hammett criteria,[16−18] this linear acidity−rate relationship indicated (1) the involvement of protonation of the *O*-monoprotonated phenyl enone **3** in the cyclization reaction to give the indanones **2** and

Table 3. Rate Constants for Acid-Catalyzed Cyclizations of **1b**−**1h**[a]

1b[b]		**1c**[b]		**1d**[b]	
H_0	10^5k (s^{-1})	H_0	10^5k (s^{-1})	H_0	10^5k (s^{-1})
−12.7	28.43	−12.7	13.05	−12.7	13.74
−12.4	23.56	−12.4	11.31	−12.3	10.00
−11.4	15.37	−12.2	10.58	−11.4	7.86
−10.6	8.64	−11.9	8.79	−11.0	7.27
−9.5	6.07	−11.3	7.33	−9.9	4.68
−9.0	5.64	−10.9	6.26	−8.8	3.08
		−10.7	5.76		

1e[b]		**1f**[b]		**1g**[c]		**1h**[c]	
H_0	10^5k (s^{-1})	H_0	10^5k (s^{-1})	H_0	10^5k (s^{-1})	H_0	10^5k (s^{-1})
−12.7	23.12	−12.7	54.84	−12.7	66.04	−12.7	52.91
−12.3	17.18	−12.3	36.68	−12.3	46.49	−12.4	43.08
−11.4	12.74	−11.4	27.26	−11.4	30.90	−11.4	29.28
−10.6	7.17	−10.8	20.64	−10.6	19.26	−10.7	18.97
−9.9	5.23	−9.8	12.13	−10.0	14.90	−10.0	15.35
−8.9	3.76	−9.0	10.37	−9.0	10.08	−9.0	8.91

[a] Corrected values of the acidity function of the reaction media (see Table 2 and ref 14). [b] At 0 °C. [c] At 25 °C.

(2) a fairly low level (i.e., concentration) of formation of the diprotonated species.

No deuterium exchange, including the C_2-position, of 1-phenyl-2-propen-1-one (**1a**) was observed in deuterated trifluoromethanesulfonic acid (TFSA-d_1) at 25 °C for 1 h. The 1-indanone (**2a**) formed in TFSA-d_1, after isolation, was found to be monodeuterated at the C_2-position; i.e., no additional deuterium incorporation was observed at the C_2- and C_3–positions. These observations clearly exclude any contribution of protonation of the olefin moiety of 1-phenyl-2-propen-1-one (**1a**) in TFSA. It was also found that no deuterium exchange, in particular of the olefinic carbon atoms, was observed in TFSA-d_1 in the case of chalcone, wherein a phenyl substituent might stabilize the cation (like **6**) formed upon *C*-protonation of the olefin moiety.[12] It was also demonstrated experimentally that *O*,*O*-diprotonation of mesityl oxide (4-methyl-3-penten-2-one) is thermodynamically favored over *O*,*C*-diprotonation.[19] Therefore, the intervention of *O*,*O*-diprotonated species **4** is concluded to be involved in the electrocyclizations of 1-phenyl-2-propen-1-ones **1**. Studies in other[20,21] and our laboratories[12,22] have demonstrated the involvement of superelectrophilic activation due to *O*,*O*-diprotonation of ketones, i.e., oxonium−carbenium dications, in some Friedel−Crafts reactions. The onium−carbenium dication character of **4** leads to increased delocalization of positive charge over the aromatic ring of **4**, resulting in enhanced pentadienium character, which facilitates the ground-state 4π-electrocyclization.

Substituent Effects. As judged from the kinetic data, substituent effects on the reaction rates are rather small among the compounds with aromatic substituents **1b**−**1f** (the deviation of the rates in 100% TFSA is only 6-fold at most), even though substituents on the benzene ring are diverse, from the electron-donating CH_3 to the electron-withdrawing CF_3. These small substituent effects can be interpreted in terms of the concerted nature of the 4π-electrocyclization rather than the polar transition

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(22) Saito, S.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1995**, *117*, 11081−11084.

states of the Friedel−Crafts-type reactions. A close scrutiny reveals a subtle substituent effect: substitution of the benzene ring at the C_1-position (i.e., **1c** and **1d**) retards the reaction to some extent as compared with the unsubstituted case (**1b**), irrespective of the nature of the substituent, an electron-withdrawing CF_3 (**1c**) or an electron-donating CH_3 (**1d**). A substituent on the benzene ring at the C_2-position modifies the reaction in a different manner: the electron-withdrawing CF_3 (**1e**) retards the reaction, and the electron-donating CH_3 (**1f**) enhances the reaction.

Kinetic measurements also revealed slower reactions of the enones **1g** and **1h** bearing alkyl substituents at the C_2-position as compared with the aromatic compounds **1b**−**1f**. Alkyl substituents (**1g** and **1h**) slow the reaction 8−10 times more as compared with **1b** (on the basis of the reaction rates of **1b** in TFSA extrapolated to 25 °C).[23] However, the similarity of the acidity−rate relationships to those of the diphenyl compounds suggests a common reaction mechanism involving the dicationic intermediate. The divergent rate constants of the alkyl compounds are considered to stem from the different basicity of the intermediate (*O*-protonated enones) in terms of the Zucker−Hammett criteria:[16−18] the lower the basicity, the slower the reaction.

***Ab Initio* Calculations of Dicationic Electrocyclization. Protonated 1,4-Pentadien-3-one.** In order to evaluate the geometrical and energetic effects of protonation on the electrocyclization,[24,25] we first carried out *ab initio* calculations based on the density functional theory,[26,27] and the second-order Møller−Plesset perturbation,[29] using 1,4-pentadien-3-one (divinyl ketone) **7** as a simple model (Chart 1). Although the intermediacy of the *O*-monoprotonated divinyl ketones such as **8** is well-established in the Nazarov-type cyclization,[1,2] we assume here a hypothetical *O*,*O*-diprotonation of the divinyl ketone (i.e., **9**) in order to consider the effect of *O*,*O*-diprotonation on geometry and energy. Previous studies[28] showed that several stationary structures of neutral 1,4-pentadien-3-one (divinyl ketone) **7** and *O*-protonated 1,4-pentadien-3-one **8** are possible. In neutral 1,4-pentadien-3-one (divinyl ketone) **7**, the stability of the conformers is in the order *s-cis*,*s-cis* geometry **7c** < *s-trans*,*s-trans*-**7a** < *s-trans*,*s-cis* -**7b**, while in *O*-protonated 1,4-pentadien-3-one **8**, the order is *s-cis*,*s-trans* geometry **8b** < *s-trans*,*s-trans* structure **8a** < *s-cis*,*s-trans* geometry **8c** < the w-shaped **8d** (Chart 1). For example, the *s-cis*,*s-trans* geometry of the *O*-protonated 1,4-pentadien-3-one **8b** is more stable than the *s-trans*,*s-trans* structure **8a**, a direct substrate for the cyclization, by 2.3 kcal/mol (B3LYP/6-31G*) or 0.76 kcal/mol (MP2/6-31G*) (Table 4). Another *s-cis*,*s-trans* geometry (**8c**) is less stable than **8b** (by 1.8 kcal/mol (MP2/6-31G*)). Thus, there are no large energy differences among possible structures. In addition, the barrier to the rotation of the olefin moiety from the minimum energy structure **8b** to **8a** is 7.6 kcal/mol (B3LYP/6-31G*) through the transition structure **8r** (Table 5) (Chart 1). Because the interconversion barrier is rather small, all possible structures of the monocation **8** can exist as an equilibrating mixture, the distribution being diverse. Thus, even though the fraction of **8a** is small, the cyclization will take place from **8a** rather than from the minimum energy structure **8b**.

Upon further *O*-protonation, i.e., *O*,*O*-diprotonation, two possible stationary structures are obtained (Chart 1), the energy difference being small (Table 4): the most favorable geometry of *O*,*O*-diprotonated 1,4-pentadien-3-one **9** is the *s-trans*,*s-trans* geometry **9a** rather than the *s-cis*,*s-trans* counterpart **9b**, the

Table 4. Relative Energies (kcal/mol) of Pentadienyl Cation Derivatives[a]

structure	symmmetry	MP2/6-31G*	+ZPE[b]	B3LYP/6-31G*	+ZPE[c]
8a	C_1	0.52	0.76	2.14	2.31
8b	C_1	0.00	0.00	0.00	0.00
8c	C_1	1.23	1.76		
9a	C_1	0.00	0.00	0.00	0.00
9b	C_1	2.65	2.78	1.05	1.39
10a	C_2	2.85	2.97	4.59	4.57
10b	C_1	0.00	0.00	0.00	0.00

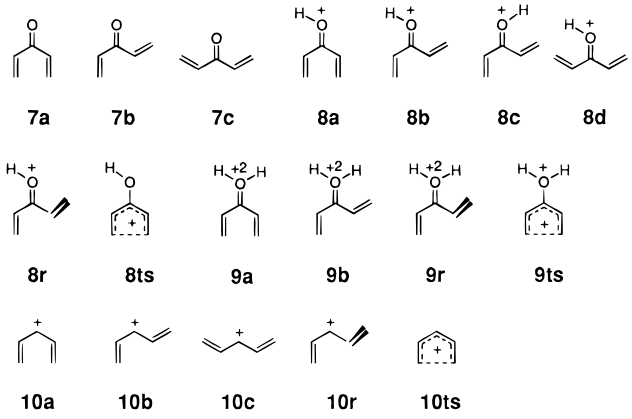
[a] All the structures are minima. [b] Scaled (by 0.95). Reference 29b. [c] Unscaled. Reference 26c.

Table 5. Energy Barriers to Rotation, Protonation, and Conrotatory Electrocyclization of Pentadienyl Cation Derivatives[a]

process	MP2/6-31G*	+ZPE[a]	B3LYP/6-31G*	+ZPE[b]
rotation				
8b → 8r	8.18	6.99	10.40	7.58
9a → 9r	11.03	10.14	11.46	10.71
10b → 10r	17.81	13.84	19.51	13.62
protonation				
8b → 9a	49.97	44.28	52.00	46.50
cyclization				
8a → 8ts	15.39	14.92	18.89	18.27
9a → 9ts	1.87	1.76	6.21	6.16
10a → 10ts	1.26	1.00	5.33	5.03

[a] Scaled (by 0.95). Reference 29b. [b] Unscaled. Reference 26c.

Chart 1



(23) The rate constant of the cyclization reaction of **1b** in TFSA, extrapolated to 25 °C is 52.8×10^{-4} s^{-1}. The rate constants of **1g** and **1h** in TFSA at 25 °C are 6.6×10^{-4} and 5.3×10^{-4} s^{-1}, respectively (see Table 3).

(24) Gaussian 94, Revision B.2: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart,M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.

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(26) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Bauschlicher, Jr.; Paartridge, H. *J. Chem. Phys.* **1995**, *103*, 1788. (d) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian Inc.: Pittsburgh, 1993.

(27) A superior description of transition structures of concerted Diels−Alder cyclizations in terms of density-functional theories rather than MP electron correlations was discussed in Goldstein, E.; Beno, B.; Houk, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 6036−6043.

(28) Smith, D. A.; Ulmer, C. W., II. *Tetrahedron Lett.* **1991**, *32*, 725−728.

(29) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Scott, A. P.: Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345−350. (c) Hehre, W. J.; Radom, L.; Schleyer, P. V. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley and Sons, Inc.: New York, 1986.

(30) The *s-cis* structure **11b** is also favored in the neutral 1-phenyl-2-propenone **11** over the *s-trans* isomer **11a** (1.34 kcal/mol, HF/6-31*, data not shown).

energy difference being 1.4 kcal/mol (B3LYP/6-31G*) or 2.8 kcal/mol (MP2/6-31G*). This *s-trans,s-trans* conformation (**9a**) brings the two terminal carbon atoms close together. The *O*-protonation of the monoprotonated 1,4-pentadien-3-one **8b** to form the *O,O*-diprotonated dication **9a** is found to be exothermic by 46.5 kcal/mol (B3LYB/6-31G*). An interconversion barrier (10.7 kcal/mol (B3LYP/6-31G*)) from the *s-trans,s-trans*-**9a** to *s-cis,s-trans* conformer **9b** is also predicted through the transition structure **9r**, the barrier being accessible (Chart 1). Thus, the possible conformers of the dication **9** can interconvert, with the *s-trans,s-trans* conformer **9a** being predominant.

The structures of the parent pentadienyl cation **10** were also studied previously,[27,31] the order of their stability being as follows: the w-shaped **10c** < the sickle-shaped **10b** < the u-shaped **10a** (Chart 1). The w-shaped **10c** is the global minimum energy structure, and the sickle-shaped **10b** is the next lowest energy structure. The u-shaped **10a**, which is assumed to be the direct substrate for the cyclization, is less stable than **10b** by 4.6 kcal/mol (B3LYP/6-31G*) (Table 4). In addition, the interconversion of **10b** into **10a** through the transition structure **10r** involves a larger barrier (13.6 kcal/mol (B3LYP/6-31G*)) than that of **9a** to **9r** (Chart 1). Even though the fraction of **10a** is very small among the possible conformers, the small activation energy of the cyclization (*vide post*) of **10a** might strongly favor the cyclization. This postulate is consistent with the experimental observation of the facile cyclization reaction of methyl-substituted pentadienyl cations.[3]

The transition structures **8ts** and **10ts** which represent the conrotatory electrocyclization reactions of *O*-protonated 1,4-pentadien-3-one **8** and the parent pentadienyl monocation **10** were identified at the B3LYP/6-31G* and MP2/6-31G* levels (Chart 1 and Table 5). The structures of **8ts** and **10ts** are consistent with those previously obtained.[28,31b] For the sake of comparison, the transition structure representing the conrotatory electrocyclization of *O,O*-diprotonated 1,4-pentadien-3-one **9ts** was also calculated. The resultant activation energy of the cyclization starting from the *s-cis,s-trans O*-protonated divinyl ketone (**8a** to **8ts**) is 18.3 kcal/mol (B3LYP/6-31G*) or 14.9 kcal/mol (MP2/6-31G*), which is larger than that of the parent pentadienium cation (**10a** to **10ts**) (B3LYP/6-31G*, 5.0 kcal/mol; MP2/6-31G*, 1.0 kcal/mol). This is a reasonable outcome of stabilization of the cationic center of the pentadienium cation due to the electron-donating hydroxy oxygen atom. The same conclusion was put forward on the basis of MP3/6-31G* single-point calculations.[28] In contrast, the *O,O*-diprotonated divinyl ketones showed a significantly lower barrier to the cyclization (**9a** to **9ts**) (B3LYP/6-31G*, 6.2 kcal/mol; MP2/6-31G*, 1.8 kcal/mol), which is comparable to that of the parent pentadienyl cation **10**. Futhermore, in terms of the longer distances between the bonding terminal carbon atoms in the transition structures, earlier transition states are predicted in the cases of the parent monocation **10ts** and the oxonium-substituted pentadienyl dication **9ts** as compared with the hydroxy-substituted counterpart **8ts** [B3LYP/6-31G* (MP2/6-31G*)]: **8ts**, 2.109 Å (2.139 Å); **9ts**, 2.290 Å (2.460 Å); **10ts**, 2.314 Å (2.457 Å) (Chart 1). While the *O*-monoprotonated species of the divinyl ketone was identified as a reaction intermediate, and the intervention of the *O,O*-diprotonated divinyl ketone is hypothetical, this energetic comparison demonstrates the activation of the reaction in the dicationic electrocyclization as compared with the monocationic electrocyclization.

Protonated 1-Phenyl-2-propenones. A similar energetic advantage of dicationic electrocyclization is also found in the case of 1-phenyl-2-propenones **1**, for which the kinetic measurements favored the intervention of discrete *O,O*-diprotonated species **4**. We consider here the protonation of the parent 1-phenyl-2-propenone **11** (renumbered from **1a**) (Chart 2). The *O*-protonated 1-phenyl-2-propenone **12** (renumbered from **3a**) has several possible conformers, the energy differences being small (Chart 2): the *s-cis* geometry **12b** with respect to the enone moiety is most favored over other rotamers (**12a**, **12c**, and **12d**). For example, the energy difference between **12b** and the more stable isomer **12a** of the two *s-trans* geometries **12a** and **12c** is 1.0 kcal/mol (B3LYP/6-31G*) or 1.1 kcal/mol (HF/6-31G*) (Table 6).[30] While the *s-cis* isomer **12b** is the minimum energy structure, the interconversion barrier of **12b** to **12c** through the rotational transition structure **12r** is rather small (8.4 kcal/mol (B3LYP)) (Table 7). Thus, all the possible conformers of the monocation **12** can equilibrate, though the fractions of the *s-cis* isomers **12a** and **12c**, both of which are available for the cyclization, are small.

On the other hand, the *O,O*-diprotonated 1-phenyl-2-propenone **13** (renumbered from **4a**) has two stationary structures,

Table 6. Relative Energies (kcal/mol) of Phenylallyl Cation Derivatives[a,d]

structure	symmetry	HF/6-31G*	+ZPE[b]	B3LYP/6-31G*	+ZPE[c]
12a	*C*1	1.11	1.12	0.99	1.03
12b	*C*1	0.00	0.00	0.00	0.00
12c	*C*1	1.80			
12d	*C*1	0.59			
13a	*C*1	0.00	0.00	0.00	0.00
13b	*C*1	1.41	1.31	0.79	0.75
15a	*C*1	0.00	0.00	0.00	0.00
15b	*C*1	2.75	2.76	2.83	2.82
16a	*C*1	0.00	0.00	0.00	0.00
16b	*C*1	3.53	3.53	3.29	3.23

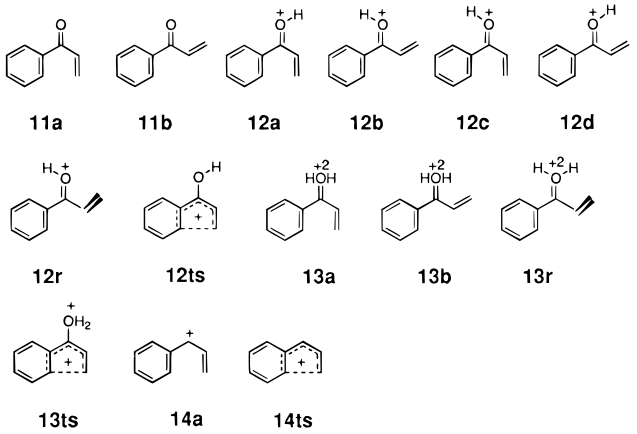
[a] All strucures are minima. [b] Scaled (by 0.95). Reference 29b. [c] Unscaled. Reference 26c.

Table 7. Energy Barriers (kcal/mol) of Rotation, Protonation, and Conrotatory Electrocyclization of Phenylallyl Cation Derivatives

process	HF/6-31G*	+ZPE[a]	B3LYP/6-31G*	+ZPE[b]
rotation				
12b → 12r	9.32	8.73	9.17	8.38
13a → 13r	5.64	5.08	8.16	7.26
protonation				
12b → 13a	66.74	60.76	70.35	64.55
15a → 16a	69.60	64.15	74.23	68.53
cyclization				
12a → 12ts	35.88	35.08	24.60	24.92
13a → 13ts	19.50	19.10	12.69	12.37
14a → 14ts	23.66	23.15	15.21	14.62
15a → 15ts	33.78	32.35	22.43	21.53
16a → 16ts	14.99	14.40	9.48	8.95

[a] Scaled (by 0.95). Reference 29b. [b] Unscaled. Reference 26c.

Chart 2



(31) (a) Schleyer, P. von R.; Bentley, T. W.; Koch, W.; Kos, A. J.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 6953−6957. (b) Kallel, E. A.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 6006−6008.

the *s-trans* geometry **13a** and the *s-cis* geometry **13b**, **13a** being more stable than **13b**: the energy difference between **13a** and **13b** is as small as 0.75 kcal/mol (B3LYP/6-31G*) or 1.3 kcal/mol (HF/6-31G*). The *O*-protonation of the monoprotonated **12b** to form the *O*,*O*-diprotonated enone **13a** is exothermic by 64.6 kcal/mol (B3LYP/6-31G*), which is considerably larger than the calculated proton affinity of *O*,*O*-diprotonation of 1,4-pentadien-3-one (46.5 kcal/mol, **8b** to **9a**). Because the rotation barrier with respect to the olefin moiety from the *s-trans*-**13a** to the *s-cis* conformer **13b** through the rotational transition structure **13r** is not large (7.3 kcal/mol (B3LYP/6-31G*)), the dication **13** should be an equilibrium mixture of structures, with *s-trans*-**13a**, a direct substrate for the cyclization, being favored.

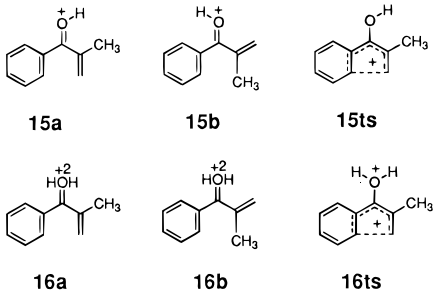
The transition structures **12ts** and **13ts**, representing the conrotatory electrocyclization of the *O*-protonated monocation **12** and the *O*,*O*-diprotonated dication **13**, were identified using B3LYP/6-31G* and HF/6-31G* basis sets (Chart 2). The distances between the two bonding carbon atoms in the transition structures indicate an earlier transition state in the cyclization of the dication **13** as compared with that of the monocation **12** [B3LYP/6-31G* (HF/6-31G*)]: **12ts**, 2.048 Å (2.057 Å); **13ts**, 2.252 Å (2.250 Å). The activation energy of the electrocyclization of the *O*-protonated enone (**12a** to **12ts**) amounts to 24.9 kcal/mol (B3LYP/6-31G*) (HF/6-31G*, 35.1 kcal/mol) (Table 7), which is larger than that of the nonaromatic *O*-monoprotonated 1,4-pentadien-3-one (**8a** to **8ts**) (B3LYP/6-31G*, 18.3 kcal/mol; HF/6-31G*, 15.4 kcal/mol). This indicates the resistance to the electrocyclization of phenyl vinyl ketones, because the participation of the aromatic π-bond in the 3-hydroxy-1,4-pentadiene system is discouraged.

It has been experimentally well-established that phenylallyl cations readily undergo intramolecular cyclization to give the corresponding indenyl cations even in a superacid, where cations are long-lived.[32] The calculated activation energy of this cyclization of the parent phenylallyl cation, from the *s-cis*-**14a** to the transition structure **14ts**, is 14.6 kcal/mol (B3LYP/6-31G*) or 23.2 kcal/mol (HF/6-31G*) (Chart 2). Thus, the electron-donating hydroxy substituent of *O*-protonated 1-phenyl-2-propanone **12** stabilizes the phenylallyl cationic nature, resulting in deactivation of the cyclization. The activation energy of the electrocylization of *O*,*O*-diprotonated 1-phenyl-2-propenone (**13a** to **13ts**) is significantly decreased to 12.4 kcal/mol (B3LYP/6-31G*) or 19.1 kcal/mol (HF/6-31G*) (Chart 2), the barrier being comparable to that of the parent phenylallyl cation **14a**. Therefore, the present calculations support the idea that *O*,*O*-diprotonative activation is requisite for the benzene ring to participate in the Nazarov-type electrocyclization of 1-phenyl-2-propen-1-ones.

As shown experimentally, a substituent at the C_2-position of 1-phenyl-2-propenone facilitates the electrocyclization. A methyl substituent at the C_2-position diminishes the activation energy of the dicationic electrocyclization: the activation energy of the electrocyclization of the *O*,*O*-diprotonated *s-trans*-1-phenyl-2-methyl-2-propenone (**16a**) (renumbered from **4g**) through the transition structure **16ts** is 9.0 kcal/mol (B3LYP/6-31G*) or 14.4 kcal/mol (HF/6-31G*), which is smaller than that of the unsubstituted *O*,*O*-diprotonated *s-trans*-1-phenyl-2-propenone (**13a** to **13ts**) (Tables 6 and 7, Chart 3). A similar reduction of the activation barrier due to the methyl substituent is also found in the cyclization of *O*-protonated *s-trans*-1-phenyl-2-methyl-2-propenone (**15a**) (renumbered from **3g**) as compared to that of *O*,*O*-diprotonated *s-trans*-1-phenyl-2-propenone (**12a** to **12ts**).

(32) (a) Deno, N. C.; Pittman, C. U., Jr.; Turner, J. O. *J. Am. Chem. Soc.* **1965**, *87*, 2153−2157. (b) Olah, G. A.; Asensio, G.; Mayr, H. *J. Org. Chem.* **1978**, *43*, 1518−1520. (c) Prakash, G. K. S.; Krishnamurthy, V. V.; Olah, G. A.; Farnum, D. G. *J. Am. Chem. Soc.* **1985**, *107*, 3928−3935. See also: Bergmann, F.; Israelashwili, S. *J. Am. Chem. Soc.* **1946**, *68*, 1−5.

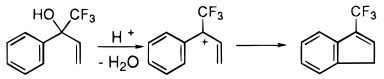
Chart 3



However, the activation barrier of **15a** (21.5 kcal/mol (B3LYP/6-31G*)) is still definitely larger than that of **16a**. The *O*-protonation of the monoprotonated **15a** to form the diprotonated **16a** is exothermic by 68.5 kcal/mol (B3LYP/6-31G*), which is larger by 4 kcal/mol than the proton affinity of the unsubstituted **12b** (to **13a**). This energetic advantage due to the methyl substituent at the C_2-position provides at least a partial rationale for the activation of the cyclization of **1b**−**1h** as compared with the parent 1-phenyl-2-propenone (**1a**).[33]

Conclusion

We found facile and efficient electrocyclization reactions of 1-phenyl-2-propen-1-one and its 2-substituted derivatives to give indanone derivatives, catalyzed by TFSA. The linear acidity−rate relationships observed in the kinetic measurements support the involvement of the oxonium−carbenium dication, i.e., *O*,*O*-diprotonated 1-phenyl-2-propen-1-ones, in the electrocyclizations. *Ab initio* calculations also highlight the energetic favorability of these dicationic electrocyclizations over the monocationic mechanism.



The trifluoromethyl-substituted phenylallyl cation has been shown to generate and to cyclize to the indene derivative under comparably mild conditions (with methanesulfonic acid at 45 °C for 10 min).[34] Therefore, the oxonium group of *O*,*O*-diprotonated 1-phenyl-2-propen-1-ones is considered to behave as *a net electron-withdrawing group* in a manner similar to that of the trifluoromethyl group, *restoring* the intrinsic cyclization reactivity of the phenylallyl cation.

All the results described here are consistent with previous observations that Nazarov-type electrocyclization reactions involving participation of a benzene ring require a strong acid catalyst.[4−7]

Experimental Section

General Methods. All the melting points were measured with a Yanagimoto hot-stage melting point apparatus (MP-500) and are uncorrected. Proton NMR spectra were measured on JEOL GX and GSX 400-MHz NMR spectrometers with TMS as an internal reference in $CDCl_3$ as the solvent. All coupling constants (*J*) are given in hertz in parentheses, and chemical shifts are reported in parts per million. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broad). High-resolution mass spectra (HRMS) were recorded on a JEOL SX-102 instrument. The combustion analyses were carried out in the microanalytical laboratory of this facility.

(33) The rate-enhancing influence of the C_2-substituent is rationalized at least partially in terms of the reduction of the distance (Å) between the terminal carbon and the cyclizing aromatic carbon: (B3LYP/ HF) **16a** (3.146/3.176) as compared with **13a** (3.227/3.248). This compression, probably arising from the C_2-substituent, would reduce the entropy change required for the cyclization.

(34) Gassman, P. G.; Ray, J. A.; Wenthold, P. G.; Mickelson, J. N. *J. Org. Chem.* **1991**, *56*, 5143−5146.

Trifluoromethanesulfonic acid (TFSA) was purchased from Central Glass Co., Japan, and used after distillation twice under reduced pressure with a Widmer condenser (bp 98 °C, 60 mmHg). Trifluoroacetic acid (TFA) was obtained from Wako Pure Chemicals Co., Japan, and was distilled at atomospheric pressure in the presence of a trace amount of potassium permanganate (0.1 g per 1 kg of the acid), followed by another distillation at atomospheric pressure without potassium permanganate (bp 72.5 °C).[13]

Preparation of 1-Phenyl-2-propen-1-one Derivatives. The precursors of 1-phenyl-2-propen-1-ones, i.e., 2-subsitituted 3-(dimethylamino)-1-propiophenones, were prepared by means of the Mannich reaction as previously described.[10] The hydrochloride salts of the precursor amine (prepared by dissolving in 4 N aqueous HCl) were transformed to 2-substituted 1-phenyl-2-propen-1-ones **1a**−**1h** by the elimination of the dimethylamine group, during steam distillation (in the case of **1a**) or in the presence of sodium acetate at 95 °C for 15 min (in the cases of **1b**−**1h**).[8,10]

1-Phenyl-2-propen-1-one (**1a**): ^{1}H-NMR δ 5.94 (1H, dd, 1.8, 10.6 Hz), 6.45 (1H, dd, 1.8, 17.2 Hz), 7.17 (1H, dd, 10.6, 17.2 Hz), 7.49 (2H, td, 1.5, 7.7 Hz), 7.58 (1H, tt, 2.2, 7.3 Hz), 7.95 (2H, dd, 1.3, 8.2 Hz); HRMS calcd for C_9H_8O 132.058, found 132.057.

1,2-Diphenyl-2-propen-1-one (**1b**): mp 29 °C (recrystallized from MeOH); ^{1}H-NMR δ 5.65 (1H, s), 6.08 (1H, s), 7.32−7.38 (3H, m), 7.41−7.46 (4H, m), 7.54 (1H, tt, 1.3, 7.3 Hz), 7.91 (2H, dt, 1.5, 7.0 Hz). Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.35; H, 5.76.

2-Phenyl-1-[4-(trifluoromethyl)phenyl]-2-propen-1-one (**1c**): mp 62−63 °C (recrystallized from *n*-hexane); ^{1}H-NMR δ 5.71 (1H, s), 6.14 (1H, s), 7.34−7.41 (5H, m), 7.70 (2H, d, 8.4 Hz), 7.98 (2H, d, 8.1 Hz). Anal. Calcd for $C_{16}H_{11}F_3O$: C, 69.56; H, 4.01. Found: C, 69.33; H, 3.93.

1-(4-Methylphenyl)-2-phenyl-2-propen-1-one (**1d**): bp 129−135 °C, 0.07 mmHg; ^{1}H-NMR δ 2.40 (3H, s), 5.60 (1H, s), 6.03 (1H, s), 7.23 (2H, d, 7.7 Hz), 7.31−7.36 (3H, m), 7.42 (2H, dd, 1.7,7.9 Hz), 7.82 (2H, d, 8.4 Hz). Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.19; H, 6.21.

1-Phenyl-2-[4-(trifluoromethyl)phenyl]-2-propen-1-one (**1e**): mp 48−49 °C (recrystallized from MeOH); ^{1}H-NMR δ 5.79 (1H, s), 6.18 (1H, s), 7.46 (2H, td, 1.5, 7.7 Hz), 7.55 (2H, d, 8.1 Hz), 7.59 (1H, td, 1.1, 7.3 Hz), 7.62 (2H, d, 8.4 Hz), 7.90 (2H, td, 1.5, 8.1 Hz). Anal. Calcd for $C_{16}H_{11}F_3O$: C, 69.56; H, 4.01. Found: 69.57; H, 3.75.

1-(4-Methylphenyl)-1-phenyl-2-propen-1-one (**1f**): mp 35 °C (recrystallized from *n*-hexane); ^{1}H-NMR δ 2.34 (3H, s), 5.58 (1H, s), 6.02 (1H, s), 7.15 (2H, d, 7.7 Hz), 7.31 (2H, d, 8.1 Hz), 7.42 (2H, tt, 1.5, 7.5 Hz), 7.54 (1H, tt, 1. 5, 7.3 Hz), 7.90 (t 2H,d, 1.7, 8.4 Hz). Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.33; H, 6.09.

2-Methyl-1-phenyl-2-propen-1-one (**1g**): bp 60 °C, 3 mmHg; ^{1}H-NMR δ 2.08 (3H, s), 5.63 (1H, s), 5.92 (1H, d, 1.5 Hz), 7.43 (2H, t, 7.5 Hz), 7.53 (1H, t, 7.3 Hz), 7.73 (2H, dd, 1.5, 7.0 Hz); HRMS calcd for $C_{10}H_{10}O$ 146.073, found 146.071.

2-Ethyl-1-phenyl-2-propen-1-one (**1h**): bp 85 °C, 5 mmHg; ^{1}H-NMR δ 1.13 (3H, t, 7.3 Hz), 2.50 (2H, q, 7.5 Hz), 5.58 (1H, d, 0.73 Hz), 5.83 (1H, s), 7.43 (2H, tt, 1.8, 7.5 Hz), 7.54 (1H, tt, 1.7, 7.5 Hz), 7.76 (2H, td, 1.7, 7.0 Hz); HRMS calcd for $C_{11}H_{12}O$ 160.089, found 160.088.

Acid-Catalyzed Cyclization Reactions. Reaction of 1-Phenyl-2-propen-1-one (1a) in TFSA. 1-Phenyl-2-propen-1-one (**1a**) (134 mg, 1 mmol) was added to TFSA ((9.0 mL, 100 mmol) at 25 °C with stirring. The resultant solution was stirred at 25 °C for 120 h. The whole was poured into ice−water and extracted with CH_2Cl_2 (150 mL). The organic layer was washed with brine (100 mL), dried over Na_2SO_4, filtered, and evaporated to give a residue, which was flash-chromatographed (CH_2Cl_2−*n*-hexane 1:2 to 1:1) to give 1-indanone (**2a**) (84 mg, 63% yield), together with recovered **1a** (8 mg, 6% yield). **2a**: mp 40−42 °C (recrystallized from *n*-hexane); ^{1}H-NMR δ 2.70 (2H, t, 5.9 Hz), 3.15 (2H, t, 5.5 Hz), 7.37 (1H, t, 7.7 Hz), 7.48 (1H, d, 7.7 Hz), 7.59 (1H, t, 7.7 Hz), 7.77 (1H, d, 7.7 Hz); HRMS calcd for C_9H_8O 132.058, found 132.057.

Reaction of 1,2-Diphenyl-2-propen-1-one (1b) in TFSA. 2b: mp 76−77 °C (recrystallized from *n*-hexane); ^{1}H-NMR δ 3.28 (1H, dd, 4.0, 17.6 Hz), 3.70 (1H, dd, 8.1, 17.6 Hz), 3.91 (1H, dd, 4.0, 8.4 Hz), 7.19 (2H, dt, 1.5, 7.0 Hz), 7.26 (1H, tt, 1.5, 7.4 Hz), 7.33 (2H, tt, 1.5, 7.2 Hz), 7.43 (1H, t, 7.0 Hz), 7.54 (1H, d, 7.7 Hz), 7.66 (1H, td, 1.1, 7.6 Hz), 7.82 (1H, d, 7.7 Hz). Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.60; H, 5.73.

Reaction of 2-phenyl-1-[4-(trifluoromethyl)phenyl]-2-propen-1-one (1c) in TFSA. 2c: mp 145−146 °C (recrystallized from CH_2Cl_2−*n*-hexane); ^{1}H-NMR δ 3.36 (1H, dd, 4.2, 17.8 Hz), 3.77 (1H, dd, 8.4, 18.0 Hz), 3.97 (1H, dd, 4.4, 8.4 Hz), 7.18 (2H, d, 7.7 Hz), 7.28 (1H, dt, 0.7, 7.0 Hz), 7.34 (2H, t, 7.5 Hz), 7.69 (1H, d, 8.1 Hz), 7.82 (1H, s), 7.92 (1H, d, 8.1 Hz); HRMS calcd for $C_{16}H_{11}F_3O$ 276. 076, found 276.075.

Reaction of 1-(4-methylphenyl)-2-phenyl-2-propen-1-one (1d) in TFSA. 2d: mp 70−71 °C (recrystallized from *n*-hexane); ^{1}H-NMR δ 2.48 (3H, s), 3.21 (1H, dd, 4.0, 17.6 Hz), 3.64 (1H, dd, 8.2, 17.4 Hz), 3.88 (1H, dd, 3.9, 8.2 Hz), 7.18 (2H, td, 1.5, 7.0 Hz), 7.23−7.26 (2H, m), 7.29−7.33 (3H, m), 7.72 (1H, d, 7.7 Hz). Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.61; H, 6.33.

Reaction of 1-Phenyl-2-[4-(trifluoromethyl)phenyl]-2-propen-1-one (1e) in TFSA. 2-[4-(Trifluoromethyl)phenyl]-1-indanone (**2e**): mp 91−92 °C (recrystallized from *n*-hexane); ^{1}H NMR δ 3.28 (1H, dd, 4.2, 17.4 Hz), 3.73 (1H, dd, 8.4, 17.2 Hz), 3.97 (1H, dd, 4.4, 8.4 Hz), 7.32 (2H, d, 8.1 Hz), 7.45 (1H, t, 7.0 Hz), 7.55 (1H, d, 7.7 Hz), 7.58 (2H, d, 8.1 Hz), 7.68 (1H, dt, 1.1, 7.3 Hz), 7.83 (1H, d, 7.3 Hz). Anal. Calcd for $C_{16}H_{11}F_3O$: C, 69.56; H, 4.01. Found: C, 69.58; H, 3.98.

Reaction of 1-(4-Methylphenyl)-1-phenyl-2-propen-1-one (1f) in TFSA. 2-(4-Methylphenyl)-1-indanone (**2f**): mp 75−76 °C (recrystallized from *n*-hexane); ^{1}H-NMR δ 2.32 (3H, s), 3.25 (1H, dd, 4.1, 17.3 Hz), 3.68 (1H, dd, 8.3, 17.3 Hz), 3.86 (1H, dd, 4.1, 8.3 Hz), 7.07 (2H, d, 8.1 Hz), 7.13 (2H, d, 8.5 Hz), 7.42 (1H, t, 7.5 Hz), 7.52 (1H, d, 7.7 Hz), 7.64 (1H, t, 7.5Hz), 7.81 (1H, d, 7.3 Hz). Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.21; H, 6.33.

Reaction of 2-Methyl-1-phenyl-2-propen-1-one (1g) in TFSA. 2-Methyl-1-indanone (**2g**): bp 93−95 °C, 4 mmHg; ^{1}H-NMR δ 1.32 (3H, d, 7.3 Hz), 2.70−2.77 (2H, m), 3.41 (1H, dd, 8.8, 18.0 Hz), 7.37 (1H, t, 7.3 Hz), 7.46 (1H, d, 7.7 Hz), 7.59 (1H, dt, 1.1, 7.5 Hz), 7.76 (1H, d, 7.7 Hz); HRMS calcd for $C_{10}H_{10}O$ 146.073, found 146.071.

Reaction of 2-Ethyl-1-phenyl-2-propen-1-one (1h) in TFSA. 2-Ethyl-1-indanone (**2h**): bp 90 °C, 3.5 mmHg; ^{1}H-NMR δ 1.02 (3H, dt, 0.86, 7.5 Hz), 1.52−1.58 (1H, m), 1.95−2.00 (1H, m), 2.60−2.64 (1H, m), 2.83 (1H, dd, 3.7, 17.2 Hz), 3.32 (1H, dd, 8.1, 17.2 Hz), 7.36 (1H, t, 7.5 Hz), 7.46 (1H, dd, 0.7, 7.0 Hz), 7.58 (1H, t, 7.5 Hz), 7.75 (1H, d, 7.7 Hz); HRMS calcd for $C_{11}H_{12}O$ 160.089, found 160.093.

Kinetic Measurement. A mixture of the acid, TFSA, and TFA was prepared in a polyethylene glovebox (AtomosBag, Aldrich) under an argon atmosphere. To a weighted phenyl vinyl ketone (typically 6−10 mg) was added a precooled acid mixture (−45 °C, dry ice and acetonitrile) (100 equiv, typically 2 mL) in the dry glovebox. After a good solution was obtained, the solution was transferred to an NMR tube which involved a small quantity of methanol-free methylene chloride, as an internal standard of signal integrations. The spectra were recorded at a specified temperature. The NMR probe temperature was controlled with a variable-temperature apparatus, NM-ALTAS/L and NM-AVT1A (JEOL, Japan). Errors in the controlled temperature were ±0.1 °C. The disappearance of the starting material was monitored in terms of signal integration, with a GSX 500-MHz NMR spectrometer.

Computational Methods. Geometries were initially optimized without any symmetry restriction (except **10a** and **10ts** (C_2 symmetry)) with the split valence HF/3-21G basis set, and with the heavy atom d-polarized HF/6-31G* basis set.[24] The geometries were further optimized with a hybrid density-functional theory method, Becke3-LYP (B3LYP) with the HF/6-31G* optimized geometries.[26] In the cases of divinyl derivatives **8**−**10** the structures were also optimized in the second-order Møller−Plesset (MP2(Full)) perturbation. All the structures of the reactants shown in Tables 4 and 6 were minima, and the transition structures which represent rotation and cyclization processes were characterized by frequency calculations. Zero-point vibrational energies (ZPE) were scaled by 0.95 in the cases of the HF and MP2 levels, and unscaled in the case of the B3LYP level.[29]

Supporting Information Available: Tables of total energies and figures of optimized stuctures (6 pages). See any current masthead page for ordering and Internet access instructions.

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