Superacid-Catalyzed Electrocyclization of Diphenylmethyl Cations to Fluorenes. Kinetic and Theoretical Revisit Supporting the Involvement of Ethylene Dications

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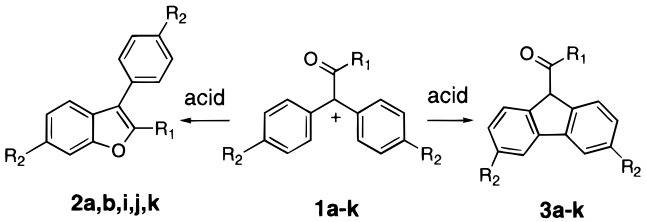
Received January 8, 1998

Abstract: In superacid media, diphenylmethyl cations bearing an α-carbonyl group generate fluorene compounds. We have obtained chemical evidence showing the acidity dependence of this fluorene cyclization process. A linear relationship was found between the rate of the fluorene cyclization and the acidity of the reaction media in kinetic studies, strongly supporting the intervention of an additional proton transfer to the diphenylmethyl monocation in the fluorene cyclization, that is, the involvement of a dication in the form of the diphenylmethyl cation bearing an O-protonated carbonyl group. Ab initio calculations employing Becke3-LYP density functional theory provided theoretical support for the idea that the dicationic fluorene cyclization is energetically more favorable than monocationic electrocyclization to give the benzofuran or the fluorene. The magnitudes of the predicted activation barriers of the dicationic fluorene cyclization are compatible with the experimental values for the fluorene cyclization and with the experimental dependence of the reaction aptitude on the α-carbonyl substituent (ester, acid, or acetyl group).

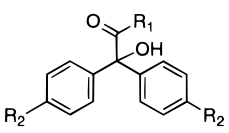
Introduction

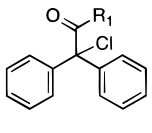
Diphenylmethyl cations (**1**) and related diarylmethyl cations substituted with electron-withdrawing groups constitute a typical class of destabilized cations, i.e., carbocations bearing electron-withdrawing groups directly attached to the carbenium center.[1] The prototype diphenylmethyl cations (**1** (R_2 = H)) bearing electron-withdrawing substituents have been generated in the presence of acids,[3] or more recently by flash-laser photolysis,[4] and characterized as discrete stable ions. The cations **1** were proposed to undergo three modes of reaction depending on the electron-withdrawing substituent (Scheme 1): (1) cyclization to form benzofurans, (2) cyclization to give fluorenes, and (3) electrophilic reaction onto the carbenium center. Unresolved discrepancies were encountered in the former two cyclization reactions with respect to the reaction conditions, the substituent effect, and in particular, the reactive intermediates. In the case of the cations substituted with a ketone (for example, **1a** and **1i**), it was reported that α-benzoyldiphenylmethanol **4a** and α-acetyldiphenylmethanol **4i** in $CHCl_3/H_2SO_4$ underwent electrocyclization between the benzene ring and the carbonyl group (Scheme 2), resulting in the formation of benzofurans **2a** and **2i**, respectively,[3,5] although the formation of the fluorene derivative **3a** has also been reported from **4a** under similar conditions.[6] In contrast to this heteroatom cyclization process, the acid, ester, and amide analogues underwent electrocyclic coupling of the two aromatic rings, leading to the fluorene

Scheme 1



a: R_1=Ph R_2=H
b: R_1=p-anisyl R_2=OCH_3
c: R_1=OCH_3 R_2=H
d: R_1=OCH_3 R_2=Br
e: R_1=OCH_3 R_2=CH_3
f: R_1=OCH_3 R_2=F
g: R_1=OH R_2=H
h: R_1=OH R_2=CH_3
i: R_1=CH_3 R_2=H
j: R_1=CH_3 R_2=CH_3
k: R_1=H R_2=H





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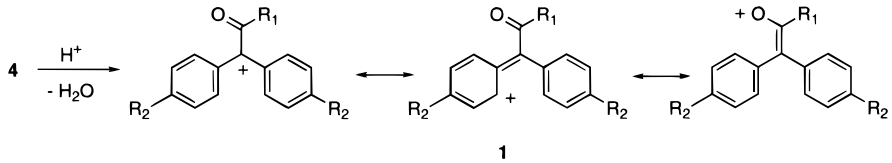
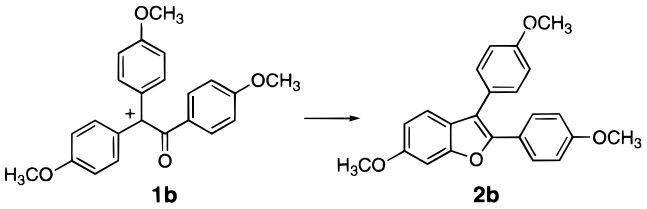
S0002-7863(98)00090-0 CCC: $15.00
Published on Web 04/30/1998

Scheme 2



Scheme 3



derivatives: for example, α-(methoxycarbonyl)diphenylmethanol **4c** gave 9-(methoxycarbonyl)fluorene **3c**.[3,7] These cyclizations were proposed to take place through the monocation **1**.[3]

The isolation of the relevant carbocation, the di-*p*-anisyl(*p*-methoxybenzoyl)methyl cation **1b** (R_1 = *p*-methoxyphenyl, R_2 = OCH_3), as a stable crystalline antimony pentafluoride salt was reported by Takeuchi et al., who showed that heating of the salt **1b** in a neutral solvent such as 1,2-dichloroethane gave the benzofuran **2b** (Scheme 3).[2] This study clearly demonstrated that the benzofuran cyclization of the cation **1** does not require acid catalysis.

A decade ago, the chemical behaviors of the monocations **1**, generated under neutral and strongly acidic conditions were reported from this laboratory[8] and were divergent from those described above: α-benzoyldiphenylmethanol **4a** (R_1 = Ph, R_2 = H), a precursor of the unsubstituted cation (**1a**), reacted in trifluoromethanesulfonic acid (TFSA) at −50 °C to afford the fluorene **3a**, along with the phenanthrene derivative, 9-phenylphenanthr-10-ol. No benzofuran was obtained in TFSA. This superacid-catalyzed fluorene cyclization of **4a** was also reported by Olah and Wu in the same acid,[9] although the yields were a little different. The monocation **1a** could be generated as a stable entity at −50 °C by the reaction of the α-chloro ketone **5** with silver salts. However, no fluorene or benzofuran was formed under these neutral conditions. When the stable cation was added to TFSA at −50 °C, the fluorene and the phenanthrene were produced. This led to the proposals that the fluorenes **3** do not arise directly from the monocation **1** and that the real intermediate is the dication **6** (Scheme 4), formed by protonation of the α-carbonyl group by TFSA, although an attempt at direct spectroscopic observation of the dication (**6a** and **6c**) was unsuccessful.[8] Since the review of these discrepancies in the behavior of the cations **1** in *Chemical Reviews* by Creary,[1a] there has been no advance toward achieving a consistent understanding of the features of the acid-catalyzed fluorene cyclization. This cyclization represents an acid-catalyzed electrocyclization wherein two aromatic rings participate and is of synthetic interest.[3b] Here we revisit the superacid-catalyzed cyclization of the diphenylmethyl cations **1**, aiming (1) to establish chemically and kinetically the acidity dependence of the fluorene cyclizations, and the intervention of an additional proton transfer to the monocation **1**, and (2) to demonstrate theoretically the energetic favorability of the dicationic electrocyclization to give the fluorene over the monocationic electrocyclization to give the benzofuran or the fluorene. We also show that the magnitudes of the predicted activation barriers of the dicationic fluorene cyclization are consistent with the experimental values for the fluorene cyclization and with the observed dependence of the reaction aptitude on the α-carbonyl substituent (ester, acid, or acetyl group).

Results

Acidity Dependence of the Reactions. Formation of 9-(methoxycarbonyl)fluorene **3c** was observed when α-(methoxycarbonyl)diphenylmethanol **4c** was dissolved in TFSA at −45 °C.[8] The cyclization depends on the acidity of the reaction medium, as judged from the yields of the product (Table 1). In TFA ($H_0 \approx -2.7$), the cyclization of **4c** to give the fluorene **3c** did not take place. As the acidity was increased to $H_0 \approx -11.8$ (56% TFSA- 44% TFA), the reaction of **4c** started, though slowly. The reaction in TFSA was rapid, and the fluorene **3c** was formed in high yield. A similar acceleration of the reaction with increase of the acidity was observed in the cases of the bis(*p*-bromophenyl) (**4d**) and bis(*p*-methylphenyl) (**4e**) derivatives. The cyclization of α-(methoxycarbonyl)bis(*p*-fluorophenyl)methanol **4f** in TFSA was slow, and the yield was moderate.

The pK_{R^+} values of the α-carbonyl-substituted monocations **1** are not available,[4] while those of the parent diphenylmethyl cations are −6.9 (diphenylmethyl cation), −7.2 (bis(*p*-chlorophenyl)methyl cation), and −5.1 (bis(*p*-methylphenyl)methyl cation),[12] as calibrated in terms of the H_0 scale.[13] The pK_{R^+} value of the dibromo derivative bearing an α-ester (**4d**) is estimated to be around −10 (H_0) on the basis of the following observation: a solution of the bis(*p*-bromophenyl)methanol **4d** in 40% TFSA−60% TFA ($H_0 \approx -11$, 1000 equiv of the acid), prepared at −45 °C, was quenched with a large excess of methanol to give, in 94% yield, a methoxy derivative, which is formed by the addition of methanol to the corresponding bis(*p*-bromophenyl)methyl cation **1d**. This experiment suggests at least 90% ionization of the alcohol **4d** to the cation **1d** at $H_0 \approx -11$. If substitution of an ester group in the diphenylmethanols has a consistent retarding effect upon ionization to the diphenylmethyl cations, the pK_{R^+} values of the alcohols bearing an α-ester group (**4**) should be around −10 (**4c**) and −8 (**4e**), respectively.

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Scheme 4

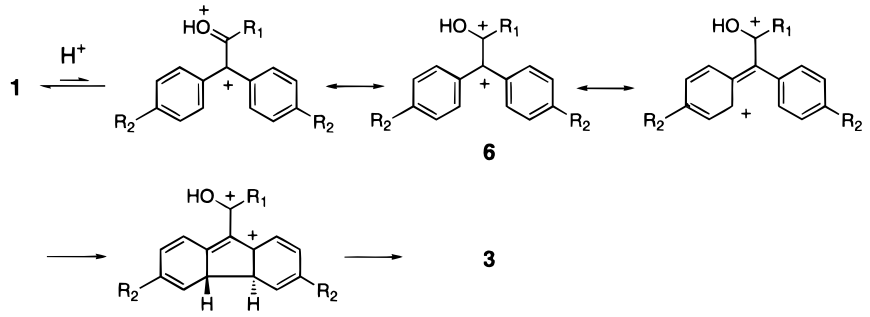

Table 1. Acid-Catalyzed Cyclization of Diarylmethanols Substituted with a Carbonyl Group and Its Acidity Dependence

	R_1	R_2	acid	$-H_0$[a]	time (h)	temp (°C)	recovery (%)	yield (%)
4c	OCH_3	H	TFA	2.7	1	−20	100	0
			56% TFSA−44% TFA	11.8	1	−45	75	20
			TFSA	13.2	1	−45	0	94[b]
4d	OCH_3	Br	54% TFSA−46% TFA	12.0	5	10	47	49
			TFSA	13.2	5	10	0	100
4e	OCH_3	CH_3	31% TFSA−69% TFA	11.0	5	0	80	15
			TFSA	13.2	5	0	0	94[c]
4f	OCH_3	F	TFSA	13.2	144	20	0	44
4g	OH	H	TFSA	13.2	1	0	0	65[d]
4h	OH	CH_3	TFSA	13.2	2	−20	0	82[e]
4i	CH_3	H	55% TFSA−45% TFA	12.0	15 min	−45	65	19[f]
			TFSA	13.2	15 min	−45	0	86[g,h]
4j	CH_3	CH_3	30% TFSA−70% TFA	10.9	15 min	−45	79	0[i]
			TFSA	13.2	15 min	−45	0	65[j]

[a] Corrected values of acidity function of the reaction media (see Table 7 and ref 10). [b] 81% yield (ref 8a). [c] 94% (ref 8b). [d] Reference 8a. [e] Reference 8b. [f] The fluorene dimer (**7**) (see the Experimental section) (16%) and fluorene (3%). [g] 70% yield (ref 8a). [h] The fluorene dimer (**7**) is also formed (1.8%). [i] Benzofuran (**2j**) 1.5%. [j] Benzofuran (**2j**) 6.5%.

Similarly, benzilic acid (**4g**) was reported to give fluorene-9-carboxylic acid in 65% yield in TFSA[8a] and α-carboxybis(*p*-methylphenyl)methanol (**4h**) gave the fluorene **3h** in 82% yield in TFSA.[8b] The reaction of **4h** was faster than that of the corresponding ester **4e** under similar reaction conditions (in TFSA), the ratio being approximately 9 (**4h**/**4e**).[8b] The observed rate ratio is due to the inductive stabilization of the cationic intermediate by the substituent (CH_3) at the carbonyl group.

α-Acetyldiphenylmethanol **4i** also gave 9-acetylfluorene **3i** (86% yield) in TFSA at −45 °C, indicating that the benzoyl group is not necessary for the fluorene formation (Table 1).[8,14] At $H_0 \approx -12.0$ (in 55% TFSA−45% TFA), the reaction is very slow. In TFSA ($H_0 \approx -13.2$) the reaction was accelerated, being completed within 15 min. The reaction of α-acetylbis(*p*-methylphenyl)methanol **4j** is also dependent on the acidity of the medium: in 30% TFSA−70% TFA ($H_0 \approx -10.9$), the reaction is too slow to detect, although ionization to the bis(*p*-methylphenyl)methyl cation **1j** should occur to a large extent, as judged from the estimated pK_{R^+} value (−8) of the bis(*p*-methylphenyl)methanol **4e**. Under this condition, a trace (1.5% yield) of the benzofuran derivative **2j** was detected. In TFSA ($H_0 \approx -13.2$), the fluorene cyclization was very rapid (the yield was increased to 65% yield) and was accompanied with the formation of the benzofuran derivative **2j** (6.5% yield). The isolated benzofuran derivative **2j** was stable in TFSA at −30 °C for 1 h (monitored by ^1H NMR spectroscopy), showing no transformation to the fluorene derivative **3j**. These results indicate that the benzofuran cyclization of the bis(*p*-methylphenyl)methyl monocation **1j** is much slower at −45 °C than the fluorene cyclization. The fluorene cyclization reactions of the α-acetyl derivatives were too fast even at −45 °C to allow kinetic measurements to be made (vide infra), in contrast to those of the ester analogues. Therefore the experimental reaction aptitude for the fluorene cyclization is in the order ester < acid ≪ acetyl. Nevertheless, the similar acidity dependences of the reaction of the α-acetyl cations (**1i** and **1j**) strongly suggest a similar reaction mechanism of the cyclization to that in the case of the ester derivatives.

Table 2. Rate Constants for Acid-Catalyzed Cyclizations of **4c**−**e**[a,b]

4c[c]		**4d**[c]		**4e**[c]	
H_0	10^5k (s^{-1})	H_0	10^5k (s^{-1})	H_0	10^5k (s^{-1})
−12.7	82.55	−13.2	11.34	−13.2	37.20
−12.6	70.96	−12.7	6.35	−12.7	24.04
−12.2	39.53	−12.6	5.55	−11.7	6.32
−11.9	21.83	−12.2	3.38	−11.5	2.78
−11.7	15.58	−11.9	1.77	−11.1	1.46
		−11.6	1.19	−10.7	0.61
		−11.3	0.75		

[a] Corrected values of acidity function of the reaction media (see Table 7 (Experimental Section) and refs 10 and 11). [b] Errors of rates, ±2%. [c] At 0 °C.

Kinetic Evidence for Proton Transfer in the Fluorene Cyclization. We measured the reaction rates of the fluorene cyclization of several α-methoxycarbonyldiarylmethanols (**4c**, **4d**, and **4e**) in the TFSA−TFA acid system (Table 2). The acidity rate profiles of the reactions of the α-(methoxycarbonyl)diphenylmethyl cation **1c** and the α-(methoxycarbonyl)bis(*p*-bromophenyl)methyl cation **1d** were linear, with slopes of 0.71 and 0.63, respectively (Figure 1). This linearity supports the intervention of the additional proton transfer to the diphenyl-

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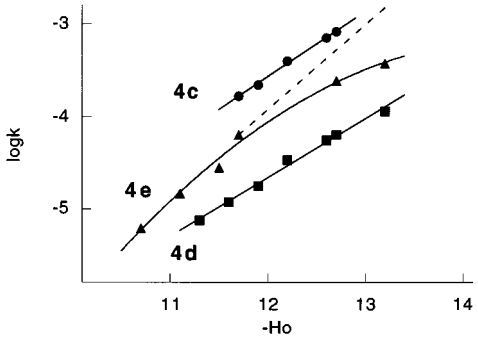

Figure 1. Acidity rate profiles of the fluorene cyclizations.

methyl cations in the cyclization, in accordance with the Zucker−Hammett criteria.[11,15−17] The α-(methoxycarbonyl)-bis(*p*-methylphenyl)methyl cation **1e** also showed a linear acidity rate profile in the region between −10.6 and −11.7 (H_0), the slope being 0.92. This linear acidity rate dependence again indicates the intervention of the additional proton transfer. However, in the dimethyl case, distinct curvature of the plot appears in the acidity region higher than −12 (Figure 1). This can be interpreted in terms of a leveling effect, i.e., the concentration of the dicationic species **6e** is increased significantly in the highly acidic medium, as judged from the estimated pK_{BH^+} value (vide infra).[18] In TFSA−SbF_5 (2.5:1) a proton on the carbonyl group of the bis(*p*-methylphenyl)methyl cation **1e** was observed in the NMR spectrum, supporting the formation of the dication **6e**.[8] A comparison of the chemical shifts of the ions formed in TFSA with those of the dication formed in TFSA−SbF_5 acid indicated the discrete formation of the dication **6e** in TFSA at −30 °C.[8] The acidity of TFSA−SbF_5 (2.5:1) is stronger than −16 (H_0 < −16), so the pK_{BH^+} of the diphenylmethyl cation **1e** is estimated to be around −12 to −13. This stable formation of the dication **6e** can be attributed to conjugative stabilization by the two methyl substituents on the phenyl groups. Such acidity rate behavior is also compatible with the Zucker−Hammett criteria, which predict linearity when the concentration of the active species is low.[15]

The fact that the reaction of the dimethyl substrate **4e** was slower than that of unsubstituted **4c** despite the higher basicity of the monocation **1e** (as an oxygen base) supports the involvement of a rate-determining cyclization process, rather than a rate-determining protonation.[19]

Theoretical Evaluation of the Fluorene and Benzofuran Cyclizations. The effects of protonation on the structures and electrocyclization reactions were evaluated on the basis of the ab initio calculations employing the density functional theory.[20,21]

Diphenylmethyl Monocations. Becke3-LYP/6-31G*-optimized structures of the experimentally examined diphenylmethyl cations bearing α-methoxycarbonyl (**1c**), α-carboxyl (**1g**), α-acetyl (**1i**), and the simplest substituent α-formyl (**1k**), are shown in Figure 2.[20] With respect to the isomerism of the

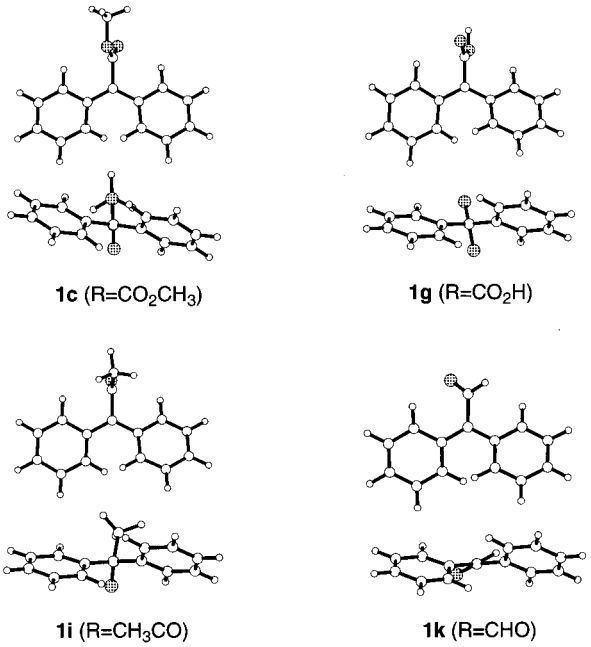

Figure 2. B3LYP/6-31G*-optimized structures of diphenylmethyl monocations substituted with an α-carbonyl group (R) (above, top view; below, side view).

hydroxyl group in the carboxyl substituent, the species **1g** has *s-cis* conformation. The *s-trans* conformation with respect to the hydroxyl group is higher in energy by 11.2 kcal/mol (HF/3-21G, data not shown) than the *s-cis* conformation **1g**. Thus, we focus on the *s-cis* conformer **1g** hereafter. These energy-minimized structures (**1c**,**1g**, **1i**, and **1k**) show a tendency to take bisected forms with respect to the central C−C bond. The transition structures (**ts1**) were also identified at the Becke3-LYP/6-31G* level (Figure 3) and represent those of the conrotatory electrocyclization reactions of the diphenylmethyl monocations to yield the fluorenes in the cases of the methoxycarbonyl (**1c-ts1**), the carboxyl (**1g-ts1**), the acetyl (**1i-ts1**), and the formyl (**1k-ts1**) substituents. The transition structures (**ts2**) which represent the cyclization to give the benzofurans were also located in the cases of the acetyl (**1i-ts2**) and the formyl substituents (**1k-ts2**). The predicted activation energies (B3LYP/6-31G*+ZPE) for the fluorene cyclizations are 22.7 kcal/mol (for the ester, **1c** → **1c-ts1**), 21.6 kcal/mol (for the carboxyl group, **1g** → **1g-ts1**), 25.0 kcal/mol (for the acetyl group, **1i** → **1i-ts1**), and 21.9 kcal/mol (for the formyl group, **1k** → **1k-ts1**), respectively (Tables 3 and 4). The distances between the cyclizing aromatic carbon atoms (**1i-ts1**, 1.951 Å < **1c-ts1**, 1.963 Å < **1k-ts1**, 1.966 Å < **1g-ts1**, 1.972 Å) also correspond well to an early location of the transition states along the reaction coordinate (the earlier the transition state, the less exothermic the reaction, as represented in terms of the predicted activation barrier) (see also Figure 5). The activation energies of the benzofuran cyclization are 17.0 kcal/mol (for the acetyl group, **1i** → **1i-ts2**, B3LYP/6-31G* + ZPE), and 17.9 kcal/

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(18) A referee pointed out that a straight line (slope 0.72) rather than a curved line is obtained even in the case of **4e**, if all six data are used. Although the correlation coefficient is high (regression coefficient r = 0.986), we prefer to interpret the kinetic data in the high-acidity region in terms of leveling-off, because of our experimental observations by NMR spectroscopy of the facile formation of the relevant dication (ref 8).

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

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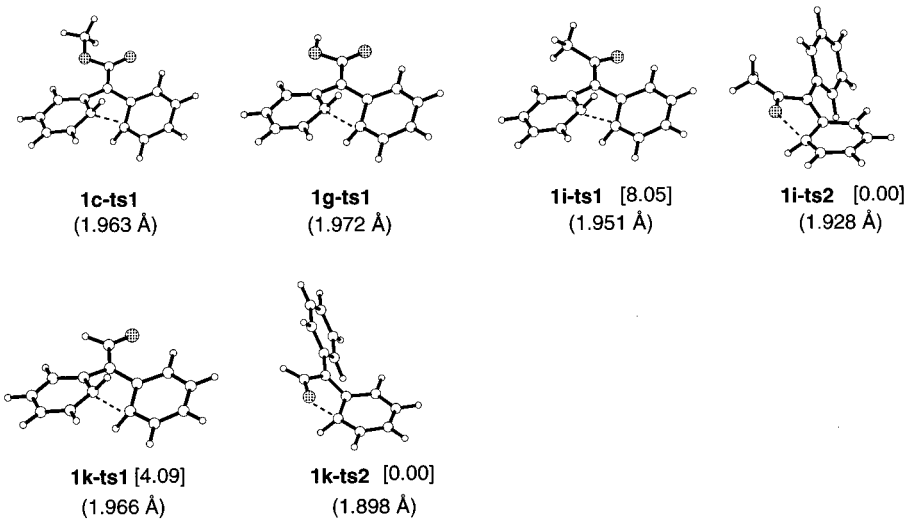


Figure 3. B3LYP/6-31G*-optimized transition structures of the fluorene cyclizations (**ts1**) and the benzofuran cyclizations (**ts2**) of the diphenylmethyl monocations bearing an α-carbonyl group. Distances between the cyclizing atoms are shown in parentheses. Relative energy differences (in kcal/mol) of the two modes of cyclization are shown in brackets.

Table 3. Total Energies (in hartrees) and Zero-Point Energies (in kcal/mol) of Diphenylmethyl Cation Derivatives and Transition Structures for Cyclizations[a]

structure	symm	HF/3-21G	HF/6-31G*	ZPE[b]	B3LYP/6-31G*
		Monocations and Transition Structures			
1c	C_1	−721.03529 (0)	−725.09019 (0)	162.98	−729.61709
1c-ts1	C_1	−720.99653 (1)	−725.04000 (1)	162.64	−729.58042
1g	C_1	−682.21700 (0)	−686.05919 (0)	144.44[c]	−690.30621
1g-ts1	C_1	−682.18008 (1)	−686.01064 (1)	143.73	−690.27078
1i	C_1	−646.57484 (0)	−650.21687 (0)	158.68	−654.38302
1i-ts1	C_1	−646.52849 (1)	−650.16116 (1)	158.57	−654.34296
1i-ts2	C_1	−646.54081 (1)	−650.17401 (1)	158.59	−654.35582
1k	C_1	−607.74142 (0)	−611.16644 (0)	140.24	−615.05392
1k-ts1	C_1	−607.69836 (1)	−611.11692 (1)	139.76	−615.01828
1k-ts2	C_1	−607.70315 (1)	−611.12263 (1)	140.17	−615.02538
		Dications and Transition Structures			
6c	C_1	−721.23660 (0)	−725.28782 (0)	170.49	−729.81890
6c-ts1	C_1	−721.21044 (1)	−725.25354 (1)	170.19	−729.79529
6g	C_1	−682.40262 (0)	−686.24278 (0)	151.77	−690.49531
6g-ts1	C_1	−682.37998 (1)	−686.21215 (1)	151.32	−690.47485
6i	C_1	−646.76592 (0)	−650.40846 (0)	166.45	−654.57939
6i-ts1	C_1	−646.74669 (1)	−650.37996 (1)	166.43	−654.56579
6k	C_1	−607.91670 (0)	−611.34357 (0)	148.36	−615.24227
6k-ts1	C_1	−607.90473 (1)	−611.32520 (1)	147.80	−615.23155

[a] The number of imaginary frequencies is shown in parentheses. [b] Unscaled (in kcal/mol). [c] HF/3-21G ZPE; 184.02 kcal/mol (HF/6-31G*).

Table 4. Energy Barriers (in kcal/mol) of Conrotatory Electrocyclizations of Diphenylmethyl Cation Derivatives

process	HF/3-21G	HF/6-31G*	B3LYP/6-31G*	B3LYP/6-31G*+ZPE[a]
		Monocationic Fluorene Cyclizations		
1c → 1c-ts1	24.33	31.50	23.01	22.67
1g → 1g-ts1	23.17	30.47	22.23	21.60
1i → 1i-ts1	29.09	34.96	25.14	25.04
1k → 1k-ts1	27.02	31.07	22.36	21.94
		Monocationic Benzofuran Cyclizations		
1i →1i-ts2	21.35	26.90	17.07	16.99
1k → 1k-ts2	24.01	27.49	17.91	17.85
		Dicationic Fluorene Cyclizations		
6c → 6c-ts3	16.42	21.51	14.82	14.52 (13.99)[b]
6g → 6g-ts3	14.21	19.22	12.84	12.44
6i → 6i-ts3	12.07	17.88	8.53	8.52
6k → 6k-ts3	7.51	11.53	6.73	6.23

[a] Scaled by 0.89, based on the values obtained in HF/6-31G* calculations. [b] The value thermally corrected to 273.15 K is shown in parentheses.

mol (for the formyl group, **1k → 1k-ts2**, B3LYP/6-31G* + ZPE). The distances between the carbonyl oxygen atom and the cyclizing aromatic carbon atom (**1i-ts2**, 1.928 Å; **1k-ts2**, 1.898 Å) also indicate that the transition states lie at an early point along the reaction coordinate. The calculated activation barriers for the monocationic fluorene cyclizations are apparently

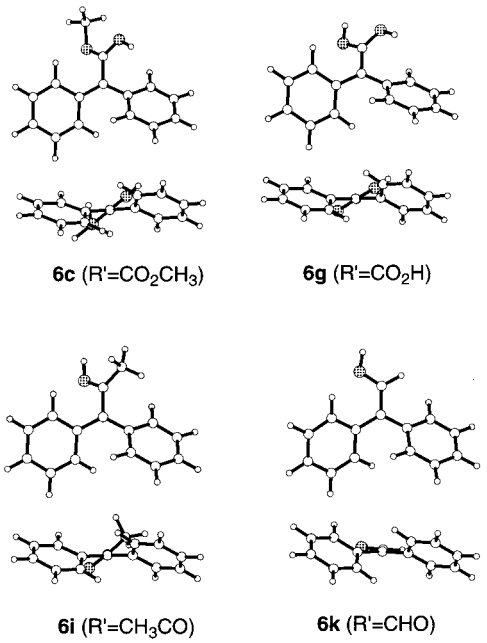


Figure 4. B3LYP/6-31G*-optimized structures of the dications of the diphenylmethyl cations bearing an O-protonated α-carbonyl group ($R'H^+$) (above, top view; below, side view).

larger than those of the corresponding benzofuran cyclizations: in the case of the acetyl group, the energy difference between **1i-ts1** and **1i-ts2** is 8.05 kcal/mol (B3LYP/6-31G*+ZPE); in the case of the formyl group, that between **1k-ts1** and **1k-ts2** is 4.09 kcal/mol (B3LYP/6-31G*+ZPE). These energetic differences of the two modes of cyclization are in complete agreement with the experimentally observed exclusive formation of the benzofuran derivative **2b** upon heating of the di-*p*-anisyl(*p*-methoxybenzoyl)methyl cation **1b** in a neutral solvent.[2] Thus, the cyclization to the benzofuran is favored, but nevertheless has a high activation barrier, which may be compatible with the experimental observation that the formation of the benzofuran from the acetyl substrate (**4i**) is very slow at −45 °C even though the monocation (**1i**) is discretely formed. On the basis of the calculated activation energies, the reaction aptitude for the monocationic fluorene cyclization is predicted to be in the order acetyl < ester < acid. However, the acetyl substrates (**4i** and **4j**) cyclized much faster than the corresponding ester derivatives (**4c** and **4e**).

Diphenylmethyl Cations Substituted with O-Protonated Carbonyl Groups. The structures of the corresponding dications **6**, formed upon O-protonation of the carbonyl group of α-(methoxycarbonyl)- (**1c**), α-carboxy- (**1g**), α-acetyl- (**1i**), and α-formyl- (**1k**) diphenylmethyl cations, were also optimized with Becke3-LYP/6-31G* basis sets (Figure 4). With respect to possible conformations due to the geometries of the O-protonated carboxy group, the sickle-shaped conformation **6g** was chosen, because the w-shaped and u-shaped conformers are higher in energy than the sickle **6g** by 7.75 kcal/mol (HF/3-21G, data not shown) and 16.10 kcal/mol (HF/3-21G, data not shown), respectively. We also assumed the sickle-shaped conformation (as in **6c**) of the O-protonated methoxycarbonyl group in the case of the dication bearing an O-protonated ester group. We focused on the *s-cis* conformations of the O-protonated acetyl group of **6i** and the O-protonated formyl group of **6k**, because the *s-trans* counterparts are less stable (1.33 kcal/mol over the *s-cis* **6i**; 1.81 kcal/mol over the *s-cis* **6k**, HF/3-21G, data not shown). The dications (**6c**, **6g**, **6i**, and **6k**) can be regarded as ethylene dications substituted with two aryl groups and (an) oxygen group(s) or a methyl group or a hydrogen atom. These structural preferences are consistent with the theoretically predicted effects of substitutions of the ethylene dications with an electron-donating group such as a phenyl, hydroxyl, methyl, or methoxyl group:[22] as the number of substituents is increased, the favored geometry of the ethylene dication ($CH_2^+-CH_2^+$) changes from the intrinsic perpendicular structure toward the planar state. However, a completely planar structure of tetra-substituted ethylene dications is unfavorable owing to steric repulsion.[22b] The transition structures (**ts3**) which represent the conrotatory electrocyclization of the dications to give the fluorenes were also located at the B3LYP/6-31G* level (Figure 5). The activation energies (B3LYP/6-31G*+ZPE) are 14.5 kcal/mol (**6c** → **6c-ts3**), 12.4 kcal/mol (**6g** → **6g-ts3**), 8.5 kcal/mol (**6i** → **6i-ts3**), and 6.2 kcal/mol (**6k** → **6k-ts3**), respectively (Tables 3 and 4). These barriers are greatly attenuated as compared with those of the monocationic fluorene cyclizations, overwhelming the monocationic benzofuran cyclization. This energy difference can explain the experimental reality that the α-acetyl substrates **4i** and **4j** gave predominantly the fluorenes over the benzofurans in TFSA. The activation barriers for the dicationic fluorene cyclization of the cations bearing the ester (**6c**) and the carboxylic acid group (**6g**) are larger than those of the ketone analogues (**6i** and **6k**): the reaction aptitude is predicted to be in the order ester < acid ≪ acetyl. This order is consistent with the experimental results. Furthermore, the fact that the ketone substrates (**4i** and **4j**) reacted faster than the corresponding ester substrates (**4c** and **4e**) is consistent with rate-determining cyclization rather than rate-determining protonation, because the oxygen basicity of the carbonyl group of the monocation **1** is in reverse order as judged from the calculated proton affinities (B3LYP/6-31G*+ZPE; **1c** → **6c**, 120.0 kcal/mol; **1i** → **6i**, 116.3 kcal/mol). The stability of the dication **6** is relevant to the reaction aptitude. Finally it is worthwhile to compare these predicted activation barriers with the experimentally available thermochemical parameters (activation energies E_a and enthalpy of activation $\Delta H^{\ddagger}$), obtained from the rates at different temperatures in 55% TFSA−45% TFA ($H_0 = -11.8$) (Table 5).[23,24] After

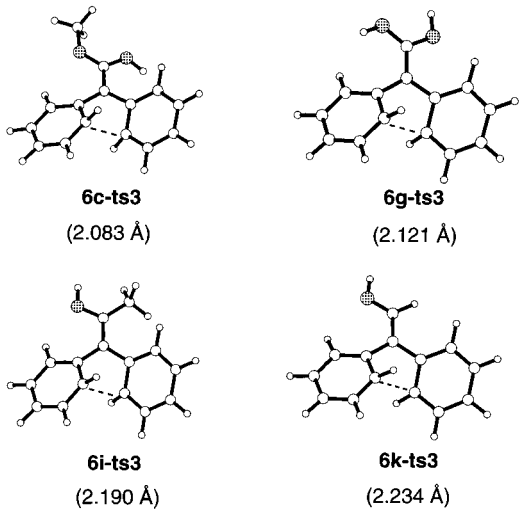


Figure 5. B3LYP/6-31G*-optimized transition structures of the fluorene cyclizations (**ts3**) of the dications of the diphenylmethyl cations bearing an O-protonated α-carbonyl group. Distances between the cyclizing atoms are shown in parentheses.

(22) (a) Lammertsma, K.; Barzaghi, M.; Olah, G. A.; Pople, J. A.; Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, *105*, 5252. (b) Frenking, G. *J. Am. Chem. Soc.* **1991**, *113*, 2476−2481.

Table 5. Thermochemical Data for Acid-Catalyzed Cyclizations of **4d** and **4e**

		rate constants 10^5k (s^{-1}) at T (°C)						
	$-H_0$[a]	−10	0	10	E_a (kcal/mol)[b]	$\Delta G^{\ddagger}$ (kcal/mol)[c]	$\Delta H^{\ddagger}$ (kcal/mol)[d]	$\Delta S^{\ddagger}$ (eu)[e]
4d	11.8	0.53	1.39	3.21	13.3	22.0	12.8	−33.8
4e	11.8	1.83	4.55	10.02	12.7	21.4	12.2	−33.6
4e	13.2	14.0	37.2	75.0	12.5	20.3	11.9	−30.5

[a] Corrected values of acidity function of the media (Table 7). [b] Errors ±0.3 kcal/mol. [c] Errors ±0.5 kcal/mol. [d] Errors ±0.3 kcal/mol. [e] Errors ±1.0 eu, at 273.15 K (0 °C).

thermal correction to 273.15 K, the predicted barrier of the ester substrates (**6c** → **6c-ts3**) is 14.0 kcal/mol.

The magnitudes of the experimental enthalpies of activation of the ester substrates ($\Delta H^{\ddagger}$, for **4d**, 12.2 kcal/mol and for **4e**, 12.8 kcal/mol) agree well with the predicted activation energy of the dicationic fluorene cyclization (**6c** → **6c-ts3**) rather than with that of the monocationic fluorene cyclization (**1c** → **1c-ts1**).[24] This coincidence also supports the intervention of dicationic electrocyclization in the fluorene cyclization of the diphenylmethyl cations.

Charge Delocalization. The charge distributions of the energy minima (**1c**, **1g**, **1i**, **1k**, **6c**, **6g**, **6i,** and **6k**) and transition structures (**ts1**, **ts2,** and **ts3**) of ions, based on natural bond orbital (NBO) population analysis are shown in Table 6.[25] The total aromatic ring charge was obtained by summing the NBO population net charges associated with the carbon atoms and the hydrogen atoms belonging to the benzene ring. The total substituent charge was obtained by summing the NBO charges of the carbonyl substituent. In terms of aromatic ring charges (the summation of the two aromatic ring charges of the dications **6** is +1.04 to +1.27; that of the monocations **1** is +0.68 to +0.75), the dications **6** (**6c**, **6g**, **6i**, and **6k**) can be regarded as carbodications with positive charge substantially delocalized over the aromatic rings, which suggests enhanced pentadienium character of the ground-state dications **6** as compared with the corresponding monocations **1**.[26] More positive charges are localized into the aromatic rings of the transition structures for both mono- (**ts1**) and dicationic (**ts3**) fluorene cyclization as compared with the starting minima structures, suggesting enforced pentadienium character in the transition structures. A similar increase of the positive charge is also found in the cyclizing aromatic ring of the transition structures (**ts2**) in the case of the benzofuran cyclization. In the transition structures of the monocationic fluorene (**ts1**) and benzofuran (**ts2**) cyclizations, the α-carbon atom has a fractional negative charge, while the carbonyl carbon and the aromatic ipso carbons bear large positive charges. In the cases of the transition structures (**ts3**) of the dicationic fluorene cyclizations, the α-carbon atom has a definite negative charge, and therefore, charge alternation is encouraged, which leads to internal Coulombic stabilization of the ions.[27] This charge alternation mechanism provides at least a partial rationale for the stabilization of the transition structures of the dicationic fluorene cyclization (**ts3**), resulting in the reduction of the activation energies.

Table 6. Natural Bond Orbital Populations (Becke3-LYP/6-31G*) of Ion Precursors and Transition Structures

	aromatic ring[b]	α-carbon center	substituent	total
1c	+0.347, +0.354 (+0.702)	+0.163	+0.135	+1.000
1c-ts1	+0.496, +0.474 (+0.970)	−0.057	+0.086	+1.000
1g	+0.364, +0.359 (+0.723)	+0.151	+0.126	+1.000
1g-ts1	+0.505, +0.486 (+0.991)	−0.070	+0.079	+1.000
1i	+0.316, +0.364 (+0.680)	+0.176	+0.143	+1.000
1i-ts1	+0.508, +0.448 (+0.956)	−0.046	+0.090	+1.000
1i-ts2	+0.578,[a] +0.190	−0.008	+0.240	+1.000
1k	+0.347, +0.408 (+0.756)	+0.121	+0.123	+1.000
1k-ts1	+0.515, +0.469 (+0.985)	−0.067	+0.082	+1.000
1k-ts2	+0.607,[a] +0.209	−0.036	+0.221	+1.000
6c	+0.466, +0.575 (+1.041)	+0.031	+0.929	+2.000
6c-ts3	+0.596, +0.677 (+1.272)	−0.130	+0.858	+2.000
6g	+0.619, +0.485 (+1.104)	+0.002	+0.893	+2.000
6g-ts3	+0.711, +0.621 (+1.332)	−0.143	+0.811	+2.000
6i	+0.521, +0.576 (+1.097)	+0.033	+0.870	+2.000
6i-ts3	+0.707, +0.662 (+1.370)	−0.096	+0.726	+2.000
6k	+0.639, +0.630 (+1.269)	−0.029	+0.759	+2.000
6k-ts3	+0.709, +0.729 (+1.438)	−0.113	+0.675	+2.000

[a] The charge of the cyclizing aromatic rings. [b] The summation of the charges of the two aromatic rings is shown in parentheses.

Conclusion

The chemical and kinetic characterizations of the fluorene cyclization of diphenylmethyl cations bearing an α-carbonyl group described herein provide conclusive support for the idea that an additional proton transfer is required to induce efficient electrocyclization of the diphenylmethyl cations.[9] The benzo-

(23) The rates were measured in 55% TFSA−45% TFA ($H_0 = -11.8$) because leveling-off of the reaction rates of **4e** was found in TFSA (see Table 2 and Figure 1). A preliminary report of the thermochemical parameters of the reaction of **4e** in TFSA (ref 8b) gave values in reasonable agreement with those obtained in this work. The activation parameters of **4e** in a higher-acidity region (in TFSA) are similar to those obtained at $H_0 = -11.8$. See also ref 18.

(24) The observed rate constant k_{obs} is related to k_r/K_e where k_r is the rate constant for cyclization and K_e is the equilibrium constant associated with the protonation of the monocation (i.e., the ionization constant of the carbodication). If k_r and K_e are temperature-dependent in different ways, k_{obs} will be affected by temperature in a complex manner. It has been shown that the H_0 is temperature-dependent in a $H_2SO_4-H_2O$ solvent system (see: Johnson, C. D.; Katritzky, A. R.; Shapiro, S. A. *J. Am. Chem. Soc.* **1969**, *91*, 6654−6662). Therefore, the validity of the pK_{BH^+} of bases (indicator and the relevant monocations) and H_0 values at different temperatures may be questioned. However, the changes of H_0 and pK_{BH^+} should essentially cancel each other out, and the protonation states of the bases should not be significantly affected by the temperature. The excellent linear relationships (regression coefficient $r > 0.99$) obtained in the estimation of activation parameters support the postulation that the changes of H_0 and pK_{BH^+} are canceled out in the TFSA−TFA acid system and, thus, that k_{obs} is affected by k_r and not K_e at the different temperatures (Table 5).

(25) NBO Version 3.1: Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. A. Reed, E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.

(26) Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1989**, *111*, 34−40.

(27) (a) Klein, J. *Tetrahedron* **1983**, *39*, 2733. (b) Klein, J. *Tetrahedron* **1983**, *48*, 2928. (c) Wiberg, K. *J. Am. Chem. Soc.* **1990**, *112*, 4177−4182.

furan cyclization was much slower than the fluorene cyclization at −45 °C in TFSA in the case of the acetyl substrates. This can be at least partially rationalized in terms of the predicted activation barriers of the dicationic fluorene cyclization, which are smaller than those of the monocationic benzofuran or fluorene cyclization reactions. We hypothesize a similar contribution of the dicationic species in the alternative cyclization of the cation **1a** to the phenthrol[9] and probably also in the superacid-catalyzed cyclization of pinacols to phenanthrenes.[28]

Experimental Section

Materials. α-(Methoxycarbonyl)bisphenylmethanol (**4c**) and α-(methoxycarbonyl)bis(*p*-methylphenyl)methanol (**4e**) were prepared as described previously.[8a,b] Other α-(methoxycarbonyl)bisarylmethanols were prepared similarly by esterification (with catalytic sulfuric acid in methanol at ambient temperature) of the corresponding α-carboxybisarylmethanols, which were prepared by utilizing the benzilic acid rearrangement reactions of the substituted benzils.

α-(Methoxycarbonyl)bis(*p*-bromophenyl)methanol (**4d**): mp 73.5−74.0 °C (recrystallized from *n*-hexane); ^{1}H NMR 7.47 (4H, d, J = 8.4 Hz), 7.27 (4H, d, J = 8.4 Hz), 4.21 (1H, s), 3.86 (3H, s). Anal. Calcd for $C_{15}H_{12}Br_2O_3$: C, 45.03; H, 3.02; N, 0.00. Found: C, 44.83; H, 2.92; N, 0.00.

α-(Methoxycarbonyl)bis(*p*-fluorophenyl)methanol (**4f**): colorless oil (molecular distillation 190 °C/2 mmHg); ^{1}H NMR 7.37 (4H, ddd, J = 7.0, 5.1, 2.2 Hz), 7.02 (4H, t, J = 8.8 Hz), 4.24 (1H, s), 3.86 (3H, s). Anal. Calcd for $C_{15}H_{12}F_2O_3$: C, 64.75; H, 4.35; N, 0.00. Found: C, 64.45; H, 4.24; N, 0.00.

α-Acetylbis(phenyl)methanol (**4i**) and α-acetylbis(*p*-methylphenyl)-methanol (**4j**) were prepared by the acid-catalyzed desilylation of the corresponding trimethylsiloxy derivatives, which were prepared by addition of the anion of [1-(diethoxyphosphinyl)ethoxy]trimethylsilane to benzophenone or 4,4-dimethylbenzophenone:[14] that is, to a stirred solution of 12 mL of diisopropylamine in 60 mL of dry THF at −78 °C was added 52 mL of *n*-butyllithium (1.6 M in hexane). The mixture was stirred at −78 °C for 20 min, and then the cooling bath was replaced with an ice−water bath. The mixture was stirred for 15 min and then cooled to −78 °C, and 27.1 g of [1-(diethoxyphosphinyl)-ethoxy]trimethylsilane (prepared from trimethylsilyl chloride, triethyl phosphite, and acetaldehyde (Merck, 99%)) was added dropwise over 10 min at −78 °C. The mixture was stirred at −78 °C for 75 min, and then a solution of benzophenone (13.46 g) in 10 mL of THF was added over 10 min. The resultant yellow solution was stirred and warmed to room temperature and then further stirred at room temperature for 37 h. It was poured into 400 mL of water, and the mixture was extracted with methylene chloride. The organic layer was washed with 1 N aqueous hydrogen chloride, followed by brine, and dried over sodium sulfate. Evaporation of the solvent gave 7.40 g of the residue, which was flash-chromatographed (ethyl acetate−*n*-hexane 2:98) to give 5.66 g of 1,1-diphenyl-1-(trimethylsiloxy)propan-2-one. A solution of this trimethylsiloxy derivative in 60 mL of methanol and 0.2 mL of concentrated hydrochloric acid was heated at 43 °C for 30 min. Evaporation of methanol gave the residue, which was extracted with methylene chloride. The organic layer was washed with brine and dried over sodium sulfate. Evaporation of the solvent gave the residue (4.296 g), which was flash-chromatographed (ethyl acetate−*n*-hexane 1:12) to give 2.77 g of α-acetylbisphenylmethanol **4i**. For **4i**: mp 66.0−66.5 °C (colorless flakes, recrystallized from *n*-hexane); ^{1}H NMR 7.363 (10H, m), 4.844 (1H, s, OH), 2.258 (3H, s). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24; N, 0.00. Found: C, 79.38; H, 6.24; N, 0.00.

α-Acetylbis(*p*-methylphenyl)methanol **4j** was prepared similarly from 4,4′-dimethylbenzophenone in 62% (total yield). The crude alcohol was purified by flash column chromatography (ethyl acetate−*n*-hexane 1:15) to give a viscous, colorless oil of **4j**: ^{1}H NMR 7.251 (4H, d-like, J = 8.43 Hz), 7.174 (4H, d, J = 8.06 Hz), 4.772 (1H, s, OH), 2.362 (6H, s), 2.249 (3H, s); HRMS calcd for $C_{17}H_{18}O_2$ 254.1306, found 254.1320.

(28) Olah, G. A.; Klumpp, D. A.; Wang, N. Q. *Synthesis* **1996**, 321−323.

Acid-Catalyzed Fluorene Cyclization Reactions in TFSA. General Procedure. The diphenylmethanol (**4**) (1 mmol) was added to precooled TFSA ((44 mL, 500 mmol) at the specified temperature (−45 or 0 °C) with stirring. The resultant solution was stirred for the specified time. 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 2:3) to give the fluorene compounds (**3**).

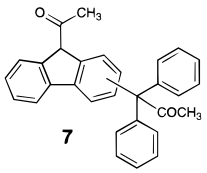
Acid- Catalyzed Reaction of α-(Methoxycarbonyl)bisphenylmethanol (4c). 9-(Methoxycarbonyl)fluorene **3c**: mp 63.5−64.5 °C (recrystallized from *n*-hexane); ^{1}H NMR 7.76 (2H, d, J = 7.5 Hz), 7.66 (2H, dd, J = 0.74, 7.5 Hz), 7.43 (2H, ddd, J = 0.74, 7.5, 7.5 Hz), 7.34 (2H, ddd, J = 1.3, 7.5, 7.5 Hz), 4.88 (1H, s), 3.76 (3H,s).

Acid-Catalyzed Reaction of α-(Methoxycarbonyl)bis(*p*-bromophenyl)methanol (4d). 9-(Methoxycarbonyl)-3,6-dibromofluorene **3d**: mp 182−183 °C (recrystallized from *n*-hexane); ^{1}H NMR 7.84 (2H, d, J = 1.5 Hz), 7.54 (2H, d, J = 8.4 Hz), 7.49 (2H, dd, 1.8, 8.1 Hz), 4.76 (1H, s), 3.98 (3H, s); HRMS calcd for $C_{15}H_{10}Br_2O_2$ 379.905, found 379.907.

Acid-Catalyzed Reaction of α-(Methoxycarbonyl)bis(*p*-methylphenyl)methanol (4e). 9-(Methoxycarbonyl)-3,6-dimethylfluorene **3e**: mp 104.0 °C (recrystallized from *n*-hexane); ^{1}H NMR 7.54 (2H, s), 7.50 (2H, d, J = 7.7 Hz), 7.13 (2H, d, J = 8.1 Hz), 4.78 (1H, s), 3.70 (3H, s), 2.44 (6H, s). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39; N, 0.00. Found: C, 80.63; H, 6.19; N, 0.00.

Acid-Catalyzed Reaction of α-(Methoxycarbonyl)bis(*p*-fluorophenyl)methanol (4f). 9-(Methoxycarbonyl)-3,6-difluorofluorene **3f**: mp 134−135 °C (recrystallized from *n*-hexane); ^{1}H NMR 7.61 (2H, dd, J = 5.0, 8.3 Hz), 7.37 (2H, dd, J = 8.6, 2.4 Hz), 7.05 (2H, ddd, J = 10.6, 8.6, 2.4 Hz), 4.80 (1H, s), 3.76 (3H, s); HRMS calcd for $C_{15}H_{10}F_2O_2$ 260.065, found 260.065.

Acid-Catalyzed Reaction of α-Acetylbisphenylmethanol (4i). A solution of the diphenylmethanol (**4i**) (1 mmol, 227 mg) in 1.5 mL of methanol-free methylene chloride was added to precooled TFSA ((44 mL, 500 mmol) at −45 °C (acetonitrile−dry ice) with stirring over 1 min. The resultant solution was stirred for 15 min. The whole was poured into ice−water (300 mL) and extracted with CH_2Cl_2 (300 mL). The organic layer was washed with brine (100 mL), dried over Na_2SO_4, filtered, and evaporated to give a residue (232 mg), which was flash-chromatographed (CH_2Cl_2−*n*-hexane 1:1) to give 9-acetylfluorene **3i** (180 mg, 86%), together with the fluorene dimer **7** (4 mg, 1.8%). 9-Acetylfluorene **3i**: mp 73.5−74.0 °C (colorless cubes, recrystallized from *n*-hexane); ^{1}H NMR 7.828 (2H, d, J = 7.5 Hz), 7.809 (2H, d, J = 7.5 Hz), 7.467 (2H, dd, J = 7.5, 7.5 Hz), 7.356 (2H, dd, J = 7.5, 7.5 Hz), 4.800 (1H, s), 1.617 (3H, s). Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.80; N, 0.00. Found: C, 86.80; H, 5.89; N, 0.00. The fluorene dimer **7**: ^{1}H NMR 7.826 (2H, d, J = 7.7 Hz), 7.481−7.110 (15H, m), 4.847 (1H, s), 4.799 (1H, s), 2.271 (3H, s), 1.615 (3H, s); MS *m*/*e* 416 (M^+).



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Acid-Catalyzed Reaction of α-Acetylbis(*p*-methylphenyl)methanol (4j). A solution of the diphenylmethanol (**4j**) (1 mmol, 260 mg) in 1.5 mL of methanol-free methylene chloride was added to precooled TFSA ((44 mL, 500 mmol) at −45 °C (acetonitrile−dry ice) with stirring over 1 min. The resultant solution was stirred for 15 min. The whole was poured into ice water (300 mL) and extracted with CH_2Cl_2 (300 mL). The organic layer was washed with brine (100 mL), dried over Na_2SO_4, filtered, and evaporated to give a residue (246 mg), which was flash-chromatographed (CH_2Cl_2−*n*-hexane 2:3) to give 9-acetyl-3,6-dimethylfluorene **3j** (158 mg, 65%), together with 3-(*p*-methylphenyl)-2,6-dimethylbenzofuran **2j** (15.8 mg, 6.5%). 9-Acetyl-3,6-dimethylfluorene **3j**: mp 100.5−101.5 °C (colorless plates, recrystallized from *n*-hexane); ^{1}H NMR 7.611 (2H, s), 7.361 (2H, d, J = 7.69 Hz),

Table 7. Corrected Values of Acidity Function of the Acid Media in the Presence of Water

acid[a]	acid/water[b]	uncorrd H_0[c]	corrd H_0[d]
100% TFSA	511 equiv	−14.12	−13.18
84.2% TFSA−15.8% TFA	503 equiv	−12.93	−12.59
71.2% TFSA−28.8% TFA	497 equiv	−12.51	−12.18
57.2% TFSA−42.8% TFA	492 equiv	−12.10	−11.80
55.8% TFSA−44.2% TFA	490 equiv	−12.06	−11.76
24.3% TFSA−75.7% TFA	516 equiv	−10.69	−10.66

[a] Weight percent of the composite acids. [b] Mole ratios of acid and water. [c] Reference 10. [d] See also ref 11.

7.153 (2H, d, 8.43 Hz), 4.697 (1H, s), 2.471 (6H, s), 1.595 (3H, s). Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83; N, 0.00. Found: C, 86.46; H, 7.11; N, 0.00. 3-(*p*-Methylphenyl)-2,6-dimethylbenzofuran **2j**: mp 77−80 °C; ^{1}H NMR 7.434 (1H, d, J = 8.06 Hz), 7.392 (2H, d, J = 8.06 Hz), 7.285 (2H, d, J = 8.06 Hz), 7.247 (1H, s), 7.037 (1H, d, J = 7.32 Hz), 2.505 (3H, s), 2.467 (3H, s), 2.417 (3H, s); HRMS calcd for $C_{17}H_{16}O$ 236.1201, found 236.1201.

The Acid Systems. In strong acid of more than $H_0 = -10$ (see the text), the alcohols **4** is ionized almost completely to yield one equivalent amount of water and the diphenylmethyl cation **1** and the resultant water behaves as an oxygen base, thus reducing the acidity of the reaction medium. The carbonyl group of the diphenylmethyl cations **1** may also behave as an oxygen base, particularly in the region of high acidity. We therefore estimated the lowering of the acidity of the reaction medium by measuring the acidity of TFSA−TFA (500 equiv with respect to water) in the presence of water at acidity levels stronger than $H_0 \approx -9$ (Table 7).[10,11] Naturally, addition of water to 100% TFSA caused the largest lowering of the acidity, and the effect of water was attenuated as the acidity of the medium decreased upon the addition of TFA.

Ionization of α-(Methoxycarbonyl)bis(*p*-bromophenyl)methanol (4d). A solution of α-(methoxycarbonyl)bis(*p*-bromophenyl)methanol (**4d**) (80.3 mg, 0.2 mmol) in 18 mL (1000 equiv) of 40.2% w/w TFSA−59.8% w/w TFA was prepared at −45 °C. The solution was poured into methanol (300 mL), followed by the addition of methylene chloride (300 mL). The organic layer was washed with three portions of water (200 mL) and dried over sodium sulfate. The solvent was evaporated to give α-(methoxycarbonyl)-α-methoxybis(*p*-bromophenyl)methane as a colorless oil (78.3 mg, 94% yield): ^{1}H NMR 7.46 (4H, d, J = 8.8 Hz), 7.29 (4H, d, J = 8.8 Hz), 3.77 (3H, s), 3.16 (3H, s).

Kinetic Measurement. Acid mixtures of TFSA and TFA were prepared in a polyethylene glovebox (AtmosBag, Aldrich) under an argon atmosphere. A precooled acid mixture (−45 °C, dry ice−acetonitrile) (1000 equiv (50 mmol), typically, 4.4 mL) was added to a weighed diphenylmethanol (**1**, 0.05 mmol), in the dry glovebox. A good solution was obtained, and a portion (ca. 0.6 mL) of it was transferred to an NMR tube, which contained a small quantity of methanol-free methylene chloride as an internal standard for signal integrations. The spectra were recorded at a specified temperature. The NMR probe temperature was controlled to within ±0.1 °C using a variable-temperature apparatus, NM-ALTAS/L and NM-AVT1A (JEOL, Japan). The disappearance of the starting material was monitored in terms of the integrated signal intensity with a GSX 500-MHz NMR spectrometer. Errors of rates, derived from the signal integration, are ±2%.

Computational Methods. Computations were carried out with the GAUSSIAN 94 ab initio programs. Geometries were initially optimized without any symmetry restriction with the split valence HF/3-21G basis set, and with the heavy atom d-polarized HF/6-31G* basis set.[29] The geometries were further optimized with a hybrid density-functional theory method, Becke3-LYP (B3LYP) with the HF/6-31G* optimized geometries.[21] All the structures of the reactants shown in Figures 2 and 4 were minima, and the transition structures (Figures 3 and 5), which represent cyclization processes, were characterized by frequency calculations at the HF/6-31G* level. Zero-point vibrational energy (ZPE) corrections were made on the basis of the values scaled by 0.89 obtained in the HF/6-31G* calculations.[30] For comparison with experimental data ($\Delta H^{\ddagger}$) (Table 5), the activation barrier (**6c** → **6c-ts3**) was thermally corrected to 273.15 K.

JA980090W

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