Structures and Reactivities of Ethylene Dication Electrophiles

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Abstract: 1,2-Dicarbonyl compounds such as 2,3-butanedione reacted with benzene in the presence of a strong acid, trifluoromethanesulfonic acid, to give *gem*-diphenylated ketones in high yield. The monoxime derivative of 1,2-diones also reacted with benzene in the acid, but slowly enough to allow discrimination of monophenylated and diphenylated oximes. The reactive electrophiles in these Friedel−Crafts reactions are considered to be O,O-diprotonated 1,2-dicarbonyl species and N,O-diprotonated ketoxime, i.e., related ethylene dications differentiated by a single different heteroatom substituent, a hydroxy or a hydroxyamino group. The reactivity depends on the electron-donating ability of substituents adjacent to the reaction center.

High-level theoretical calculations were successful in predicting the unusual anti-van't Hoff perpendicular structure, rather than planar geometry, of the ethylene dication ($C_2H_4^{2+}$).[1] *Ab initio* calculations also revealed that multiple substitution of the ethylene dication with π-donating groups such as hydroxy,[2a,3] fluoro,[2b] or amino groups[4] tends to stabilize the planar geometry relative to the perpendicular geometry. For example, in the cases of fluoro and amino substitutions, the mono- and disubstituted dications $C_2H_3X^{2+}$ and 1,1-$C_2H_2X_2^{2+}$ take perpendicular structures, whereas the tri- and tetrasubstituted dications $C_2HX_3^{2+}$ and $C_2X_4^{2+}$ favor planar structures.[1] Apart from the intriguing structural dichotomy, the ethylene dications can be regarded as reactive electrophiles involving (at least formally) adjacent carbenium centers, i.e., gitonic superelectrophiles.[5,6] Ethylene dications substituted with two *gem*-diphenyl groups undergo facile electrocyclization to give fluorene derivatives.[3a,c] However, the electrophilic behavior of ethylene dications in Friedel−Crafts reactions is still little understood.[7] Diprotonation of 1,2-diones in strong acids has been shown to afford O[1],O[2]-diprotonated 1,2-diones, i.e., 1,2-dihydroxyethylene dications **4**,[8] and therefore we chose to examine the Friedel−Crafts reaction of 1,2-diones **1** and some derivatives with benzene in the presence of trifluoromethanesulfonic acid (TFSA). While 1,2-diones react readily with two benzenes to give *gem*-diphenyl ketones **2**, an oxime derivative of a 1,2-dione reacts slowly, allowing discrimination of monophenylation and diphenylation. Reactive electrophiles in these Friedel−Crafts reactions have been demonstrated by direct observation to be O,O-diprotonated 1,2-dicarbonyl species and N,O-diprotonated ketoxime, i.e., related ethylene dications differentiated by a single different heteroatom substituent (a hydroxy or a hydroxyamino group) adjacent to the reaction center.

Results and Discussion

Acid-Catalyzed Reaction of 2,3-Butanedione. 2,3-Butanedione (**1a**) reacted with benzene in the presence of trifluoromethanesulfonic acid (TFSA) at 5 °C to give 3,3-diphenyl-2-butanone (**2a**) in 94% yield (Scheme 1) (Table 1). The product is probably formed through diphenylation of one of the carbonyl groups. The reaction depends on the acidity of the medium, as judged from the yield of the product. At $H_0 = -8$ to -9, where the medium is sufficiently acidic to monoprotonate the dione (at least partially) to give the monocation **3** (Scheme 2),[9,10] essentially no reaction takes place. But, an increase of the acidity to -11 (H_0) gave **2a** in a yield of 62%, and the conversion was quantitative in 50% TFSA−50% TFA ($H_0 = -12$). In TFSA the reaction is very rapid. The heterogeneity of the reaction precludes quantitative kinetic studies.[11] However this acidity-dependent behavior of the reaction implies that an additional protonation is required to increase the electrophilicity of the attacking cation **3**. The ^{1}H and ^{13}C chemical shifts of the species formed from **1a** in TFSA−SbF_5 (mole ratio 2.5:1) correspond well to those of the O,O-diprotonated 2,3-butanedione **4** formed in FSO_3H−SbF_5 (see Tables 2 and 3).[12] Therefore, the efficient conversion of **1a** at high acidities is consistent with the intervention of the O,O-diprotonated 2,3-

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

(1) Observation: Benoit, C.; Horsley, J. A. *Mol. Phys.* **1975**, *30*, 557. Theoretical calculations: Lammertsma, K.; Barzaghi, M.; Olah, G. A.; Pople, J. A.; Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, *105*, 5252.

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(4) Frenking, G. *J. Am. Chem. Soc.* **1991**, *113*, 2476−2481.

(5) Olah, G. A. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 767−788.

(6) Olah, G. A.; Hartz, N.; Rasul, G.; Burrichter, A.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 6421−6427.

(7) A part of the work has been communicated: Yamazaki, T.; Saito, S.; Ohwada, T.; Shudo, K. *Tetrahedron Lett.* **1995**, *36*, 5749−5752.

(8) Olah, G. A.; Calin, M. *J. Am. Chem. Soc.* **1968**, *90*, 4672−4675. Olah, G. A.; Grant, J. L.; Westerman, P. W. *J. Org. Chem.* **1975**, *40*, 2102−2108.

(9) The acidity (H_0) of the trifluoromethanesulfonic acid (TFSA)−trifluoroacetic acid (TFA) system has been described: Saito, S.; Saito, S.; Ohwada, T.; Shudo, K. *Chem. Pharm. Bull.* **1991**, *39*, 2718−2720. See also: Saito, S.; Sato, Y.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1994**, *116*, 2312−2317, footnote 8.

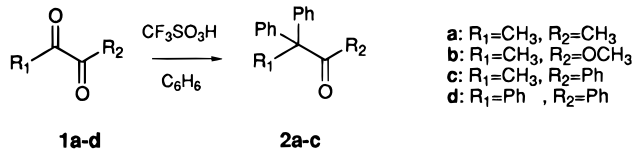
(10) (a) Protonation of ketones: Paspaleev, E.; Kojucharova, A. *Monatsch. Chem.* **1969**, *100*, 1213. (b) Protonation of imines: Childs, R. F.; Dickie, B. D. *J. Am. Chem. Soc.* **1983**, *105*, 5041. (c) Protonation of oximes: Allen, M.; Roberts, J. D. *Can. J. Chem.* **1981**, *39*, 451−458.

(11) The possible solubility increase of benzene in the case of the higher acidity seems to affect the rate of reactions. However, the increase of benzene may be caused by the production of benzenium ions which may not be a substrate for the electrophile. Even if this was the case, the very slow reaction in the medium which is acidic enough to monoprotonate the substrate completely definitely eliminates the possibility of the participation of the monoprotonated species.

(12) Though some difference in solvent effect may exist, the presence of the same diprotonated species in TFSA is in accordance with the normal acid−base equilibrium.

S0002-7863(95)03623-7 CCC: $12.00

Scheme 1



1a-d **2a-c**

Table 1. Acid-Catalyzed Reactions of 1,2-Diones and Their Derivatives with Benzene

substrate	acid[a]	temp (°C)	time	monophenyl product	diphenyl product
1a	6% TFSA-94% TFA	5	20 min		**2a** (0%)
1a	20% TFSA-80% TFA	5	20 min		**2a** (62%)
1a	50%TFSA-50% TFA	5	20 min		**2a** (94%)
1a	TFSA	5	5 min		**2a** (94%)
1b	TFSA	5	5 min		**2b** (72%)
1c	TFSA	5	60 min		**2c** (34%)[b]
7a	TFSA	5	5 min	**8** (58%)	**9** (37%)
7a	TFSA	5	145 min	**8** (50%)	**9** (39%)
7a	TFSA	5	72 h	**8** (6%)	**9** (75%)
7a	50%TFSA-50% TFA	5	20 h	**8** (78%)	**9** (0%)
7a	TFSA (10 equiv)	5	145 min	**8** (94%)	**9** (0%)
8	TFSA	5	75 h		**9** (64%)[c]
8	10% SbF5−90% TFSA	5	15 min		**9** (85%)

[a] One hundred equivalents of the acid was used. [b] 2-Phenyl-1-indanone (36%). [c] Recovery of **8** (11%).

butanedione (**4a**), i.e., 1,2-dihydroxybutenium dication, as a genuine electrophile. Phenylation can take place through this 1,2-dihydroxybutane dication (**4a**), resulting in the formation of a ketol intermediate, **5a**. Although we could not detect the monophenylated intermediate **5a** even at a short reaction time in the case of **1a**, a dehydroxylated derivative (1,2-diphenyl-2-propen-1-one) of the monophenylated intermediate was isolated in the case of 1-phenyl-1,2-propanedione (**1c**), supporting the intermediate formation of the ketol **5**. This ketol **5** is postulated to ionize to another ethylene dication, **6a**, stabilized by the phenyl and hydroxy groups, in a strongly acidic medium (Scheme 2). It is known that related ethylene dications are formed from ketol precursors.[3a] The dication **6a** is likewise very active and can alkylate a second benzene to give **2a**. Another possible mechanism would be a pinacol−pinacolone rearrangement after diphenylation at the two individual carbonyl groups,[13,14] but the behavior of methyl pyruvate (**1b**) excluded this alternative: this keto ester **1b** reacted similarly with benzene to give methyl 2,2-diphenylpropionate (**2b**). The ester group survived the reaction, and the product was formed rapidly even at lower temperature (−40 °C in methylene chloride as a cosolvent).[15] A similar diphenylation reaction of the ketoxime also excluded this mechanism.

Acid-Catalyzed Reaction of 2,3-Butanedione Monoxime. 2,3-Butanedione monoxime (**7a**) reacted with benzene in the presence of a large amount of TFSA (100 equiv) to give the monophenylated ene oxime **8** (58% yield), together with 37% yield of the diphenylated oxime **9** after 5 min (Scheme 3) (Table 1).[16] The monophenyl product **8** was derived by the C_1-phenylation of the ketoxime **7a**, and the diphenyl product **9** was formed by double phenylation of the C_1 position, as in the reaction of 2,3-butanedione (**1a**). The isolated monophenyl derivative **8** was converted to **9** under the same reaction conditions.

In a weaker acid, 50% (w/w) TFSA−50% (w/w) TFA (H_0 = −12), the ketoxime **7a** provided the monophenyl product **8** in 78% yield after 20 h at 5 °C. The use of a smaller amount of the acid catalyst (10 equiv) has an effect similar to that of the reduction of the acidity of the acid. In the presence of 10 equiv of TFSA, the ketoxime **7a** gave the monophenyl product **8** in 94% yield after 2.5 h. In TFSA−TFA or with a small excess (10 equiv) of TFSA, the concentration of the conjugate base (trifluoroacetate in the former case or trifluoromethanesulfonate anions in the latter case) would increase, and the base would catalyze the proton elimination of the intermediate dication **13** to give the monophenyl ene oxime **8** (see Scheme 4). The long reaction time required to complete the monophenylation is in contrast to the very rapid monophenylation reaction (within 20 min) of the 1,2-dione **1a** even in a weaker acid, 50% (w/w) TFSA−50% (w/w) TFA. Therefore, the monophenylation of the ketoxime **7a** is essentially slow, but is accelerated by the increase of the acidity to that of TFSA. The pK_{BH^+} of 2,3-butanedione monoxime was reported to −3.49.[17] In 50% TFA-50% TFSA (H_0 = −12) the monoxime is completely monoprotonated without doubt.

The phenylation of the monophenyl oxime **8** to give the diphenylated oxime **9** was also slow, as judged from the fact that an extended reaction time (145 min) did not significantly change the yields of **8** and **9** from **7a** in TFSA (50% and 39%, respectively). A much longer time (72 h, optimal) is required to complete the conversion of **8** to **9** in TFSA. Slow conversion of **8** to **9** was also observed in the reaction of the isolated **8** with benzene in TFSA, giving the diphenylated **9** in 64% yield after 75 h.

Similar ethylene dications **11a** and **13**, corresponding to the dications **4** and **6** of the 1,2-diones, are presumed to participate in the reaction. The reactions of these dications **11a** and **13** are slower than those of 1,2-diones. As judging from the higher basicity of the imino nitrogen atom of the oxime group compared with that of the oxygen atom of the carbonyl group,[10,17] the ketoxime **7a** is also diprotonated in TFSA to give the N,O-diprotonated ketoxime **11a**, probably through the N-protonated monocation **10a**. The dication **11a** reacts with benzene to give the hydroxy oxime **12**, from which another ethylene dication, **13**, is generated. This dication **13** equilibrates with the N-protonated ene oxime **8** (**14**) via elimination of a methyl proton. The formation of the ene oxime **8a** is consistent with the intermediacy of the hydroxy oxime **12**. The dication **13** can react with another benzene to give the diphenylated oxime **9**, like the dication **6a**. The phenylation reaction of the dication **11a** is much slower than the corresponding reaction of the dication **4a** of the diketone **1a**, as judged from the reaction time. Involvement of the dicationic species **13** in this second phenylation process was supported by the fact that the addition of SbF_5 to TFSA (10% SbF_5−90% TFSA) significantly accelerated the reaction of **8a** to **9a**, and the reaction was completed in a very short time (15 min) (Table 1). Deuterium exchange of methylene protons of the isolated ene oxime **8a** in TFSA-*d* definitely takes place, though it is slow even at ambient

(13) March, J. *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure*, 4th ed; John Wiley & Sons: New York, 1992; pp 1072−1079 and references cited therein.

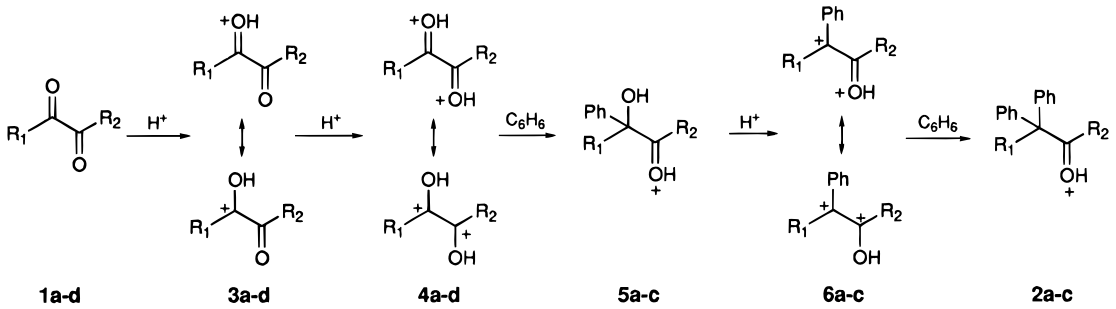
(14) Probable pinacol intermediates will not give the ketol products in a strong acid. The pinacol ionizes to the ethylene dications in TFSA and gives another product: 1,1,2,2-tetraphenylethanediol gave 9,10-diphenylphenanthrene in TFSA through a tetraphenylethylene dication intermediate (see ref 3a,c). In the reactions of dicarbonyl compounds, such cyclized products cannot be detected.

(15) The relative reactivity and regioselectivity data described in this paper are very easily rationalized in terms of cation stability. Generally more basic compounds form stabler cation species upon protonation. Reported pK_{BH^+} values of acetone, acetophenone, acetic acid (in place of methyl acetate), and acetone oxime are −7.2, −6.17, −6.10, and −1.9, respectively (Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 223−403). Thus, the cation centers of protonated species are stabilized in this order.

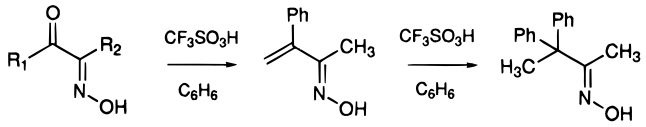
(16) 2,3-Butanedione monoxime was a single isomer with respect to the oxime group, as judged from the NMR data.

(17) Hall, N. F. *J. Am. Chem. Soc.* **1930**, *52*, 5115−5128.

Scheme 2



Scheme 3



a: R_1=CH_3, R_2=CH_3
b: R_1=Ph , R_2=Ph

temperature, indicating that the concentration of the equilibrating cation **13** is low.

NMR Spectroscopic Observation of Dications. Direct NMR spectroscopic observation of diprotonated 1,2-diketones was accomplished in the so-called magic acid system (FSO_3H-SbF_5).[8] On the basis of the coincidence of the ^1H and ^{13}C chemical shifts, 2,3-butanedione (**1a**) and benzil (**1d**) are also diprotonated in TFSA−SbF_5 (2.5:1). Their chemical shifts are listed in Tables 2 and 3, together with the data for reference compounds (O-protonated ketones (acetone and acetophenone)[18] and N-protonated oximes (acetone oxime and acetophenone oxime)).[10c] The dication formed from benzil is stable and did not react with benzene at 0 °C. A related stable species is formed from benzil monoxime (**7b**) in TFSA and TFSA−SbF_5 (2.5:1 mole ratio) at −30 °C, and it was assigned as the N,O-diprotonated benzil monoxime (**11b**), i.e., a hydroxyamino-substituted ethylene dication (Scheme 4). In the ^1H NMR spectra in TFSA−SbF_5 (2.5:1 mole ratio), three sets of singlet absorptions were observed at 14.76, 13.44, and 10.67 ppm, which can reasonably be assigned to a C═OH^+, a C═NH^+, and an oxime OH group, respectively.[18] In the ^{13}C NMR spectra, the chemical shifts of the C_1 and C_2 carbons seemed to be unperturbed or even slightly shielded upon diprotonation, as compared with the neutral precursors. O-protonation of acetophenone and N-protonation of acetophenone oxime resulted in a large deshielding by 21 and 18 ppm, respectively, at the trigonal carbons. The "high-field" shifts of the adjacent electron-deficient centers suggest a strong contribution of the protonated carbonyl (C═OH^+) and protonated imino (C═NH^+) resonance structures rather than the hydroxycarbenium (C^+—OH) and aminocarbenium (C^+—NH) centers. A similar counterpoising effect of the adjacent carbenium centers is also observed in the ^{13}C NMR spectra of diprotonated 2,3-butanedione (**1a**) (in TFSA−SbF_5 (2.5:1)) and benzil (**1d**) (in TFSA), where the low-field shifts of the carbonyl carbons are much smaller (6.2 and 2.3 ppm) than the corresponding low-field shifts of the carbonyl carbons of acetone (41.1 ppm, TFSA−SbF_5 (2.5:1)) and acetophenone (21.0 ppm, TFSA) upon O-monoprotonation. Finally, we also prepared a solution of the ion from 2,3-butanedione monoxime (**7a**) in TFSA−SbF_5 (2.5:1) at −30 °C. The observed species was assigned as N,O-diprotonated 2,3-butanedione monoxime (**11a**). While the C_1 carbon atom is deshielded by 22 ppm in the ^{13}C NMR spectrum as compared with that of the neutral precursor, the C_2 carbon atom is rather shielded by 0.8 ppm, indicating an overwhelming predominance of the imino resonance structure over the keto resonance structure. In the ^1H NMR spectrum, low-field shifts of two methyl groups were observed, as compared with the methyl groups of O-protonated acetone and N-protonated acetone oxime. Two singlet absorptions at 14.49 (C═OH^+) and 12.47 ppm (C═NH^+) were also observed, though even in the TFSA−SbF_5 (2.5:1) acid system at −30 °C, proton exchange with the solvent began to cause merging of the former absorption (C═OH^+) with the acid peak, giving a signal integration value of less than one proton.[19]

The acidity of TFSA−SbF_5 (2.5:1) is stronger than −16 (H_0 < −16)[20] where the NMR study was performed and the dications were observed, so the second pK_{BH^+} of 2,3-butanedione and 2,3-butanedione monoxime is around −17 to −19. Thus, in TFSA (H_0 = −14) where the reactions are performed, 10^{-3}−10^{-5} formation of the dication is estimated, which is sufficient for the reaction to proceed. The Zucker−Hammett criteria indicate that even the small concentration of the active species warrants the linearity between the acidity and rate (and therefore the yield).[21]

Conclusion

We have directly observed the dications (discrete gitonic superelectrophiles) formed from 1,2-diones and their derivatives in Friedel−Crafts reactions. These are analogous to the previously reported O,O-diprotonated nitronaphthalenes,[22a] O,O-diprotonated nitrostyrenes,[22b] and *gem*-diphenylethylene dications.[3a,c] Several recent studies have indicated a nonplanar structure of tetrasubstituted ethylene dications, presumably owing to steric repulsion: an X-ray structure analysis showed that the tetra-*p*-anisylethylene dication has a 41° twist around the central C−C bond,[23] and the dibromo and dichloro salts of the tetrakis(dimethylamino)ethylene dication have twisting angles around the C−C bond of 76° (chloro salt) and 67° (bromo salt).[24] This nonplanar geometry is not rigid in solution. For

(18) Brookhart, M.; Levy, G. C.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 1735.

(19) This spectroscopic investigation of diprotonated 2,3-butanedione monooxime in TFSA−SbF_5 suggested a predominant hydroxyiminium resonance structure, which is consistent with the observed reactivity as an electrophile (see ref 15).

(20) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Super Acids*; Wiley-Interscience: New York, 1985.

(21) (a) Sato Y.; Yato, M.; Ohwada, T.; Saito, S.; Shudo, K. *J. Am. Chem. Soc.* **1995**, *117*, 3037−3043. (b) Saito, S.; Sato, Y.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1994**, *116*, 2312−2317. (c) Ohwada, T. *Rev. Heteroatom Chem.* **1995**, *12*, 179−209.

(22) (a) Ohta, T.; Shudo, K.; Okamoto, T. *Tetrahedron Lett.* **1984**, 325−328. (b) Ohwada, T.; Ohta, T.; Shudo, K. *J. Am. Chem. Soc.* **1986**, *108*, 3029−3032.

(23) Baenziger, N. C.; Buckles, R. E.; Simpson, T. D. *J. Am. Chem. Soc.* **1967**, *89*, 3405.

(24) Bock, H.; Ruppert, K.; Merzweiler, K.; Fenske, D.; Goesmann, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1684−1685.

Scheme 4

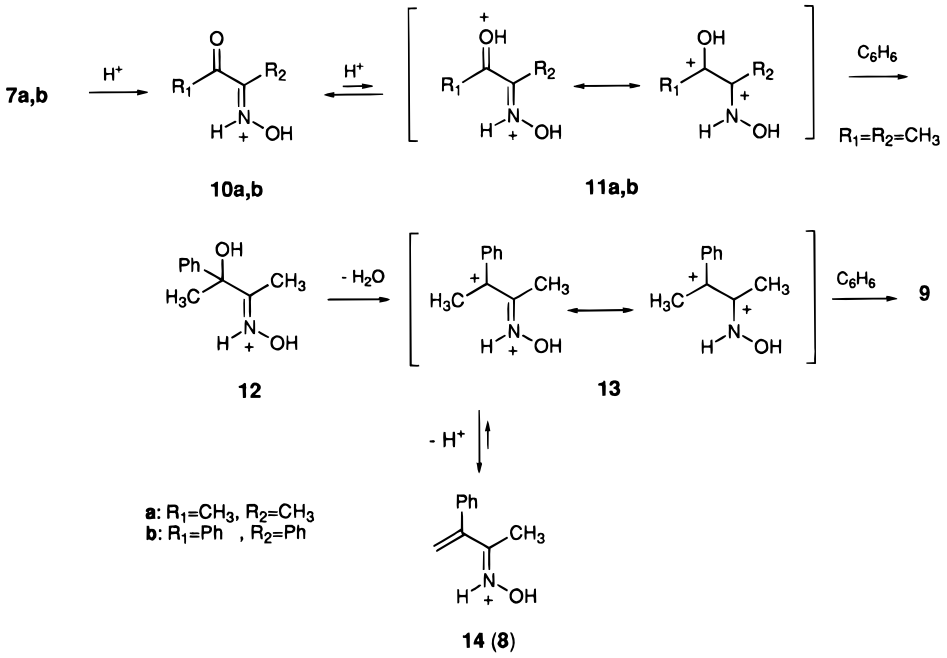


Table 2. ^{1}H NMR Spectroscopic Data of Ions[a]

substrate	acid	temp (°C)	δ(NH/OH)	δ(H_o)	δ(H_m)	δ(H_p)	δ(CH_3)
1a	TFSA−SbF_5	−30	ND[b]				4.33
	FSO3H−SbF_5[c]	−60	ND				4.0
1d	TFSA[d]	−30	11.65 (═OH)[e]	8.64 (d, 7.32)	8.17 (t, 7.33)	8.55 (t, nd)	
	TFSA−SbF_5	−30	ND	9.57 (br d)	8.72 (br t)	9.27 (br t)	
				8.79 (br d)	8.54 (br t)		
7a	TFSA−SbF_5	−30	14.49 (═OH)[e]				4.17, 3.58
			12.47 (═NH)				
7b	TFSA	−30	12.66 (═NH)	8.48 (d, 7.8)	7.96 (t, 7.3)	8.25 (t, nd)	
				8.38 (t, 7.8)		8.19 (t)	
	TFSA−SbF_5	−30	14.73 (═OH)	9.54 (br d)	8.64 (br t)	9.16 (br t)	
			13.44 (═NH)	8.81 (br d)	8.48 (br t)	8.38 (nd)	
			10.67 (OH)	8.64 (br d)	8.38 (nd)		
				8.38 (nd)			
acetone	TFSA	−30	ND				3.26
	TFSA−SBF_5	−30	14.76 (═OH)				3.61, 3.55
	TFA	−10	ND				2.41
acetophenone	TFSA	−30	13.80 (═OH)[e]	8.70 (d, 7.81)	7.97 (t, 7.81)	8.37 (t, 7.32)	3.51
	TFSA−SbF_5	−30	13.32 (═OH)	9.06 (br d)	8.30 (br t)	8.71 (br t)	3.84
acetone oxime	TFSA	−30	11.56 (═NH)				2.67, 2.64
	TFSA−SbF_5	−30	11.47 (═NH)				3.00, 2.95
acetophenone oxime	TFSA	-30	12.06 (═NH)	8.18 (d, 7.33)	8.08 (t, 6.84)	8.27 (t, nd)	3.29
	TFSA−SbF_5	−30	11.47 (═NH)	7.96 (d, 7.33)	7.85 (t, 7.33)	8.02 (t, 7.33)	3.10

[a] Coupling modes and coupling constants in hertz are shown in parentheses, d = doublet, t = triplet, br d = broad doublet, br t = broad triplet, nd = not determined. [b] ND = not detected. [c] Reference 8a. [d] Reference 3c. [e] Signal integration values were less than expected.

example, the O-protonated[(*p*-methoxyphenyl)carbonyl]bis(*p*-methoxyphenyl)methyl dication (akin to **6**) exhibited equivalent *gem*-aromatic rings of the dication in the ^{1}H NMR spectra, supporting an intermediate structure between the perpendicular and planar geometries, with equilibration between possible conformations by rotation about the central C−C bond.[3a] Therefore, although tetrasubstitution, as in the dications **4**, **6**, **11**, and **13**, of course, exhibited different steric effects,[25] the much attenuated reactivity of the dication formed from 2,3-butanedione monoxime (**7a**), as compared with the 1,2-dicarbonyl counterpart **1a**, can be interpreted in terms of the divergent electron-donating ability of a substitent, rather than the size of the substitents. The geometrical preference (planar vs perpendicular) of these dications may determine the electronic nature of these Friedel−Crafts electrophiles. Futher studies will address this possibility with the assistance of theoretical calculations.

Experimental Section

General Methods. All the melting points were measured with a Yanagimoto hot-stage melting point apparatus (MP-500) and are uncorrected. Proton (400 MHz) and carbon (100 MHz) NMR spectra were measured on a JEOL GX-400 NMR spectrometer with TMS (^{1}H) and the middle peak of $CDCl_3$ (77.0 ppm, ^{13}C) as internal references in $CDCl_3$ as the solvent. Coupling constants are given in hertz. Flash column chromatography was performed on silica gel (Kieselgel 60, 230−400 mesh, Merck) with the specified solvent.[26] Combustion analyses were carried out in the microanalytical laboratory of this

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Table 3. ^{13}C NMR Spectroscopic Data of Ions and Neutral Precursors

substrate	acid	temp (°C)	$\delta(C_1)$	$\delta(C_2)$	$\delta(C_{ipso})$	$\delta(C_o)$	$\delta(C_m)$	$\delta(C_p)$	$\delta(CH_3)$
1a	TFSA−SbF_5	−30	203.3						24.7
	FSO_3H−SbF_5[a]	−60	204.0						25.5
	$CDCl_3$	23	197.1						23.4
1d	TFSA[b]	−20	196.9		128.3	135.0	130.8	144.3	
	FSO_3H[a]	−60	197.3		128.3	136.2	131.4	145.6	
	$CDCl_3$	23	194.6		132.9	129.9	129.0	134.9	
7a	TFSA−SbF_5	−30	219.2	156.4					29.2, 13.2
	$CDCl_3$	23	197.2	157.2					25.1, 8.1
7b	TFSA	−20	188.2	159.9	131.4	133.7	129.9	139.9	
					122.4	132.2	129.9	138.8	
	TFSA−SbF5	−20	192.4	157.2	126.4	142.1	131.9	155.3	
					120.4	138.0	130.9	143.8	
						133.6			
						133.3			
	$CDCl_3$	23	194.2	157.0	134.5	134.6	128.9	130.5	
					130.8	129.4	126.4	129.0	
acetone	TFSA	−30	241.9						25.5
	TFSA−SBF_5	−30	248.0						30.8, 29.6
	$CDCl_3$	23	206.9						30.8
acetone oxime	TFSA	−30	179.2						20.6, 17.0
	TFSA−SbF_5	−30	181.1						20.7, 17.0
	$CDCl_3$	23	155.6						21.7, 14.9
acetophenone	TFSA	−30	219.1		128.8	130.3	130.3	144.8	24.1
	TFSA−SbF_5	−30	219.0		128.6	130.5	130.5	145.4	24.1
	$CDCl_3$	23	198.1		137.0	133.0	128.5	133.0	26.5
acetophenone oxime	TFSA	−20	174.5		126.8	129.8	127.4	135.9	15.4
	$CDCl_3$	23	156.0		136.5	128.5	113.9	129.3	12.3

[a] Reference 8b. [b] Reference 3c.

faculty. Trifluoromethanesulfonic acid (TFSA) was purchased from Central Glass Co., Japan, and used after distillation under reduced pressure with a Widmer condenser as described previously.[8] Trifluoroacetic acid (TFA) was obtained from Wako Pure Chemical Co., Japan, and was distilled at atmospheric pressure.[8] Antimony pentafluoride was purchased from Aldrich Chemical Co. and was used after distillation under reduced pressure. 2,3-Butanedione (**1a**), methyl pyruvate (**1b**), and 1-phenyl-1,2-propanedione (**1c**) were purchased from Wako Pure Chemical Co., and were used after distillation under reduced pressure. 2,3-Butanedione monoxime (**7a**) was obtained from Aldrich, and was further purified by recrystallization.

TFSA-Catalyzed Reaction of 2,3-Butanedione (1a) with Benzene. A solution of 2,3-butanedione (**1a**) (215 mg, 2.5 mmol) in dry benzene (2.7 mL, total amount of benzene was 75 mmol, 30 equiv with respect to **1a**) was added in portions to a well-stirred mixture of dry benzene (4 mL) and trifluoromethanesulfonic acid (TFSA) (22.2 mL, 100 equiv) over 2 min at 5 °C in an ice−water bath. The whole mixture was stirred for 5 min, then poured into ice−water (300 mL), and extracted with methylene chloride (three portions of 100 mL). The organic phase was washed with brine (100 mL), dried over Na_2SO_4, and evaporated to give the crude residue (570 mg), which was flash-chromatographed (ethyl acetate−*n*-hexane (1:50)) to give the diphenylated ketone **2a** (525 mg, 94% yield):[27] colorless powder; mp 39.0−39.5 °C (recrystallized from *n*-hexane); ^1H NMR δ 7.36−7.18 (10H, m), 2.11 (s, 3H, $OCCH_3$), 1.87 (3H, s, CH_3). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.92; H, 7.28.

TFSA-Catalyzed Reaction of Methyl Pyruvate (1b) with Benzene. The reaction of methyl pyruvate (**1b**) with benzene in the presence of TFSA (100 equiv) was conducted at 5 °C in the same manner as described for **1a** to give a 72% yield of methyl 2-diphenylpropionate (**2b**) as a colorless oil after column chromatography (ethyl acetate−*n*-hexane (1:15)). Satisfactory NMR and IR spectroscopic data were obtained.

TFSA-Catalyzed Reaction of 1-Phenyl-1,2-propanedione (1c) with Benzene. 1-Phenyl-1,2-propanedione (**1c**) (374 mg) was allowed to react with benzene (total amount of benzene was 6.7 mL, 30 equiv) in the presence of TFSA (100 equiv, 22.1 mL) at 5 °C. After 60 min, aqueous workup as described above gave a crude product (660 mg), which was flash-chromatographed (ethyl acetate−*n*-hexane (1:60)) to give 241 mg (34% yield) of 1,2,2-triphenylpropan-1-one (**2c**) and 173 mg (33% yield) of 2-phenyl-1-indanone. Data for **2c**: colorless needles; mp 91−92 °C (recrystallized from ethanol); ^1H NMR δ 7.52 (2H, d, 7.0), 7.4−7.3 (5H, m), 7.3−7.2 (8H, m), 2.03 (3H, s). Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 87.80; H, 6.19. Data for 2-phenyl-1-indanone: colorless prisms; mp 74−74.5 °C (recrystallized from ethanol); ^1H NMR δ 7.82 (1H, d, 7.3), 7.65 (1H, t, 7.5), 7.53 (1H, d, 7.7), 7.43 (1H. t, 7.3), 7.32 (2H, t, 7.3), 7.2 (1H, not determined), 7.19 (2H, d, 7.0), 3.90 (1H, dd, 8.4, 4.0), 3.70 (1H, dd, 7.6, 4.4), 3.28 (1H, dd, 7.2, 4.0). Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.26; H, 5.70.

TFSA-Catalyzed Reaction of 2,3-Butanedione Monoxime (7a) with Benzene. A solution of the monoxime **7a** (253 mg, 2.5 mL) in dry benzene (2.7 mL, total amount of benzene was 75 mL, 30 equiv with respect to **7a**) was added in portions over 2 min to a well-stirred mixture of dry benzene (4 mL) and trifluoromethanesulfonic acid (TFSA) (22.2 mL, 100 equiv) at 5 °C in an ice−water bath. The whole mixture was stirred for 5 min, then poured into ice−water (300 mL), and extracted with methylene chloride (two portions of 100 mL). The organic phase was washed with brine (100 mL), dried over Na_2SO_4, and evaporated to give a crude residue (456 mg), which was flash-chromatographed (ethyl acetate−*n*-hexane (1:10)) to give the monophenylated **8** (232 mg, 58% yield) and the diphenylated **9** (221 mg, 37%). Data for **8**: colorless cubes; mp 155.1−155.4 °C (recrystallized from *n*-hexane);[28] ^1H NMR δ 8.58 (1H, s, OH), 7.32−7.20 (10H, m), 1.91 (1H, s, CH_3), 1.78 (3H, s, CH_3). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.60; H, 7.40; N, 5.85. Data for **9**: colorless powder; mp 90.5−91 °C (recrystallized from *n*-hexane−CH_2Cl_2);[29] ^1H NMR δ 7.84 (1H, s, OH), 7.36−7.30 (5H, m), 5.58 (1H, s, methylene), 5.44 (1H, s), 2.08 (3H, s, CH_3). Anal. Calcd for $C_{10}H_{11}NO$: C, 74.50; H, 6.88; N, 8.69. Found: C, 74.20; H, 6.95; N, 8.76.

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. Measurements and calibration of chemical shifts were conducted as previously described.[3c]

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