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Reaction of Diphenylmethyl Cations in a Strong Acid. Participation of Carbodications with Positive Charge Substantially Delocalized over the Aromatic Rings

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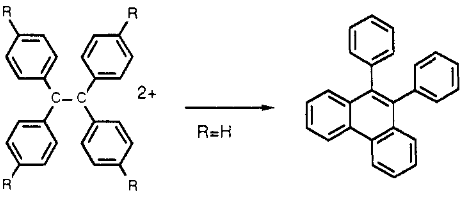
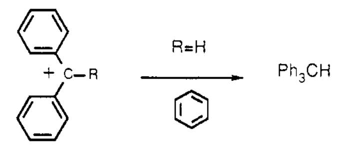
Abstract: Diphenylmethanol bearing a carbonyl group such as benzoyl, acetyl, methoxycarbonyl, or carboxyl gave the 9-substituted fluorene in high yield in the presence of trifluoromethanesulfonic acid (TFSA) at −50 °C. In the case of the benzoyl substituent, 9-phenylphenanthr-10-ol was formed together with the fluorene. The diphenylmethyl cations substituted with electron-withdrawing ketone, ester, and cyano groups were shown to be stable species by silver ion assisted ionization of the corresponding diphenylmethyl chlorides. The reaction of diphenylmethyl cations bearing ketone and ester groups to give the fluorenes and phenylphenanthrol requires the presence of a strong acid. We propose the participation of the carbodications with adjacent carbenium centers, the O-protonated carbonyldiphenylmethyl dications, in TFSA. The conjugate carbenium centers of the carbodications are significantly stabilized by enhanced delocalization of the positive charge over the aromatic rings, as in the well-known tetraarylethylene dications. NMR spectroscopic studies on the ions from bis(*p*-methoxyphenyl)methanol bearing a carbonyl group in highly acidic media demonstrate the formation of the stabilized carbodications with adjacent carbenium centers.

Scheme I



1 (R=OCH$_3$, H) 2

Scheme II



3 (R=H, CH$_3$)

In the last two decades, experimental and theoretical studies of doubly charged cations have become a very active field of chemical and physical research.[1] Various dipositively charged dications are now known to be formed in acidic media, and several are stable enough to be directly observed by spectroscopic methods.[1b] These stable dications are stabilized by conjugation with aromatic rings or by aromaticity; for example, tetraarylethylene dications **1** are discrete dications stabilized by conjugating aromatic rings.[2] In these dications, the adjacent carbenium centers are stabilized by the delocalization of substantial positive charge over the aromatic rings.[3] The parent tetraphenylethylene dication **1** (R = H) can be observed by NMR spectroscopy at low temperature, while at elevated temperature this dication yields 9,10-diphenylphenanthrene (**2**; Scheme I).[3,4] This π electrocyclization of the hexadienylium system to the phenanthrene was attributed to the substantial delocalization of positive charges over the benzene nuclei. Such adjacent positive centers could also be effectively stabilized by lone-pair electrons of a heteroatom in place of an aromatic nucleus.[5] We will describe here the involvement of adjacent carbodications stabilized by an oxygen atom in the reactions of diphenylmethyl cations **11–13** in a strong acid, trifluoromethanesulfonic acid.[6] Cyclization of the diphenylmethyl cations to corresponding 9-substituted fluorenes (**6**, **8**, and **10**, respectively) was found when the substituents at the cationic center were carbonyl groups. Several cyclization reactions of diphenylmethanol to fluorenes have appeared in the literature. Benzilic acid in the presence of aluminum trichloride gave fluorene-9-carboxylic acid.[7] A similar reaction was also catalyzed by concentrated sulfuric acid.[8] The intermediacy of diphenylmethyl cations substituted with a carboxyl group has been postulated in these reactions. Even when these reactions were carried out in the presence of benzene, an intermolecular reaction of benzene to triphenylacetic acid was not observed.[7,8] These results are in contrast to the reaction of cyanodiphenylmethyl cation, which does not cyclize to the fluorene in the presence of aluminum trichloride as a catalyst but gives triphenylacetonitrile in benzene.[9,10b] Diphenylmethyl cations in an acidic medium seem to

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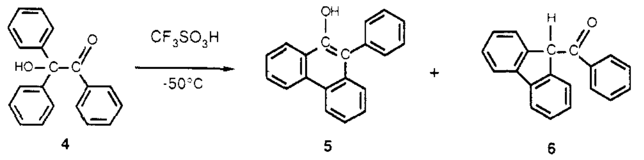
Scheme III



have diverse reactivities depending on the substituents on the carbenium ion centers. Several reports have recently appeared describing the formation and reaction of the antimony pentafluoride salt of di-*p*-anisyl(*p*-methoxybenzoyl)methyl cation and showing that it undergoes diverse reactions to form benzofuran derivatives.[10a,11] The carbonyl-substituted diphenylmethanol was reported to give benzofurans, catalyzed by sulfuric acid,[12a] though the formation of the fluorene has also been reported under similar conditions.[12b] This and other discrepancies in the literature[13] suggested that further investigation of the acid-catalyzed reactions of diphenylmethyl cations under unified reaction conditions would be worthwhile.

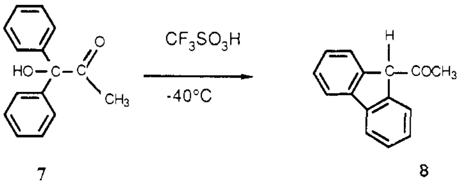
Cyclization of benzoyldiphenylmethanol (**4**) catalyzed by TFSA gave 9-benzoylfluorene (**6**) and 9-phenylphenanthr-10-ol (**5**). The formation of the latter can be explained by involvement of the 1,1,2-triphenyl-2-hydroxyethylene dication **14**, the ethylene dication stabilized by three aromatic rings and an oxygen lone pair of the hydroxyl group. It seems reasonable to conclude that benzoylfluorene was formed via the same dication. This conclusion is supported by the findings that the diphenylmethyl cations (**11**, **12**) bearing a π-electron-withdrawing group are stable under neutral conditions and a strong acid was required for cyclization to the fluorene and phenanthrol from these diphenylmethyl cations. Similar reactions occurred with diphenylmethyl cations bearing a carboxy or methoxycarbonyl group. These results are compatible with the recent investigation on carbenium ions substituted with π-electron-withdrawing substituents;[10] it was found both kinetically and spectroscopically that these cations are stable in spite of conjugation with an electron-withdrawing substituent at the cationic centers.

Results and Discussion

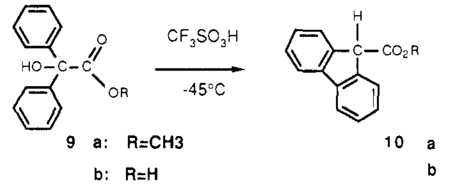
Reactions of Diphenylmethyl Cations in TFSA. The parent diphenylmethyl cation **3** (R = H), prepared by dissolving benzhydrol in TFSA, was not stable even at −50 °C. In the presence of benzene, triphenylmethane was obtained quantitatively (Scheme II), indicating that the electrophilicity at the central carbon atom is high enough to allow reaction with nonactivated benzene. This reaction was also catalyzed by equimolar TFSA. α–Methyldiphenylmethyl cation **3** (R = CH_3) was considered to be in equilibrium with 1,1-diphenylethylene in an acidic medium.[13] In TFSA solution, the cation was stable enough to be observed by direct NMR spectroscopy, and quenching of the solution with water yielded quantitatively 1,1-diphenylethylene even in the presence of benzene. These results demonstrate the localization of positive charge at the α position in these simple diphenylmethyl cations.

Reactions of Diphenylmethyl Cations Substituted with Carbonyl Groups in TFSA. α-Benzoyldiphenylmethanol (**4**) gave 9-benzoylfluorene (**6**) in 74% yield, together with 9-phenylphenanthr-10-ol (**5**) in a yield of 8.4% when **4** was dissolved in an excess of TFSA (500 equiv) at −50 °C, followed by the usual aqueous workup (Scheme III). The reaction was very rapid even at −50 °C, and the starting material disappeared immediately after the addition. The reaction was very clean, and no benzofuran compound was found.[12] The assignments of both compounds were confirmed by alternative synthesis.[14] Even in the presence of a large excess of benzene these products were formed, but no triphenylmethane derivative was found. Neither the fluorene nor phenylphenanthrol was formed when the reaction was catalyzed by an equimolar or smaller amount of TFSA with benzene as a cosolvent. Both products are reasonably stable in TFSA at 0 °C, and on quenching of the acid solution with water, the material was recovered quantitatively. The fluorene is concluded to be formed by cyclization between the benzene ring attached to the C_α atom, and the phenanthrol is formed via cyclization between the benzene ring of the benzoyl group and the benzene at the C_α atom. Complete recovery of the fluorene **6** from the TFSA solution excludes the formation of the phenanthrol **5** by a mechanism involving ring expansion and rearrangement of the phenyl ring of the fluorene **6**.[15] No phenanthrene derivative was obtained in the acid-catalyzed reaction of α-acetyldiphenylmethanol (**7**) (vide infra), which also excludes the above mechanism. Formation of 9-benzoylfluorene was observed, though in only 4% yield, when the catalytic acid was replaced with 97% sulfuric acid (0 °C, 1 min). Sulfuric acid is not a suitable catalyst, since the acid is not strong enough and the isolated fluorene product is rapidly converted to water-soluble materials (presumably sulfonated compounds).[12]

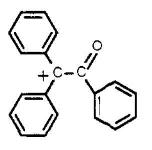
Scheme IV



Scheme V



To demonstrate the generality of the carbonyl substituent effect the reaction of α-acetyldiphenylmethanol (**7**) in TFSA was also examined.[16] α-Acetyldiphenylmethanol gave 9-acetylfluorene (**8**) in 70% yield at −40 °C in the presence of TFSA (Scheme IV). This reaction shows that the phenyl group of the benzoyl substituent is not crucial for the reaction. Previous reports indicated that benzofurans were formed from carbonyl-substituted diphenylmethanols by the action of sulfuric acid, and it was proposed that the benzofurans were formed by electrocyclization of the diphenylmethyl cations **11** and **12** as the oxypentadienyl cations.[12,13] The results described here, however, are in contrast to the previous reports. The higher acidity of TFSA possibly decreases the resonance contribution of the oxypentadienyl cation in the diphenylmethyl cations **11** and **12** and inhibits the carbonyl oxygen nucleophilic transfer discussed previously.[12,13] These results suggest second protonation on the carbonyl oxygen atom of the



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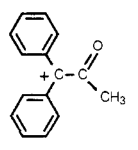

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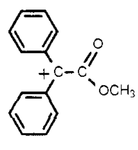

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[15] It was shown that ring expansion of fluorenyl derivatives in the presence of acidic reagents afforded phenanthrenes: Werner, A.; Grob, A. *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 2887. Mathieu, A.; Boyer, J. *C. R. Seances Acad. Sci., Ser. C* **1968**, *267*, 1078. Rouzaud, J. *Ibid.* **1959**, *249*, 1523. *Bull. Soc. Chim. Fr.* **1968**, 4851. The ring expansion reaction may be suppressed by protonation on the fluorene ring in the acid system.

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Table I. Reactions of α-Benzoyldiphenylmethanol and α-Benzoyldiphenylmethyl Chloride with Electrophilic Catalysts

		conditions				product yield, %			
run	substr	catalyst	time, min	temp, °C	treatment[a]	**4**	**16**	**5**	**6**
1	**4**	CF_3SO_3H[b]	30	-48	A	0	0	9	76
2	**16**	$AgBF_4$[c]	60	-57	A	50	33	0	0
3	**16**	CF_3CO_2Ag[c]	50	-58	A	58	33	0	0
4	**16**	$AgBF_4$[c]	50	-59	B	0	0	6	69
5	**16**	CF_3CO_2Ag[c]	50	-59	B	0	0	5	79

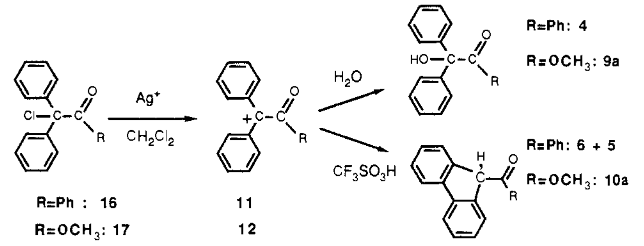
[a] A, aqueous workup; B, added to precooled CF_3SO_3H at -50 °C and stirred at this temperature for 30 min, followed by aqueous workup as in A. [b] 500 equiv was used. [c] 2 equiv was used with CH_2Cl_2 as a cosolvent.

Table II. Reactions of (α-Methoxycarbonyl)diphenylmethanol and (α-Methoxycarbonyl)diphenylmethyl Chloride with Electrophilic Catalysts

		conditions				product yield, %		
run	substr	catalyst	time, min	temp, °C	treatment[a]	**9a**	**17**	**10a**
1	**9a**	CF_3SO_3H[b]	55	-55	A	0	0	79
2	**17**	$AgBF_4$[c]	55	-58	A	100	0	0
3	**17**	CF_3SO_3Ag[c]	50	-59	A	97	0	0
4	**17**	$AgBF_4$[c]	55	-59	B	0	0	85
5	**17**	CF_3SO_3Ag[c]	55	-58	B	0	0	96

[a] A, aqueous workup; B, added to precooled CF_3SO_3H at -50 °C and stirred at this temperature for 30 min, followed by aqueous workup as in A. [b] 500 equiv was used. [c] 2 equiv was used with CH_2Cl_2 as a cosolvent.

Scheme VI

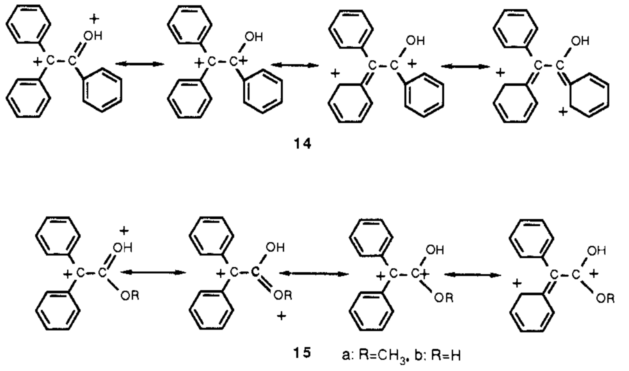


carbonyl-substituted diphenylmethyl cations.

Formation of the fluorene was also observed in the reaction of (α-methoxycarbonyl)diphenylmethanol (**9a**) in TFSA when the diphenylmethanol was dissolved in TFSA at -45 °C (2 h): **9a** gave 9-(methoxycarbonyl)fluorene (**10a**) in 81% yield (Scheme V). In a similar manner, benzilic acid (**9b**) reacted to give fluorene-9-carboxylic acid (**10b**) in 65% yield in TFSA. The fluorene could be recovered after dissolving it in TFSA at the same temperature. It was reported that the fluorene was formed by sulfuric acid catalysis, and the product was found to be unstable in this acid.[12] While divergent behaviors were reported in the reactions of diphenylmethyl cations bearing carbonyl groups in sulfuric acid,[12] we have now established the convergent reaction conditions for compounds with an electron-withdrawing substituent such as a carbonyl, an ester, or an acid group, catalyzed by TFSA. In order to clarify the reactivity of the electron-deficient diphenylmethyl cations and the role of the acid in the formation of fluorenes, the reactivities of the diphenylmethyl cations, prepared under neutral conditions, were investigated.

Silver Ion Assisted Ionization of Diphenylmethyl Chlorides. The diphenylmethyl cations were obtained by the silver ion assisted ionization of the corresponding diphenylmethyl chlorides in dry dichloromethane.[10a] The reaction products from cations formed in neutral conditions were analyzed after aqueous workup or after treatment with a large amount of TFSA at low temperature (followed by aqueous workup). The reaction conditions and results are summarized in Tables I and II. A solution of the chloride **16** in dichloromethane[17] was treated with a 2-fold molar excess of silver trifluoroacetate or silver tetrafluoroborate at low temperature (-57 °C) to yield a red solution of the corresponding diphenylmethyl cation, accompanied with precipitates of silver chloride (Scheme VI). The solution is stable even at 0 °C for more than 0.5 h. After aqueous workup, the products were the diphenylmethanol **4** and the recovered diphenylmethyl chloride **16**: the yields are similar with both silver salts (silver trifluoroacetate, 58% and 33%; silver tetrafluoroborate, 50% and 33%, respectively) (Table I, runs 2 and 3). No trace of benzoylfluorene **6** or phenylphenanthrol **5** was detected.[12] In the absence of silver ion the diphenylmethyl chloride **16** was not hydrolyzed to the corresponding alcohol **4** and was recovered unchanged on aqueous workup. When the red solution of the diphenylmethyl cation **11** in dichloromethane was added to an excess of TFSA at -50 °C instead of water, the fluorene **6** and phenylphenanthrol **5** were formed in yields comparable with those obtained in the reaction of the diphenylmethyl alcohol **4** with TFSA (Table I, runs 4 and 5).

Scheme VII



A similar investigation was performed on the diphenylmethyl cation **12** substituted with a methoxycarbonyl group. It is noteworthy that the diphenylmethyl cation **12** prepared from the corresponding precursor[18] by silver ion assisted ionization ($AgBF_4$ and silver triflate were used) was stable, and the fluorene was not formed (Table II, runs 2 and 3). The reaction is independent of the counterparts of the catalytic silver salts. The fluorene was not formed even at 0 °C from the diphenylmethyl cation **12**. The presence of excess TFSA is required for the formation of the fluorene **10a** from the preformed diphenylmethyl cation[13] (Table II, runs 4 and 5).

These results strongly indicate the requirement of an acid for the formation of fluorenes. Consequently, intervention of the diphenylmethyl dications **14** and **15** with a protonated carbonyl group is proposed (Scheme VII). These dications would have more positive charge delocalization into the aryl rings owing to the resonance contribution of adjacent cation-cation repulsive interactions.

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Table III. ^{1}H NMR Spectroscopic Data for Ions in Superacids[a,b]

	acid syst[c]	temp, °C	OH	H_o	H_m	p-OCH_3	others
21	A	-30		8.25 (d, 8.8)	7.73 (d, 8.8)	4.55 (s)	4.84 (s, CH_3)
	B	-30	13.82 (s)	7.98 (br s)	7.67 (br s)	4.83 (s)	4.98 (s, CH_3)
27	A	-30		8.35 (d, 8.8)	7.77 (d, 8.8)	4.58 (s)	
	B	-36	14.08 (br s)	8.09 (br s)	7.72 (br s)	4.88 (s)	
25	A	-30		8.56 (d, 8.8)	7.61 (d, 8.8)	4.44 (s)	9.12 (s, CH)

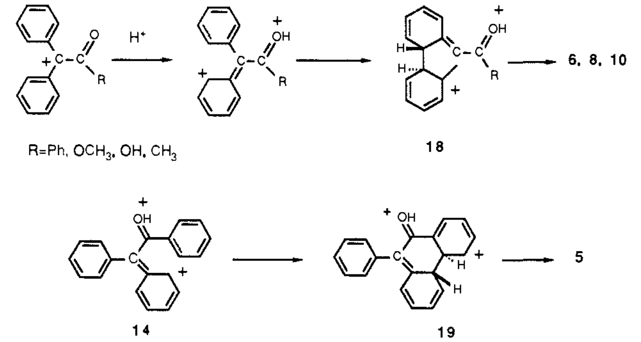
[a] Chemical shifts (ppm) from external capillary Me_4Si in acetone-d_6. [b] Coupling modes and ^{1}H–^{1}H coupling constants in hertz are shown in parentheses: d = doublets, br s = broad singlet, s = sharp singlet. [c] A, CF_3SO_3H; B, CF_3SO_3H–SbF_5 (2.5:1, mole ratio).

Table IV. ^{13}C NMR Spectroscopic Data for Ions in Superacids[a,b]

	acid syst[c]	temp, °C	C_o	C_m	C_p	C_{ipso}	C_1	C_2	OCH_3	CH_3
21	A	-20	143.9 (167.3)	119.3 (170.2)	174.7	127.6	176.0	168.6	57.7 (146.7)	58.4 (145.2)
	B	-20	142.7 (170.2)	122.8 (173.8)	173.6	134.7	181.6	151.1	68.1 (158.4)	68.1 (158.4)
27	A	-20	143.8 (164.4)	119.3 (170.2)	174.8	127.3	176.1	168.8	57.7 (149.6)	
25	A	-20	144.3 (166.5)	118.0 (167.2)	174.0	129.6	178.6 (155.6)		56.9 (146.7)	
1[d]		-30	144.7	119.4	175.3	135.3	181.9		58.4	

[a] Chemical shifts (ppm) are calibrated from Me_4Si in $CDCl_3$. [b] ^{13}C–^{1}H coupling constants are shown in parentheses in hertz. [c] See footnote *c* in Table III. [d] R = OCH_3, in SO_2. See ref 3.

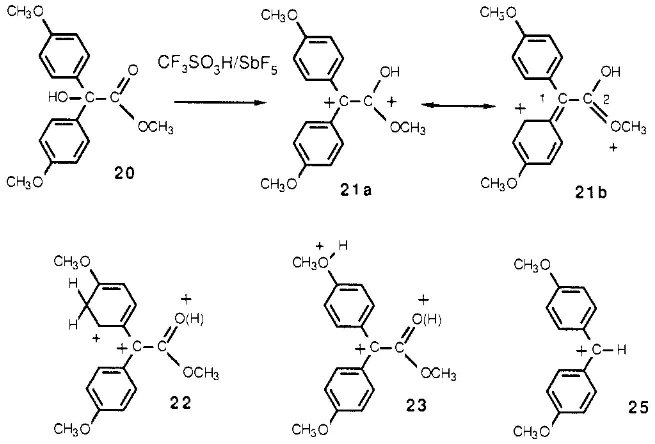
Scheme VIII



Proposed Mechanism. The increased delocalization of positive charge facilates 4π electrocyclization in the conrotatory manner[19] to the intermediates **18** and then to the fluorenes (Scheme VIII). The intermediates **18** are known to be aromatized to fluorenes. Conventional 4π electrocyclization of the diphenylmethyl cations (**11–13**) was excluded since those ions prepared by silver ion ionization from the chloride precursors gave no cyclization product. The carbonyl-protonated diphenylmethyl dications (**14**, **15**), a kind of adjacent dication, participate in the cyclization reaction. The positive charge of this ion is, because of charge–charge repulsion, greatly delocalized into the aromatic rings. The species with the positive charge substantially delocalized over the aromatic rings has the pentadienylium character. Thus, the proposed protonated diphenylmethyl cations obtain an effective overlap of the π orbitals for the electrocyclization to fluorenes. This is in agreement with the fact that benzophenone did not give a Nazarof-type reaction product,[20] fluorenol or its derivatives, in TFSA even at 80 °C.

In the case of the benzoyl substituent, another cyclization occurred: the 4π ground-state electrocyclization between the benzoyl moiety and the phenyl group in the conrotatory manner (**14** → **19**) to give 9-phenylphenanthr-10-ol (**5**). This reaction was very similar to that of the tetraphenylethylene dication **1** (R = H). The tetraarylethylene dications **1** are established to be carbodications with adjacent carbenium centers. On TFSA catalysis at -50 °C, tetraphenylethylene diol gave 35% yield of phenylpinacol and 36% yield of 9,10-diphenylphenanthrene (**2**), indicating the formation and cyclization of the tetraphenylethylene dication under these conditions.[2,3] The charge–charge repulsion causes the charge to delocalize substantially over the aromatic rings. The formation of 9-phenylphenanthr-10-ol (**5**) by the reaction of α-benzoyldiphenylmethanol (**4**) in a strong acid demonstrates the presence of a similar resonance contribution in the hydroxytriphenylethylene dication **14** to that in the tetraphenylethylene dication **1** (R = H).

Scheme IX



Similar dications (**15**) are proposed in the acid-catalyzed reactions of the (α-methoxycarbonyl)diphenylmethyl cation (**12**) and the carboxydiphenylmethyl cation. The dications (**15a**, **15b**) were thought to be relatively stable ones in which the neighboring carbenium centers are stabilized by two pairs of nonbonding electrons of the two oxygen atoms. The formation of the fluorene derivatives previously described in the presence of sulfuric acid from (methoxycarbonyl)diphenylmethanol (**9a**) and benzilic acid (**9b**) can also be reasonably interpreted in terms of the participation of dications such as **15**.

NMR Spectroscopic Studies of the Stable Carbodications with Adjacent Carbenium Centers. For direct observation of the proposed carbodications with adjacent carbenium centers (such as **14** and **15**), NMR measurement was performed on a solution of (α-methoxycarbonyl)diphenylmethanol (**9a**) in TFSA at -40 °C. The observed species was assigned as protonated 9-(methoxycarbonyl)fluorene (**10a**) (the site of protonation was the methoxycarbonyl group as judged from the chemical shifts), suggesting that the cyclization reaction to the fluorene is fast even at -40 °C. A solution of the ion from (α-methoxycarbonyl)diphenylmethanol in FSO_3H–SbF_5 (1:1) was prepared at -50 °C, but the transient color of the solution immediately changed and the spectrum obtained was essentially the same as that of protonated **10a**. However, the ion formed from (α-methoxycarbonyl)bis(p-methoxyphenyl)methanol (**20**; Scheme IX) both in TFSA and in TFSA–SbF_5 is sufficiently stable[21] and gives clear NMR signals

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[19] Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic: New York, 1970; Chapter 5. Deno, N. C.; Pittman, C. U., Jr.; Turner, J. O. *J. Am. Chem. Soc.* **1965**, *87*, 2153. Sorensen, T. S. *Can. J. Chem.* **1964**, *42*, 2768; *J. Am Chem. Soc.* **1967**, *89*, 3782, 3794.

[20] Nazarov, I. N.; Zaretskaya, I. I. *Zh. Obsh. Khim.* **1957**, *23*, 693. Reviews: Santelli-Rouvier, C.; Santelli, M. *Synthesis* **1983**, 429.

[21] (a) Ford-Moore, A. H. *J. Chem. Soc.* **1947**, 952. (b) Shacklett, C.; Smith, H. A. *J. Am. Chem. Soc.* **1953**, *75*, 2654. (c) Bachmann, W. E.; Sternberger, H. R. *Ibid.* **1934**, *56*, 170.

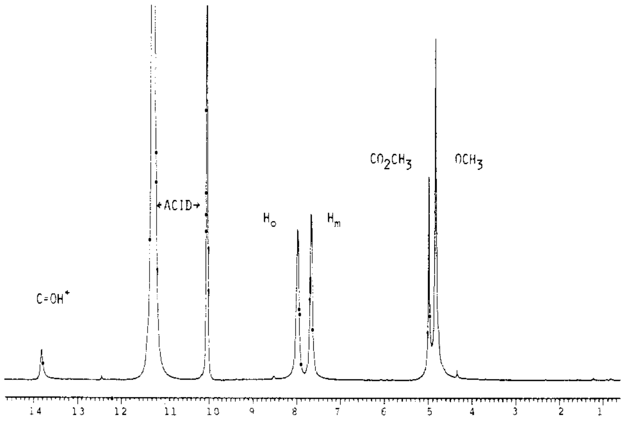


Figure 1. 400-MHz ^1H NMR spectrum of (α-methoxycarbonyl)bis(*p*-methoxyphenyl)methanol (**20**) in TFSA-SbF_5 (2.5:1) at −30 °C. The C=OH^+ signal is observed.

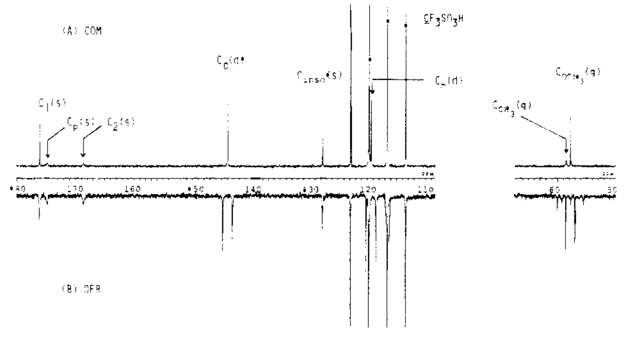
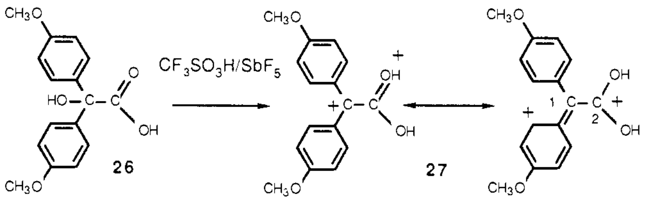
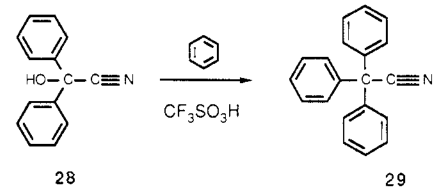


Figure 2. 100-MHz ^{13}C NMR spectrum of (α-methoxycarbonyl)bis(*p*-methoxyphenyl)methanol (**20**) in TFSA at −20 °C: (A) proton complete decoupling, (B) proton off-resonance decoupled spectrum.

Scheme X



Scheme XI



even at 0 °C (Figures 1 and 2). The chemical shifts of the ion are listed in Tables III and IV, together with the data for the bis(*p*-methoxyphenyl)methyl cation (**25**) formed from the bis(*p*-methoxyphenyl)methanol (**24**) and those for the tetrakis(*p*-methoxyphenyl)ethylene **1** (R = OCH_3).[3] (α-Methoxycarbonyl)bis(*p*-methoxyphenyl)methanol (**20**) gave a deep purple solution in TFSA, and aqueous quenching of the solution of TFSA cooled at 0 °C yielded the starting material quantitatively. No deuterium exchange of protons of the ion from **20** was observed in CF_3SO_3D from −30 °C to 0 °C. This excludes C-protonation on the aromatic rings in the acid, such as in structure **22**. For direct observation of the O-protonation, we prepared the ions in a more acidic system: TFSA containing SbF_5 (mole ratio TFSA:SbF_5 = 2.5:1 or 1:1). In the ^1H NMR spectra (in TFSA:SbF_5 = 2.5:1 at −30 °C), a singlet absorption was observed at 13.82 ppm, which can reasonably be assigned to a C=OH^+ group.[22] Five sets of absorptions in the ratio 1:4:4:3:6 (from lower field) can be seen (Figure 1).[23] The two anisyl groups are equivalent, and the aromatic OCH_3 groups give singlet absorptions.[24] These results exclude the O-protonation of the aromatic OCH_3 group, such as in structure **23**. Although general high-field shifts of absorptions were observed on addition of SbF_5, especially in the ^1H NMR spectra (see Table III), it could reasonably be concluded that the same ion was formed in both the acid systems. The differences should be due mainly to the effect of the medium, because the relative positions of these absorptions in the ^1H NMR spectra were almost the same. The ^{13}C NMR data in the two acid systems (Figure 2: in TFSA at −20 °C) support this conclusion. In the ^1H NMR spectra, the methoxycarbonyl group (CH_3) of **21** exhibited the largest deshielding (1.00 ppm deshielded from neutral **20**) upon protonation, indicating a significant contribution of the resonance structue **21b** (C=OCH_3^+). In the ^{13}C NMR spectra, the chemical shifts of the ion formed from **20** both in TFSA and TFSA-SbF_5 (2.5:1) were well correlated to those of the tetrakis(*p*-methoxyphenyl)ethylene dication **1** (R = OCH_3) previously reported.[3] These spectroscopic results provided strong evidence for the postulation that (α-methoxycarbonyl)bis(*p*-methoxyphenyl)methanol (**20**) gives the 1,1-bis(*p*-methoxyphenyl)-2-hydroxy-2-methoxyethylene dication (**21**) in TFSA. The dication **21** is very stable and gives no fluorene compound. This great stability of dication **21** is due to the strong electron-donating ability of OCH_3 on the aromatic rings. These observations are completely compatible with the well-established chemistry of the tetraarylethylene dications: the dication **1** (R = OCH_3) is sufficiently stable, while the parent dication **1** (R = H) yields 9,10-diphenylphenanthrene (**2**).[2-4]

Similar NMR studies were performed on the ions formed from 4,4′-dimethoxybenzilic acid (**26**) under the same superacid conditions (Scheme X). These results are summarized in Tables III and IV. the acid **26** also gave a purple solution in both TFSA and TFSA-SbF_5, and quenching with water gave the starting material in quantitative yield.[25] In the TFSA-SbF_5 (2.5:1) acid system at −36 °C, C=OH^+ groups equivalent to two protons were observed at 14.08 ppm,[22] indicating protonation of the carbonyl oxygen atom.[26] C-Protonation on the aromatic rings is excluded by the ^1H NMR spectra recorded in CF_3SO_3D. These results suggested that the acid **26**, as well as the ester **20**, yields the dipositively charged species, i.e., the 1,1-bis(*p*-methoxyphenyl)-2,2-dihydroxyethylene dication (**27**). This conclusion was supported by the ^{13}C NMR data for the ion in TFSA, which correspond reasonably well with those for the dication **21** formed from the ester **20**.

The ions (**21**, **27**) formed from the ester **20** and the acid **26** in TFSA were studied by means of UV spectroscopy. While the absorptions of the bis(*p*-methoxyphenyl)methyl cation (**25**) were at 500 nm (λ_{max}; log ϵ 4.61) and 360 nm (log ϵ 2.53) in TFSA at 0 °C, both the ester **20** and the acid **26** have an absorption maximum at 549 nm (log ϵ 5.05, 4.67, respectively), together with

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[22] Direct observations of C=OH^+ groups of protonated esters and carboxylic acids are described as follows. Ester: (a) Fraenkel, G. *J. Chem. Phys.* **1961**, *34*, 1466. (b) Birchall, T.; Gillespie, R. J. *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.

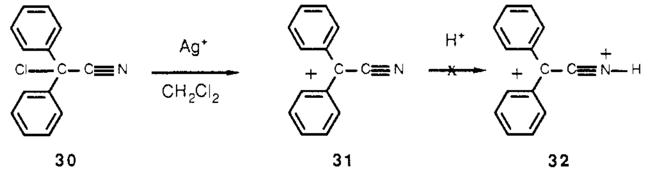
[23] At higher temperature (−5 °C) the proton exchange with the solvent is sufficiently rapid to cause merging of the C=OH^+ absorption with the acid peak. In TFSA-SbF_5 (1:1) the C=OH^+ signal was observed at 13.49 ppm at −10 °C.

[24] If O-protonation of the aromatic OCH_3 group occurred, the OCH_3 absorption would be observed as a doublet in the ^1H NMR spectra. See: Olah, G. A.; Comisarow, M. B.; Namanworth, E.; Ramsey, B. *J. Am. Chem. Soc.* **1967**, *89*, 5259.

[25] The purple color produced when **26** was dissolved in sulfuric acid was described in ref 21b. It could reasonably be concluded that the dication **27** was formed in sulfuric acid.

[26] In the TFSA-SbF_5 (2.5:1) acid system at −30 °C, the proton exchange with the solvent began to cause merging of the C=OH^+ absorption with the acid peak.

Scheme XII



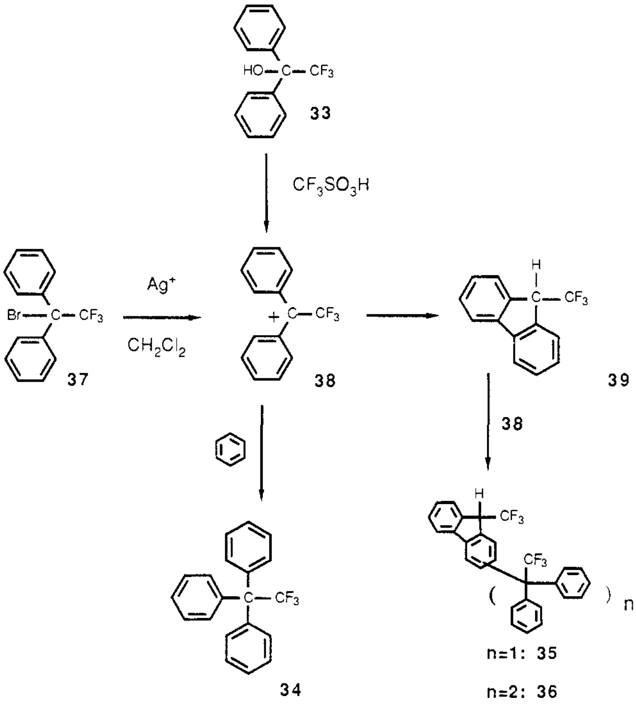
an absorption at 346 nm (log ε 3.56, 3.45, respectively) under the same conditions. The bathochromic absorption (549 nm) of the ions **21** and **27**, in comparison with that of the monocation **25** (500 nm), suggested strong perturbation arising from the carbenium center (C_2).

These NMR and UV spectroscopic studies provided supporting evidence for the formation of the carbodications with adjacent carbenium centers in the reaction of the diphenylmethyl cations in a strong acid.

Reaction of Cyanodiphenylmethanol in TFSA. Benzophenone cyanohydrin[27] (**28**) forms the stable cyanodiphenylmethyl cation (**31**) in a strong acid (HSO_3F-SbF_5).[10b] In spite of the electron-withdrawing ability of the cyano group, no fluorene compound was obtained in TFSA even at room temperature. The cyanodiphenylmethyl cation (**31**) prepared by the silver ion assisted ionization from cyanodiphenylmethyl chloride **30** was stable,[28] and aqueous quenching gave cyanodiphenylmethanol (**28**). In the presence of benzene, the cyanodiphenylmethanol (**28**) gave cyanotriphenylmethane (**29**) in 74% yield (Scheme XI), which is in contrast to the above cases. The preformed ion **31** was treated with TFSA, but no cyclization product was formed. This result is consistent with the previous result of the reaction of benzoyl cyanide with benzene catalyzed by aluminum trichloride through a postulated reaction intermediate cyanodiphenylmethyl cation.[9] By means of kinetic studies and NMR spectroscopic studies, a significant contribution of the mesomeric structures with delocalization of the π electrons of the cyano group to the cation center was demonstrated in the cyanodiphenylmethyl cation (**31**).[10b] A positive charge character was observed on the nitrogen atom of the cyano group owing to the resonance contribution. Therefore, protonation of the cyanodiphenylmethyl cation to **32** was not observed even in magic acid by NMR spectroscopic studies (Scheme XII).[10b] A high-energy barrier to protonation of the significantly positively charged nitrogen atom of the cyanodiphenylmethyl cation (**31**) is suggested on the basis of the different reactivity of the cation in a strong acid. Furthermore, the results are well compatible with the findings that the carbonyl-substituted diphenylmethyl *monocations* were stable and did not yield a fluorene product.

Reaction of (Trifluoromethyl)diphenylmethyl Cation in TFSA. Formation of the fluorene has been reported from (trifluoromethyl)diphenylmethanol (**33**) in concentrated sulfuric acid in a low yield.[13,29] The reaction was also catalyzed by TFSA (Scheme XIII). In the presence of benzene, the diphenylmethanol **33** gave (trifluoromethyl)triphenylmethane (**34**) in 26% yield, accompanied by the fluorene dimer **35** (23%) and fluorene trimer **36** (46%) when the catalytic acid was TFSA. The optimum yield (43%) of **34** was obtained by the use of a less acidic medium, 20% TFSA in TFA (v/v; H_0 −10), with the formation of dimer **35** (6%) and trimer **36** (31%). These results indicated that the reaction can be catalyzed by a rather weak acid. Dissolving the diphenylmethanol **33** in TFSA gave a deep red solution, and aqueous quenching of the solution after standing at −50 °C for 30 min yielded a fluorene **39** in 3% yield, accompanied by a large amount of polymeric products (dimer **35**, 3%; trimer **36**, 32%). It was evident that the diphenylmethyl cation **38** exhibited ambident reactivity both on the central carbon and on the aryl ring carbon.[13] Even in a dilute solution in TFSA, the dimeric and trimeric products **35** and **36** were formed in large amounts, while the yield of the parent fluorene **39** was low. These results indicated that the reaction of the cation **38** to give the fluorene is slow. It seems reasonable, therefore, that cation **38** could be observed by NMR spectroscopy in magic acid at a lower temperature.[30] In terms of Hammett constants, the cation **38** is considered to have more positive charge in the aryl rings than those diphenylmethyl cations bearing a *free* carbonyl or cyano group because of the potent electron-withdrawing ability of the trifluoromethyl group. The extent of charge delocalization over the aromatic nucleus in **38** is significant, but insufficient for ready electrocyclic reaction, based on the finding that the fluorene formation in this case is slow even at higher temperature, and the yield was low. To clarify the reactivity of the (trifluoromethyl)diphenylmethyl cation, the cation was prepared by silver ion (AgOTf) assisted ionization from the corresponding bromide **37** in CH_2Cl_2 at −50 °C.[31] It gave the fluorene trimer **36** in 35% yield and undefined fluorene derivatives, though the fluorene monomer was not obtained. It was found that the fluorene was formed in the absence of the catalytic acid from the diphenylmethyl cations when the substituent is trifluoromethyl. The result also constitutes a stringent test of the general applicability of the silver ion assisted ionization conditions for probing the formation of fluorenes from the diphenylmethyl cations.

Scheme XIII



Conclusion. It was found that diphenylmethanol bearing a carbonyl group such as a benzoyl, acetyl, methoxycarbonyl, or carboxyl group gave the 9-substituted fluorene in high yield in the presence of CF_3SO_3H at −50 °C. In the case of the benzoyl substituent, 9-phenylphenanthr-10-ol was formed together with the fluorene. The diphenylmethyl cations substituted with electron-withdrawing ketone, ester, and cyano groups were shown to be stable species by silver ion assisted ionization of the corresponding diphenylmethyl chlorides. The reaction of the diphenylmethyl cations bearing ketone and ester groups to give the fluorenes and phenylphenanthrol requires the presence of a strong acid. Thus, we propose the participation of the carbodications with adjacent carbenium centers, the O-protonated carbonyldiphenylmethyl dications, in TFSA. The conjugate carbenium centers of the carbodications are significantly stabilized by enhanced delocalization of the positive charge over the aromatic rings as in the well-known tetraarylethylene dications. The pentadie-

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(27) Gassman, P. G.; Talley, J. J. *Tetrahedron Lett.* **1978**, 3773.

(28) Kiyooka, S.; Fujiyama, R.; Kawaguchi, K. *Chem. Lett.* **1984**, 1979.

(29) Cohen, S. *J. Am. Chem. Soc.* **1957**, *79*, 1499. Kailuszyner, A.; Cohen, S. *Tetrahedron* **1960**, *11*, 252.

(30) Olah, G. A.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 3210.

(31) Liu, K.-T.; Sheu, C.-F. *Tetrahedron Lett.* **1980**, *21*, 4091. Liu, K.-T.; Kau, M.-Y.; Shu, C.-F. *J. Am. Chem. Soc.* **1982**, *104*, 211.

nylium character facilates the electrocyclization to fluorenes or phenanthrol. This mechanism is compatible with most of the reported reactions of related diphenylmethyl cations in acid. Direct observations of the stable O-protonated carbonylbis(*p*-methoxyphenyl)methyl dication by NMR spectroscopy supported these postulations. Possible contributions of other related carbodications to the reactions are under investigation.

Experimental Section

General Methods. All the melting points were measured with a Yanagimoto hot-stage melting point apparatus and are uncorrected. Proton NMR spectra were obtained on either a JEOL FX 100-MHz NMR spectrometer or a JEOL GX 400-MHz NMR spectrometer with tetramethylsilane as an internal reference and $CDCl_3$ as the solvent unless otherwise specified. ^{13}C NMR spectra were recorded on either a JEOL FX-100 (at 25.5 MHz) or a JEOL GX-400 (at 100 MHz). Chemical shifts are reported (ppm) in terms of Me_4Si; the spectra were referenced by the assignment of the middle resonance of deuteriochloroform as 77.0 ppm. Infrared spectra were measured on a Shimadzu IR 408 spectrometer as a solid suspension in KBr. Mass spectra were recorded with a JEOL JMS-DX300 or JEOL JMS-D300. Flash column chromatography[32] was performed over silica gel (Merck, Kieselgel 60, 230–400 mesh) with a specified solvent. High-performance liquid chromatography was run on a Shimadzu LC-2 system on LiChrosorb Si60 (Merck) packing (4.6 mm × 20 cm, 3.0 g) with 1:10 chloroform–*n*-hexane as the eluent. Ultraviolet spectra were measured on a Shimadzu UV200S at 0 °C in acidic media. Combustion analyses were carried out in the microanalytical laboratory of this faculty.

Materials. Trifluoromethanesulfonic acid (TFSA) was purchased from 3M Co. and was purified by distillation under reduced pressure [bp 62.5 °C (13 mmHg)]. Antimony pentafluoride (SbF_5) was available from Aldrich Chemical Co. and was purified by distillation under reduced pressure [bp 81.5 °C (61 mmHg)]. Deuteriumtrifluoromethanesulfonic acid (CF_3SO_3D) was prepared by heating of a mixture of deuterium oxide (99.7 atom % D) and an equivalent amount of trifluoromethanesulfonic anhydride[33] at 80 °C for 2 h, followed by distillation [bp 67–69 °C (19 mmHg)]. Silver trifluoromethanesulfonate (TfOAg) and silver trifluoroacetate were obtained from Aldrich and were used without further purification. Silver tetrafluoroborate was from Wako Chemical Co. and was used after repeated washing with *n*-pentane. Methylene chloride, used for silver ion assisted ionization experiments was washed with saturated aqueous $CaCl_2$ solution, dried over $CaCl_2$, and purified by distillation. All the substituted diphenylmethanols were prepared and purified by recrystallization as follows. **4**: α-Benzoyldiphenylmethanol was prepared from benzil by the reaction of the Grignard reagent prepared from bromobenzene; white needles; mp 87–88 °C (recrystallized from *n*-hexane). **7**: α-Acetyldiphenylmethanol was prepared by condensation of benzophenone with methyl acetate by the use of 5 equiv of lithium metal.[16] The crude reaction mixture was purified by flash column chromatography twice with CH_2Cl_2–*n*-hexane (2:3) as the eluent to give a colorless oily material, which was solidified after molecular distillation [40 °C, external bath temperature (<1 mmHg)], mp 64–65 °C. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.40; H, 6.24. **9a**: (α-Methoxycarbonyl)diphenylmethanol was prepared by the usual esterification of benzilic acid and was recrystallized from *n*-hexane; mp 71.5–72 °C. **28**: Benzophenone cyanohydrin was obtained by hydrolysis of the corresponding trimethylsilyl ether, which was prepared by addition of trimethylsilyl cyanide in the presence of a catalytic amount of zinc iodide;[27] mp 116–119 °C (recrystallized from benzene–*n*-hexane) as colorless needles. **33**: (α,α,α-Trifluoromethyl)diphenylmethanol was prepared from α,α,α-trifluoroacetophenone by the action of Grignard reagent prepared from bromobenzene and recrystallized from *n*-hexane; colorless cubes; mp 76.5–77 °C.

All the corresponding diphenylmethyl halides were prepared as follows. **16**: Several drops of acetic anhydride were added to a solution of α-benzoyldiphenylmethanol (**4**; 1 g) in acetic acid (5 mL), and the solution was heated to reflux. Under reflux, dry HCl gas was introduced into the solution for 3 h. Addition of ice and water yielded crude **16** as a white precipitate (72%), mp 81.5–82 °C (recrystallized from *n*-hexane).[17] Anal. Calcd for $C_{20}H_{15}OCl$: C, 78.30; H, 4.93; N, 0.0. Found: C, 78.04; H, 4.89; N, 0.0. **17**: (α-Methoxycarbonyl)diphenylmethyl chloride was prepared by esterification of 2-chlorodiphenylacetyl chloride, which was obtained from diphenylacetic acid by the action of 5.5 equiv of thionyl chloride and 1.2 mol of iodine (reflux for 2 h)[18] and purified by molecular distillation [44.5 °C (external temperature) (0.5 mmHg)]. Anal. Calcd for $C_{15}H_{13}O_2Cl$: C, 69.10; H, 5.03. Found: C, 69.04; H, 4.90. **30**: (α-Diphenylmethyl)cyano chloride was obtained by the reaction of trimethylsilyl cyanide with benzophenone in the presence of titanium tetrachloride.[28] To a solution of benzophenone (907.3 mg, 4.98 mmol) in methylene chloride (10 mL) was added 1.2 equiv of titanium tetrachloride (0.61 mL) dropwise with stirring at 0 °C. The mixture was allowed to stand for 30 min at 0 °C, and a solution of an equimolar amount of trimethylsilyl cyanide (512.2 mg) in methylene chloride (2 mL) was added to the resultant yellow solution at 0 °C. Stirring was continued at ambient temperature for 17 h. After addition of 50 mL of cold water and 50 mL of methylene chloride, the organic layer was separated and washed with saturated sodium bicarbonate solution and brine. The organic layer was dried over Na_2SO_4, and the solvent was evaporated off to yield a colorless oil. Flash column chromatography (CH_2Cl_2–*n*-hexane 1:2) gave pure **30**: 680 mg (60% yield); colorless oil; ^{13}C NMR 137.7 (s), 129.4 (d), 128.6 (d), 118.3 (s), 63.3 (s). **37**: (Trifluoromethyl)diphenylmethyl bromide was obtained by bromination of the corresponding alcohol **33** with phosphorus tribromide.[31] Freshly distilled phosphorus tribromide [bp 61 °C (16 mmHg); 2.16 g, 1.2 equiv] was added to a solution of the alcohol **33** (1.654 g, 50 mmol) in methylene chloride (10 mL) at 0 °C. After removal of the ice bath, the solution was refluxed at 53 °C for 7.5 h. The solution was poured into 100 mL of ice–water and extracted with CH_2Cl_2. The extract was washed with brine, dried over Na_2SO_4, and evaporated to give a mixture of **37** and the starting material. Flash column chromatography (*n*-hexane as the eluent) gave pure **37**: 732 mg (35% yield); colorless plates; mp 34–34.5 °C. **26**: 4,4′-Dimethoxybenzilic acid was prepared by the benzilic acid rearrangement reaction of the *p*-anisil (available from Aldrich:[21a,b] *p*-anisil (5.06 g, 18.7 mmol) was added to a solution of potassium hydroxide (2.50 g) in boiling *n*-butanol (18 mL) during 10 min, and the mixture was refluxed for 15 min. After aqueous treatment as previously described,[21a,b] crude **26** was obtained: 81% yield (4.39 g); mp 155–157 °C (colorless fine needles, recrystallized from AcOEt–*n*-hexane (1:2)); ^1H NMR ($CDCl_3$) 7.40 (d, 4 H, H_o, $J = 9.2$ Hz), 6.88 (d, 4 H, H_m, $J = 9.2$ Hz), 3.81 (s, 6 H, OCH_3); ^{13}C NMR ($CDCl_3$, DMSO-d_6) 176.2 (s), 158.8 (s), 134.7 (s), 128.4 (d, $J = 160.0$ Hz), 113.0 (d, $J = 158.5$ Hz), 79.7 (s), 55.0 (q, $J = 143.8$ Hz). Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.65; H, 5.59; N, 0.0. Found: C, 66.35; H, 5.59; N, 0.0. (α-Methoxycarbonyl)bis(*p*-methoxyphenyl)methanol (**20**): The ester was obtained by treatment of the acid **26** with an ethereal solution of diazomethane;[21c] mp 107.5–108.5 °C; colorless cubes (recrystallized from *n*-hexane); ^1H NMR ($CDCl_3$) 7.32 (d, 4 H, $J = 8.8$ Hz), 6.86 (d, 4 H, $J = 8.8$ Hz), 3.84 (s, 3 H), 3.80 (s, 6 H); ^{13}C NMR ($CDCl_3$) 175.3 (s), 159.2 (s), 134.2 (s), 128.5 (d, $J = 160.0$ Hz), 113.3 (d, $J = 158.5$ Hz), 80.4 (s), 55.2 (q, $J = 143.8$ Hz), 53.4 (q, $J = 146.7$ Hz). Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.53; H, 6.00; N, 0.0. Found: C, 67.44; H, 5.99; N, 0.0. **24**: bis(*p*-Methoxyphenyl)methanol was prepared from 4,4′-dimethoxybenzophenone (Aldrich) by reduction with $LiAlH_4$ in THF. After reflux for 5 h, aqueous workup gave **24** in 90% yield: mp 67.5–68.5 °C; colorless needles (recrystallized from *n*-hexane); ^1H NMR ($CDCl_3$) 7.25 (d, 4 H, H_o, $J = 8.8$ Hz), 6.84 (d, 4 H, H_m, $J = 8.8$ Hz), 5.29 (s, 1 H, CH), 3.76 (s, 6 H); ^{13}C NMR ($CDCl_3$) 158.8 (s), 136.4 (s), 128.4 (d, $J = 160.0$ Hz), 113.7 (d, $J = 158.5$ Hz), 75.2 (d, $J = 143.8$ Hz), 55.2 (q, $J = 143.8$ Hz). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60; N, 0.0. Found: C, 73.86; H, 6.62; N, 0.0.

Reaction of Diphenylmethyl Cations Substituted with Carbonyl Groups in TFSA Reaction of α-Benzoyldiphenylmethanol (4) in TFSA. An aliquot of 42 mL of TFSA was cooled to −50 °C in a dry ice–ethanol bath, and then **4** (274.5 mg) was added in portions with vigorous stirring. The solution was stirred for 30 min at −50 °C before the usual aqueous workup. The resultant crude products were purified by flash column chromatography with CH_2Cl_2–*n*-hexane (1:4) as the eluent to give 189.8 mg (74% yield) of **6** and 21.6 mg (8.4%) of 9-phenylphenanthr-10-ol (**5**). **5**: mp 144–145.5 °C (recrystallized from *n*-hexane as slightly yellow plates); ^1H NMR (400 MHz) 8.72 (ddd, 1 H, H_4, $J = 8.1, 1.3, 0.6$ Hz), 8.67 (ddd, 1 H, H_5, $J = 8.2, 1.3, 0.6$ Hz), 8.39 (ddd, 1 H, H_1, $J = 8.0, 1.6, 0.6$ Hz), 7.72 (ddd, 1 H, H_3, $J = 8.2, 7.6, 1.5$ Hz), 7.66 (ddd, 1 H, H_2, $J = 8.1, 6.9, 1.3$ Hz), 7.62 (m, 2 H, H_m), 7.54 (m, 1 H, H_p), 7.50 (ddd, 1 H, H_6, $J = 7.4, 7.4, 1.7$ Hz), 7.48 (m, 2 H, H_o), 7.43 (ddd, 1 H, H_7, $J = 7.4, 7.4, 1.3$ Hz), 7.39 (ddd, 1 H, H_8, $J = 8.2, 1.7, 0.6$ Hz); ^{13}C NMR 145.9 (s), 134.4 (s), 132.2 (s), 131.3 (d), 130.9 (s), 129.6 (d), 128.5 (d), 127.1 (d), 126.7 (d), 126.7 (d), 126.5 (d), 126.3 (d), 125.2 (d), 124.9 (d), 123.9 (d), 122.9 (d), 122.4 (d), 117.1 (s). Anal. Calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22; N, 0.0. Found: C, 88.59; H, 5.12; N, 0.0. **6**: recrystallized from *n*-hexane as slightly yellow plates; mp 138–138.5 °C; ^1H NMR (400 MHz) 7.845 (d, 2 H, $J = 7.6$ Hz), 7.578 (dd, 2 H, $J = 1.1, 7.6$ Hz), 7.503 (ddt, 1 H, $J = 7.4, 7.4, 1.1$ Hz), 7.431 (dd, 2 H, $J = 7.6, 7.6$ Hz), 7.387 (dd, 2 H, $J = 1.1, 7.4$ Hz), 7.356 (dd, 2 H, $J = 7.6, 7.6$ Hz), 7.267 (ddd, 2 H, $J = 7.4, 7.4, 1.1$ Hz), 5.608 (s, 1 H); mass spectrum, *m/e* 270 (M^+). Anal. Calcd for $C_{20}H_{14}O$: C, 88.86;

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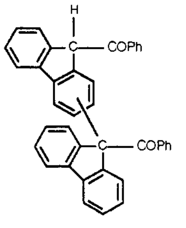
(33) Gramstad, T.; Haszeldine, R. N. *J. Chem. Soc.* **1956**, 173. Stang, P. J.; Duebber, T. E. *Org. Synth.* **1974**, *54*, 79.

H, 5.22. Found: C, 88.84; H, 5.21. The ^1H NMR absorptions of both **6** and **5** were assigned on the basis of INDOR and NOE enhancement experiments.

Acid-Catalyzed Reaction of α-Benzoyldiphenylmethanol (4) in the Concentrated Solution. (a) In the Presence of Benzene. A solution of 145.7 mg of **4** in 2.4 mL of benzene (total amount of benzene was 100 equiv) was added in portions to an ice-cooled solution of 0.44 mL (10 equiv) of TFSA in 2 mL of benzene with vigorous stirring. The solution was stirred for 30 min before the usual aqueous workup. The crude mixture was flash chromatographed with CH_2Cl_2–*n*-hexane (1:2) as the eluent to give 24.9 mg (18%) of benzoylfluorene, 47.1 mg (34%) of α,α-diphenylacetophenone and 21 mg (15%) of the fluorene dimer **40**.



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The last two products were formed by hydride transfer of the H_9 proton of the benzoylfluorene to the diphenylmethyl cation to give diphenylacetophenone and 9-benzoylfluorenium cation. The latter cation reacted with 9-benzoylfluorene to yield the fluorene dimer. No triphenylmethyl derivative was obtained in the presence of benzene.

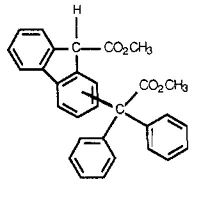
(b) In the Absence of Benzene. The same redox reaction products were also formed in the reaction catalyzed by 100 equiv of TFSA (0 °C, 15 min). The yields were as follows: **6**, 29%; α,α-diphenylacetophenone, 27%; fluorene dimer **40**, 17%. The reaction proceeded similarly when the reaction temperature was −50 °C.

Independent Synthesis of 6 and 5. 9-Benzoylfluorene was prepared by Friedel–Crafts reaction of 9-fluorenecarboxylic acid with benzene catalyzed by TFSA. A mixture of 9-fluorenecarboxylic acid (213.7 mg, ca. 1.0 mmol) and 0.88 mL (10 equiv with respect to 9-fluorenecarboxylic acid) in 8.8 mL (100 equiv) of dry benzene was heated at 63 °C for 4 h. The solution was poured into 200 mL of ice and water and extracted with methylene chloride. The separated organic layer was washed with saturated sodium bicarbonate solution and brine. The aqueous layer was neutralized with aqueous hydrogen chloride solution to give the recovered carboxylic acid, 65.2 mg (31%). The organic layer was dried over Na_2SO_4, and the solvent was evaporated off to yield crude 9-benzoylfluorene, 164.0 mg (60%). 9-Phenylphenanthr-10-ol was prepared from 2-iodobiphenyl as previously described.[14] The IR and NMR spectra of these prepared compounds are identical with those of **6** and **5**, respectively.

Reaction of α-Acetyldiphenylmethanol (7) in TFSA. To 17.7 mL of TFSA cooled to −48 °C in a dry ice–ethanol bath was added 91.2 mg (0.40 mmol) of α-acetyldiphenylmethanol (**7**) in portions with vigorous stirring. Stirring was continued at the same temperature for 1.5 h, and then the solution was poured into ice and water (200 mL) and extracted with CH_2Cl_2. The organic layer was washed with brine, and the solvent was evaporated off. The residue was flash chromatographed with CH_2Cl_2–*n*-hexane (2:3) as the eluent to give 58.4 mg (70% yield) of **8** as colorless cubes: mp 72.5–73.5 °C (recrystallized from *n*-hexane); mass spectrum, *m/e* 208 (M^+); ^1H NMR (400 MHz) 7.828 (d, 2 H, H_4, J = 7.5 Hz), 7.809 (d, 2 H, H_1, J = 7.5 Hz), 7.467 (dd, 2 H, H_3, J = 7.5, 7.5 Hz), 7.356 (dd, 2 H, H_2, J = 7.5, 7.5 Hz), 4.800 (s, 1 H), 1.617 (s, 3 H, CH_3); ^{13}C NMR (25.5 MHz) 206.1 (s), 141.9 (s), 140.9 (s), 128.2 (d), 127.5 (d), 124.9 (d), 120.2 (d), 63.4 (d), 25.1 (q). Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.37; H, 5.83.

Reaction of (α-Methoxycarbonyl)diphenylmethanol (9a) in TFSA. Addition of **9a** to TFSA (12.2 mL, 500 equiv) cooled to −50 °C in a dry ice–ethanol bath yielded a fluorene **10a** after the usual aqueous workup (2 h) in 81% yield. **10a**: mp 63.5–64.5 °C (recrystallized from *n*-hexane); ^1H NMR 7.760 (d, 2 H, J = 7.51 Hz), 7.657 (dd, 2 H, J = 0.74, 7.51 Hz), 7.425 (ddd, 2 H, J = 0.74, 7.51, 7.51 Hz), 7.340 (ddd, 2 H, J = 1.28, 7.51, 7.51 Hz), 4.880 (s, 1 H), 1.562 (s, 3 H); mass spectrum, *m/e* 224 (M^+).

When the reaction was conducted in a more concentrated solution (TFSA, 100 equiv at −50 °C), 41% yield of **10a** and 37% yield of the fluorene dimer **41** were obtained after the usual aqueous workup and flash column chromatography (CH_2Cl_2–*n*-hexane 3:4 as the eluent). Fluorene dimer **41**: colorless oil; ^1H NMR ($CDCl_3$) 7.72 (d, 1 H), 7.64 (d, 2 H), 7.52–7.00 (m, 14 H), 4.8 (s, 1 H), 3.80 (s, 3 H), 3.65 (s, 3 H). The fluorene dimer was thought to be formed by the intermolecular electrophilic reaction of the diphenylmethyl cation with the 9-methoxycarbonylfluorene.



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Reaction of Benzilic Acid (9b) in TFSA. Benzilic acid (233 mg) was added in portions to an ice-cooled solution of 1.76 mL (20 equiv) of TFSA in 17.6 mL (200 equiv) of benzene with vigorous stirring. The solution was stirred for 1 h before the usual aqueous workup. The aqueous solution was extracted with AcOEt, and the organic layer was washed with saturated sodium bicarbonate solution. The aqueous layer was neutralized with 2 N aqueous HCl solution and was extracted with AcOEt. The organic layer was dried over Na_2SO_4 and was evaporated to give crude **10b** (139.9 mg, 65% yield). The product was identical with an authentic sample in terms of IR and NMR spectra.

Generation of Diphenylmethyl Cations by Silver Ion Assisted Ionization of Diphenylmethyl Halides. General Procedure. A solution of a diphenylmethyl halide (**16**, **17**, **30**, **37**; 0.5 mmol) in methanol-free methylene chloride (1 mL) was added in one portion with vigorous stirring to a solution of 1 mmol of silver salt ($AgBF_4$, $AgSO_3CF_3$, CF_3CO_2Ag) in 1 mL of methanol-free CH_2Cl_2 cooled to −58 °C in a dry ice–ethanol bath. During stirring at this temperature for 40 min a red solution of diphenylmethyl cation was obtained. At the specified time (50 min) after the addition of reagents, the solution was submitted to the usual aqueous workup or added to TFSA precooled at −50 °C. The yields of the reaction products were determined by high-performance liquid chromatography. Yields of the reaction products were estimated in terms of peak areas, which were approximated by the product of the peak height and the width of the peak at half-height; a weighed amount of dimethyl terephthalate was used as an internal standard. The results are summarized in Tables I and II.

Formation and Reaction of Tetraphenylethylene Dication 1 (R = H) in TFSA. Tetraphenylethylenediol (184.2 mg, 0.5 mmol) was added in portions to 4.4 mL (100 equiv) of TFSA cooled in a dry ice–ethanol bath at −51 °C, with vigorous stirring. The solution was stirred at the same temperature for 30 min, followed by aqueous workup. The obtained mixture of products was purified by flash column chromatography with AcOEt–*n*-hexane (1:80) as the eluent to give 63.8 mg (36%) of a pinacol rearrangement product, α,α,α-triphenylacetophenone, and 50.7 mg (31%) of 9,10-diphenylphenanthrene (**2**). **2**: mp 238.5–239.0 °C (recrystallized from *n*-hexane; colorless needles; ^1H NMR (400 MHz) 8.817 (d, 2 H, J = 8.43 Hz), 7.669 (ddd, 2 H, J = 1.1, 7.60, 7.60 Hz), 7.562 (dd, 2 H, J = 8.43, 1.10 Hz), 7.488 (ddd, 2 H, J = 7.56, 7.56, 1.1 Hz), 7.266–7.147 (m, 10 H). Anal. Calcd for $C_{26}H_{18}$: C, 94.51; H, 5.49; N, 0.0. Found: C, 94.28; H, 5.49; N, 0.0.

Recovery Experiment by Quenching of Ion Solutions with Water. Dissolving (α-methoxycarbonyl)bis(*p*-methoxyphenyl)methanol (**20**) or 4,4′-dimethoxybenzilic acid (**26**; 0.2 mmol) in TFSA (3.5 mL, 200 equiv with respect to the organic compound) at 0 °C in an ice bath yielded a purple solution. After standing at this temperature for 2 h, the TFSA solution was poured dropwise into ice–water, followed by extraction with methylene chloride. The CH_2Cl_2 layer was washed with brine and dried over Na_2SO_4. The material obtained after evaporation of the solvent proved to be the pure starting material in both cases.

Preparation and NMR Studies of Ions in TFSA and TFSA–SbF_5. NMR spectra of ions were measured on JEOL GX400 spectrometers equipped with a variable-temperature apparatus. All samples were prepared below −30 °C in a dry ice–ethanol bath. The ^1H NMR spectra were obtained without deuterium locking, and the chemical shifts were referred to Me_4Si in acetone-d_6 in a capillary. The ^{13}C NMR spectra were also recorded without deuterium locking, and the chemical shifts were calibrated on the basis of Me_4Si in $CDCl_3$.

The ^1H NMR spectra of **20** and **26** were also measured in CF_3SO_3D, and no deuterium exchange of any proton was observed from −40 to 0 °C.

Reaction of Cyanodiphenylmethanol (28) with Benzene Catalyzed by TFSA. Benzophenone cyanohydrin (**28**; 214.1 mg) was added to an ice-cooled solution of 0.88 mL of TFSA (10 equiv) and 8.8 mL of benzene (100 equiv) with vigorous stirring. Stirring was continued at 0–5 °C for 2 h, followed by the usual aqueous workup; extraction with CH_2Cl_2 and flash column chromatography (CH_2Cl_2–*n*-hexane 1:1) gave cyanotriphenylmethane (**29**): 187.4 mg (yield 74%); mp 129 °C (recrystallized from *n*-hexane); ^{13}C NMR 140.0 (s), 128.63 (d), 128.51 (d), 127.98 (d), 123.29 (s), 57.37 (s). Anal. Calcd for $C_{20}H_{15}N$: C, 89.18;

H, 5.61; N, 5.20. Found: C, 89.36; H, 5.64; N, 5.38. Benzophenone cyanohydrin was partially decomposed to benzophenone on the silica gel column.

In the absence of benzene, no fluorene compound was formed in the presence of TFSA even at room temperature. The only products were benzophenone and benzophenone cyanohydrin. 9-Cyanofluorene was not formed from the cyanohydrin when the catalytic acid was replaced with SbF_5-FSO_3H (1:1).

Formation and Reaction of Cyanodiphenylmethyl Cation (31) Prepared by Silver Ion Assisted Ionization of Cyanodiphenylmethyl Chloride (30). A solution of cyanodiphenylmethyl chloride (**30**) in 2.4 mL of dry benzene was added in one portion to a solution of 158.9 mg of TfOAg (1.1 equiv with respect to the chloride) in 2 mL of dry benzene at 0–5 °C with stirring. After 4 h at that temperature, the solution was poured into ice–water and worked up as usual. The crude products were flash chromatographed (CH_2Cl_2–*n*-hexane 2:3) to give a triphenylmethyl cyanide (**29**; 111.7 mg, yield 85%). These results are the same as those in the reactions catalyzed by TFSA, suggesting that the electrophilic reaction of cyanodiphenylmethyl cation with benzene does not require a strong acid. In the absence of benzene, the stable red solution was obtained even at 0 °C. NMR spectroscopic measurements indicated the formation of cyanodiphenylmethyl cation (**31**). The ^{13}C NMR absorptions of **31** in TFSA at −30 °C were as follows: 168.5 (s, C^+), 153.3 (d, C_p), 146.0 (d, C_o, br), 138.4 (s, C_{ipso}), 133.57 (d, C_m), 111.8 (s, CN). These spectroscopic results are consistent with previous spectra obtained in other acid systems.[10b]

Acid-Catalyzed Reactions of (Trifluoromethyl)diphenylmethanol (33) in the Presence of Benzene. To an ice-cooled solution of 0.44 mL (10 equiv) of TFSA in 4.4 mL (100 equiv) of dry benzene was added 127.5 mg (ca. 0.5 mmol) of **33** in portions. Stirring was continued at 0–5 °C for 15 min, followed by the usual aqueous workup. Evaporation of the solvent and flash column chromatography with *n*-hexane as the eluent gave 41.7 mg of (trifluoromethyl)triphenylmethane (**34**), 27.4 mg of fluorene dimer **35**, and 54.6 mg of fluorene trimer **36**. The dimeric and trimeric products (**35**, **36**) were formed by the intermolecular electrophilic reactions of the diphenylmethyl cation with the formed fluorene.

When the reaction was catalyzed with a less acidic system (TFSA–TFA 1:4 v/v 0–5 °C, 1 h), the yields of products were as follows: **34**, 43%; **35**, 6%; **36**, 31%. The increase in the yield of **34** indicated that the cyclization reaction to fluorenes does not require a strong acid catalyst. **34**: mp 164 °C (recrystallized from *n*-hexane); mass spectrum, *m/e* 312 (M^+). **35**: viscous oil; HRMS calcd for $C_{28}H_{18}F_6$ 468.13134, found 468.1304; ^1H NMR 7.80–7.48 (m, 4 H), 7.48–6.92 (m, 14 H), 4.60 (q, 1 H, J_{HF} = 9.76 Hz). **36**: mp 163–163.5 °C (recrystallization from *n*-hexane); HRMS calcd for $C_{42}H_{27}F_9$ 702.19701, found 702.1963; ^1H NMR 7.80–7.48 (m, 4 H), 7.48–6.92 (m, 24 H), 4.60 (q, 1 H, J_{HF} = 9.80 Hz).

Reaction of (Trifluoromethyl)diphenylmethanol (33) in TFSA. To 4.4 mL (500 equiv) of TFSA cooled to −53 °C in a dry ice–methanol bath was added **33** in portions with vigorous stirring. The resultant red solution was stirred for 30 min at −53 °C before the usual aqueous workup. The crude mixture was flash chromatographed with *n*-hexane as the eluent to give 7.3 mg (3%) of 9-(trifluoromethyl)fluorene (**39**), 8.3 mg (3%) of fluorene dimer **35**, and 75.3 mg (32%) of fluorene trimer **36**. The product **39** was identical with an authentic sample in terms of NMR and IR spectra. **39**: HRMS calcd for $C_{14}H_9F_3$ 234.06543, found 234.0654; ^1H NMR: 7.82–7.67 (5 H, m), 7.55–7.28 (5 H, m), 4.60 (1 H, q, J_{HF} = 9.80 Hz).

Reaction of (Trifluoromethyl)diphenylmethyl Cation (38) Prepared by Silver Ion Assisted Ionization of (Trifluoromethyl)diphenylmethyl Bromide (37). A solution of the bromide **37** (314 mg, 1 mmol) in 2 mL of CH_2Cl_2 was added in one portion to a solution of AgOTf (489.2 mg, 1.9 equiv) in 4 mL of CH_2Cl_2 with vigorous stirring at −50 °C in a dry ice–ethanol bath. After being stirred at −50 °C for 1 h, the resulting red solution was poured into ice and water and extracted with CH_2Cl_2. The residue was flash chromatographed with CH_2Cl_2–*n*-hexane (1:8) to give fluorene trimer **36** (80.7 mg, 35% yield) and undefined fluorene derivatives.

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Theoretical Elucidation of the Origin of the Anomalously High Acidity of Meldrum's Acid

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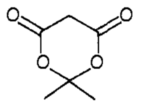
Abstract: The acidity of methyl acetate in syn and anti conformations has been investigated with ab initio calculations and the 3-21G, 6-31G*, and 6-31+G* basis sets. The deprotonation of the anti conformation requires 5.4 kcal/mol less energy than deprotonation of the syn conformation. The constraint of two ester groups in a dilactone to anti conformations should decrease the deprotonation energy by about 11 kcal/mol, essentially the amount by which Meldrum's acid is more acidic than malonic ester in DMSO solution. The higher acidity of the anti conformation is attributed to electrostatic (dipole–dipole) repulsion effects. An electrostatic effect, rather than the usually invoked resonance effect, is also proposed to be responsible for the lower acidity of esters as compared with ketones.

Arnett and Harrelson recently studied a variety of systems in order to understand the unusually high acidity of Meldrum's acid[1] (**1**). This dilactone has a considerably higher acidity (pK_a 7.3) than acyclic analogues such as dimethyl malonate (**2**; pK_a 15.9), or even the diketone analogue **3** (pK_a 11.2). These pK_a's were all measured in DMSO, in which the acidities are uncomplicated by aggregation or counterions. Arnett and Harrelson proposed that the anomalously high acidity of **1** is connected to the he unfavorable anti conformations that the ester groups are forced to adopt in Meldrum's acid. However, Arnett and Harrelson left a tantalizing sense of mystery about the origin of the effect.[2a]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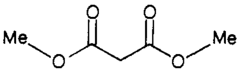

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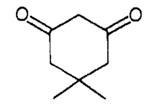
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[1] (a) Meldrum, A. N. *J. Chem. Soc., Trans.* **1908**, *93*, 589. (b) Davidson, D.; Bernhard, S. A. *J. Am. Chem. Soc.* **1948**, *70*, 3426. (c) Arnett, E. M.; Harrelson, J. A. *Gazz. Chim. Ital.*, in press. (d) Pfluger, C. E.; Boyle, P. D. *J. Chem. Soc., Perkin Trans. 2*, 1985, 1547.

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