Acknowledgment.—We thank Mr. Paul G. Elsey and Mr. Dale Stoy of the Ethyl Corporation for a generous supply of methylphosphonous dichloride. We also acknowledge the research work of Dr. B. C. Trivedi on several of the compounds described herein.

Registry No.—**1a**, 40084-63-7; *cis*-**1b**, 40084-64-8; *trans*-**1b**, 40084-65-9; *cis*-**1c**, 35616-95-6; *trans*-**1c**, 35616-97-8; **4a**, 35624-08-9; **4b**, 35624-09-0; **5**, 40085-35-6; **5** cis isomer, 22434-52-2; **5** methiodide, 26339-55-9; **6a**, 39990-53-9; **6b**, 39990-54-0; **6** phosphorane form, 39981-51-6; **7a**, 40084-68-2; **7b**, 40084-69-3; **10a**, 39990-55-1; **10b**, 39990-56-2; **10** phosphorane form, 39981-52-7; **11a**, 39990-57-3; **11b**, 39990-58-4; **11** phosphorane form, 39981-53-9; *cis*-**12**, 25145-23-7; *trans*-**12**, 25145-24-8; *cis*-**16**, 39990-60-8; *trans*-**16**, 39990-63-1; **16** phosphorane form, 20699-83-6; *cis*-**16** $AlCl_4$ derivative, 40084-70-6; *trans*-**16** oxide, 35623-32-6; **17**, 30092-42-3; **17a**, 30092-44-5; **17b**, 39981-57-2; **18**, 36044-91-4; **19**, 39981-59-4; **20**, 39981-60-7; **21**, 39981-61-8; **22**, 39990-66-4; **22** phosphorane form, 39981-62-9; *cis*-**23**, 39990-67-5; *trans*-**23**, 39990-68-6; **24**, 39981-63-0; phenyl phosphonous dichloride, 644-97-3; *cis*-1,2,2,3,4,4-hexamethylphosphetane, 35622-00-5; *trans*-1,2,2,3,4,4-hexamethylphosphetane, 35621-97-7; *cis*-1-phenyl-2,2,3,4,4-pentamethylphosphetane, 22434-51-1; *trans*-1-phenyl-2,2,3,4,4-pentamethylphosphetane, 16083-95-7; 1-*tert*-butyl-2,2,3,4,4-pentamethylphosphetane 1-oxide HBr adduct, charged form, 40088-36-6; 1-*tert*-butyl-2,2,3,-4,4-pentamethylphosphetane 1-oxide HBr adduct, neutral form, 9981-10-0.

Stable Carbocations. CLI.[1] Protonation of Cyclic Carboxylic Acid Anhydrides in FSO_3H-SbF_5 ("Magic Acid")-SO_2 Solution

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Protonation of a series of cyclic carboxylic acid anhydrides (1–16) in SO_2 solutions containing varying amounts of 1:1 mol/mol FSO_3H-SbF_5 was studied by nmr spectroscopy. O-Protonated cyclic carboxylic acid anhydrides formed undergo rapid intermolecular hydrogen exchange with the acid solvent system or excess anhydride, even at the lowest accessible temperatures. Unsaturated cyclic carboxylic acid anhydrides (1–3), as well as cyclic aromatic carboxylic acid anhydrides (4–10), were not cleaved in magic acid solution up to 0°, in sharp contrast to the behavior of acyclic saturated cyclic carboxylic acid anhydrides.

Protonation of acyclic carboxylic acid anhydrides in superacids has been studied in our preceding work.[2] A preliminary study of protonation of cyclic anhydrides, including succinic and glutaric anhydrides, was also carried out in $FSO_3H-SbF_5-SO_2$ solution.[3,4] Protonated cyclic anhydrides such as succinic and glutaric anhydrides could not be observed even when the solutions were prepared and examined at −80°, as they were cleaved in "magic acid" giving the corresponding alkyleneoxocarbenium–carboxonium ions, $^+OC(CH_2)_n$-$COOH_2^+$ (n = 2 and 3, respectively).[5] On the other hand, succinic anhydride was reported to be only partially protonated in sulfuric acid.[6]

In continuation of our studies, we presently wish to report the results of protonation of a series of cyclic (both aliphatic and aromatic) carboxylic acid anhydrides (**1–16**) in SO_2 solutions containing varying amounts of 1:1 mol/mol FSO_3H-SbF_5.

Results and Discussion

The chemical behavior of cyclic carboxylic acid anhydrides in $FSO_3H-SbF_5-SO_2$ is different from that of acyclic anhydrides. In particular cyclic aromatic anhydrides **4–10** are not cleaved even with large excess of FSO_3H in SO_2 solution at 0°. They are protonated in the superacid and undergo rapid intermolecular hydrogen exchange with the solvent system. Intramolecular hydrogen exchange seems to be less feasible since the position of the two carbonyl groups are rigidly fixed and consequently their distance is too large. Intermolecular hydrogen exchange processes must be extremely rapid, since static mono- or diprotonated cyclic anhydrides were not observed even at the lowest possible temperature (*ca.* −90°) under the experimental conditions. Consequently, the proton chemical shifts of protonated cyclic anhydrides are dependent upon the concentration of both substrate and superacid used. Pmr parameters of cyclic carboxylic acid anhydrides protonated in SO_2 solutions containing varying amounts of magic acid and their precursors (in SO_2) are summarized in Table I (also showing the proportions of superacid and anhydride in the system).

Unsaturated cyclic carboxylic acid anhydrides including maleic (**1**), dimethylmaleic (**2**), and 3,4,5,6-tetrahydrophthalic anhydride (**3**) show similar behavior in $FSO_3H-SbF_2-SO_2$ solutions. When **maleic anhydride** (**1**) was protonated with 0.5 equimolar magic acid in SO_2 solution, the pmr absorption of the two vinylic protons was deshielded from δ 6.83 (s) to 7.21 (s). A very deshielded pmr singlet absorption (~0.5 proton intensity) is found at δ 14.5 and is assigned to the OH proton of protonated maleic anhydride, which undergoes intermolecular hydrogen exchange with **1**. The pmr singlet absorption of the two vinylic protons in protonated maleic anhydride **1a** was further deshielded at δ 7.63 when equimolar magic acid was used. The OH proton was slightly shielded to δ 13.5. These data suggest that another intermolecular H exchange process may occur (eq 1). When **1** was treated with a large excess of 1:1 mol/mol FSO_3H-SbF_5 in SO_2 or with neat magic acid solution, the pmr spectra of the resulting solution showed two more deshielded singlets at δ 8.09 and 8.30, respectively. The OH proton is not observed

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(1) Part CL: G. A. Olah, G. Liang, G. D. Mateescu, and J. L. Riemenschneider, *J. Amer. Chem. Soc.*, in press.

(2) G. A. Olah, K. Dunne, Y. K. Mo, and P. Szilagyi, *J. Amer. Chem. Soc.*, **94**, 4200 (1972).

(3) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **89**, 4752 (1967).

(4) G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, **70**, 561 (1970).

(5) For a discussion of the general concept of carbocations and differentiation of trivalent carbenium ion from penta- (or tetra-) coordinated carbonium ions, see G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

(6) R. J. Gillespie and J. A. Leisten, *Quart. Rev., Chem. Soc.*, **8**, 40 (1954).

TABLE I

PMR PARAMETERS OF CYCLIC CARBOXYLIC ACID ANHYDRIDES IN SO_2 SOLUTIONS CONTAINING VARYING MOLAR AMOUNTS OF 1:1 MOL/MOL $FSO_3H–SbF_5$[a]

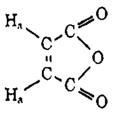
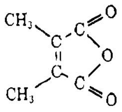
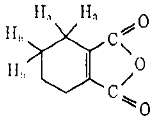
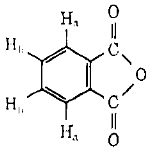
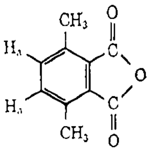
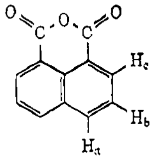
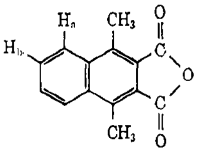
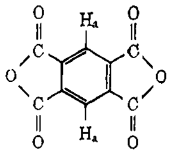
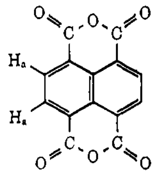
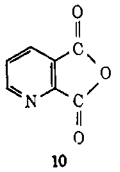
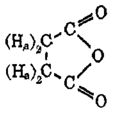
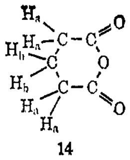
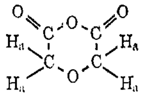
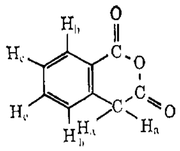
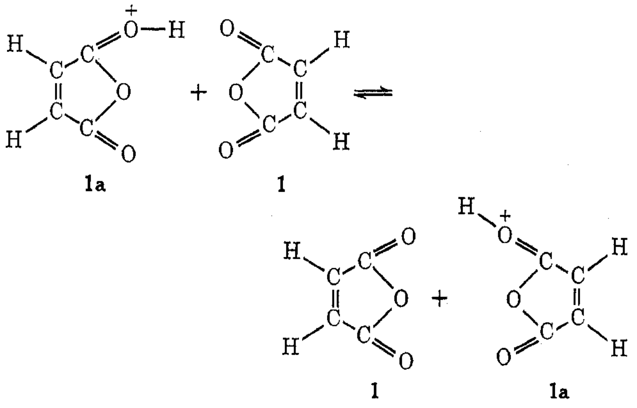
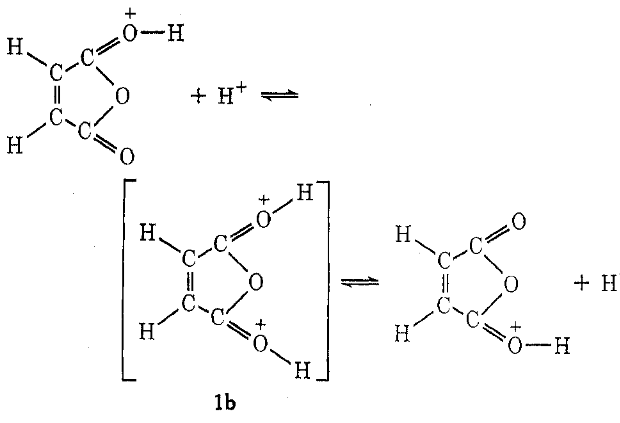
Cyclic carboxylic acid anhydride	Solvent[b] system	δ_{H_a}	δ_{H_b}	δ_{H_c}	δ_{CH_3}	Other
 1	SO_2	6.83 (s)				
	0.5 *M* MA	7.21 (s)				14.5 (OH)
	1.0 *M* MA	7.63 (s)				13.5 (OH)
	Excess MA	8.09 (s)				*c*
	Neat MA	8.30 (s)				*c*
 2	SO_2				1.88 (s)	
	0.5 *M* MA				1.97 (s)	14.0 (OH)
	1.0 *M* MA				2.11 (s)	13.2 (OH)
	Excess MA				2.42 (s)	*c*
	Neat MA				2.90 (s)	*c*
 3	SO_2	2.18 (m)	1.50 (m)			
	0.5 *M* MA	2.36 (m)	1.71 (m)			14.6 (OH)
	1.0 *M* MA	2.70 (m)	1.90 (m)			12.9 (OH)
	Excess MA	2.80 (m)	2.10 (m)			*c*
	Neat MA	3.10 (m)	2.40 (m)			*c*
 4	SO_2	7.73 (s)	7.73 (s)			
	1.0 *M* MA	8.03 (s)	8.03 (s)			14.0 (s, br, OH)
	2.0 *M* MA	8.35 (m)	8.35 (m)			*c*
	4.0 *M* MA	8.50 (m)	8.50 (m)			*c*
	Excess MA	9.38 (m)	9.03 (m)			*c*
	Neat MA	9.80 (m)	9.45 (m)			*c*
 5	SO_2	7.30 (s)			2.25 (s)	
	1.0 *M* MA	8.00 (s)			2.75 (s)	14.5 (OH)
	Excess MA	8.18 (s)			2.90 (s)	*c*
	Neat MA	8.93 (s)			3.70 (s)	*c*
 6	SO_2	9.2 (m)	7.6 (m)	9.2 (m)		
	Excess MA	9.70 (d, 8)	8.68 (t, 8)	9.85 (d, 8)		*c*
	Neat MA	10.3 (d, 8)	9.31 (t, 8)	10.3 (d, 8)		*c*
 7	*d*					
	Excess MA	8.9 (m)	8.3 (m)		3.3 (s)	*c*
	Neat MA	9.3 (m)	9.3 (m)		4.0 (s)	*c*
 8	SO_2	8.42 (s)				
	1.0 *M* MA	9.55 (s)				14.5 (OH, s, br)
	Excess MA	9.73 (s)				*c*
 9	*d*					
	Excess MA	9.50 (s)				*c*
	Neat MA	10.61 (s)				*c*
 10	SO_2	8.20 (dd, 8, 2)	7.73 (dd, 8, 4)	8.83 (dd, 4, 2)		
	Excess MA	9.3 (m)	8.7 (m)	9.3 (m)		9.7 (s, br, NH) *c*

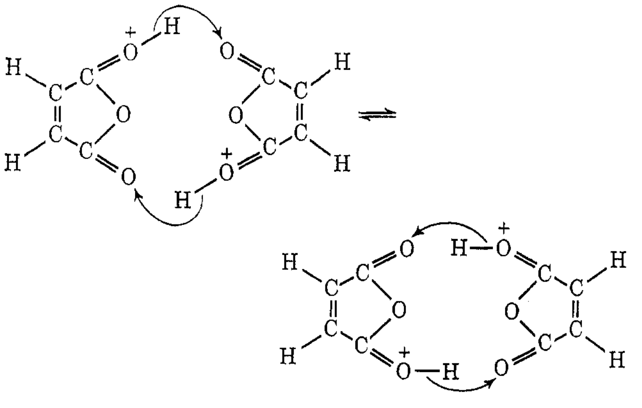
TABLE I (*Continued*)

Cyclic carboxylic acid anhydride	Solvent[b] system	δ_{H_a}	δ_{H_b}	δ_{H_c}	δ_{CH_3}	Other
 **13**	SO_2	2.73 (s)				
	0.25 *M* MA	2.90 (s)				14.8 (OH, s, br)
	1.0 *M* MA	3.00 (s)				13.2 (OH, s, br)
	3.0 *M* MA	3.80 (s)				*c*
	4.0 *M* MA	4.60 (s, br)				*c*
	Excess MA[e]	4.47, 5.15				14.43 (OH)
	Wet MA[f]	4.08 (s)				13.6 (s, br)
	Neat MA[g]	5.10 (s)				
 14	SO_2	2.53 (t, 6)	1.80 (qu, 6)			
	1.0 *M* MA	2.68 (t, 6)	2.00 (qu, 6)			16.1 (OH, s, br)
	Wet MA[f]	3.85 (t, 6)	2.80 (qu, 6)			12.7 (OH, s)
	Excess MA[e]	4.40 (t, 6)	3.11 (qu, 6)			13.0 (OH, s)
	Neat MA[g]	5.20 (t, 6)	4.10 (qu, 6)			
 15	SO_2	4.20 (s)				
	0.5 *M* MA	4.30 (s)				13.0 (OH, s, br)
	1.0 *M* MA	4.40 (s)				12.8 (OH, s, br)
	Excess MA[e]	5.58 (s) 6.58 (s)				13.3 (OH, s, br)
	Wet MA[f]	5.40 (s)				13.2 (OH, s, br)
 16	SO_2	3.90 (s)	7.5 (m)	7.5 (m)		
	1.0 *M* MA	4.10 (s)	8.0 (m)	7.5 (m)		12.3 (OH, s, br)
	Excess MA[e]	4.91 (s) 5.03 (s)	8.0-9.0 (m) 8.0-9.0 (m)			13.1 (OH, s, br) 13.3 (OH, s, br)
	Neat MA[g]	5.50 (s)	8.80 (t, 6)	9.60 (d, 6) 9.32 (d, 6)		

[a] Proton chemical shifts are reported in parts per million (δ) from external (capillary) TMS. Abbreviation: s, singlet; d, doublet; t, triplet; qu, quintet; m, multiplet; br, broad. The coupling constants are shown in parentheses. [b] Used equimolar amount of magic acid (MA) in SO_2: excess, more than 5 mol equiv of magic acid; wet, excess magic acid containing 10% water; neat, neat magic acid at room temperature. [c] The OH protons are not observable because of rapid intermolecular hydrogen with the solvent system. [d] Insoluble in SO_2. [e] Formation of oxocarbenium-carboxonium ions. [f] Formation of diprotonated dicarboxylic acids. [g] Formation of dioxocarbenium ions.


1a 1
1 1a


1b



since it now rapidly exchanges with the superacid system. It is suggested that under these conditions diprotonated maleic anhydride **1b** may be involved in the intermolecular exchange process. The deshielding of the vinylic protons is proportional to the molar concentration of magic acid used.

Dimethylmaleic anhydride (2)[7] **and 3,4,5,6-tetrahydrophthalic anhydride (3)** show similar deshielding effects of the methyl and methylene protons, respectively, in magic acid solutions. The pmr data of **2** and **3** in solutions containing varying amounts of magic acid are summarized in Table I.

It is known that acyclic and saturated cyclic acid anhydrides are cleaved in excess magic acid.[2] However, unsaturated carboxylic acid anhydrides (**1–3**) are not cleaved under similar conditions. Furthermore, the olefinic double bonds in **1–3** are not protonated in the same media. This behavior is similar to that observed in the protonation of α,β-unsaturated alde-

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(7) Dimethylmaleic anhydride was made available by Dr. H. Bosshard of CIBA-GEIGY Limited, Basel, Switzerland.

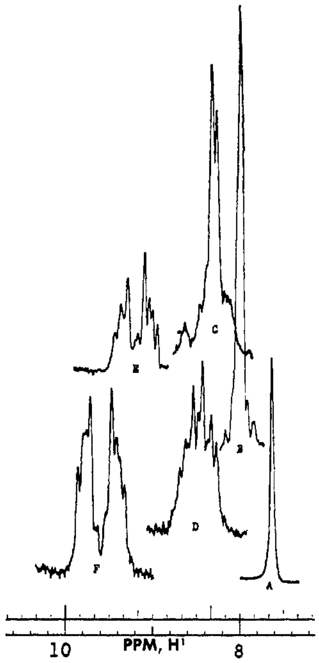
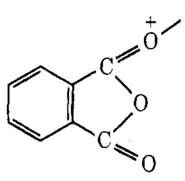


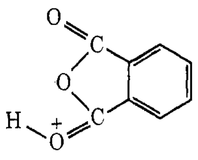
Figure 1.—Pmr spectra of phthalic anhydride (4) in SO_2 (A), in 1.0 equiv mol of magic acid (B), in 2.0 equiv mol of magic acid (C), in 4.0 equiv mol of magic acid (D), in excess magic acid (E), and in neat magic acid (F) solutions.

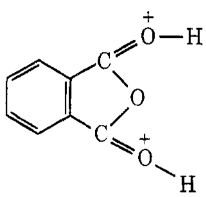
hydes and ketones in superacids.[8] Magic acid solutions of cyclic carboxylic acid anhydrides (**1–3**) when quenched with ice–water regenerate the starting anhydrides unchanged.

Protonation of the olefinic double bonds in unsaturated cyclic carboxylic acid anhydrides can take place only if they are not directly attached to the carbonyl groups. For example, 1,2,3,6-tetrahydrophthalic anhydride reacted with magic acid at −80° giving complicated and yet unidentified products. The pmr spectrum of the resulting solution shows the absence of olefinic protons and the presence of carboxonium groups ($COOH_2^+$).[9] These data indicate that protonation of double bond in 1,2,3,6-tetrahydrophthalic anhydride has occurred, as well as cleavage of the acid anhydride group.

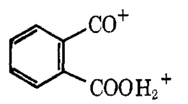
Aromatic Cyclic Acid Anhydrides.—Phthalic anhydride (**4**) was studied with different molar equivalents of 1:1 mol/mol $FSO_3H–SbF_5$ in SO_2 solution at low temperature. The pmr spectra of the resulting solutions are shown in Figure 1. The deshielding of the aromatic protons (which show a singlet absorption at δ 7.73 in SO_2 solution) after protonation is proportional to the molar equivalents of magic acid used. When **4** was treated with equimolar 1:1 mol/mol $FSO_3H–SbF_5$ in SO_2 solution at −78°, the pmr spectrum of the solution shows a singlet absorption at δ 8.03 for the aromatic protons and a very deshielded broad singlet absorption at δ 14.0 for the rapidly exchanging OH proton. The aromatic singlet absorption was further deshielded and split into a multiplet at δ 8.35 when 2 mol equiv of 1:1 mol/mol $FSO_3H–SbF_5$ in SO_2 was used (Figure 1, C trace). The OH absorption is shifted upfield, presumably due to rapid exchange with the superacid system. The multiplet absorption was slightly broadened and further deshielded to δ 8.50 when 4 mol equiv of 1:1 mol/mol $FSO_3H–SbF_5$ in SO_2 solution was used (Figure 1, D trace). The pmr spectrum of **4** in excess 1:1 mol/mol $FSO_3H–SbF_5–SO_2$ became two multiplets at δ 9.38 and 9.03 (Figure 1, E trace). This solution was then added to a solution of **4** in SO_2. The pmr spectrum of the resulting solution is dependent upon the concentration of **4** in SO_2 and is similar to those previously obtained (Figure 1, B, C, and D traces). Thus, the process is reversible. Under all of the experimental conditions studied, no static OH proton absorption of either mono- or diprotonated phthalic anhydride was observed. This behavior is very similar to that of **1** in similar magic acid solutions. Thus, intermolecular hydrogen exchange processes involving mono- or diprotonated phthalic anhydride, such as **4** + **4a** $\rightleftharpoons$ **4a** + **4**, **4a** + **4b** $\rightleftharpoons$ **4b** + **4a**, and **4a** + H^+ $\rightleftharpoons$ **4c** $\rightleftharpoons$ **4b** + H^+, are taking place.


4a


4b


4c

Phthalic anhydride was not cleaved, however, to **4d**


4d

even in neat 1:1 mol/mol $FSO_3H–SbF_5$ at room temperature. The pmr spectrum of this solution shows again two further deshielded multiplets at δ 9.80 and 9.45. Quenching of the solution quantitatively regenerated starting phthalic anhydride. If **4d** would be formed or involved in the intermolecular hydrogen exchange processes, phthalic acid should have been obtained from the quenching experiment.[10]

In addition, we have also studied the behavior of phthalic acid with varying molar amounts of 1:1 mol/mol $FSO_3H–SbF_5$ in SO_2 solution at low temperature. The pmr spectra of either **4** or phthalic acid in the same magic acid solution are identical, except for the intense H_3O^+ peak in the latter. These data clearly show that phthalic acid dehydrated in $FSO_3H–SbF_5–SO_2$ solution to phthalic anhydride **4**.

Other aromatic cyclic carboxylic acid anhydrides, such as 3,6-dimethylphthalic anhydride (**5**), 1,8-naphthalic anhydride (**6**), 1,4-dimethyl-2,3-naphthalic anhydride (**7**), 1,2,4,5-benzenetetracarboxylic acid dianhydride (**8**), 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (**9**), and 2,3-pyridinedicarboxylic acid anhydride (**10**), were also studied with varying molar amounts of 1:1 mol/mol of $FSO_3H–SbF_5$ in SO_2 solution, at low temperature. They behave very similarly to phthalic anhydride in these media. Their pmr parameters are tabulated in Table I. The aromatic, as well as the methyl, protons of **5–10** are increasingly more deshielded with higher molar equivalents of 1:1 mol/

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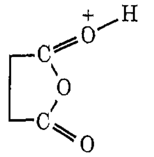
[8] G. A. Olah, Y. Halpern, Y. K. Mo, and G. Liang, *J. Amer. Chem. Soc.*, **94**, 3554 (1972).

[9] The carboxonium groups ($COOH_2^+$) generally show two nonequivalent OH absorptions at δ 12.0–13.5 [see G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **89**, 3591 (1967)].

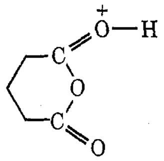
[10] A referee has pointed out, however, that quenching experiments would not exclude **4d** as a low concentration, steady-state intermediate.

mol FSO_3H–SbF_5 in SO_2 solution. Data indicate that intermolecular hydrogen exchange of monoprotonated, as well as diprotonated, aromatic cyclic carboxylic acid anhydrides with the superacid solvent system takes place. None of the cyclic carboxylic acid anhydrides **5–10** or tetrachloro- (bromo-) phthalic anhydride (**11–12**) were cleaved in the superacid solutions, even at 0°, in sharp contrast to acyclic and also saturated cyclic acid anhydrides (see subsequent discussion). Quenching of the solution again quantitatively regenerated starting anhydrides.

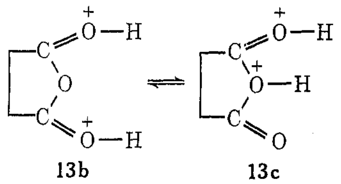
Saturated Cyclic Anhydrides and Their Cleavage.—Protolytic cleavage of succinic and glutaric anhydrides (**13** and **14**, respectively) has been observed in excess FSO_3H–SbF_5–SO_2 solution.[3] However, observation of protonated succinic and glutaric anhydrides **13a** and **14a**, respectively, under stable ion conditions have not yet been achieved. As an extension of this work, we have now examined **13** and **14** with different molar equivalents of 1:1 mol/mol FSO_3H–SbF_5 in SO_2 solution with a hope to observe directly the mono- and diprotonated anhydrides. The pmr spectrum of **13** in SO_2 at −60° displays a singlet absorption at δ 2.73. This singlet absorption was deshielded to δ 2.90 and 3.00 when **13** was treated with 0.25 and 1.00 molar equiv amounts of 1:1 mol/mol FSO_3H–SbF_5 in SO_2 solution, respectively. Two OH absorptions were also observed at δ 14.8 and 13.2, respectively, in their pmr spectra. These data indicate that **13** was protonated and underwent intermolecular hydrogen exchange with the superacid systems. Static monoprotonated succinic anhydride **13a** was not observed even at −90°. The pmr spectra of **13** in SO_2 solutions containing 3 and 4 mol equiv of FSO_3H–SbF_5 displayed two further deshielded singlets at δ 3.80 and 4.60 (slightly broadened), respectively. These data suggest that intermolecular hydrogen exchange in these system may involve diprotonated succinic anhydride (**13b** and **13c**). Intramolecular hydrogen exchange through **13b** and **13c** is less probable. It can be suggested that diprotonated succinic anhydrides **13b** and **13c** are also involved in the cleavage reaction of **13** in large excess of superacid to give oxocarbenium–carboxonium ion $OC^+(CH_2)_2COOH_2^+$ (**13d**). The cleavage reaction of **13** in excess superacid has been reported previously.[3] Consequently, the slight broadening of the CH_2 absorption at δ 4.60 (when **13** was treated with 4 mol equiv of FSO_3H–SbF_5 in SO_2 solution) may be due to involvement of **13d**.



13a



14a

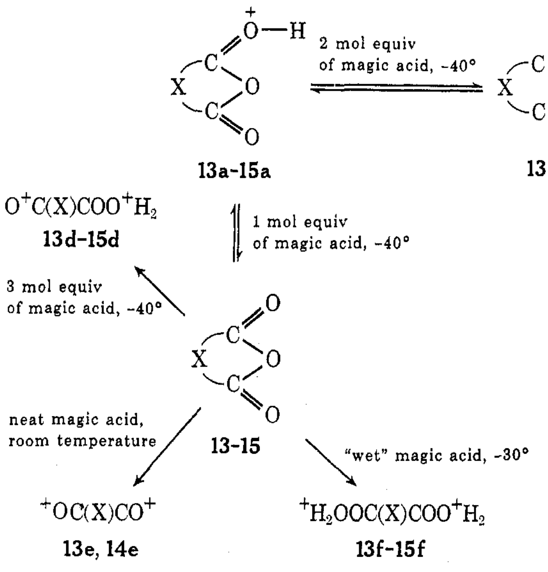


13b **13c**

When **13** was treated with "wet" magic acid (*i.e.*, containing ~10 mol % of H_3O^+), diprotonated succinic acid was formed in addition to **13d**. The amount of diprotonated succinic acid formed is proportional to the concentration of hydronium ion (H_3O^+) originally present in the magic acid solution. In neat 1:1 mol/mol FSO_3H–SbF_5 solution, at room temperature, **13** was cleaved and dehydrated to the diacyl cation, $OC^+(CH_2)_2CO^+$ (**13e**).

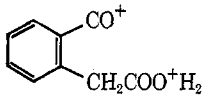
Glutaric anhydride (14) and diglycolic anhydride (15) behave very similarly to **13** with varying amounts of magic acid (Scheme I). The pmr data of **13–15** in these solutions are tabulated in Table I. Diglycolic anhydride (**15**) decomposed with CO_2 evolution when treated with neat magic acid at room temperature. The ethereal oxygen atom of **15** was not observed in protonated form under any other studied conditions,[11] although it may be involved in the cleavage processes.

SCHEME I

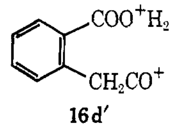


13, 13a, b, d–f, $X = (CH_2)_2$
14, 14a, b, d–f, $X = (CH_2)_3$
15, 15a, b, d, f, $X = CH_2OCH_2$

Protonation of homophthalic anhydride (**16**) was also studied in different magic acid media. With 1 and 2 mol equiv of 1:1 mol/mol FSO_3H–SbF_5 in SO_2 solution, **16** behaved similarly to **13–15**. In excess magic acid, **16** was cleaved to give equal amounts of acylcarboxonium ions **16d** and **16d′**. The pmr spectrum of the solution shows two (equal intensity) singlet absorptions at δ 4.95 and 5.05 for the methylene protons of **16d** and **16d′**, respectively. These singlet absorptions are independent of the temperature in the range from −80 to −10°, indicating that interconversion of **16d** and **16d′** through **16b** and **16c** does not occur. The OH absorptions of **16d** and **16d′** were not observed in the pmr spectra owing to rapid exchange with the acid solvent system.



16d



16d′

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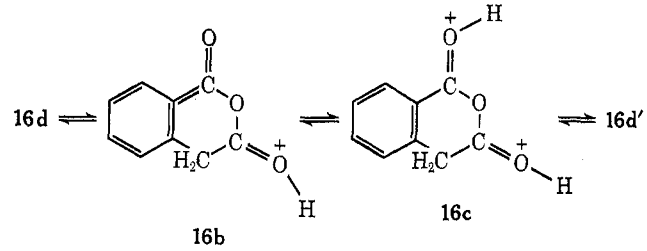
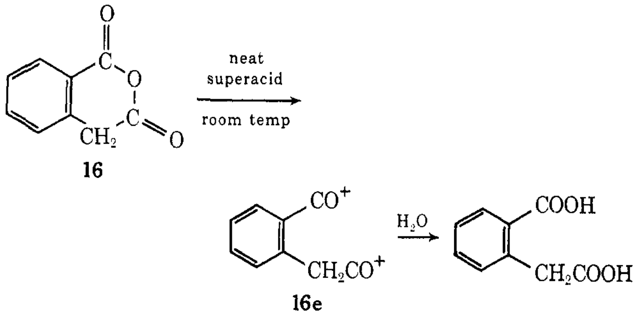
(11) G. A. Olah and D. H. O'Brien, *J. Amer. Chem. Soc.*, **89**, 1725 (1967).



In neat magic acid at room temperature, **16** was cleaved and dehydrated to the corresponding diacyl cation **16e**. The methylene protons of **16e** show a singlet absorption at δ 5.50. Quenching of the solution with ice–water gave homophthalic acid exclusively.



In conclusion cyclic carboxylic acid anhydrides behave differently from their acyclic analogs in superacid solutions. Aromatic and unsaturated cyclic anhydrides (in which the carbonyl carbons are directly attached to the sp^2 olefinic carbons) are not cleaved, even in neat magic acid at room temperature. Maleic anhydride and related unsaturated anhydrides thus show remarkable stability in superacid media. One possible explanation is that they contain four adjacent sp^2 carbon atoms and thus favor for the formation of a five-membered ring. Even if this would be cleaved in superacid media, the recyclization process may be extremely rapid. This is evidenced by the ease of cyclodehydration of phthalic and maleic acid in neat magic acid at room temperature to the corresponding anhydrides. In contrast acyclic saturated dicarboxylic acids (such as glutaric acid) are dehydrated to diacyl cations.

Experimental Section

Materials.—Carboxylic acid anhydrides used, when not otherwise indicated, were commercial material of high purity (Aldrich Chemical Co.). They were used without further purification. Dimethylmaleic anhydride was made available by Dr. H Bosshard of CIBA-GEIGY Limited, Basel, Switzerland, and we are grateful for his assistance. 3,6-Dimethylphthalic anhydride (**4**) and 1,4-dimethyl-2,3-naphthalic anhydride (**7**) were gifts from Professor M. S. Newman. Antimony pentafluoride and fluorosulfuric acid were purified as previously described.[12] Magic acid solutions were stored in Teflon bottles.

Nmr Spectra.—A Varian Associates Model A-56/60A spectrometer with variable temperature probe was used for all spectra. Chemical shifts are reported in parts per million (δ) from external (capillary) TMS.

Protonation of Cyclic Carboxylic Acid Anhydrides.—Protonated cyclic acid anhydrides were prepared by slow addition, with efficient stirring (vortex mixer), of generally a 10% (w/w) solution of the anhydride in SO_2 to a SO_2 solution of fluorosulfuric acid–antimony pentafluoride (in proportions of the reagents indicated in Table I). Samples were transferred to a precooled nmr tube and studied by nmr.

Quenching of protonated anhydrides was carried out by adding, with efficient stirring, their solution to ice-water. The quenched products were isolated and analyzed by comparison with authentic samples of starting material or their corresponding carboxylic acids by glc, ir, and nmr. Details of all studies were similar to those reported previously in the case of acyclic anhydrides[2].

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Registry No.—**1**, 108-31-6; **2**, 766-39-2; **3**, 2426-02-0; **4**, 85-44-9; **5**, 5463-50-3; **6**, 81-84-5; **7**, 40682-58-4; **8**, 89-32-7; **9**, 81-30-1; **10**, 699-98-9; **13**, 108-30-5; **14**, 108-55-4; **15**, 4480-83-5; **16**, 703-59-3.

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[12] G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **89**, 5692 (1967).

Stable Carbocations. CLVIII.[1a] Degenerate 1,2-Hydrogen Shifts in Fluorobenzenium Ions and Their Comparison with Those in Methylbenzenium Ions[1b]

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Protonation of fluorinated benzenes was studied in fluoroantimonic acid SbF$_5$–HF (1:1 mol:mol)–SO$_2$ClF (1:1 v:v) solution at low temperature. Temperature dependent nmr (^{1}H and ^{19}F) spectra of protonated fluorobenzene, *o*- and *p*- difluorobenzene, and 1,2,3,4-tetrafluorobenzene were observed indicating stepwise 1,2-hydrogen shifts in all these benzenium ions. The activation energies for the two, different, stepwise processes in the 3,4-difluorobenzenium ion were found to be 5.7 ± 0.8 and 11.2 ± 0.9 kcal/mol.

In previous studies of protonation of fluorinated benzenes in FSO$_3$H–SbF$_5$ solution, *o*-difluorobenzene, 1,2,3,4-tetrafluorobenzene, pentafluorobenzene, and hexafluorobenzene were not observed to be protonated.[2] We have consequently applied the more suitable superacid medium, SbF$_5$–HF (1:1 mol:mol)–SO$_2$ClF (1:1 v:v), for the protonation of some weak aromatic bases.[3] The advantages of this superacid system are the increased solubility of substrate, lower freezing

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[1] (a) G. A. Olah, S. Kobayashi, and Y. K. Mo, *J. Org. Chem.*, submitted. (b) A preliminary communication has appeared: G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 9241 (1972).

[2] G. A. Olah and T. E. Kiovsky, *ibid.*, **89**, 5692 (1967).

[3] G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and Gh. D. Mateescu, *ibid.*, **94**, 2034 (1972).