α or γ free position can be successfully utilized. Moreover, the experimental conditions are extremely simple and mild (the reaction is exothermic and completed in a few minutes, starting at room temperature), and the reagents and the catalyst are particularly inexpensive.

Preliminary results[4,20] have shown that other simple sources of methyl radicals ((AcO_2), t-BuOOH, $(t\text{-BuO})_2$, MeCOMe + H_2O_2, MeCOOH + $S_2O_8^{2-}$) are also suitable for the alkylation of heteroaromatic bases by alkyl iodides and for several other selective reactions. Nucleophilic alkyl radicals, generated from alkyl iodides, can in fact also be utilized in the selective alkylation of diazonium salts, pyrylium salts, iminium salts, quinones, electron-poor olefins, biacetyl, and oximes, whereas electrophilic radicals (with electron-withdrawing groups in the α-position; in these cases, the iodine abstraction by the methyl radical is still easier[21] compared with the unsubstituted alkyl iodides) can be utilized for the oxidative alkylation of olefins and aromatics.

Experimental Section

All the reaction products were identified by comparison (GLC, NMR, MS) with authentic samples, previously prepared by a different procedure developed by us[22] (alkylation by silver-catalyzed decarboxylation of carboxylic acid by peroxydisulfate).

General Procedures. (i) Secondary Alkyl Iodides. H_2O_2 (30%; 7.5 mmol) was added dropwise over 2 min at room temperature to a stirred solution of 2.5 mmol of heteroaromatic base, 2.5 mmol of H_2SO_4, and 0.3 mmol of $FeSO_4{\cdot}7H_2O$ in 25 mL of DMSO. A fast reaction took place, and the temperature rose to 40–50 °C. Additional $FeSO_4$ (0.2–0.4 mmol) was added in small portions until the temperature kept on rising (in any case, a moderate excess of $FeSO_4$ has no significant influence on the yields). The solution was stirred for 15 min, diluted with water, made basic with NaOH, and extracted with CH_2Cl_2. The reaction products were analyzed by GLC with the same procedures previously utilized (quinaldine or lepidine as internal standard).[22] The GLC of the low-boiling reaction products, carried out in the case of isopropyl iodine and lepidine, revealed the presence of 1.7 mmol of methyl iodide. No significant product of methylation of the heteroaromatic base was observed.

(ii) Primary Alkyl Iodides. The procedure is similar to i with the difference that more H_2O_2 (13 mmol) and alkyl iodide (13 mmol) were utilized; the temperature spontaneously rose to 70–80 °C, and 1–2% of methylation of the heteroaromatic base was observed as a byproduct.

(iii) Tertiary Alkyl Iodides. Tertiary alkyl iodides react with DMSO at room temperature, giving the corresponding oxyalkylsulfonium iodides. Procedure i has been slightly modified in order that the alkyl iodide is always present in the reaction medium. Thus 7.5 mmol of 30% H_2O_2 and 7.5 mmol of the tertiary alkyl iodide were separately and simultaneously added dropwise over 5 min to a stirred solution of 2.5 mmol of heteroaromatic base, 2.5 mmol of H_2SO_4, and 0.5 mmol of $FeSO_4{\cdot}7H_2O$ in 25 mL of DMSO at room temperature. The solution was stirred for an additional 15 min and worked up as in procedure i. No product of methylation of the heteroaromatic base was observed.

Registry No. DMSO, 67-68-5; i-PrI, 75-30-9; i-BuI, 513-38-2; PrI, 107-08-4; BuI, 542-69-8; t-BuI, 558-17-8; H_2O_2, 7722-84-1; $FeSO_4$, 7720-78-7; lepidine, 491-35-0; quinaldine, 91-63-4; quinoline, 91-22-5; isoquinoline, 119-65-3; acridine, 260-94-6; 4-cyanopyridine, 100-48-1; 4-acetylpyridine, 1122-54-9; 4-methylpyridine, 108-89-4; pyrazine, 290-37-9; quinoxaline, 91-19-0; benzothiazole, 95-16-9; cyclohexyl iodide, 626-62-0; 2-isopropyllepidine, 91879-71-9; 2-isobutyllepidine, 123005-14-1; 2-cyclohexyllepidine, 56947-80-9; 2-propyllepidine, 99878-27-0; 2-butyllepidine, 30980-47-3; 2-*tert*-butyllepidine, 97691-25-3; 4-isopropylquinaldine, 123005-15-2; 4-cyclohexylquinaldine, 37597-46-9; 4-butylquinaldine, 37520-55-1; 2-isopropylquinoline, 17507-24-3; 4-isopropylquinoline, 17507-25-4; 2,4-diisopropylquinoline, 22493-98-7; 2-isobutylquinoline, 93-19-6; 4-isobutylquinoline, 7661-51-0; 2,4-diisobutylquinoline, 123005-16-3; 2-cyclohexylquinoline, 1613-43-0; 4-cyclohexylquinoline, 33357-38-9; 2,4-dicyclohexylquinoline, 123005-17-4; 2-propylquinoline, 1613-32-7; 4-propylquinoline, 20668-44-4; 2,4-dipropylquinoline, 33538-25-9; 2-butylquinoline, 7661-39-4; 4-butylquinoline, 74808-78-9; 2,4-dibutylquinoline, 123005-18-5; 2-*tert*-butylquinoline, 22493-94-3; 1-isopropylisoquinoline, 20922-03-6; 1-cyclohexylisoquinoline, 33538-11-3; 9-isopropylacridine, 33538-07-7; 9-cyclohexylacridine, 35242-12-7; 4-cyano-2-isopropylpyridine, 33538-10-2; 4-cyano-2,6-diisopropylpyridine, 33538-08-8; 4-cyano-2-cyclohexylpyridine, 40114-95-2; 4-cyano-2,6-dicyclohexylpyridine, 83001-42-7; 2-*tert*-butyl-4-cyanopyridine, 33538-09-9; 4-cyano-2,6-di-*tert*-butylpyridine, 37581-48-9; 4-acetyl-2-isopropylpyridine, 123005-19-6; 4-acetyl-2,6-diisopropylpyridine, 123005-20-9; 2-cyclohexyl-4-methylpyridine, 15787-48-1; 2-cyclohexylpyrazine, 53190-45-7; 2-cyclohexylquinoxaline, 40115-00-2; 2,3-dicyclohexylquinoxaline, 123005-21-0; 2-cyclohexylbenzothiazole, 40115-03-5.

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Ethylene Dications Substituted with Electron-Donating Groups

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Direct spectroscopic observations were made of substituted ethylene dications bearing π-stabilizing groups such as an aryl, a hydroxy, or a methoxy group in a strong acid, trifluoromethanesulfonic acid (TFSA). Based on the spectroscopic evidence, we reached the following conclusions. (1) 1,1-Diaryl-2-hydroxy-2-methoxyethylene dications, 1,1-diaryl-2,2-dihydroxyethylene dications, and 1,1,2-triaryl-2-hydroxyethylene dications are *discrete* intermediates in the electrocyclization reaction to yield the fluorene and phenanthrol in TFSA. (2) Several dications bearing methoxy substituents on the aromatic rings are formed in trifluoroacetic acid (TFA). (3) NMR spectra suggested the nonplanar structures of O-protonated α-carbonyl diarylmethyl dications at the central C–C bond. (4) 1,2-Diaryl-1,2-dihydroxyethylene dications and 1-aryl-1,2,2-trihydroxyethylene dications are very stable. Ab initio MO calculations showed that 1,2-dihydroxyethylene dications are more stable than 1,1-dihydroxyethylene dications.

The generation and detection of small doubly charged cations in the gas phase are well-established owing to modern experimental techniques such as charge stripping (CS) mass spectrometry.[1] The properties of such ions can

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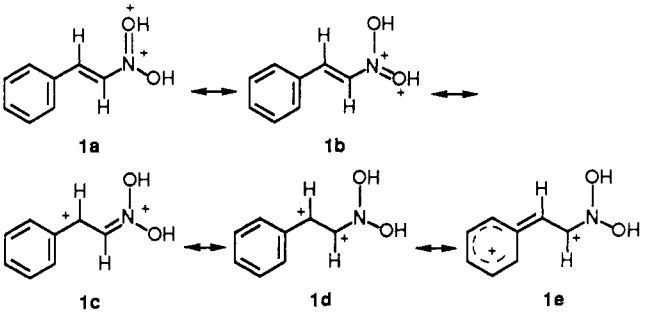
Table I. ^{1}H NMR Spectroscopic Data for 1,1-Diaryl-2-methoxy-2-hydroxyethylene Dications and 1,1-Diaryl-2,2-dihydroxyethylene Dications[a,b]

	acid	temp, °C	OH	H_o	H_m	p-(O)CH_3	others
6A	TFSA[c]	−30	−	8.25 (d, 8.8)	7.73 (d, 8.8)	4.55 (s)	4.84 (s, CH_3)
	TFSA–SbF_5[c]	−30	13.82 (s)	7.98 (b s)	7.67 (b s)	4.83 (s)	4.98 (s, CH_3)
	TFA	−5	−	8.10 (d, 7.3)	7.51 (d, 8.3)	4.34 (s)	4.37 (s, CH_3)
6B	TFSA[c]	−30	−	8.35 (d, 8.8)	7.77 (d, 8.8)	4.58 (s)	−
	TFSA–SbF_5[c]	−36	14.08 (b s)	8.09 (b s)	7.72 (b s)	4.88 (s)	−
	TFA	−5	−	8.23 (d, 9.3)	7.52 (d, 8.8)	4.35 (s)	−
7A	TFSA	−30	−	8.36 (d, 8.3)	8.19 (d, 8.3)	3.13 (s)	4.80 (s, CH_3)
	TFSA–SbF_5	−30	15.00 (b s)	7.96 (b s)	7.96 (b s)	2.88 (s)	5.17 (s, CH_3)
7B	TFSA	−40	−	8.35 (d, 7.8)	8.11 (d, 7.8)	3.04 (s)	−
8	TFSA	−30	−	8.56 (d, 8.8)	7.61 (d, 8.8)	4.44 (s)	9.12 (s, CH)
	TFA	−5	−	8.40 (d, 8.3)	7.45 (d, 8.8)	4.29 (s)	8.94 (s, CH)
9	TFSA	−30		8.48 (b d)	7.97 (b d)	2.91 (s)	9.65 (s, CH)

[a] Chemical shifts are in ppm from external capillary Me_4Si in acetone-d_6. [b] Coupling modes and ^{1}H–^{1}H coupling constants in hertz are shown in parentheses; d = doublet, b s = broad singlet, s = sharp singlet. [c] Reference 6.

Scheme I



also be deduced by high-level ab initio molecular orbital calculations.[2] The formation of dications with two interacting cation centers in the through-space mode[3a] or in the through-bond mode[3b] is very interesting in the field of cation chemistry. We have recently reported an extraordinary dipositively charged O,O-diprotonated nitro olefin 1, where the two cation centers are conjugated in a canonical resonance structure (Scheme I).[4] The formation of such simple acyclic dications was proposed to involve an enhanced stabilization by Y-delocalization of 6π electrons (**1a–c**).[5] From an alternative point of view, these dipositive systems can be regarded as ethylene dications (**1d,e**), which are stabilized by lone-pair electrons of the nitrogen atom of the *N,N*-dihydroxyamino and π-electron-donating phenyl groups in the case of nitrostyrenes. These considerations led us to investigate the formation and reaction of substituted ethylene dications, since there has been no systematic investigation of the formation and reaction of ethylene dications in solution.[6]

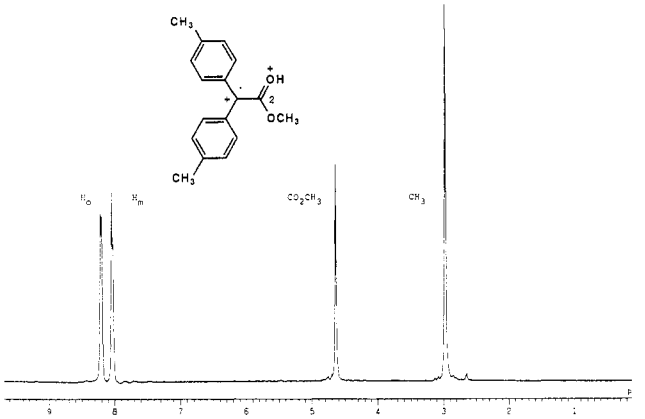
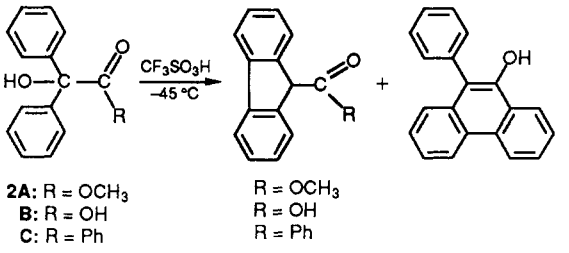


Figure 1. 400-MHz ^{1}H NMR spectrum of α-(methoxycarbonyl)bis(p-methylphenyl)methanol (**4A**) in TFSA at −30 °C.

Scheme II



The previous study revealed that α-(methoxycarbonyl)diphenylmethanol (**2A**) reacted in trifluoromethanesulfonic acid (TFSA) to give 9-carbomethoxyfluorene in high yield, and α-benzoyldiphenylmethanol (**2C**) also reacted in TFSA to give 9-benzoylfluorene and 9-phenylphenanthr-10-ol (Scheme II).[6] In this paper we will present evidence for the characterization of O-protonated α-carbonyldiarylmethyl dications (**5**) as the *discrete* intermediates in the electrocyclization reaction to yield the fluorene and phenanthrol in TFSA. Further studies also revealed that several dications bearing methoxy substituents on the aromatic rings are formed in trifluoroacetic acid (TFA). Magnetically equivalent substituents suggested nonplanar structures of O-protonated α-carbonyldiarylmethyl dications at the central C–C bond.

Substituted ethylene dications in TFSA were prepared by replacement of the substituents: 1,2-diaryl-1,2-dihydroxyethylene dications, 1-aryl-1,2-dihydroxy-2-methoxyethylene dications, and 1-aryl-1,2,2-trihydroxyethylene

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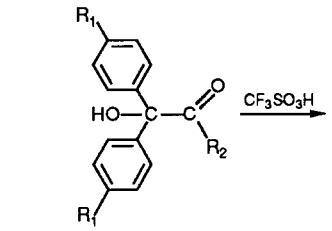
Table II. ^{13}C NMR Spectroscopic Data for 1,1-Diaryl-2-methoxy-2-hydroxyethylene Dications and 1,1-Diaryl-2,2-dihydroxyethylene Dications in Acids[a,b]

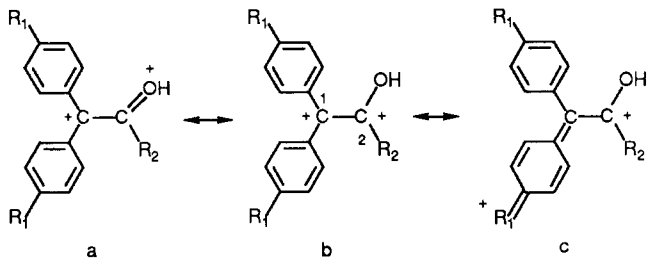
	acid	temp, °C	C_o	C_m	C_p	C_{ipso}	C_1	C_2	p-(O)CH_3	others
6A	TFSA[c]	−20	143.9	119.3	174.7	127.6	176.0	168.6	57.7	58.4
			(167.3)	(170.2)					(146.7)	(145.2)
	TFSA–SbF_5[c]	−20	142.7	122.8	173.6	134.7	181.6	151.1	68.1	68.1
			(170.2)	(173.8)					(158.4)	(158.4)
	TFA	−10	146.0	120.8	170.3	129.6	177.8	177.8	59.2	56.6
			(164.4)	(170.2)					(149.6)	(149.6)
6B	TFSA[c]	−20	143.8	119.3	174.8	127.3	176.1	168.8	57.7	–
			(164.4)	(170.2)					(149.6)	
	TFSA–SbF_5[c]	−20	142.7	122.8	173.7	135.0	182.4	150.3	68.2	–
			(170.2)	(173.1)					(158.1)	
	TFA	−10	146.1	120.7	172.1	129.1	177.7	178.0	59.2	–
			(167.3)	(170.3)					(146.8)	
7A	TFSA	−25	143.4	133.7	167.6	132.3	184.2	170.7	23.1	53.3
			(167.2)	(167.2)					(129.1)	(125.5)
	TFSA–SbF_5	−35	144.5	135.3	168.9	133.5	183.7	173.0	24.1	68.7
			(br)	(187.8)					(132.0)	(158.5)
7B	TFSA	−40	143.4	133.8	167.8	131.9	183.4	171.0	23.1	–
			(d, nd)	(167.2)					(q, nd)	
8	TFSA	−20	144.3	118.0	174.0	129.6	178.6	–	56.9	–
			(166.5)	(167.2)			(155.6)		(146.7)	
	TFA	−10	146.4	120.7	176.9	131.6	180.3	–	58.7	–
			(164.3)	(167.3)			(155.7)		(146.7)	
9	TFSA	−20	142.8	132.9	164.6	134.3	191.7	–	22.6	–
			(167.3)	(167.3)			(158.5)		(129.1)	

[a] Chemical shifts (in ppm) are calibrated from Me_4Si in $CDCl_3$. [b] C–^{1}H coupling constants are shown in parentheses in hertz (nd = not determined). [c] Reference 6.

Scheme III



2A: R_1 = H; R_2 = OCH_3
B: R_1 = H; R_2 = OH
C: R_1 = H; R_2 = Ph
3A: R_1 = OCH_3; R_2 = OCH3
B: R_1 = OCH_3; R_2 = OH
C: R_1 = OCH_3; R_2 = p-CH_3OPh
4A: R_1 = CH_3; R_2 = OCH_3
B: R_1 = CH_3; R_2 = OH
C: R_1 = CH_3; R_2 = p-CH_3Ph



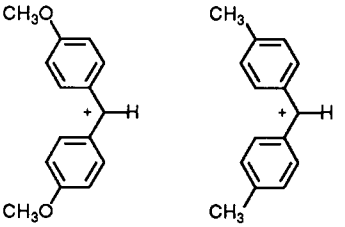
5A: R_1 = H; R_2 = OCH_3
B: R_1 = H; R_2 = OH
C: R_1 = H; R_2 = Ph
6A: R_1 = OCH_3; R_2 = OCH3
B: R_1 = OCH_3; R_2 = OH
C: R_1 = OCH_3; R_2 = p-CH_3OPh
7A: R_1 = CH_3; R_2 = OCH_3
B: R_1 = CH_3; R_2 = OH
C: R_1 = CH_3; R_2 = p-CH_3Ph

dications are very stable in TFSA even at 23 °C. Spectroscopic information on these ethylene dications and experimental estimation of their reactivities (or stabilities) in solution should provide valuable insights into the structures and stabilities of simple ethylene dications which were observed in the gas phase[1] and were discussed theoretically.[2,7]

Results and Discussion

Formation and Reaction of O-Protonated α-(Methoxycarbonyl)diarylmethyl Dications and O-Protonated α-Carboxydiarylmethyl Dications. While an attempt to observe the parent dications **5A** and **5B** by NMR spectroscopy was unsuccessful owing to their high reactivity even at −50 °C in TFSA, we could prepare stable ions O-protonated α-carbomethoxybis(*p*-methoxyphenyl)methyl dication (**6A**), and O-protonated α-carboxybis(*p*-methoxyphenyl)methyl dication (**6B**) in TFSA and TFSA–SbF_5 (2.5:1).[6] These ions are so stable that they did not cyclize to the fluorene or phenanthrol.

The chemical species (**7A**) formed in TFSA from α-(methoxycarbonyl)bis(*p*-methylphenyl)methanol (**4A**) was also stable at −30 °C and gave a well-resolved spectrum shown in Figure 1 (Scheme III). The spectroscopic data for this dication are summarized in Tables I and II, together with the data for **6A** and **6B**, and the data for the bis(*p*-methoxyphenyl)methyl cation **8** and the bis(*p*-methylphenyl)methyl cation **9** (formed from bis(*p*-methoxy- or *p*-methylphenyl)methanol, respectively, in TFSA at −30 °C). The ion formed in TFSA–SbF_5 (2.5:1) is the

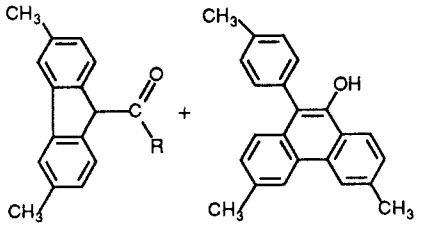


8 **9**

same, judging from the ^{13}C NMR chemical shifts of the ions formed in the two acid systems, and was reasonably assigned as the O-protonated α-(methoxycarbonyl)bis(*p*-methylphenyl)methyl cation (**7A**) based on the signal of the C=OH^+ group at 15.00 ppm in TFSA–SbF_5 (2.5:1) at −30 °C.[8] The equivalence of the two aromatic rings of the

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

dication **7A** in the ^1H and ^{13}C NMR spectra suggested a nonplanar structure at the central C–C bond. In TFSA at −30 °C, the dication slowly cyclized to yield the 9-(methoxycarbonyl)-3,6-dimethylfluorene **10A**, and the reaction took place effectively at 0 °C to give **10A** in 94% yield.



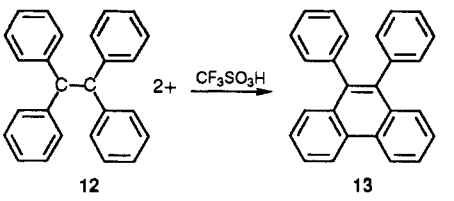
10A: R = OCH_3
B: R = OH
C: R = *p*-CH_3Ph

11c

Similarly, the 1,1-bis(*p*-methylphenyl)-2,2-dihydroxyethylene dication **7B** was formed from α-carboxybis(*p*-methylphenyl)methanol (**4B**) in TFSA at −30 °C. This conclusion was based on the good correspondence of the chemical shifts of the ion **7B** in TFSA with those of the dication **7A** in both the ^1H and the ^{13}C NMR spectra. The presence of OH signals equivalent to two protons also supports the formation of the dication. The formation of these related dipositive systems under the same conditions was very reasonable, but the dication **7B** was more reactive than the dication **7A**: the dication **7B** was gradually converted to the fluorene **10B** even at −20 °C in 82% yield over 1.5 h. Both of the dications **7A** and **7B** showed good first-order kinetics: the rate of disappearance of the dications **7A** and **7B** are identical with the rate of appearance of the cyclized products **10A** and **10B**, respectively. These observations are strongly consistent with the conclusion that these dications are discrete intermediates in the cyclization reactions. The activation parameters are as follows: **7A**, enthalpy of activation $\Delta H^{\ddagger}$ = 10.1 kcal/mol, entropy of activation $\Delta S^{\ddagger}$ = −36.4 eu; **7B**, $\Delta H^{\ddagger}$ = 11.1 kcal/mol, $\Delta S^{\ddagger}$ = −28.7 eu. The entropy of activation suggested that the transition state is a highly ordered.[11b] The calculated rate constants of **7A** and **7B** at 0 °C were 4.65×10^{-4} s^{-1} and 4.03×10^{-3} s^{-1}, respectively. Based on a simple consideration of the difference in the Hammett σ^* or σ^I constant, the methoxy group is a superior stabilizing substituent to the hydroxy group.[9] The observed rate ratio (8.7) between **7A** and **7B** is due to the inductive stabilization of the dications by the substituent (CH_3). These results provided evidence for involvement of **7A**, **7B**, **5A**, and **5B**, as real intermediates to the fluorenes.

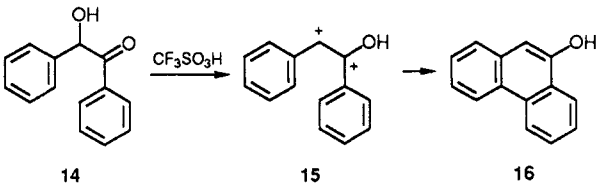
Formation and Reaction of 1,1,2-Triaryl-2-hydroxyethylene Dications. The reaction of α-benzoyldiphenylmethanol (**2C**) in TFSA to give the fluorene was regarded as the same electrocyclization as that of O-protonated (α-methoxycarbonyl)diphenylmethyl dication **5A** to the fluorene (Scheme II). This reaction was interpreted in terms of the participation of the O-protonated benzoyldiphenylmethyl dication **5C**, i.e., the

Scheme IV



12 **13**

Scheme V



14 **15** **16**

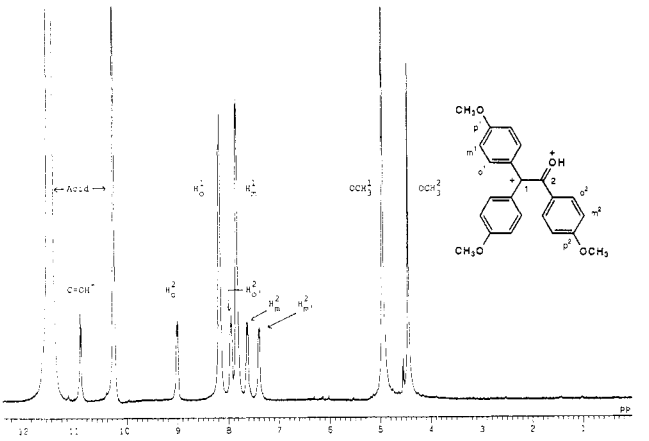


Figure 2. 400-MHz ^1H NMR spectrum of α-(*p*-methoxybenzoyl)bis(*p*-methoxyphenyl)methanol (**3C**) in TFSA–SbF_5 (2.5:1) at −30 °C.

1,1,2-triphenyl-2-hydroxyethylene dication in TFSA. The reaction to form phenanthrol (from **2C**) was also an electrocyclization similar to that of the tetraphenylethylene dication **12** to 9,10-diphenylphenanthrene **13** (Scheme IV).[6,10] A similar phenanthrene formation occurred in the reaction of benzoin **14** in TFSA: **14** reacted in TFSA (200 equiv with respect to **14**) at 0 °C for 45 min to give 9-phenanthrol **16** in 11% yield; the 1,2-diphenyl-1-hydroxyethylene dication (**15**) may participate in this reaction (Scheme V).

Spectroscopic evidence for the formation of the proposed dication **5C** could not be obtained owing to its high reactivity. However, an ion **6C** formed from α-(*p*-methoxybenzoyl)bis(*p*-methoxyphenyl)methanol (**3C**) in TFSA was stable enough to give a clear NMR spectrum even at 50 °C (Scheme III). Aqueous quenching of the solution of TFSA after standing at 0 °C recovered **3C** quantitatively (99%). The spectroscopic data for the ion **6C** are summarized in Tables III and IV, together with the data for the stable (*p*-methoxybenzoyl)bis(*p*-methoxyphenyl)-methyl monocation **17** (in $CDCl_3$).[11a] The assignment of

(8) Ester: (a) Fraenkel, G. *J. Chem. Phys.* **1961**, *34*, 1466. (b) Birchall, T.; Gillespie, R. *Can. J. Chem.* **1965**, *43*, 1045. (c) Olah, G. A.; O'Brien, D. H.; White, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 5694. Carboxylic acid: (d) Hogeveen, H.; Bickel, A. F.; Hilbers, C. W.; Mackor, E. L.; Maclean, C. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 687. (e) Hogeveen, H. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 809. (f) Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 3591.

(9) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row Publishers: New York, 1981; Chapter 2. Isaacs, N. S. *Physical Organic Chemistry*; Longman Scientific & Technical: Birmingham, AL, 1987; Chapter 4.

(10) Mandelung, W.; Oberwegner, M. *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 2469. Wizinger, R. *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 1377. Baenzziger, N. C.; Buckles, R. E.; Simpson, T. D. *J. Am. Chem. Soc.* **1967**, *89*, 3405. Buckles, R. E.; Wonner, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 5055. Buckles, R. E.; Erickson, R. E.; Snyder, J. D.; Person, W. B. *J. Am. Chem. Soc.* **1960**, *82*, 2444. Olah, G. A.; Grant, J. L.; Spear, R. J.; Bollinger, J. M.; Seranz, A.; Sipos, G. *J. Am. Chem. Soc.* **1976**, *98*, 2501. Schmidlin, J.; Escher, R. V. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1153. Hart, H.; Sulzberg, T.; Rafos, R. R. *J. Am. Chem. Soc.* **1963**, *85*, 1800.

Table III. ^{1}H NMR Spectroscopic Data for 1,1,2-Triaryl-2-hydroxyethylene Dications[a,b]

	acid	temp, °C	OH	$H_o(1)$	$H_m(1)$	$H_o(2)$	$H_m(2)$	$CH_3(1)$	$CH_3(2)$
6C	TFSA	−30	–	8.33 (d, 9.2)	7.79 (d, 8.8)	9.26 (d, 9.2) 8.12 (d, 9.2)	7.84 (d, 9.2) 7.48 (d, 9.2)	4.60 (s)	4.60 (s)
	TFSA–SbF_5	−30	10.90	8.14 (b s)	7.80 (b s)	8.98 (b s) 7.92 (b s)	7.60 (b s) 7.36 (b s)	4.93 (s)	4.43 (s)
	TFA	−10	–	8.05 (d, 9.2)	7.39 (d, 9.3)	8.05 (d, 9.2)	7.13 (b s)	4.22 (s)	3.99 (s)
7C	TFSA	−30	–	8.24 (b s)	8.11 (b s)	9.13 (b s) 8.11 (b s)	8.02 (b s) 7.80 (b s)	3.03 (s)	2.95 (s)
	TFSA–SbF_5	−30	12.90	8.04 (b s)	8.04 (b s)	9.03 (b s) 7.98 (b s)	7.81 (b s) 7.69 (b s)	2.89 (s)	2.84 (s)
17[c]	CD_2Cl_2	35	–	7.96 (d, 9.6)	7.28 (d, 9.6)	7.81 (d, 9.0)	6.98 (d, 9.0)	4.13 (s)	3.87 (s)

[a] Chemical shifts are in ppm from external capillary Me_4Si in acetone-d_6. [b] (1) and (2) mean the aromatic groups attached at the C_1 carbon atom and at the C_2 carbon atom, respectively. [c] Reference 11a.

Table IV. ^{13}C NMR Spectroscopic Data for 1,1,2-Trisaryl-2-hydroxy Ethylene Dication in Acids[a-c]

	acid	temp, °C	C_o	C_m	C_p	C_{ipso}	C_1	C_2	p-(O)CH_3
6C	TFSA	−20	143.9 (1) (167.3) 146.6 (2) (161.4) 139.9 (2) (170.1)	119.7 (1) (167.2) 120.5 (2) (167.2) 118.4 (2) (170.2)	176.6 (1) 168.0 (2)	129.7 (1) 123.1 (2)	180.3	190.3	58.4 (149.7) (2) 57.9 (149.7) (1)
	TFSA–SbF_5	−20	147.0 (2) (nd) 143.1 (1) (164.3)	140.6 (2) (nd) 122.1 (1) (nd)	172.4 (1) 181.8 (2)	134.8 (1) 123.1 (2)	164.1	185.2	67.3 (155.6) (1) 58.9 (149.7) (2)
	TFA	−10	145.6 (1) (167.3) 136.3 (2) (180.5)	120.8 (1) (167.3) 117.4 (2) (164.3)	186.3 (2) 177.4 (1)	130.3 (1) 129.9 (2)	169.9	197.7	59.1 (149.6) (1) 57.3 (146.7) (2)
7C	TFSA	−20	143.8 (1) (173.1) 143.7 (2) (173.1) 136.5 (2) (nd)	134.7 (1) (nd) 133.8 (2) (nd) 133.2 (2) (nd)	170.4 (1) 170.4 (2)	134.2 (1) 127.7 (2)	180.1	199.7	23.7 (129.1) (1) 23.5 (132.1) (2)
	TFSA–SbF_5	−25	143.6 (1) (nd) 144.5 (2) (167.3) 137.1 (2) (176.1)	135.0 (1) (167.3) 134.4 (2) (167.2) 133.7 (2) (nd)	171.1 (1) 173.1 (2)	134.4 (1) 127.7 (2)	178.9	198.8	23.9 (129.1) (1) 23.9 (129.1) (2)
17	CD_2Cl_2[d]	25	143.5 (1) 133.4 (2)	118.9 (1) 114.8 (2)	174.5 (1) 166.6 (2)	128.1 (1, 2)	185.1	193.1	58.1 (1) 56.0 (2)

[a] Chemical shifts (in ppm) are calibrated from Me_4Si in $CDCl_3$. [b] ^{13}C–^1H coupling constants are shown in parentheses in hertz (nd = not determined). [c] (1) and (2) mean the aromatic groups attached at the C_1 carbon atom and at the C_2 carbon atom, respectively. [d] Reference 11a.

the dication **6C** was supported by the good agreement with **6A** in terms of chemical shifts, especially in the ^{13}C NMR spectra. In the TFSA–SbF_5 (2.5:1) acid system at −30 °C, a C=OH^+ group equivalent to one proton was observed at 10.90 ppm as a singlet in the ^{1}H NMR spectra, indicating protonation of the carbonyl oxygen atom (Figure 2).[12] Based on the ^{13}C NMR data for the ions in TFSA and TFSA–SbF_5 (2.5:1) there existed reasonable correspondence in the chemical shifts for two acid systems. Although there may be a difference in solvent effect on the chemical shifts, the relative chemical shifts between the dication **6C** and monocation **17** are significantly different: in the ^{13}C NMR spectra, the ortho and meta carbon atoms of the *p*-methoxybenzoyl aromatic ring of the dication have absorptions at lower field. These downfield shifts supported the existence of the cation center at the *p*-methoxybenzoyl moiety of the dication.

(11) (a) Okamoto, K.; Nitta, I.; Shingu, H. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1464. Takeuchi, K.; Kitagawa, T.; Okamoto, K. *J. Chem. Soc., Chem. Commun.* **1983**, 7. (b) Maleki, M.; Hopkinson, A. C.; Lee-Ruf, E. *Tetrahedron Lett.* **1983**, 4911. Hopkinson, A. C.; Dao, L. H.; Duperrouzel, P.; Maleki, M.; Lee-Ruf, E. *J. Chem. Soc., Chem. Commun.* **1983**, 727. Dao, L. H.; Maleki, M.; Hopkinson, A. C.; Lee-Ruf, E. *J. Am. Chem. Soc.* **1986**, *108*, 5237.

(12) Protonation of ketones: Olah, G. A.; O'Brien, D. H.; Calin, M. *J. Am. Chem. Soc.* **1967**, *89*, 3582. Brouwer, D. M. Recl. Trav. Chim. Pays-Bas. 1967, 86, 879. Brookhart, M.; Levy, G. C.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 1735. See also ref 8b.

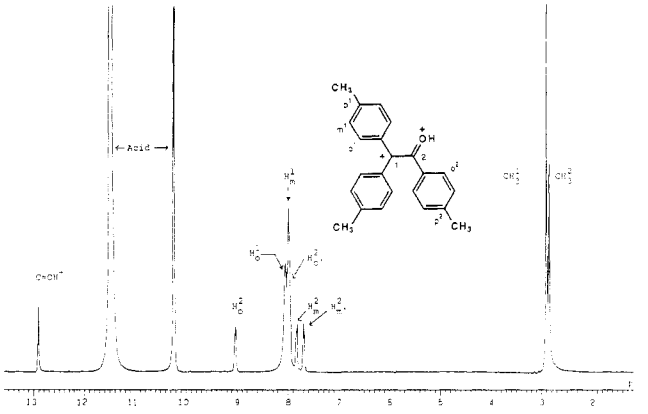


Figure 3. 400-MHz ^1H NMR spectrum of α-(*p*-methylbenzoyl)bis(*p*-methylphenyl)methanol (**4C**) in TFSA–SbF_5 (2.5:1) at −30 °C.

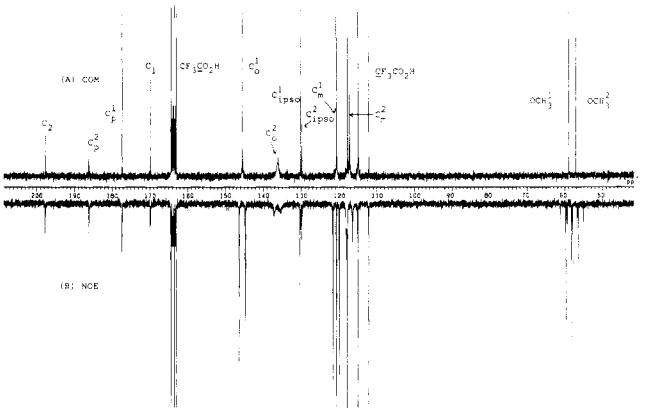


Figure 4. 100-MHz ^{13}C NMR spectrum of α-(*p*-methoxybenzoyl)bis(*p*-methoxyphenyl)methanol (**3C**) in TFA at −10 °C: (A) proton complete decoupling (COM); (B) gated nondecoupling (NOE) spectrum.

The ion formed from α-(*p*-methylbenzoyl)bis(*p*-methylphenyl)methanol (**4C**) both in TFSA and in TFSA–SbF_5 (2.5:1) was stable at −30 °C and is the 1,1,2-tris(*p*-methylphenyl)-2-hydroxyethylene dication **7C** (Figure 3). In TFSA–SbF_5 (2.5:1), a C=OH^+ absorption was observed at 12.90 ppm.[12] The ^1H NMR and ^{13}C NMR data for the ion **7C** are summarized in Tables III and IV. The spectra observed in TFSA and TFSA–SbF_5 were almost the same, indicative of the formation of the same dication, **7C**, in both solutions. This dication **7C** was stable at −30 °C in TFSA, but it converted effectively to the fluorene **10C** and phenanthrol **11C** in 70% and 14% yields, respectively, at 0 °C for 3 h. This reaction was very similar to that of the parent α-benzoyldiphenylmethanol (**2C**) in TFSA, and therefore it was deduced that the 1,1,2-triphenyl-2-hydroxyethylene dication **5C** participates in the cyclization of **2C**. In the case of **6C** and **7C**, while the protons at ortho and meta positions and all carbon atoms of the aryl rings on the C_2 position are nonequivalent, the proton and carbon absorptions of the geminal aromatic rings at the C_1 position were nuclear magnetically equivalent in the NMR spectra. The ^1H NMR spectra of **6C** was not dependent on temperature (−30 °C to 50 °C). The spectra of **6C** and **7C** are consistent with a structure in which the C_1-aryl bonds are free to rotate, and the C_1–C_2 bond is fixed in the perpendicular C_1- and C_2-p-orbital geometry, as in the case of the dications **6A** and **7A**. On the other hand, recent theoretical calculations showed that substitution of stabilizing groups on the parent ethylene dication tends to change the preferred structures from perpendicular geometries to planar ones.[2e,7] These results suggested that these dications take nonplanar structures intermediate between the planar and perpendicular structures.

Proton and carbon chemical shifts have been found to be proportional to π-electron densities (or charge densities) in aromatic systems.[13] Based on a consideration of the difference in the calculated charge densities of the benzene rings of simple benzyl cation and phenylethylene dication,[7] the relative chemical shifts between the monocation and the dication would be significantly different. Rather small signal perturbations (deshielding) of aromatic protons and of carbon atoms of dication **6** or **7**, as compared with those of the corresponding monocation **8** or **9**, respectively, are considered to be due to a more extensive delocalization of the positive charge over the para substituents. This was shown by low-field shifts of the protons and of the carbon atoms of the para substituents CH_3O of **6** and CH_3 of **7** from those of the monocation **8** and **9**.

The OH proton chemical shifts can be used to estimate the degree of the contribution of protonated carbonyl structures (C=O^+H) and of hydroxy-substituted cations (C^+-OH): very low chemical shifts (15 ppm) imply the former structures and higher shifts such as 10–11 ppm imply the latter structures.[12] Ion **7A** in TFSA/SbF_5 has an OH chemical shift 15.00 ppm, suggesting that structure a is a better representation of the dication than structures b and c. Ion **6C**, with an OH chemical shift of 10.90 ppm, is better represented by structures b and c and thus is legitimately called an ethylene dication.[14]

Dications in Trifluoroacetic Acid. Further studies revealed the formations of the stable dications **6A** and **6B** bearing a *p*-methoxy group in *a weaker acid system, trifluoroacetic acid* (TFA). This conclusion was derived from the ^{13}C NMR spectra (Table II). The chemical shifts of the ion formed in TFA were very similar to those of the dications **6A** and **6B** in TFSA. Moreover, the presence of the same species in TFA and TFSA was supported by the fact that addition of TFSA to the TFA solution of **3A** or **3B** did not change the UV absorption spectra.[15] This facile formation of the dications is attributed to the great stabilizing ability of the methoxy group at the para position, while the methyl derivatives, dications **7A** and **7B**, could not be detected in TFA solution of **4A** and **4B**, judging from the UV studies: small addition of TFSA (a small amount, but in excess over the solute) to the TFA solution of **4A** or **4B** induced substantial change of the absorptions.[16]

The species formed by dissolving **3C** in trifluoroacetic acid (TFA) was the dication **6C** observed in TFSA; small signal perturbations (especially for $C_p(2)$ and C_1) in the ^{13}C NMR spectra were probably due to solvent effects (Figure 4). This conclusion was also supported by a UV

(13) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468. O'Brien, D. H.; Hart, A. J.; Russell, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410. Forsyth, D. A.; Olah, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 4086.

(14) This discussion on the chemical shifts of the O-protons was suggested by a referee.

(15) The UV spectroscopic data of the ions (λ_{max}, log $\epsilon\lambda_{max}$) are as follows. **3A**: in TFSA, 549 nm (5.05), 346 nm (3.56); in TFA, 536.5 nm (4.24), 343.5 nm (3.24). **3B**: in TFSA, 549 nm (4.67), 346 nm (3.45); in TFA, 537 nm (4.05), 342.5 nm (2.96). **3C**: in TFSA, 576.5 nm (4.68), 367 nm (4.27), 336 nm (3.43); in TFA, 539 nm (4.95), 355 nm (4.02), 330 nm (shoulder, 4.11), 313 nm (4.22). **8**: in TFSA, 500 nm (4.61), 360 nm (2.53); in TFA, 501 nm (4.40), 351 nm (2.60).

(16) The UV spectroscopic data of the ions (λ_{max}) are as follows. **4A**: 502.5, 334.5 nm. (The absorptions changed depending on time because the fluorene was formed.) In TFA, 492 and 337 nm (the absorptions were much weaker than those in TFSA).

Scheme VI

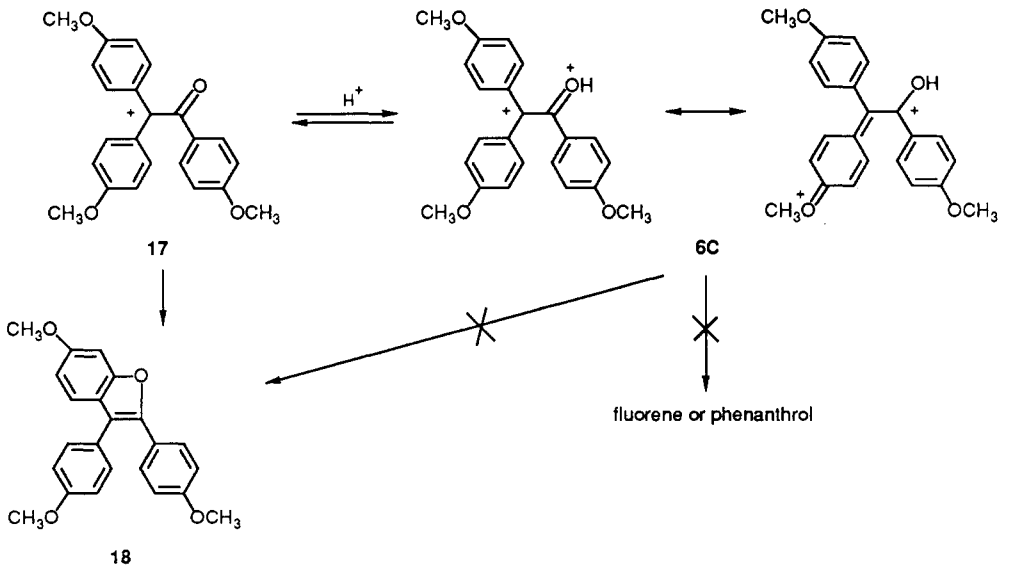


Table V. ^{1}H NMR Spectroscopic Data for 1,2-Diaryl-1,2-dihydroxyethylene Dications in Acids[a]

	acid	temp, °C	OH	H_o	H_m	H_p	(O)CH_3
22C	TFSA	-30	-	8.64 (d, 7.32)	8.17 (t, 7.33)	8.55 (t, nd)	-
23C	TFSA	-30	-	9.23 (vbr) 8.48 (vbr)	7.93 (vbr) 7.72 (vbr)	-	4.76 (s)
	TFSA-SbF_5	-30	11.32	8.91 (b s) 8.11 (b s)	7.60 (b s) 7.42 (b s)	-	4.48 (s)
24C	TFSA	-30	-	8.71 (d, 8.3)	8.15 (d, 8.3)	-	3.13 (s)
	TFSA-SbF_5	-30	13.39	8.96 (b s) 8.15 (b s)	8.09 (b s) 7.91 (b s)	-	2.95 (s)

[a] Chemical shifts are in ppm from external capillary Me_4Si in acetone-d_6; vbr = very broad.

experiment: addition of TFSA to the TFA solution induced no substantial change of the UV absorptions even after standing at room temperature.[15] While the dication formed in TFA was essentially stable even at 50 °C, the heating of the solution at 70 °C (reflux) for 1.25 h gave 2,3-dianisylbenzofuran (**18**) in high yield (96%) (Scheme VI). It was reported that the antimony hexafluoride salt of **17** undergoes the same reaction to form the benzofuran **18** in the absence of the acid catalyst.[11b] Therefore, the results of the reaction in TFA suggested the presence of a small amount of the equilibrating monocation **17** in this weak acid, and the monocation **17** cyclizes to the benzofuran. In the much more strongly acidic TFSA, the monocation **17** was completely diprotonated to the dications, which could not cyclize to benzofuran, fluorene, or phenanthrol.[11a]

Further Examples of Substituted Ethylene Dications in Solution. We could prepare additional substituted ethylene dications with reasonable stabilities in solution by replacement of aryl groups.

(A) 1,2-Diaryl-1,2-dihydroxyethylene Dications. 1,2-Diaryl-1,2-dihydroxyethylene dications could be formed by O,O-diprotonation of 1,2-diketones. Although previous studies suggested the diprotonation of 1,2-diketones in magic acid, based only on the interpretation of the highly deshielded singlet methyl absorption of 2,3-butandione in excess 1:1 FSO_3H-SbF_5-SO_2,[17a] subsequent ^{13}C NMR studies on protonation of 1,2-diketones depended on the above suggestion.[17b] Therefore, further investigation of the ion formed from 1,2-diketones would be worthwhile. The formation of 1,2-diaryl-1,2-dihydroxyethylene dications from 1,2-diketones was supported by the observation of C=OH^+ absorptions equivalent to two protons at lower field. Benzil (**19C**), 4,4′-dimethoxybenzil (**20C**), and 4,4′-dimethylbenzil (**21C**) gave stable ions in both TFSA and TFSA-SbF_5, and these were assigned as 1,2-diaryl-1,2-dihydroxyethylene dications (**22C**, **23C**, and **24C**, respectively) (Scheme VII). The spectroscopic data are given in Tables V and VI, together with previous data for benzil (**19C**) in fluorosulfuric acid reported by Olah et al.[17b] In the case of 4,4′-dimethoxybenzil (**20C**) and 4,4′-dimethylbenzil (**21C**), a singlet absorption was observed at 11.32 or 13.39 ppm in the ^{1}H NMR spectra (in TFSA-SbF_5, 2.5:1, at -30 °C), which can be reasonably assigned to C=OH^+ groups. Lesser lower field shift of the O-proton of the dication **23C** indicated a significant contribution of hydroxymethyl ion structure (b or c) to the ion. In the ^{13}C NMR spectra, the chemical shifts of the absorptions in both these acids, TFSA and TFSA-SbF_5 (2.5:1), are in good agreement with each other, supporting the formation of the identical dications. Since the proton exchange with

(17) (a) Olah, G. A.; Calin, M. *J. Am. Chem. Soc.* **1968**, *90*, 4672. (b) Olah, G. A.; Grant, J. L.; Westerman, P. W. *J. Org. Chem.* **1975**, *40*, 2102.

Table VI. ^{13}C NMR Spectroscopic Data for 1,2-Diaryl-1,2-dihydroxyethylene Dications in Acids[a,b]

	acid	temp, °C	C_o	C_m	C_p	C_{ipso}	C_1	p-(O)CH$_3$
22C	TFSA	−20	135.0 (164.4)	130.8 (165.8)	144.3 (164.4)	128.3	196.9	–
	FSO_3H[c]	−80	136.2	131.4	145.6	128.3	197.3	–
23C[d]	TFSA	15	143.3 (173.1)	120.5 (170.1)	178.6	120.4	182.0	59.1 (149.7)
		−20	vbr	vbr	177.0	118.7	181.2	58.2 (149.6)
	TFSA–SbF_5	−20	146.7 (167.3) 140.8 (176.0)	122.2 (149.7) 119.7 (176.1)	176.3	120.7	183.2	59.5 (149.7)
24C[e]	TFSA	−20	135.5 (164.3)	131.3 (164.4)	162.3	124.6	192.8	21.4 (129.1)
	TFSA–SbF_5	−20	144.6 (164.3) 138.0 (170.2)	135.4 (170.1) 134.5 (164.3)	177.5	124.6	186.9	24.7 (129.1)

[a] Chemical shifts (in ppm) are calibrated from Me_4Si in $CDCl_3$; vbr = very broad. [b] ^{13}C–^1H coupling constants are shown in parentheses in hertz. [c] Reference 17b. [d] In TFA (−10 °C): 135.9 (162.6, C_o), 117.0 (164.3, C_m), 169.0 (C_p), 127.0 (C_{ipso}), 198.6 (C_1), 57.1 (146.7, OCH_3). [e] In TFA (−10 °C): 133.0 (164.4, C_o), 132.2 (161.4, C_m), 152.4 (C_p), 131.3 (C_{ipso}), 200.3 (C_1), 22.6 (126.2, CH_3).

Table VII. ^1H NMR Spectroscopic Data for 1-Aryl-1,2-dihydroxy-2-methoxyethylene Dications in Acids[a]

	acid	temp, °C	OH	H_o	H_m	H_p	CO_2CH_3	p-(O)CH$_3$
22A	TFSA	−30	–	9.22 (d, 7.3)	8.14 (d, 6.8)	8.63 (b s)	4.62 (s)	–
	TFSA–SbF_5	−30	–	9.15 (d, 7.3) 8.81 (d, 7.3)	7.87 (d, 6.8)	8.46 (b s)	4.96 (s)	–
23A	TFSA	−30	–	9.48 (b s) 9.04 (b s)	7.62 (b s)	–	4.56 (s)	4.56 (s)
	TFSA–SbF_5	−30	–	8.97 (b s) 8.68 (b s)	7.32 (b s)	–	4.81 (s)	4.36 (s)
24A	TFSA	−30	–	9.19 (b s)	8.00 (b s)	–	4.59 (s)	2.99 (s)
	TFSA–SbF_5	−30	–	9.02 (b s) 8.70 (b s)	7.74 (b s)	–	4.92 (s)	2.72 (s)

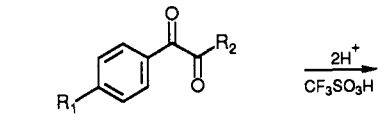
[a] Chemical shifts are in ppm from external capillary Me_4Si in acetone-d_6.

the solvent is sufficiently rapid, the C=OH^+ absorption merged with the acid peak in the case of benzil (**19C**) in TFSA–SbF_5 (2.5:1). But the chemical shifts of the ion from **19C** in TFSA corresponded well to those of the O,O-diprotonated 4,4′-dimethylbenzil **24C** in TFSA, indicative of the formation of the related dication, 1,2-diphenyl-1,2-dihydroxyethylene dication.

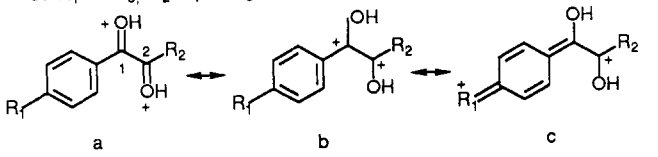
In the case of the dication bearing *p*-methoxy groups **23C**, the two aromatic rings are equivalent in both the ^1H NMR and the ^{13}C NMR spectra, but two individual protons at the ortho or meta position were nonequivalent. In the ^{13}C NMR spectrum, the ortho and meta carbon signals are broad at −20 °C, but they sharpened at 15 °C (at 143.3 and 120.5 ppm).

(B) 1-Aryl-1,2-dihydroxy-2-methoxyethylene Dications and 1-Aryl-1,2,2-trihydroxyethylene Dications. Replacement of one of the aryl groups in 1,2-diaryl-1,2-dihydroxyethylene dications by OCH_3 and OH groups yielded stable 1-aryl-1,2-dihydroxy-2-methoxyethylene dications (**22A**, **23A**, and **24A**) and 1-aryl-1,2,2-trihydroxyethylene dications (**22B**), which could be formed from the α-keto esters (**19A**, **20A**, and **21A**) and the α-keto acid **19B**, respectively (Scheme VII). The spectroscopic data are summarized in Tables VII and VIII. Although an attempt to observe directly the C=OH^+ group in the TFSA–SbF_5 (2.5:1) acid system was unsuccessful, the ^{13}C

Scheme VII



19A: R_1 = H; R_2 = OCH_3
B: R_1 = H; R_2 = OH
C: R_1 = H; R_2 = Ph
20A: R_1 = OCH_3; R_2 = OCH_3
C: R_1 = OCH_3; R_2 = *p*-CH_3OPh
21A: R_1 = CH_3; R_2 = OCH_3
C: R_1 = CH_3; R_2 = *p*-CH_3Ph



22A: R_1 = H; R_2 = OCH_3
B: R_1 = H; R_2 = OH
C: R_1 = H; R_2 = Ph
23A: R_1 = OCH_3; R_2 = OCH_3
C: R_1 = OCH_3; R_2 = *p*-CH_3OPh
24A: R_1 = CH_3; R_2 = OCH_3
C: R_1 = CH_3; R_2 = *p*-CH_3Ph

NMR spectra provided supporting evidence for the formation of these ethylene dications: significant low-field

Table VIII. ^{13}C NMR Spectroscopic Data for 1-Aryl-1,2-dihydroxy-2-methoxyethylene Dications and 1-Aryl-1,2,2-trihydroxyethylene Dications in Acids[a,b]

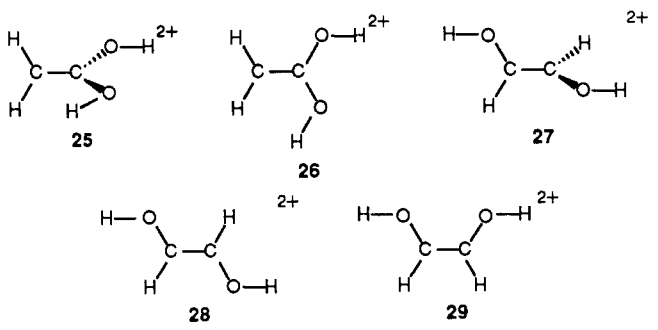
	acid	temp, °C	C_o	C_m	C_p	C_{ipso}	C_1	C_2	OCH_3	p-(O)CH_3
22A	TFSA	−20	140.3	131.3	149.0	125.4	188.8	159.5	57.2	–
			(170.1)	(170.2)	(164.3)				(152.6)	
	TFSA-SbF_5	−20	154.1	133.1	141.4	125.0	176.1	170.2	68.2	–
			(167.2)	(176.1)	(173.1)				(161.4)	
			144.5	132.8						
			(170.2)	(173.1)						
23A	TFSA	−20	147.4	120.3	178.7	118.3	180.4	160.5	56.3	58.3
			(170.2)	(nd)					(152.6)	(149.6)
			142.5	118.3						
			(179.0)	(nd)						
	TFSA-SbF_5	−20	146.6	122.8	173.3	120.8	184.8	158.8	60.4	66.3
			(155.5)	(nd)					(149.7)	(158.4)
			145.0	121.6					60.3	66.1
			(167.3)	(nd)					(149.7)	(158.4)
24A	TFSA	−20	141.3	132.9	158.9	122.7	185.1	168.8	56.5	23.1
			(170.2)	(167.2)					(152.6)	(129.1)
	TFSA-SbF_5	−20	144.5	135.1	171.3	123.4	176.1	171.1	67.5	24.5
			(170.2)	(167.3)					(158.5)	(129.2)
			141.7	134.4						
			(170.2)	(170.2)						
22B	TFSA	−20	139.3	131.1	148.1	125.9	188.3	160.2	–	–
			(167.3)	(164.3)	(158.4)					

[a] Chemical shifts (in ppm) are calibrated from Me_4Si in $CDCl_3$. [b] ^{13}C–^1H coupling constants are shown in parentheses in hertz (nd = not determined).

shifts (from 23.6 to 60.4 ppm) of the C_{para} carbon atoms compared to the C_{ipso} carbon atom are well-correlated with those of diprotonated diketones, 1,2-diaryl-1,2-dihydroxyethylene dications (**22C**, **23C**, and **24C**). The chemical shifts of the aromatic ring and the C_1 carbon atoms in the ^{13}C NMR spectra of the ions resembled those of the dications (**22C**, **23C**, and **24C**). The related dication, 1-phenyl-1,2,2-trihydroxyethylene dication **22B**, was formed in TFSA from benzoylformic acid **19B**. These results are in agreement with previous investigations on protonation of α-keto esters in magic acid.[18] This dication, however, should be regarded as a substituted ethylene dication. A previous description of diprotonated oxalic acid in magic acid can also be interpreted in terms of formation of the very stable tetrahydroxyethylene dication in solution.[19]

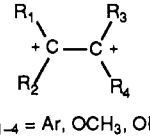
Stability of 1,1-Dihydroxy- and 1,2-Dihydroxyethylene Dications. It was apparent that 1,1-diaryl-2,2-dihydroxyethylene dications (**5B** and **7B**) were reactive to electrocyclization, while the isomeric dications, 1,2-diaryl-1,2-dihydroxyethylene dications (**22C** and **24C**), were very stable. In order to shed light on the different stabilities, we calculated the structures and energies of sickle-shaped 1,1-dihydroxyethylene dications in both perpendicular (**25**) and planar (**26**) structures[7] and the structures of 1,2-dihydroxyethylene dications, perpendicular **27**, and two possible (*Z* and *E*) planar isomers (**28** and **29**) on the basis of split-valence 4-31G basis sets (Chart I).[20] Energies relative to the most stable **28** were **25**, 28.1 kcal/mol; **26**, 31.0 kcal/mol; **27**, 4.0 kcal/mol; and **29**, 3.5 kcal/mol. In all structures calculated, 1,2-dihydroxyethylene dications were more stable than 1,1-dihydroxyethylene dications, supporting the observation of the greater reactivity of 1,1-diaryl-2,2-dihydroxyethylene dications over 1,2-diaryl-1,2-dihydroxyethylene dications.

Chart I



Conclusion

We have demonstrated the formation of substituted ethylene dications bearing π-stabilizing groups such as aryl, methoxy, and hydroxy as discrete chemical species in a strong acid, TFSA. The involvement of these dications can well interpret the electrocyclization reaction to yield the fluorenes and phenanthrols, which are not derived from the corresponding monocation (e.g. **17**). The recognition of these dications in addition to the earlier examples (including tetraarylethylene dications and diprotonated oxalic acid) provides the general formula **30**, wherein R_1–R_4 represent aryl, OCH_3, or OH and possibly other π(or n)-electron donating substituents.



30: R_{1-4} = Ar, OCH_3, OH, etc.

Experimental Section

General Methods. Proton NMR spectra were measured on a JEOL GX 400-MHz NMR spectrometer with TMS as an internal reference in $CDCl_3$ as the solvent for neutral compounds. ^{13}C NMR spectra were recorded on a JEOL GX-400 spectrometer (at 100 MHz) in $CDCl_3$, and chemical shifts are reported in ppm, referenced by assignment of the middle resonance of deuteriochloroform as 77.0 ppm from TMS. Ultraviolet spectra were measured on a Shimadzu UV 200S at 0 °C in acidic media. Flash

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(19) Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 4752.
(20) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. The calculations have been performed at the Computer Center of the University of Tokyo. The ab initio calculations were carried out by using a modified version of the GAUSSIAN 80 computer programs (GAUSSIAN 80H). We thank Dr. A. Itai and Dr. N. Tomioka, Faculty of Pharmaceutical Sciences, University of Tokyo, for their helpful advice and for the use of the calculation systems.

column chromatography was performed on silica gel (Merck, Kieselgel 60, 230–400 mesh) with a specified solvent.[21]

Materials. All the melting points were measured with a Yanagimoto micro-melting point apparatus (MP-500) and are uncorrected. Combustion analysis was carried out in the microanalytical laboratory of this faculty.

Trifluoromethanesulfonic acid (TFSA) was purchased from 3M Co. and was purified by distillation under reduced pressure [bp 84 °C (33 mmHg)]. Antimony pentafluoride (SbF_5) was from Aldrich Chemical Co. and was purified by distillation under reduced pressure [bp 81.5 °C (61 mmHg)]. Trifluoroacetic acid (TFA) was purchased from Wako Chemical Co. and used without further purification. α-(Methoxycarbonyl)bis(p-methylphenyl)methanol (**4A**) was obtained quantitatively by treatment of the corresponding acid **4B** with ethereal diazomethane. Purification by flash column chromatography (CH_2Cl_2–*n*-hexane, 3:1), and subsequently by recrystallization from *n*-hexane gave pure **4A**: mp 81.5–82 °C. ^1H NMR: δ 7.291 (d, 4 H, 8.43), 7.138 (d, 4 H, 8.06), 3.829 (s, OCH_3), 2.341 (s, CH_3, 6 H). ^{13}C NMR: δ 175.2 (s, C_2), 139.1 (s, C_p), 137.8 (s, C_{ipso}), 128.8 (d, C_o, 159.9), 127.2 (d, C_m, 151.2), 80.9 (s, C_1), 53.4 (q, OCH_3, 146.8), 21.04 (q, CH_3, 126.2). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.531; H, 6.712; N, 0.0. Found: C, 75.35; H, 6.73; N, 0.0. α-Carboxybis(p-methylphenyl)methanol (**4B**) was prepared by the benzilic acid rearrangement reaction of 4,4′-dimethylbenzil (**21C**) (available from Aldrich):[22] a solution of **21C** (2.0 g) in ethanol (8 mL) was added to an aqueous solution (4 mL) of potassium hydroxide (2.0 g). The mixture was refluxed for 25 min in a steam bath (ext 90 °C). After addition of water, the aqueous mixture was extracted with Et_2O. Acidification of the resultant aqueous layer with concentrated HCl produced the crude acid **4B** as a yellow oil. The mixture was extracted with CH_2Cl_2, and the organic layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave 1.8 g of **4B** (83% yield), mp 127–129 °C (recrystallized from n-hexane/CH_2Cl_2), as colorless cubes. ^1H NMR: δ 7.332 (d, 4 H, 8.06), 7.143 (d, 4 H, 8.06), 2.342 (s, 6 H). ^{13}C NMR: δ 178.7 (C_2, s), 138.3 (C_p, s), 138.2 (C_{ipso}), 128.9 (d, C_o), 127.2 (d, C_m), 80.9 (C_1, s), 21.1 (q, CH_3). Anal. Calcd for $C_{16}H_{10}O_3$: C, 74.978; H, 6.293; N, 0.0. Found: C, 74.986; H, 6.275; N, 0.0. Bis(p-methylphenyl)methanol: this methanol was prepared from 4,4′-dimethylbenzophenone (Wako) by reduction with $LiAlH_4$ (4.5 eq) in dry Et_2O under reflux for 2 days. Usual aqueous workup, extraction with Et_2O, and evaporation of the solvent yielded a pure alcohol in 96% yield, mp 69–69.5 °C (recrystallized from *n*-hexane: colorless needles). ^1H NMR: δ 7.250 (d, 4 H, 8.06), 7.132 (d, 4 H, 7.69), 5.777 (1 H, s), 2.321 (6 H, s). ^{13}C NMR: δ 141.07 (s, C_{ipso}), 136.99 (s, C_p), 129.05 (d, 155.6), 126.39 (d, 155.6), 75.80 (d, 146.7), 21.01 (q, 126.2). Anal. Calcd for $C_{15}H_{16}O$: C, 84.865; H, 7.598; N, 0.0. Found: C, 84.83; H, 7.60; N, 0.0. **3C**: α-(p-Methoxybenzoyl)bis(p-methoxyphenyl)methanol was prepared from 4,4′-dimethoxybenzil (**20C**) (available from Aldrich) by the reaction of the Grignard reagent prepared from 4-bromoanisole in dry Et_2O. To a solution of **20C** (5.40 g) in a mixture of benzene (40 mL) and Et_2O (20 mL) under reflux, portions of the Grignard reagent (prepared from p-bromoanisole (7.5 g)) were added. The mixture was heated at 60 °C for 30 min, poured into saturated aqueous NH_4Cl, and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated to give a crude product, which was purified by flash column chromatography (CH_2Cl_2–*n*-hexane, 2:1) to give 4.82 g (46%) of **3C**, mp 116–116.5 °C (recrystallized from *n*-hexane). ^1H NMR: δ 7.763 (d, 2 H, o^2, 8.79), 7.309 (d, 4 H, o^1, 8.79), 6.826 (d, 4 H, m^1, 8.79), 6.730 (d, 2 H, m^2, 8.80), 5.280 (s, OH), 3.745 (s, 9 H, OCH_3). ^{13}C NMR: δ 198.9 (s, CO), 163.1 (s, p^2), 159.0 (s, p^1), 134.6 (s, $C_{ipso}{}^1$), 133.4 (d, o^2, 162.9), 129.5 (d, o^1, 159.9), 127.3 (s, $C_{ipso}{}^2$), 13.5 (d, $C_m{}^1$), 113.2 (d, $C_m{}^2$). Anal. Calcd for $C_{23}H_{22}O_5$: C, 72.998; H, 5.860; N, 0.0. Found: C, 72.72; H, 5.88; N, 0.0. **4C**: α-(p-Methylbenzoyl)bis(p-methylphenyl)methanol was also prepared from 4,4′-dimethylbenzil by the reaction of the Grignard reagent prepared from 4-bromotoluene. The workup was similar to the case of **3C** (see above), mp 87–88 °C (recrystallized from *n*-hexane; colorless cubes). ^1H NMR: δ 7.654 (d, 2 H, 8.42), 7.2894 (d, 4 H, 8.42), 7.130 (d, 4 H, 8.06), 7.075 (d, 2 H, 8.06), 5.114 (1 H, s, OH), 2.335 (3 H, s), 1.573 (6 H, s). ^{13}C NMR: δ 200.36 (s, C_2), 143.82 ($C_p{}^2$, s), 139.32 ($C_{ipso}{}^1$, s), 137.72 (s, $C_p{}^1$), 132.35 (s, $C_{ipso}{}^2$), 131.15 (d, 164.4, $C_o{}^2$), 128.96 (d, 161.4, $C_o{}^1$), 128.78 (d, 158.5, $C_m{}^2$), 128.29 (d, 161.4, $C_m{}^1$), 84.50 (s), 21.60 (q, $CH_3{}^2$), 21.07 (q, $CH_3{}^1$). Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71; N, 0.0. Found: C, 83.32; H, 6.76; N, 0.0. Benzoylmethyl formate (**19A**), benzoylformic acid (**19B**), and benzil (**19C**) were obtained from Wako Chemical Co. and used after recrystallization from *n*-hexane or distillation (**19A**: 96–98 °C (2 mmHg)). The spectroscopic data were as follows. **19A**. ^1H NMR: δ 8.006 (2 H, d, d, H_o, 8.61, 1.46), 7.650 (1 H, d, d, H_p, 7.32, 1.46), 7.501 (2 H, H_m, d, d, 8.06, 7.33), 3.968 (s, 3 H). ^{13}C NMR: δ 185.97 (s), 163.93 (s), 134.86 (d, 164.4), 132.26 (s), 129.89 (d, 164.3), 128.76 (d, 164.3), 52.60 (q, 149.7). **19B**. ^1H NMR: δ 10.5761 (1 H, s), 8.2031 (2 H, d, H_o, 7.7), 7.687 (t, 1 H, H_p, 7.7), 7.519 (t, 2 H, 7.7, H_m). ^{13}C NMR: δ 185.06 (s, C_1), 164.25 (s, C_2), 135.53 (d, C_o, 160.0), 131.65 (s, C_{ipso}), 130.77 (d, C_p, 161.4), 128.93 (d, 164.4, C_m). **19C**. ^1H NMR: δ 7.967 (2 H, d, d, H_o, 8.43, 1.47), 7.636 (1 H, d, d, H_p, 7.33, 1.43), 7.490 (2 H, d, d, H_m, 7.33, 1.47). ^{13}C NMR: 194.5 (s), 134.8 (d, 161.4), 132.8 (s), 129.7 (d, 155.5), 128.9 (d, 164.4). **20C** (4,4′-dimethoxybenzil). ^1H NMR: δ 7.941 (d, 4 H, 9.16), 6.964 (d, 4 H, 8.8), 3.875 (s, 6 H). ^{13}C NMR: δ 193.47 (s, C_1), 164.83 (s, C_p), 132.32 (d, C_o, 161.4), 126.27 (s, C_{ipso}), 114.25 (d, C_m, 161.4), 55.57 (q, 143.8). **21C** (4,4′-dimethylbenzil). ^1H NMR: δ 7.853 (4 H, d, 8.42), 7.286 (4 H, d, 8.06), 2.413 (6 H, s). ^{13}C NMR: δ 194.43 (s, C_1), 146.04 (s, C_p), 130.62 (s, C_{ipso}), 129.89 (d, C_o, 161.4), 129.63 (d, C_m, 164.3), 21.80 (q, CH_3, 127.2). **20A**: (4-Methoxybenzoyl)methyl formate was prepared by oxidation of 2-bromo-4′-methoxyacetophenone with selenium dioxide (SeO_2) in the presence of methanol as previously described.[23] Purification by flash column chromatography (CH_2Cl_2–*n*-hexane, 3:4) and recrystallization (from *n*-hexane) gave pure **20A** (28% yield), mp 49–49.5 °C (colorless needles). ^1H NMR: δ 8.0171 (2 H, d, 9.16), 6.979 (2 H, d, 9.15), 3.966 (3 H, s), 3.901 (3 H, s). ^{13}C NMR: δ 184.39 (s), 165.07 (s), 164.31 (s), 132.61 (d, 162.9), 125.4 (s), 114.2 (d, 161.4), 55.60 (q, 143.8), 52.60 (q, 146.7). (4-Methylbenzoyl)methyl formate **21A** was also prepared by oxidation reaction in the same way as **20A**. The crude mixture was flash chromatographed (CH_2Cl_2–*n*-hexane) and was purified by distillation under reduced pressure (110 °C (2 mmHg)). ^1H NMR: δ 7.9048 (d, 7.32), 7.300 (d, 7.33), 3.966 (3 H, s), 2.431 (3 H, s). ^{13}C NMR: δ 185.62 (s, C_1), 164.16 (s, C_2), 146.24 (s, C_p), 130.07 (d, 161.4), 129.9 (s), 129.5 (d, 158.5), 52.5 (q, 149.7), 21.77 (q, 126.2).

Preparation and NMR Studies of Ions in Acids. NMR spectra of ions were measured on a JEOL GX 400 spectrometer equipped with a variable-temperature apparatus. The digital resolutions in the observed NMR spectra are as follows: ±0.49 Hz in ^1H NMR and ±2.93 Hz in ^{13}C NMR spectra. All samples of ions in TFSA and TFSA–SbF_5 (2.5:1, mole ratio) were prepared below −30 °C in a dry ice–ethanol bath, and samples in TFA were made at −10 °C. The ^1H NMR spectra were obtained without deuterium locking, and the chemical shifts were calibrated as follows. The chemical shifts of the methyl groups of protonated acetone in these acid systems were referred to TMS in acetone-d_6 in a capillary: in TFSA (−30 °C), 3.26 ppm; in TFSA–SbF_5 (2.5:1) (−30 °C), 3.55 ppm; in TFA (−10 °C), 2.407 ppm. There was a negligible temperature dependence of the chemical shifts between −40 and 0 °C. The ^{13}C NMR spectra were also recorded without deuterium locking. The chemical shifts in TFSA and TFSA–SbF_5 (2.5:1) were calibrated on the basis of the middle resonance of the quartet of CF_3SO_3H as 118.07 ppm from TMS in $CDCl_3$. The chemical shifts in TFA were based on the middle resonance of the quartet of CF_3CO_2D as 116.6 ppm. The ^{13}C NMR spectra were obtained in two observation modes: complete proton-decoupled mode (COM), and gated nondecoupling with NOE mode (NOE), which provided useful data (coupling constant J_{C-H} and mode of long-range coupling) for spectral assignment.

Reactions of α-(Methoxycarbonyl)bis(p-methylphenyl)methanol in TFSA. To 4.4 mL (100 equiv) of TFSA cooled at 0 °C in an ice water bath was added 135.4 mg (1 mmol) of α-(methoxycarbonyl)bis(p-methylphenyl)methanol (**4A**) in portions with vigorous stirring. The purple-red solution was stirred for

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(23) Schafer, J. P.; Corey, E. J. *J. Org. Chem.* **1959**, *24*, 1825.

5 h, poured into ice and water (400 mL), and extracted with CH_2Cl_2 (500 mL). The organic layer was dried over Na_2SO_4, and the solvent was evaporated off to give 119.0 mg (94%) of pure **10A**, mp 104 °C (recrystallized from *n*-hexane; colorless needles). ^1H NMR: δ 7.541 (s, 2 H), 7.502 (d, 2 H, 7.70), 7.135 (d, 2 H, 8.1), 4.784 (s, 1 H), 3.7059 (3 H, s), 2.438 (6 H, s). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39; N, 0.0. Found: C, 80.63; H, 6.19; N, 0.0.

Reaction of α-(Methoxycarbonyl)bis(*p*-methylphenyl)methanol in TFA. To 6.1 mL (200 equiv) of TFA cooled at 0 °C in an ice water bath was added 105.0 mg (0.4 mmol) of **4A** in portions with vigorous stirring. The orange solution was stirred for 0.5 h at 0 °C and subsequently at ambient temperature for 1.75 h. The solution was poured into ice and water (400 mL) and extracted with CH_2Cl_2 (400 mL). The organic layer was dried over Na_2SO_4, and the solvent was evaporated off to give 111.9 mg of the residue, which was flash chromatographed (CH_2Cl_2–*n*-hexane, 1:2) to give 35.9 mg (25%) of α-(methoxycarbonyl)bis(*p*-methylphenyl)methyl trifluoroacetate as a nonpolar fraction and 66.3 mg (63%) of recovered **4A**. α-(Methoxycarbonyl)bis(*p*-methylphenyl)methyl trifluoroacetate: ^1H NMR: 7.289 (d, 4 H, 8.42), 7.143 (d, 4 H), 3.845 (s, 3 H), 2.350 (s, 6 H).

Reaction of α-Carboxybis(*p*-methylphenyl)methanol in TFSA. An aliquot of 4.4 mL (100 equiv) of TFSA was cooled to −20 °C in a dry ice–ethanol bath, and then α-carboxybis(*p*-methylphenyl)methanol (**4B**) (178.8 mg) was added in portions with vigorous stirring. The solution was stirred for 2 h before usual aqueous workup as described above. The crude residue was again dissolved in CH_2Cl_2 (100 mL) and washed with 2 N NaOH (200 mL). The aqueous layer was acidified with concentrated HCl and extracted with CH_2Cl_2 (300 mL). The solvent was evaporated to give 136.3 mg (82%) of pure **10B**: mp 241–242 °C (recrystallized from *n*-hexane–CH_2Cl_2). ^1H NMR: δ 7.538 (s, 2 H, $H_{4,5}$), 7.519 (d, 2 H, 7.7), 7.136 (d, 2 H, 7.7), 4.783 (s, 1 H, H_9), 2.437 (s, 6 H). ^{13}C NMR ($CDCl_3$ + DMSO-d_6): δ 174.5 (s, C_{10}), 141.2 (s), 138.9 (s), 137.0 (s), 127.7 (d, 158.5), 125.1 (d, 161.4), 119.91 (d, 155.1), 21.2 (q, 126.2). The structure was confirmed after methyl esterification. The IR and NMR spectra were in good accordance with those of an authentic sample.

Reaction of α-(*p*-Methylbenzoyl)bis(*p*-methylphenyl)methanol in TFSA. To 10.6 mL (200 equiv) of TFSA cooled at 0 °C in an ice bath was added α-(p-methylbenzoyl)bis(*p*-methylphenyl)methanol (**4C**) (198.1 mg, 0.6 mmol) in portions with vigorous stirring. The purple-red solution was stirred at 0 °C for 3 h and poured into ice and water (400 mL). The crude residue obtained by usual extraction was purified by flash column chromatography with the solvent CH_2Cl_2–*n*-hexane (1:4) to give 130.4 mg (70%) of the fluorene **10C** and 26.0 mg (14%) of the phenanthrol **11C**. **10C**: mp 160–161.5 °C, colorless needles (recrystallized from *n*-hexane). ^1H NMR: δ 7.636 (2 H, d, 8.43), 7.625 (2 H, s), 7.246 (2 H, d, 9.15), 7.144 (2 H, d, 8.01), 7.059 (2 H, d, 7.7), 5.487 (s, 1 H), 2.444 (6 H, s), 2.351 (3 H, s). ^{13}C NMR: δ 197.91 (s), 143.85 (s), 141.69 (s), 140.08 (s), 137.66 (s), 133.98 (s), 129.19 (s), 128.26 (d), 124.76 (d), 120.93 (d), 58.23 (d), 21.57 (q). Anal. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45; N, 0.0. Found: C, 88.16; H, 6.56; N, 0.0. **11C**: oily material. Mass: *m/e* 312. ^1H NMR δ 8.483 (s, 1 H, H_4), 8.442 (s, 1 H, H_5), 8.241 (d, 1 H, H_2, 8.42), 7.472 (d, 1 H, H_1, 8.06), 7.410 (d, 2 H, H_3, 7.7), 7.344 (d, 2 H, H_m, 7.69), 7.294 (d, 1 H, H_7, 8.43), 7.238 (d, 1 H, H_8, 8.43), 5.370 (s), 2.647 (3 H, s, CH_3^3), 2.567 (3 H, s, CH_3^6), 2.490 (3 H, s, CH_3^p). ^{13}C NMR: δ 145.48 (s), 138.24 (s), 136.64 (s), 133.13 (s), 131.53 (s), 130.77 (d), 130.65 (d), 130.42 (d), 128.29 (d), 128.17 (d), 126.19 (s), 125.28 (d), 123.00 (s), 122.86 (d), 122.36 (d), 122.27 (d), 22.12 (q), 21.71 (q), 21.36 (q).

Reaction of Benzoin in TFSA. Benzoin **14** (106.9 mg) was added in portions to well-stirred TFSA (8.8 mL, 200 equiv) cooled at 0–5 °C in an ice water bath. After stirring at 0–5 °C for 45 min, usual aqueous workup was carried out. The residue obtained by the usual extraction procedure (with CH_2Cl_2) was flash chromatographed (AcOEt–*n*-hexane, 1:5) to give 11.1 mg (11%) of **16** as a major product. The yield was not optimized. **16**: ^1H NMR: δ 8.673 (dd, 1 H, 8.06, 1.46), 8.5854 (dd, 1 H, 1.83, 8.25), 8.312 (dd, 1 H, 1.47, 8.06), 7.717–7.676 (m, 2 H), 7.646 (dt, 1 H, 1.47, 7.44). The IR and NMR spectra of the product were identical with those of authentic **16**.

Reaction of α-(*p*-Methoxybenzoyl)bis(*p*-methoxyphenyl)methanol in TFA. A solution of α-(*p*-methoxybenzoyl)bis(*p*-methoxyphenyl)methanol (**3C**) (75.6 mg, 0.2 mmol) in TFA (200 equiv, 3.54 mL) was heated at 70 °C for 1.25 h and then poured into ice and water (400 mL). The mixture was extracted with CH_2Cl_2 (500 mL), and the solvent was evaporated. The residue was flash chromatographed with the solvent CH_2Cl_2–*n*-hexane (1:1) to give 68.9 mg (96%) of the benzofuran **18**, mp 85.5–87.5 °C (recrystallized from *n*-hexane). ^1H NMR: δ 7.552 (dd, 2 H, 6.96, 2.2), 7.394 (d, 2 H, 8.79), 7.317 (d, 1 H, 8.42), 7.0562 (d, 1 H, 2.2), 6.975 (d, 2 H, 8.79), 6.841 (dd, 1 H, 9.89, 2.2), 6.825 (d, 2 H, 9.16), 3.853 (6 H, s), 3.849 (3 H, s). ^{13}C NMR: δ 159.26 (s), 158.91 (s), 158.03 (s), 154.7 (s), 149.54 (s), 130.77 (d, 158.5), 127.9 (d, 161.4), 125.22 (s), 124.03 (s), 123.71 (s), 119.85 (d, 161.4), 115.47 (s), 114.36 (d, 161.4), 113.84 (d, 161.4), 111.53 (d, 161.4), 95.68 (d, 164.4), 55.72 (q, 143.7), 55.22 (q, 143.8). Anal. Calcd for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59; N, 0.0. Found: C, 76.44; H, 5.62; N, 0.0.

Reaction of α-(*p*-Methoxybenzoyl)bis(*p*-methoxyphenyl)methanol in TFSA. A solution of **3C** (76.5 mg, 0.2 mmol) in TFSA (3.5 mL, 200 equiv) was heated at 70 °C for 4 h and submitted to the usual aqueous workup. Purification by flash column chromatography (CH_2Cl_2–*n*-hexane) gave 2.1 mg (3%) of the benzofuran **18** and the 40 mg (52%) of the starting material **3C**.

NMR Spectroscopic Evidence for a Twin-Chair Conformer in Quinoxaline-Annelated Bicyclo[4.4.1]undecanones

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In NMR spectra at low temperature, it was found that diquinoxalino-, quinoxalinobenzo-, and quinoxalinonaphtho-annelated bicyclo[4.4.1]undeca-3,8-dien-11-ones, **1** and **5**, exist in equilibrium among two chair–boat conformers and a twin-chair one, which was not detected in the spectra of the corresponding dibenzo, benzonaphtho, and dinaphtho analogues.

Previously, we have reported[2] that dibenzo- and dinaphtho-annelated bicyclo[4.4.1]undecan-11-ones invert between two chair–boat conformers, and that, from the measured $\Delta G^{\ddagger}$ values (10–15 kcal/mol), their inversion

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