Studies on Electrophilic Substitutions of Aromatic Compounds Using Superacids

Mutsuo Tanaka
Osaka National Research Institute, AIST
1995

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（超強酸を用いた芳香族化合物求電子置換反応に関する研究）

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Preface

The work of this thesis has been performed under the guidance of Dr. Yoshie Souma at Osaka National Research Institute, AIST.

The author would like to express her sincerest guidance, helpful suggestion, and hearty encouragement throughout this work.

The author also wishes to make a grateful acknowledgement to Professor Shozo Yanagida (Faculty of Engineering, Osaka University), Professor Masatomo Nojima (Faculty of Engineering, Osaka University), Professor Shun-ichi Fukuzumi (Faculty of Engineering, Osaka University), Professor Toshiyuki Shono (Faculty of Engineering, Osaka Institute of Technology), Dr. Keiichi Kimura (Faculty of Engineering, Osaka University), Professor Yoshihisa Inoue (Faculty of Engineering, Osaka University), and Dr. Yuko Yamashoji (Faculty of Engineering, Osaka University) for their helpful suggestions and stimulating discussions.

The author is grateful to Dr. Yoshiko Nakahara and Dr. Masahiro Fujiwara for their invaluable assistance.

The author wishes to thank Mr. Hisanori Ando, Mr. Hidekatsu Kuino, Mr. Hideki Nakashima, and Mr. Jun Iyoda for their active collaboration.

Finally, the author would like to express his thanks to his wife Makiko for her hearty encouragement and understanding.

Ikeda, Osaka

December 1995

Mustuo Tanaka

List of Publications

1. Diformylation of Polynuclear Aromatic Compounds with CO in HF-SbF_5
   Tanaka, M.; Souma, Y.
   J. Chem. Soc., Chem. Commun. **1991**, 1551-1553.

2. Formylation of Aromatic Compounds with CO in HSO_3F-SbF_5 under Atmospheric Pressure
   Tanaka, M.; Iyoda, J.; Souma, Y.
   J. Org. Chem. **1992**, *57*, 2677-2680.

3. Sulfonation of Aromatic Compounds in HSO_3F-SbF_5
   Tanaka, M.; Souma, Y.
   J. Org. Chem. **1992**, *57*, 3738-3740.

4. Synthesis of Polynuclear Aromatic Dialdehyde in HF-SbF_5
   Tanaka, M.; Fujiwara, M.; Ando, H.; Souma, Y.
   J. Org. Chem. **1993**, *58*, 3213-3215.

5. Influence of Protonation on Gattermann-Koch Formylation Rate of Alkylbenzene in CF_3SO_3H-SbF_5
   Tanaka, M.; Fujiwara, M.; Ando, H.
   J. Org. Chem. **1995**, *60*, 2106-2111.

6. Dual Reactivity of the Formyl Cation as an Electrophile and a Brønsted Acid in Superacids
   Tanaka, M.; Fujiwara, M.; Ando, H.
   J. Org. Chem. **1995**, *60*, 3846-3850.

7. The Influence of Aromatic Compounds Protonation on the Regioselectivity in Gattermann-Koch Formylation
   Tanaka, M.; Fujiwara, M.; Ando, H.; Souma, Y.

J. Chem. Soc., Chem. Commun. in press.

8. Synthesis of Binaphthyl Derivatives Through Radical Cation Formation
   Tanaka, M.; Nakashima, H.; Fujiwara, M.; Ando, H.; Souma, Y.
   J. Org. Chem. in press.

Contents

Introduction

General Introduction

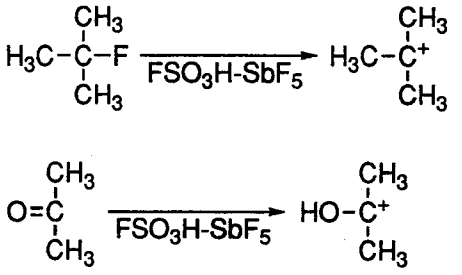
The electrophilic substitution of aromatic compounds[1] is one of classical reactions in organic chemistry and has been studied widely in the field of both pure and applied chemistry. However, some reactions have been controversial about real electrophiles in the electrophilic substitution. In addition, vigorous reaction conditions and multi-step reactions remain to be improved in industrial chemistry. It has been desired to solve these problems as well as to develop new synthetic methods for aromatic compounds.

The superacids[2] are defined as stronger acids than conc. H_2SO_4 and are generally mixtures of Brønsted acid and Lewis acid. For example, it is known that the HF-SbF_5, FSO_3H-SbF_5, CF_3SO_3H-SbF_5, HF-BF_3, CF_3SO_3H-BF_3, HF-AsF_5, HF-TaF_5, and HF-NbF_5 systems are regarded as superacids. In addition, FSO_3H and CF_3SO_3H, which are Brønsted acids, are also classified as superacids even in the absence of any Lewis acids. Recently, it was suggested that HF should be a strong Brønsted superacid. However, it is still uncertain whether HF is regarded as a superacid, or not. The acid strength has been usually evaluated by the Hammett acidity function, $-H_o$. The stronger acid has the larger $-H_o$ value. The $-H_o$ values of some strong acid systems are listed in Table 1.

Table 1. The Hammett Acidity Function, $-H_o$ for Superacid Systems[3]

Brønsted acid	$-H_o$	Brønsted-Lewis acid	$-H_o$
		HF-0.1%NbF_5	15.7
H_2SO_4	11.9	CF_3SO_3H-2%SbF_5	16.4
CF_3SO_3H	13.8	FSO_3H-5%AsF_5	16.6
FSO_3H	15.1	FSO_3H-20%SbF_5	20
(HF)	(15.1)	HF-0.5%SbF_5	21

As shown in Table 1, the acidity clearly increases by addition of Lewis acids to Brønsted acids, and the HF-SbF_5 system is recognized as the strongest superacid. The most important character of superacids is the production of various cations, namely electrophiles derived from their strong acidity. The formation of various carbonium cations in superacids (eq-1) is first discovered by G. A. Olah who won the Nobel Prize in 1994.



by G. A. Olah eq-1

After this discovery, superacids have been widely used for development of new organic reactions and also for the studies on their reaction mechanisms.

The themes of this thesis are the development of new synthetic methods in electrophilic aromatic substitutions in the presence of superacids and the elucidation of their reaction mechanisms.

In Chapter 1, the formylation of aromatic compounds with CO using HSO_3F-SbF_5 and the diformylation of polynuclear aromatic compounds using HF-SbF_5 are described.

Chapter 2 deals with the study on the formylation mechanism of aromatic compounds in the presence of superacids.

Chapter 3 refers to the sulfonation of aromatic compounds using HSO_3F-SbF_5 to produce diaryl sulfones and the reaction mechanism.

In Chapter 4, the coupling reaction of naphthalene derivatives in the presence of CF_3SO_3H-$NaNO_2$ or SbF_5 are discussed, and the mechanism in the formation of binaphthyl derivatives is described.

References and Notes

(1) (a) Olah, G. A. *Friedel-Crafts and Related Reaction* Wiley-Interscience, New York, **1964**. (b) Olah, G. A. *Interscience Monographs on Organic Chemistry: Friedel-Crafts Chemistry* Willey-Interscience, New York, **1973**. (c) Olah, G. A. *Carbocations and Electrophilic Reactions* Willey-Interscience, New York, **1974**.

(2) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids* John Wiley and Sons, New York, **1985**.

(3) (a) Gillespie, R. J.; Peel, T. E. *J. Am. Chem. Soc.* **1973**, *95*, 5173. (b) Gillespie, R. J.; Liang, J. *J. Am. Chem. Soc.* **1988**, *110*, 6053.

Chapter 1. Formylation of Aromatic Compounds

1-1. Introduction

The formylation of aromatic compounds with acid catalysts and CO is well-known as the Gattermann-Koch reaction.[1] After Gattermann and Koch published their original paper concerning the synthesis of *p*-tolualdehyde from toluene and CO in the $HCl-AlCl_3-Cu_2Cl_2$ system,[2] other catalytic systems such as $HF-BF_3$,[3] $HF-SbF_5$,[4,5] $HF-CF_3SO_3H-BF_3$,[5,6] CF_3SO_3H,[6,7] and $CF_3SO_3H-SbF_5$[6,8] have been extensively investigated for this reaction. In most cases, these formylations have been carried out under high pressure CO. There is continuing interest in the formylation of aromatic compounds with CO under milder conditions. On the other hand, diformylation of dibenzyl in the $HF-BF_3$ system[9] has been the only example so for reported. As such no diformylation example of polynuclear aromatic compounds linked by a short bond or condensed, such as diphenyl, diphenylmethane and naphthalene has been known. Thus, it may be of interest to investigate whether the diformylation of these polynuclear aromatic compounds could occur by the Gattermann-Koch reaction, or not.

It has been demonstrated that HSO_3F is the strongest Brønsted acid being a widely used as a superacid solvent.[10] Although the systems such as HSO_3F-SbF_5[11] and $HSO_3F-SbF_5-SO_3$[12] have been recognized as the most highly acidic media, the HSO_3F-SbF_5 system has not been used as a formylation catalyst. Therefore, the study was carried out to investigate whether the HSO_3F-SbF_5 system could be used as a catalytic system in the formylation of aromatic compounds under milder conditions and revealed which specific reactions occurred.

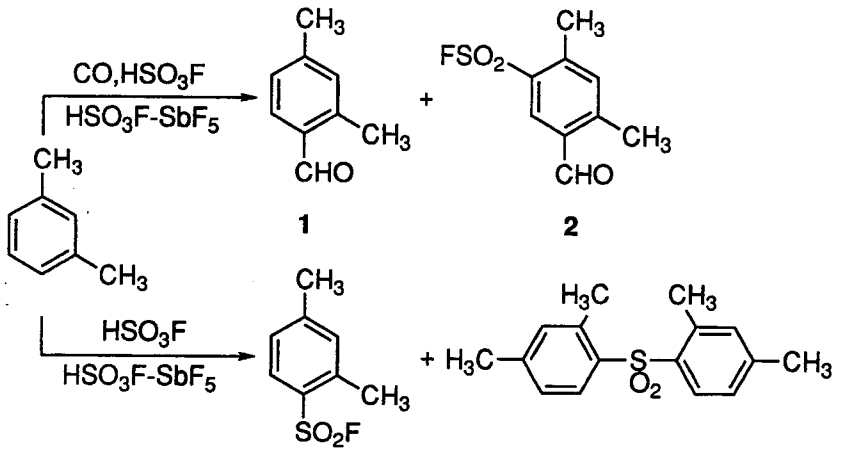
The $HF-SbF_5$ system, which has been represented to be the strongest superacid,[11-b,13] was examined as the diformylation catalyst, since the formylation occurs easily with increasing acidity of the catalyst systems.[5,6]

In this Chapter, we wish to report the formylation of aromatic compounds using HSO_3F-SbF_5 and the diformylation of polynuclear aromatic compounds using $HF-SbF_5$.

1-2. Formylation of Aromatic Compounds with CO Using HSO_3F-SbF_5

Synthesis of Aromatic Aldehydes

When *m*-xylene was slowly added to a mixture of HSO_3F and SbF_5 with vigorous stirring under atmospheric CO pressure at 0°C, four products, 2,4-dimethylbenzaldehyde **1**, 2,4-dimethyl-5-formylbenzenesulfonyl fluoride **2**, 2,4-dimethylbenzenesulfonyl fluoride **3**, and bis(2,4-dimethylphenyl) sulfone **4**, were obtained by a one-pot reaction, and **2** is a new compound (eq-1).



1 **2** **3** **4** (eq-1)

In order to study the products composition, the formylation of *m*-xylene was carried out with various compositions of HSO_3F-SbF_5, namely under various acid strength conditions. The results are given in Table 1.

Table 1. Relation between Products Composition and Acidity[a]

SbF_5 (mmol)	acidity $-H_o$[b]	products,yield(%)			
		1	**2**	**3**	**4**
0	15.1	0	0	50(83:17)[c]	48(78:22)[d]
13.8	18.3	17(100:0)[c]	0	41(80:20)[c]	36(79:21)[d]
69.0	22.4	83(100:0)[c]	4	6(100:0)[c]	2(100:0)[d]
138	22.7	79(100:0)[c]	15	0	0

a) The reaction was carried out using 20 mmol of *m*-xylene and 174 mmol of HSO_3F under atmospheric pressure of CO at 0°C for 1h. b) The value of H_o was estimated from the data of ref. 11-c. c) Isomer ratio of 2,4-dimethylbenzene derivative : 2,6-dimethylbenzene derivative. d) Isomer ratio of bis(2,4-dimethylphenyl) sulfone : 2,2',4,6'-tetramethyldiphenyl sulfone.

The Hammett acidity function, *Ho*, as reported in the literature was added to

Table 1 for comparison. When the acidity of the HSO_3F-SbF_5 system was low, only sulfonyl compounds **3** and **4** were obtained. However, formyl compounds **1** and **2** became predominant with the increase in acidity of the HSO_3F-SbF_5 system. A several-fold molar excess of SbF_5 as compared with *m*-xylene was advantageous for the formylation in the HSO_3F-SbF_5 system. The Gattermann-Koch formylation is strongly promoted by increasing the acidity of the catalyst systems.[5,6] This result is based on the fact that a high acidity is necessary for the formylation in order to produce electrophilic reactive species such as protonated CO, [HCO^+]. The role of SbF_5 in HSO_3F is to increase the acidity of the system and to produce the formyl cation (eq-2).

$$HSO_3F + SbF_5 \rightleftharpoons [H^+] + [SO_3F^-]\cdot SbF_5$$

$$[H^+] + CO \rightleftharpoons [HCO^+] \qquad \text{eq-2}$$

The formylation of toluene was carried out using analogous catalyst systems such as HSO_3F-$SbCl_5$, HSO_3Cl-SbF_5 and HSO_3Cl-$SbCl_5$. In all cases, tolualdehyde was not obtained, and only sulfonyl compounds were formed. These results seem to suggest that these systems do not have sufficient acidity for the formylation.

The formylation using HSO_3F-SbF_5 gave aromatic aldehydes in high yield with a short reaction time under atmospheric CO pressure at 0°C. These results are listed in Table 2.

Table 2. Formylation of Aromatic Compounds[a]

substrate	SbF_5 (mmol)	yield of aldehyde (%)	substrate	SbF_5 (mmol)	yield of aldehyde (%)
benzene	138	74	indan	138	71(91:9)[g]
toluene	69	95(90:10)[b]	tetralin	138	78(87:13)[h]
o-xylene	69	99(93:7)[c]	fluoro-benzene	138	92(99:1)[b]
m-xylene	69	83(100:0)[d]			
p-xylene	69	98	chloro-benzene	138	90(93:7)[b]
1,3,5-trimethyl-benzene[e]	69	53(90:10)[f]	bromo-benzene	138	88(88:12)[b]

a) The reaction was carried out using 20 mmol of substrate and 174 mmol of HSO_3F under atmospheric pressure of CO at 0°C for 1h. b) Isomer ratio of

para substituted benzaldehyde : ortho substituted benzaldehyde. c) Isomer ratio of 3,4-dimethylbenzaldehyde : 2,3-dimethylbenzaldehyde. d) Isomer ratio of 2,4-dimethylbenzaldehyde : 2,6-dimethylbenzaldehyde. e) The reaction was carried out for 24h. f) Isomer ratio of 2,4,6-trimethylbenzaldehyde : 2,4,5-trimethylbenzaldehyde. g) Isomer ratio of 5-formylindan : 4-formylindan. h) Isomer ratio of 6-formyltetralin : 5-formyltetralin.

All aromatic compounds were quickly formylated in high yields except for 1,3,5-trimethylbenzene. In the case of 1,3,5-trimethylbenzene, the formylation proceeded slowly, and the 1,2-shift of the methyl group was observed. It is known that 1,3,5-trimethylbenzene is protonated to form a σ-complex in strong acids[14] because of its high basicity,[15] and the σ-complex is considered to be the intermediate for the 1,2-shift of the methyl group.[16] In control experiments, both formylation using CF_3SO_3H-SbF_5 and sulfonation using HSO_3F-SbF_5 of 1,3,5-trimethylbenzene proceeded more slowly with increasing acidity of the acid systems. Therefore, the protonation of 1,3,5-trimethylbenzene seems to prevent the formylation and cause the 1,2-shift of the methyl group. In the case of phenol and anisole, no formylation occurred in HSO_3F-SbF_5, even in HF-SbF_5.

The formyl group was predominantly introduced into the para position of a substituent in all cases. It has been known that the Gattermann-Koch formylation is an electrophilic substitution reaction and that the formyl group is introduced into the para position of a substituent with high regioselectivity.[4,5] This characteristic has been interpreted as being due to steric hindrance where the para substitution is greatly favored if the transition state of highest energy of the reaction is like the intermediate σ-complex, where a *p*-substituent is more stabilizing than an *o*-substituent.[4,5]

Synthesis of New Compounds

The time dependence of the product composition from *m*-xylene was investigated in order to verify the formation path of the new compounds. As shown in Figure 1, 2,4-dimethylbenzaldehyde **1** was formed first, and the yield of 5-formyl-2,4-dimethylbenzenesulfonyl fluoride **2** increased in proportion to the length of reaction time and with a decrease in **1**. In control experiments, no

formylation of 2,4-dimethylbenzenesulfonyl fluoride **3** and bis(2,4-dimethylphenyl) sulfone **4** was observed under the same reaction conditions used in the formylation experiments. It is clear that the formation path of the new compounds is a two-step reaction comprised of the formylation as the first step and the sulfonation as the second step (eq-3).

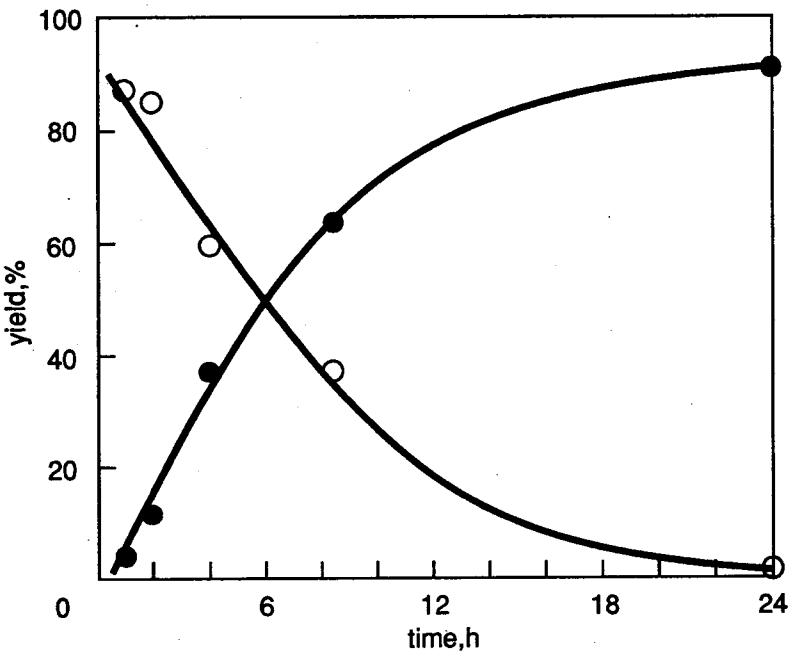
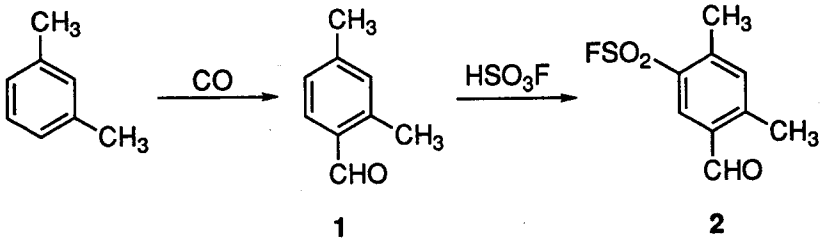


Figure 1. Time dependence of composition of products.[a]

a) The reaction was carried out using 20 mmol of *m*-xylene, 174 mmol of HSO_3F and 69.0 mmol of SbF_5 under atmospheric pressure of CO at room temperature. ○ and ● represent 2,4-dimethylbenzaldehyde and 2,4-dimethyl-5-formylbenzenesulfonyl fluoride, respectively.

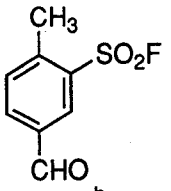
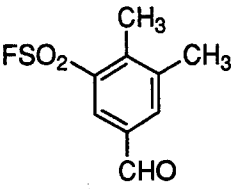
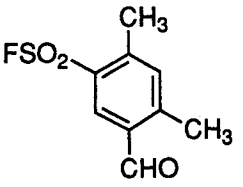
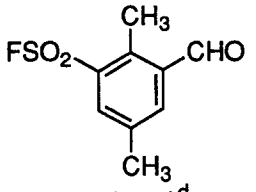
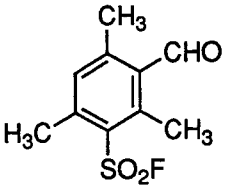
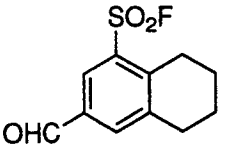


1 **2**

eq-3

Attempts to extend this reaction to a variety of aromatic compounds gave several new compounds with the results summarized in Table 3. Under adopted conditions in Table 3, only products **1** and **2** were formed.

Table 3. Synthesis of Formylalkylbenzene Sulfonyl Fluorides[a]

substrate	reaction time(h)	SbF_5 (mmol)	products,yield(%)	
			aldehyde	new compound
toluene	168	138	2	 90(76:24)[b]
o-xylene	96	138	6	 78(95:5)[c]
m-xylene	24	69	0	 93
p-xylene	96	138	6	 79(95:5)[d]
1,3,5-trimethylbenzene	48	69	48(60:40)[e]	 34
tetralin	24	138	2	 21(90:10)[f]

a) The reaction was carried out using 20 mmol of substrate and 174 mmol of HSO_3F under atmospheric pressure of CO. The structures of main products are shown. b) Isomer ratio of 3-formyl-6-methylbenzenesulfonyl fluoride : 3-formyl-4-

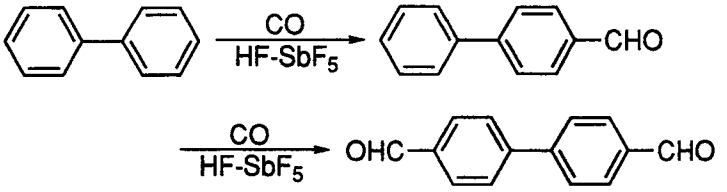
methylbenzenesulfonyl fluoride. c) Isomer ratio of 5-formyl-2,3-dimethylbenzenesulfonyl fluoride : 5-formyl-2,4-dimethylbenzenesulfonyl fluoride. d) Isomer ratio of 3-formyl-2,5-dimethylbenzenesulfonyl fluoride : 5-formyl-2,4-dimethylbenzenesulfonyl fluoride. e) Isomer ratio of 2,4,6-trimethylbenzaldehyde : 2,4,5-trimethylbenzaldehyde. f) Isomer ratio of 7-formyltetralin-5-sulfonyl fluoride : 5-formyltetralin-7-sulfonyl fluoride.

The new compounds were obtained from alkylbenzenes such as toluene, xylenes, 1,3,5-trimethylbenzene, and tetralin. The formyl group was exclusively introduced into the para position of the alkyl group in all cases. The sulfonyl group was introduced into the meta position of the formyl group. From benzene, fluorobenzene, chlorobenzene, and bromobenzene, only aldehydes were produced. When the reaction mixture from benzene was heated to 100°C, the slight formation of formylbenzenesulfonyl fluoride was observed. Consequently, the introduction of both the formyl and the sulfonyl group was difficult because of the low reactivity of these aromatics. In the case of indan and tetralin, the decomposition of the saturated ring gave unidentifiable products during the reactions in the superacid[17] and resulted in low yield, especially with indan. It became apparent that HSO_3F-SbF_5 was useful for the introduction of two different functional groups, the formyl and the sulfonyl group, into alkylbenzenes in the presence of CO by a one-pot reaction.

1-3. Diformylation of Polynuclear Aromatic Compounds with CO Using HF-SbF_5 Synthesis of Aromatic Dialdehydes

As mentioned Chapter 1. 1-2, the HSO_3F-SbF_5 system is an effective formylation catalyst system, therefore, the formylation of diphenyl was carried out under high CO pressure (60 atm) in HSO_3F-SbF_5. Although aldehyde is obtained from alkyl- and halobenzene in good yield even under atmospheric CO pressure, only sulfonation by HSO_3F proceeded, and aldehyde was not obtained in the case of diphenyl. Therefore, the HF-SbF_5 system, which is comprised of HF instead of HSO_3F and the strongest acid system,[11-b,13] was used as a formylation catalyst. When diphenyl (10 mmol) was allowed to react with CO

under 20 atm pressure in the mixture of HF (500 mmol) and SbF_5 (25 mmol) at 0°C, dialdehyde was obtained with high regioselectivity (eq-1).



eq-1

The formylation was carried out using various compositions of HF-SbF_5, and the yield of mono- and dialdehyde depending on the molar ratio of SbF_5 : diphenyl is shown in Figure 1.

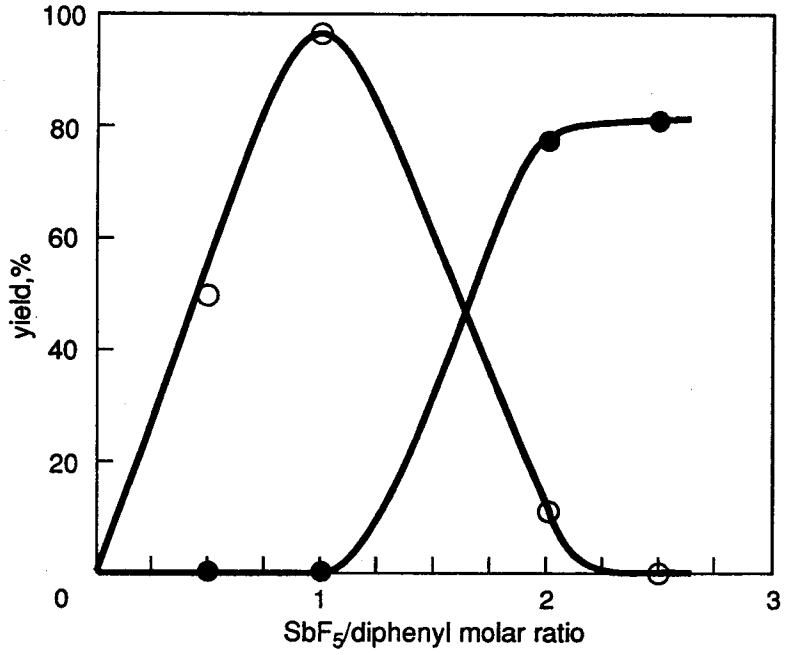


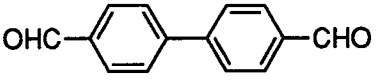
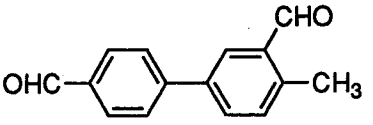
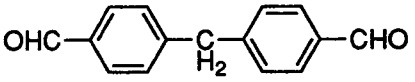
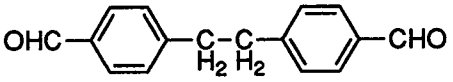
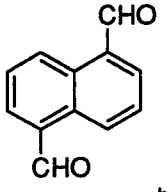
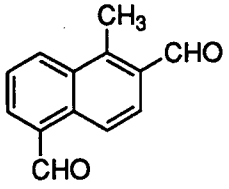
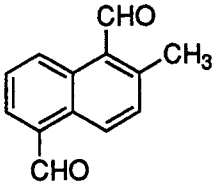
Figure 1. The composition of monoaldehyde and dialdehyde depending on the molar ratio of SbF_5 : diphenyl.[a]

a) The formylation was carried out using 10 mmol of diphenyl and 500 mmol of HF under 20 atm of CO pressure at 0°C for 3h. O and ● represent diphenylaldehyde and diphenyldialdehyde, respectively.

Only monoaldehyde was obtained when the amount of SbF_5 was less than that of diphenyl. The formation of dialdehyde was observed by the addition of SbF_5 more than that of diphenyl, and the number of introduced formyl group was almost parallel with the amount of SbF_5. The role of SbF_5 in HF is to

produce an electrophilic reactive species, formyl cation, because no formylation occurred in the absence of SbF_5. The dialdehyde synthesis from polynuclear aromatic compounds is summarized and the structures of the main products are depicted in Table 1.

Table 1. Diformylation of Polynuclear Aromatic Compounds[a]

substrate	time(h)	products,yield(%)	
		monoaldehyde	dialdehyde
diphenyl	3	0	 81(93:7:0)[b]
4-methyl-diphenyl	2	0	 27(97:3)[c]
diphenyl-methane	2	61[d]	 31(91:4:5)[e]
dibenzyl	2	0	 98(90:3:7)[f]
naphthalene[g]	2	0	 53(73:18:9:0)[h]
1-methyl-naphthalene	6	44[i]	 47(66:34)[j]
2-methyl-naphthalene	6	29[i]	 44(36:64)[k]

a) The formylation was carried out using 10 mmol of aromatics, 25 mmol of SbF_5 and 500 mmol of HF under 20 atm of CO pressure at 0°C. b) Isomer ratio of 4,4'-diphenyldialdehyde : 2,4'-diphenyldialdehyde : 2,2'-diphenyldialdehyde. c) Isomer ratio of 4-methyl-3,4'-diphenyldialdehyde : 4-methyldiphenyldialdehydes. d) Only benzaldehyde was formed, and diphenylmethanealdehyde was not obtained. e) Isomer ratio of 4,4'-diphenylmethanedialdehyde : 2,4'-diphenylmethanedialdehyde : 2,2'-diphenylmethanedialdehyde. f) Isomer ratio of 4,4'-dibenzyldialdehyde : 2,4'-dibenzyldialdehyde : 2,2'-dibenzyldialdehyde. g) The formylation was carried out using 1 mol of HF and 70 mmol of SbF_5 under 60 atm of CO pressure at 20°C. h) Isomer ratio of 1,5-naphthalenedialdehyde : 1,6-naphthalenedialdehyde : 1,7-naphthalenedialdehyde : 1,8-naphthalenedialdehyde. i) Isomer ratio could not be determined. j) Isomer ratio of 1-methyl-2,5-naphthalenedialdehyde : methylnaphthalenedialdehydes. k) Isomer ratio of 2-methyl-1,5-naphthalenedialdehyde : methylnaphthalenedialdehydes.

Diphenyl and dibenzyl gave dialdehydes with excellent yields. The yield of dialdehyde from 4-methyldiphenyl was low because of the formation of unidentifiable oily products. In the formylation of diphenylmethane, the methylene chain cleavage occurred to yield benzaldehyde as well as dialdehyde. The formation of tolualdehyde, phenylacetic acid, dibenzylbenzene, and benzyl(phenylacetyl)benzene as trace amounts of products was confirmed by mass analysis. This behavior was not observed with diphenyl and dibenzyl. This difference in behavior is derived from the easy protonation of the methylene chain of diphenylmethane to cause cleavage.[19] In the case of naphthalene and methylnaphthalenes, larger amounts of SbF_5 or a longer reaction time was necessary compared with other aromatic compounds because the formylation of these aromatic compounds proceeded more slowly than with the other aromatic compounds. The formylation of anthracene, phenanthrene, and pyrene did not occur, and the raw materials were recovered.

The isomer distribution of products showed high para regioselectivity similar to other Gattermann-Koch reactions[4,5] except for naphthalene and methylnaphthalenes. The high para regioselectivity in the Gattermann-Koch

reaction is considered to be due to steric hindrance and stability of the σ-complex like intermediate because this formylation is an electrophilic substitution by the formyl cation, protonated CO (HCO^+), and para substitution is favored if the transition state of the highest energy of the reaction is the σ-complex like intermediate, where a para substituent is more stabilizing than an ortho or meta substituent.[4,5] Therefore, the low regioselectivity in the formylation of naphthalene and methylnaphthalenes seems to be derived from the significant steric hindrance of rigid naphthalene moiety.

Acidity Influence on Formylation

As mentioned previously, it was found that only monoaldehyde is obtained under conditions when the SbF_5/substrate molar ratio is less than 1, and dialdehyde is formed when the SbF_5/substrate molar ratio is greater than 1. However, the result of dibenzyl formylation showed a different tendency as shown in Figure 2.

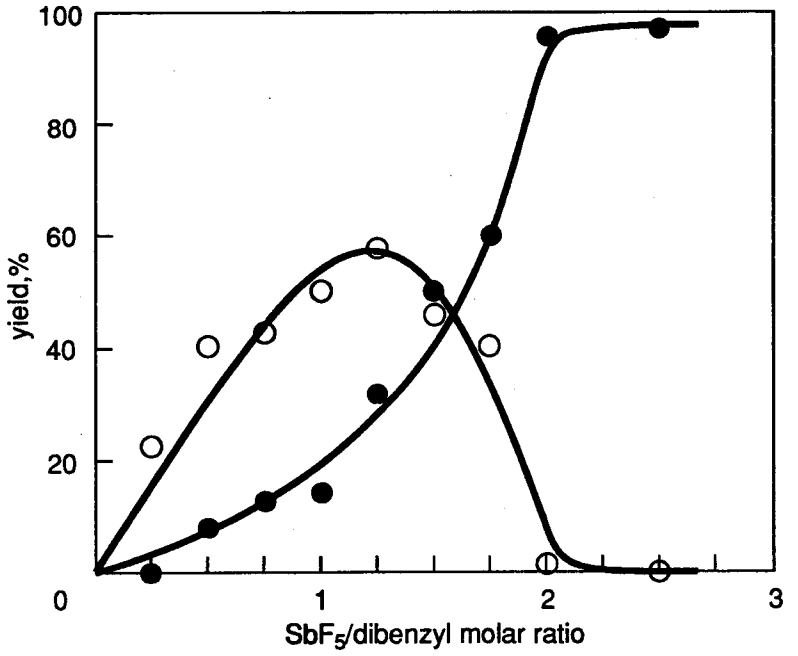


Figure 2. The composition of monoaldehyde and dialdehyde depending on the molar ratio of SbF_5 : dibenzyl.[a]

a) The formylation was carried out using 10 mmol of dibenzyl and 500 mmol of HF under 20 atm of CO pressure at 0°C for 2h. ○ and ● represent dibenzylaldehyde and dibenzyldialdehyde, respectively.

In the case of dibenzyl, dialdehyde was produced even under conditions where the SbF_5/dibenzyl molar ratio was less than 1. It is suggested that the aromatic rings of dibenzyl are independent chemically because of ethylene chain between them. These results show that the first introduced formyl group inactivates substrate strongly, therefore, a strong acid catalyst such as the HF-SbF_5 system, which is known as the strongest superacid,[11-b,13] and an excess amount of SbF_5 are necessary to obtain dialdehyde.

When the formylation of 1-methylnaphthalene was carried out using various compositions of HF-SbF_5, the formylation proceeded more slowly with the increase of the SbF_5/1-methylnaphthalene molar ratio although most formylations readily occurred with increasing acid/substrate molar ratio.[5,6] The result is shown in Figure 3.

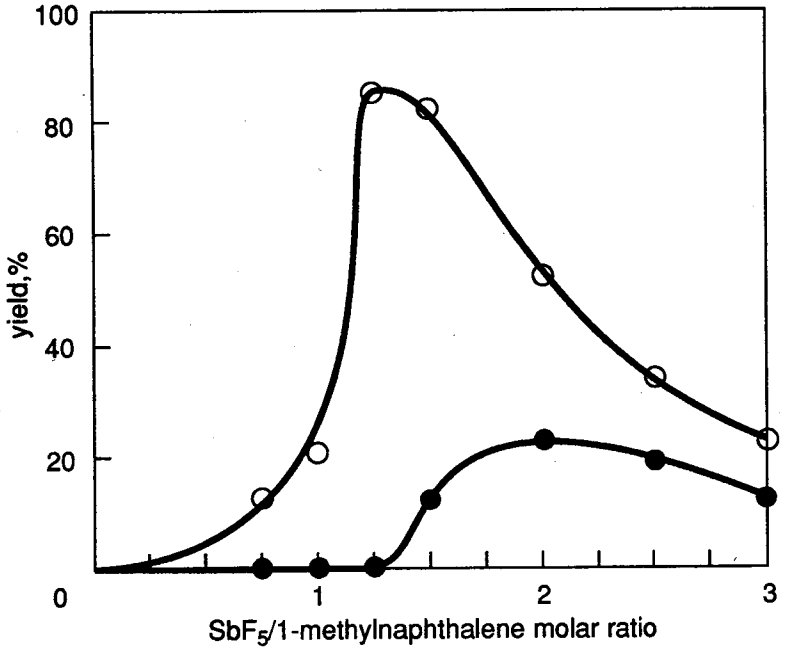


Figure 3. The composition of monoaldehyde and dialdehyde depending on the molar ratio of SbF_5 : 1-methylnaphthalene.[a]

a) The formylation was carried out using 10 mmol of 1-methylnaphthalene and 500 mmol of HF under 20 atm of CO pressure at 0°C for 2h. O and ● represent methylnaphthaldehyde and methylnaphthalenedialdehyde, respectively.

A similar tendency was observed with 2-methylnaphthalene. The slow

formylation in strong acid media was also observed with 1,3,5-trimethylbenzene in HSO_3F-SbF_5.[18] These phenomena suggest that the proton produced by SbF_5 has two roles which are the protonation of a CO and a substrate. Therefore, very high basic aromatic compounds such as anthracene, phenanthrene, and pyrene were not formylated by the protonation of substrates in HF-SbF_5.

In the formylation of methylnaphthalenes, the 1,2-shift of the methyl group was observed similarly to Friedel-Crafts alkylations and has been interpreted to proceed through the intermediate σ-complex which is formed by the protonation in strong acids.[16]

1-4. Experimental Section

All aromatic starting materials were of highest available purity and were used without further purification. HSO_3F, HSO_3Cl, CF_3SO_3H, HF, SbF_5, $SbCl_5$, and CO were all commercial reagents. The yield of products were determined by GC using the internal standard method, and the characterization of products was performed by IR, MS, ^1H,^{13}C-NMR after separation.

Formylation Procedures Using HSO_3F-SbF_5, HSO_3F-$SbCl_5$, HSO_3Cl-SbF_5, HSO_3Cl-$SbCl_5$, or CF_3SO_3H-SbF_5 under Atmospheric Pressure

The required amounts of HSO_3F-SbF_5, HSO_3F-$SbCl_5$, HSO_3Cl-SbF_5, HSO_3Cl-$SbCl_5$, or CF_3SO_3H-SbF_5 was added into a 300 mL three-necked flask equipped with a CO gas buret under atmospheric pressure at 0°C. The aromatic compounds were added slowly (40 mmol per h) into an acid mixture with vigorous stirring. After the addition of aromatic compounds was complete, the temperature was raised to room temperature. The reaction mixture was quenched in ice-water and extracted by benzene. The yields of products were determined by GC, and the products characterization was performed by IR, ^1H,^{13}C-NMR, MS, and elemental analysis after isolation by vacuum distillation or recrystallization in benzene-n-hexane systems.

Formylation Procedures Using HSO_3F-SbF_5 under Pressure

The mixture of 87 mmol of HSO_3F and 69 mmol of SbF_5 was poured into a 100-ml Hastelloy autoclave equipped with a Hastelloy magnetic stirrer bar with cooling at 0°C, and the autoclave was sealed. After 60 atm of CO was

introduced into it, 5 mmol of diphenyl was added and reacted with vigorous stirring for 1h at 0°C. After the reaction was over, the reaction mixture was quenched in ice-water, extracted by benzene, and analyzed as mentioned previously.

Formylation Procedures Using HF-SbF_5 under Pressure

The required amount of HF, SbF_5 and aromatic compounds were put into a 100-ml Hastelloy autoclave equipped with a Hastelloy magnetic stirrer bar with cooling at 0°C. The autoclave was sealed, and CO was then introduced with vigorous stirring under temperature control. After the reaction was over, the autoclave was depressurized and opened with cooling below 0°C. The reaction mixture was quenched in ice-water and extracted by benzene. Products were analyzed as mentioned previously.

Sulfonation Procedures Using HSO_3F-SbF_5

The sulfonation was carried out with the same way in the formylation procedures under atmospheric pressure, but in the absence of CO.

Products Properties

2-methyl-5-formylbenzene sulfonyl fluoride: IR(KBr): 1680 (C=O), 1395, 1175 (SO_2F) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.85 (s, 3H), 7.6-8.7 (m, 3H), 10.30 (s, 1H). ^{13}C-NMR($CDCl_3$): δ 20.8), 131.8, 133.4, 133.9, 134.9, 145.6, 189.2. Anal. Found: C, 47.91; H,3.61; M^+, 202. Calcd for $C_8H_7O_3SF$: C,47.52; H, 3.49; M, 202.

2,3-dimethyl-5-formylbenzene sulfonyl fluoride: IR(KBr): 1690 (C=O), 1405, 1195 (SO_2F) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.55 (s, 3H), 2.72 (s, 3H), 8.17 (s, 1H), 8.53 (s, 1H), 10.27 (s, 1H). ^{13}C-NMR($CDCl_3$): δ 17.1, 20.6, 129.0, 129.6, 134.1, 134.3, 136.0, 141.6, 144.1, 189.5. Anal. Found: C, 49.92; H, 4.19; M^+, 216. Calcd for $C_9H_9O_3SF$: C, 49.99; H, 4.20; M, 216.

2,4-dimethyl-5-formylbenzene sulfonyl fluoride: IR(KBr): 1680 (C=O), 1400, 1200 (SO_2F) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.75 (s, 3H), 2.80 (s, 3H), 7.50 (s, 1H), 8.60 (s, 1H), 10.35 (s, 1H). ^{13}C-NMR($CDCl_3$): δ 19.7, 20.4, 132.6, 133.0, 134.0, 136.6, 144.1, 148.2, 189.9 . Anal. Found: C, 49.63; H, 4.13; M^+, 216. Calcd for $C_9H_9O_3SF$: C, 49.99; H, 4.20; M, 216.

2,5-dimethyl-3-formylbenzene sulfonyl fluoride: IR(KBr): 1690 (C=O), 1410, 1200 (SO_2F) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.59 (s, 3H), 3.07 (s, 3H), 8.0-8.7 (m,

2H), 10.80 (s, 1H). ^{13}C-NMR($CDCl_3$): δ 14.6, 20.7, 134.4, 134.8, 135.2, 136.2, 137.6, 137.7, 138.2, 190.2. Anal. Found: C, 50.24; H, 4.11; M^+, 216. Calcd for $C_9H_9O_3SF$: C, 49.99; H, 4.20; M, 216.

2,4,6-trimethyl-3-formylbenzene sulfonyl fluoride: IR(KBr): 1695 (C=O), 1400, 1200 (SO_2F) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.58 (s, 3H), 2.70 (s, 3H), 2.79 (d, 3H, J = 2.4Hz), 7.22 (s, 1H), 10.74 (s, 1H). ^{13}C-NMR($CDCl_3$): δ 17.2, 17.3, 20.6, 23.2, 131.7, 132.1, 134.3, 134.5, 141.9, 143.8, 145.9, 192.7. Anal. Found: C, 51.80; H, 4.76; M^+, 230. Calcd for $C_{10}H_{11}O_3SF$: C, 52.16; H, 4.81; M, 230.

7-formyltetralin-5-sulfonyl fluoride: IR(KBr): 1680 (C=O), 1380, 1195 (SO_2F) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 1.7-2.1 (m, 4H), 2.8-3.4 (m, 4H), 7.95 (s, 1H), 8.37 (s, 1H), 10.05 (s, 1H). ^{13}C-NMR($CDCl_3$): δ 21.6, 21.9, 27.2, 30.1, 129.1, 129.3, 130.0, 133.8, 136.2, 142.0, 144.6, 189.7. Anal. Found: C, 54.21; H, 4.55; M^+, 242. Calcd for $C_{11}H_{11}O_3SF$: C, 54.53; H, 4.58; M, 242.

4,4'-diphenyldialdehyde: IR(KBr): 1685 (C=O) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 7.7-8.3 (m, 8H), 10.30 (s, 2H). ^{13}C-NMR($CDCl_3$): δ 128.0, 130.3, 136.1, 145.6, 191.6. Anal. Found: C, 79.77; H, 4.66; M^+, 210. Calcd for $C_{14}H_{10}O_2$: C, 79.99; H, 4.79; M, 210.

4-methyl-2,4'-diphenyldialdehyde: IR(KBr): 1680 (C=O) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.76 (s, 3H), 7.2-8.2 (m, 7H), 10.09 (s, 1H), 10.38 (s, 1H). ^{13}C-NMR($CDCl_3$): δ 19.2, 127.5, 130.3, 130.4, 132.1, 132.6, 134.6, 135.6, 138.0, 140.9, 145.6, 191.7, 192.2. Anal. Found: C, 80.38; H, 5.27; M^+, 224. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39; M, 224.

4,4'-diphenylmethanedialdehyde: IR(KBr): 1680 (C=O) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 4.08 (s, 2H), 7.1-7.8 (m, 8H), 9.87 (s, 2H). ^{13}C-NMR($CDCl_3$): δ 42.2, 129.6, 130.2, 135.0, 146.9, 191.7. Anal. Found: C, 80.32; H, 5.21; M^+, 224. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39; M, 224.

4,4'-dibenzyldialdehyde: IR(KBr): 1685 (C=O) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 3.07 (s, 4H,) 7.2-8.0 (m, 8H), 10.05 (s, 2H). ^{13}C-NMR($CDCl_3$): δ 37.5, 129.2, 130.0, 134.9, 148.1, 191.8. Anal. Found: C, 80.61; H, 5.88; M^+, 238. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92; M, 238.

1,5-naphthalenedialdehyde: IR(KBr): 1680 (C=O) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 7.6-9.8 (m, 6H), 10.49 (s, 2H). ^{13}C-NMR($CDCl_3$): δ 128.1, 130.8, 131.3, 131.9,

137.3, 193.6. Anal. Found: C, 78.28; H, 4.20; M^+, 184. Calcd for $C_{12}H_8O_2$: C, 78.25; H, 4.38; M, 184.

1,6-naphthalenedialdehyde: IR(KBr): 1670 (C=O) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 7.5-10.2 (m, 6H), 10.38 (s, 1H), 10.61 (s, 1H). ^{13}C-NMR($CDCl_3$): δ 126.1, 126.2, 126.3, 131.6, 133.1, 133.5, 133.6, 134.5, 136.4, 138.8, 191.8, 192.9. Anal. Found: C, 78.08; H, 4.40; M^+, 184. Calcd for $C_{12}H_8O_2$: C, 78.25; H, 4.38; M, 184.

1-methyl-2,5-naphthalenedialdehyde: IR(KBr): 1655 (C=O) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 3.08 (s, 3H), 7.6-9.4 (m, 5H), 10.56 (s, 1H), 10.76 (s, 1H). ^{13}C-NMR($CDCl_3$): δ 13.4, 123.2, 125.8, 127.8, 131.8, 133.2, 133.4, 137.9, 139.7, 191.8, 192.9. Anal. Found: C, 78.62; H, 4.94; M^+, 198. Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.08; M, 198.

2-methyl-1,5-naphthalenedialdehyde: IR(KBr): 1680 (C=O) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.85 (s, 3H), 7.4-9.6 (m, 5H), 10.46 (s, 1H), 11.06 (s, 1H). ^{13}C-NMR($CDCl_3$): δ 19.7, 127.6, 128.7, 131.0, 131.2, 131.5, 131.6, 132.8, 136.4, 143.2, 193.3, 193.6. Anal. Found: C, 78.59; H, 5.04; M^+, 198. Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.08; M, 198.

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Chapter 2. Formylation Mechanism of Aromatic Compounds

2-1. Introduction

In Chapter 1, we reported that HSO_3F-SbF_5 and HF-SbF_5 are also useful catalyst systems for the Gattermann-Koch formylation. Although most aromatic compounds are formylated more quickly by increasing the SbF_5/substrate molar ratio in these systems, reactive aromatic compounds such as 1,3,5-trimethylbenzene and methylnaphthalenes are formylated more slowly. The protonation of reactive aromatic compounds to form the σ-complex (arenium ion complex) under strong acidic conditions seems to decrease the apparent formylation rate because of a reduction in the aromatic concentration. The Gattermann-Koch formylation has been reported as an electrophilic substitution,[1] and the protonation of aromatic compounds inhibits its rate as it inhibits nitration[2] and acylation.[3]

The electrophilic species in Gattermann-Koch formylation has been considered the formyl cation, HCO^+, however, the existence of the formyl cation in superacids has not been confirmed yet.[1-c,4] Therefore, it is of interest to investigate the nature of the formyl cation in superacids.

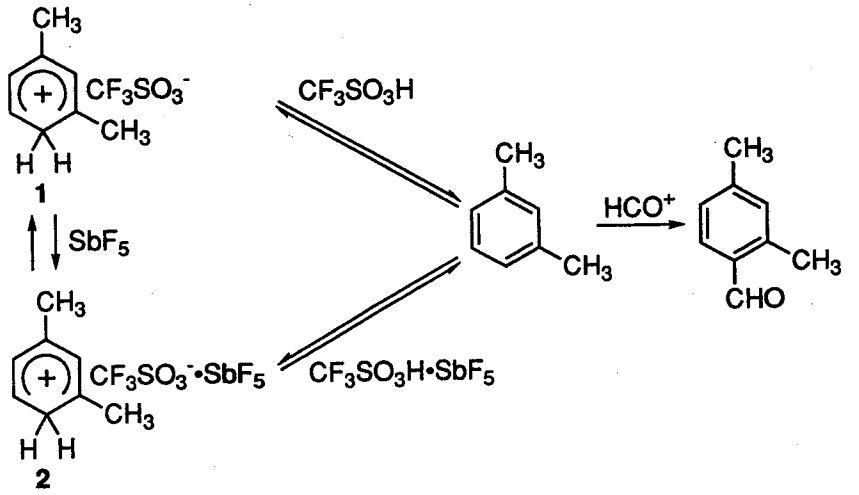
The electrophilic substitution of aromatic compounds is a very versatile reaction in organic synthesis. However, the reaction usually has a serious regioselectivity problem that produces a mixture of isomers which is difficult to separate. It has been reported that the regioselectivity of electrophilic aromatic substitutions is controlled by the electron density of the aromatic rings,[5] the nature of electrophiles and substrates,[6] and the steric hindrance of aromatic compounds[6-a,b] depending on the reaction types. On the other hand, the Gattermann-Koch formylation is known to show high regioselectivity,[1-b,d] and such a similar tendency was observed in Chapter 1. However, it was found that naphthalene and methylnaphthalenes are exceptions which show a low regioselectivity in the formylation using HF-SbF_5.

In this Chapter, we wish to report the reaction mechanism of Gattermann-Koch formylation in three aspects, the formylation rate, the nature of the formyl cation, and the regioselectivity of the formylation.

2-2. Influence of Protonation on Formylation Rate

Estimation of Protonation Equilibrium

In order to estimate the protonation ratio of an alkylbenzene in CF_3SO_3H-SbF_5, ^{1}H-NMR spectral measurements were obtained and formylation experiments of *m*-xylene were carried out using various SbF_5/*m*-xylene molar ratios in CF_3SO_3H. The results are depicted in Figures 1 and 2. When *m*-xylene was added to CF_3SO_3H, one broad singlet peak of CF_3SO_3H and benzene ring protons were observed (Figure 1). Similar ^{1}H-NMR spectra were obtained in CF_3SO_3H-SbF_5 when the SbF_5/*m*-xylene molar ratio was less than 1. Under these conditions, the ^{1}H-NMR spectra show that there is a fast proton exchange between benzene ring protons and CF_3SO_3H, and a part of the *m*-xylene is protonated by CF_3SO_3H and CF_3SO_3H•SbF_5 to form σ-complexes **1** and **2**, respectively (eq-1).[7]



eq-1

On the other hand, when the SbF_5/*m*-xylene molar ratio was greater than 1 (Figure 1), the ^{1}H-NMR spectra drastically changed and showed that most of the *m*-xylene was protonated to form σ-complex **2**.[8] This result indicates that CF_3SO_3H•SbF_5 is a far stronger acid than CF_3SO_3H, and σ-complex **2** is more stable than σ-complex **1**. On the other hand, the yield of aldehyde showed a very interesting tendency depending on the SbF_5/*m*-xylene molar ratio (Figure 2). The formylation proceeded more slowly with an increase in the SbF_5/*m*-xylene molar ratio when the SbF_5/*m*-xylene molar ratio was less than 1. This result seems to reflect the increase in the σ-complex **2**, which is a more stable ion pair than **1**, and which does not react with the formyl cation because of charge

repulsion.

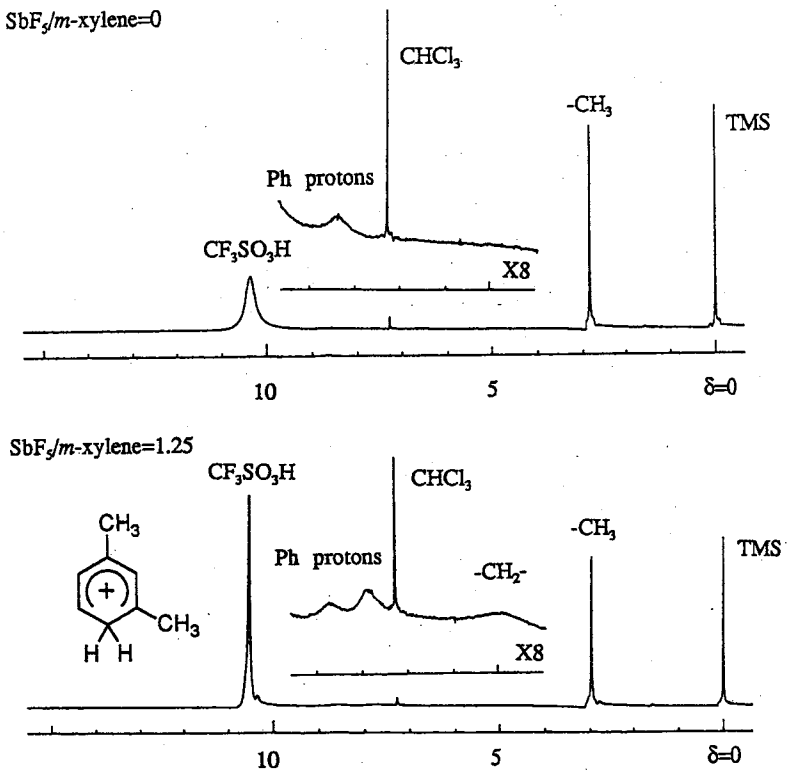


Figure 1. ^{1}H-NMR of *m*-xylene in CF_3SO_3H-SbF_5 at 0°C.

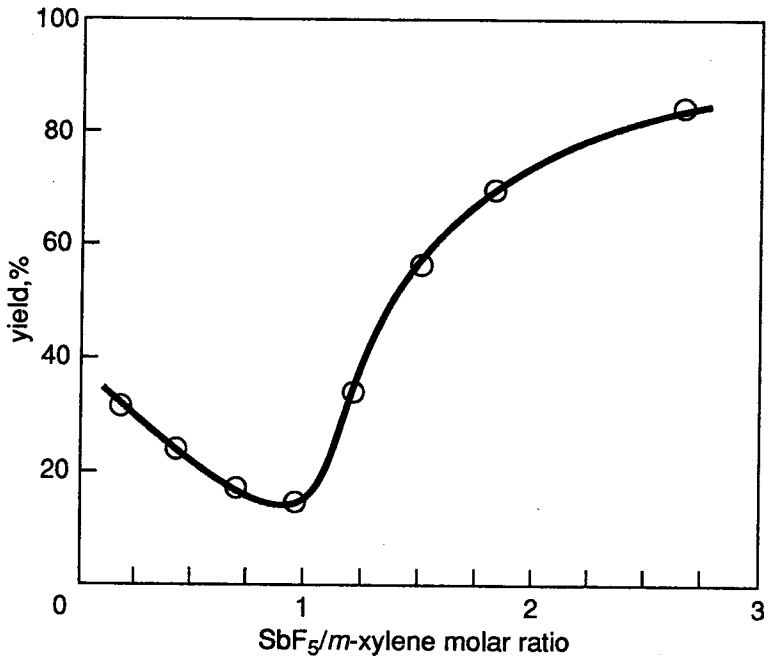


Figure 2. Apparent formylation rate of *m*-xylene in CF_3SO_3H-SbF_5.[a]

a) The reaction time was 1h.

On the contrary, the formylation proceeded more quickly with increasing SbF_5/*m*-xylene mole ratios under conditions where this ratio was greater than 1. Excess SbF_5, which does not protonate *m*-xylene, is considered to raise the formyl cation concentration and consequently increase the formylation rate.

In addition, the formylation of 1-methylnaphthalene-d_{10} was carried out in HF-SbF_5 at -78 or 0°C, and the H-D ratio was measured by ^{1}H-NMR. There was no difference in the H-D ratio between the formyl group and the aromatic ring of the produced aldehyde at 0°C. On the other hand, although formylation did not occur at all at -78°C, part of the deuterium of the aromatic ring was exchanged for hydrogen. In a control experiment, the H-D exchange of the formyl group was not observed under the same conditions. These results show that the protonation occurs faster than the formylation.

Induction of Protonation Equilibrium Equations

In view of these preliminary experimental results, we postulated that the formylation of *m*-xylene (ArH) in CF_3SO_3H-SbF_5 can be explained in two ways by considering the protonation equilibrium according to whether the SbF_5/*m*-xylene molar ratio is less than or greater than 1 (eq-2). K_{TfOH} and K_{COTf} represent the equilibrium constants for the protonation of ArH and CO by CF_3SO_3H, K_{SbF5} and K_{COSb} are the equilibrium constants for the protonation of ArH and CO by CF_3SO_3H•SbF_5, and k and k' are the rate constants of the formylation by CF_3SO_3H and CF_3SO_3H•SbF_5, respectively. In these equations, while CF_3SO_3H has two roles, which are the protonation of *m*-xylene and the production of formyl cation, CF_3SO_3H•SbF_5 acts only to protonate *m*-xylene under conditions where the SbF_5/*m*-xylene molar ratio is less than 1. On the other hand, CF_3SO_3H•SbF_5 protonates *m*-xylene and produces the formyl cation, but CF_3SO_3H is just a solvent when the SbF_5/*m*-xylene molar ratio is larger than 1. The most important concept used here is that CF_3SO_3H and CF_3SO_3H•SbF_5 are recognized as different species. CF_3SO_3H•SbF_5, being a far stronger acid, allows us to consider the equilibrium constants K_{SbF5} and K_{COSb} >> K_{TfOH} and K_{COTf}. Therefore, the formylation rate can be explained in terms of $k[HCO^+CF_3SO_3^-][ArH]$ and $k'[HCO^+CF_3SO_3^-•SbF_5][ArH]$, respectively.

SbF_5/*m*-xylene≤1

$$ArH + CF_3SO_3H \rightleftharpoons ArH_2^+CF_3SO_3^-$$

$$ArH + CF_3SO_3H{\bullet}SbF_5 \longrightarrow ArH_2^+CF_3SO_3^-{\bullet}SbF_5$$

$$CO + CF_3SO_3H \rightleftharpoons HCO^+CF_3SO_3^-$$

$$ArH + HCO^+CF_3SO_3^- \longrightarrow ArCHO + CF_3SO_3H$$

$$K_{TfOH} = \frac{[ArH_2^+CF_3SO_3^-]}{[ArH][CF_3SO_3H]}$$

$$K_{COTf} = \frac{[HCO^+CF_3SO_3^-]}{[CO][CF_3SO_3H]}$$

$$\frac{d[ArCHO]}{dt} = k[HCO^+CF_3SO_3^-][ArH]$$

SbF_5/*m*-xylene≥1

$$ArH + CF_3SO_3H{\bullet}SbF_5 \rightleftharpoons ArH_2^+CF_3SO_3^-{\bullet}SbF_5$$

$$CO + CF_3SO_3H{\bullet}SbF_5 \rightleftharpoons HCO^+CF_3SO_3^-{\bullet}SbF_5$$

$$ArH + HCO^+CF_3SO_3^-{\bullet}SbF_5 \longrightarrow ArCHO + CF_3SO_3H{\bullet}SbF_5$$

$$K_{SbF5} = \frac{[ArH_2^+CF_3SO_3^-{\bullet}SbF_5]}{[ArH][CF_3SO_3H{\bullet}SbF_5]}$$

$$K_{COSb} = \frac{[HCO^+CF_3SO_3^-{\bullet}SbF_5]}{[CO][CF_3SO_3H{\bullet}SbF_5]}$$

$$\frac{d[ArCHO]}{dt} = k'[HCO^+CF_3SO_3^-{\bullet}SbF_5][ArH] \qquad \text{eq-2}$$

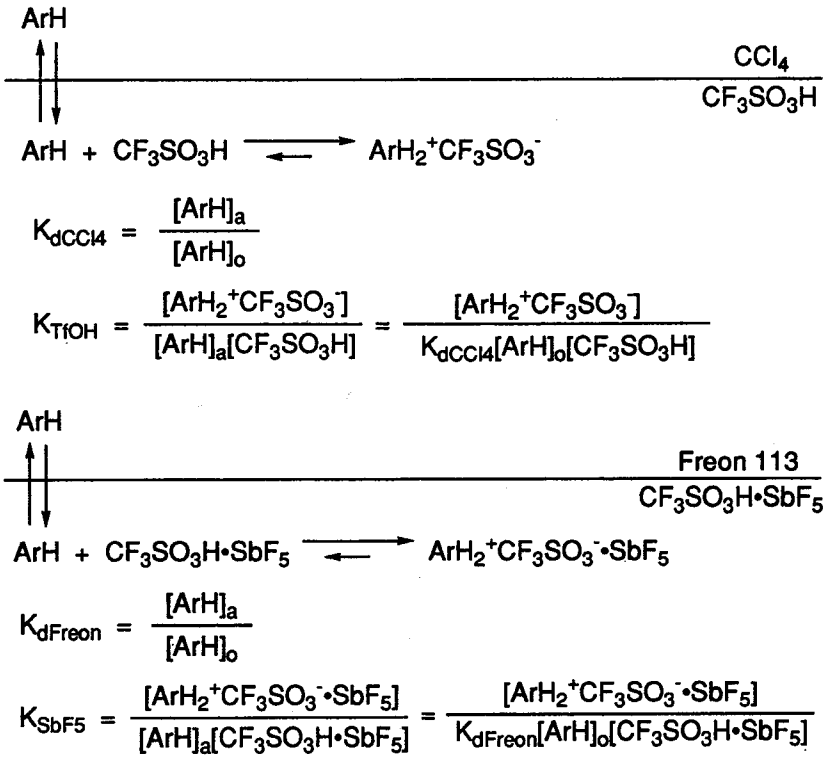
Determination of CO Protonation Equilibrium Constants

In order to determine K_{COTf} and K_{COSb}, the volume of CO absorbed by various compositions of CF_3SO_3H-SbF_5 was examined at 0°C. However, the volume was dependent only on the amount of CF_3SO_3H (18 ml of CO gas per 1 mol of CF_3SO_3H liquid). Therefore, the concentration of formyl cation seems extremely low, and [CO] is considered as the initial value $[CO]_o$ in both systems. Our results are consistent with the fact that the formyl cation has not been observed in the liquid phase.[1-c,4,9]

Determination of m-Xylene Protonation Equilibrium Constants

To determine the protonation equilibrium constants of *m*-xylene, K_{TfOH} and K_{SbF5}, the UV-VIS spectra of solutions of *m*-xylene in CF_3SO_3H-SbF_5 were obtained. However, the molar extinction coefficient of protonated *m*-xylene was too large (more than 9000 l/mol) to allows us to measure the equilibrium in this way. Therefore, the equilibrium constants were estimated by an extraction

method,[10] and *m*-xylene in the acid layer was presumed to be completely protonated under these conditions. CCl_4 and 1,1,2-trichlorotrifluoroethane (Freon 113) were chosen as the organic extraction solvents for CF_3SO_3H and $CF_3SO_3H{\bullet}SbF_5$, respectively, because they are sufficiently inert and insoluble (eq-3).



eq-3

In eq-3, K_{dCCl4} and K_{dFreon} represent the distribution constants of *m*-xylene between CCl_4 or Freon 113 and the acid layer, and $[ArH]_o$ and $[ArH]_a$ represent the concentration of *m*-xylene in the organic and acid layers, respectively. The plots of $[ArH]_o$ versus $[ArH_2^+CF_3SO_3^-]/[CF_3SO_3H]$ and $[ArH_2^+CF_3SO_3^-{\bullet}SbF_5]/[CF_3SO_3H{\bullet}SbF_5]$ gave very good linear relationships as shown in Figures 3 and 4, respectively. In view of these figures, the values were estimated as 0.2 for $K_{dCCl4}K_{TfOH}$ and 70 for $K_{dFreon}K_{SbF5}$. The distribution constants of *m*-xylene, K_{dCCl4} and K_{dFreon}, could not be determined because it was impossible to measure $[ArH]_a$, however, the distribution constants are smaller than 1 and do not seem to be very different from each other. The result is consistent with the fact that $CF_3SO_3H{\bullet}SbF_5$ is a far stronger acid than CF_3SO_3H.

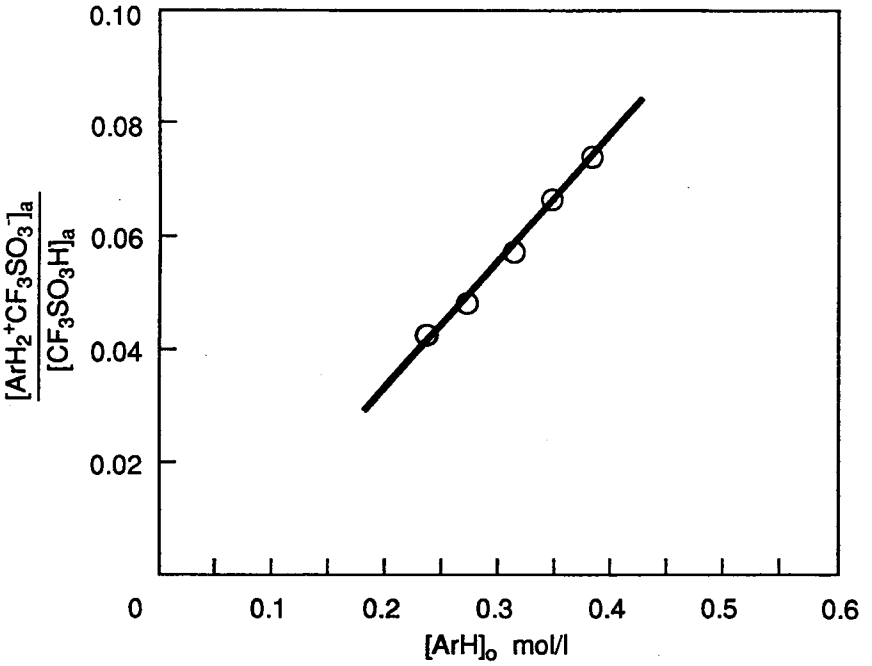


Figure 3. Correlation of $[ArH]_o$ with $[ArH_2^+CF_3SO_3^-]_a/[CF_3SO_3H]_a$.[a]

a) The amount of *m*-xylene was 6~10 mmol.

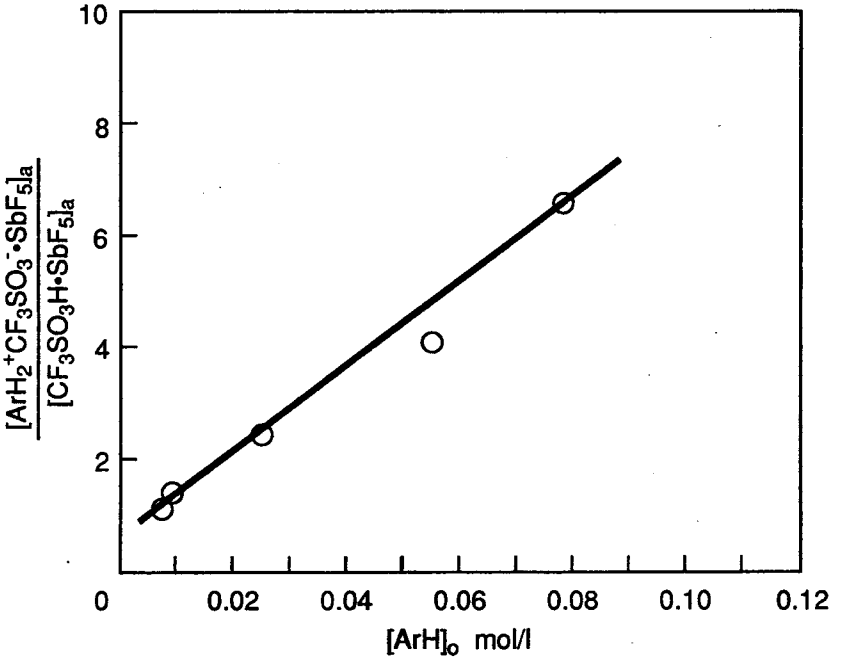


Figure 4. Correlation of $[ArH]_o$ with $[ArH_2^+CF_3SO_3^-\bullet SbF_5]_a/[CF_3SO_3H\bullet SbF_5]_a$.[a]

a) The amount of *m*-xylene was 5~9 mmol.

Kinetic Study of Formylation Rate

The kinetic study of *m*-xylene formylation was carried out based on its

equilibria (eq-2), and the initial reaction rate method was employed because SbF_5 forms a complex with produced aldehyde that changes the solution composition. The formylation rate equations were converted by using the initial values where the subscript o means the initial concentration and $[CF_3SO_3H]$ is considered constant (eq-4).

SbF_5/*m*-xylene≤1

$$[ArH] + [ArH_2^+CF_3SO_3^-] + [ArH_2^+CF_3SO_3^-\cdot SbF_5] = [ArH]_o$$

$$[ArH_2^+CF_3SO_3\cdot SbF_5] = [CF_3SO_3H\cdot SbF_5]_o$$

$$[CO] = [CO]_o$$

$$[ArH] = \frac{[ArH]_o - [CF_3SO_3H\cdot SbF_5]_o}{K_{TfOH}[CF_3SO_3H] + 1}$$

$$[HCO^+CF_3SO_3^-] = K_{COTf}[CO]_o[CF_3SO_3H]$$

$$\frac{d[ArCHO]}{dt} = k[HCO^+CF_3SO_3^-][ArH] =$$

$$\frac{kK_{COTf}[CF_3SO_3H]}{K_{TfOH}[CF_3SO_3H] + 1}[CO]_o([ArH]_o - [CF_3SO_3H\cdot SbF_5]_o)$$

SbF_5/*m*-xylene≥1

$$[ArH_2^+CF_3SO_3^-\cdot SbF_5] + [CF_3SO_3H\cdot SbF_5] = [CF_3SO_3H\cdot SbF_5]_o$$

$$[ArH] + [ArH_2^+CF_3SO_3^-\cdot SbF_5] = [ArH]_o$$

$$[CO] = [CO]_o$$

$$[ArH] = \frac{[ArH]_o}{K_{SbF5}[CF_3SO_3H\cdot SbF_5] + 1}$$

$$K_{SbF5}[CF_3SO_3H\cdot SbF_5] >> 1$$

$$[ArH] = \frac{[ArH]_o}{K_{SbF5}[CF_3SO_3H\cdot SbF_5]}$$

$$[CF_3SO_3H\cdot SbF_5] = [CF_3SO_3H\cdot SbF_5]_o - [ArH]_o$$

$$[ArH] = \frac{[ArH]_o}{K_{SbF5}([CF_3SO_3H\cdot SbF_5]_o - [ArH]_o)}$$

$$[HCO^+CF_3SO_3^-\cdot SbF_5] = K_{COSb}[CO]_o([CF_3SO_3H\cdot SbF_5]_o - [ArH]_o)$$

$$\frac{d[ArCHO]}{dt} = k'[HCO^+CF_3SO_3^-\cdot SbF_5][ArH] = \frac{k'K_{COSb}}{K_{SbF5}}[CO]_o[ArH]_o \qquad \text{eq-4}$$

The plots of $[ArCHO]/t$ versus $[CO]_o([ArH]_o-[CF_3SO_3H\cdot SbF_5]_o)$ gave an excellent linear relationship as shown in Figure 5 when the SbF_5/*m*-xylene molar ratio varied from 0 to 0.6. Similarly, the graphs of $[ArCHO]/t$ versus $[CO]_o[ArH]_o$ showed a good linear relationship as shown in Figure 6 under the conditions where the SbF_5/*m*-xylene molar ratio was from 7 to 19.

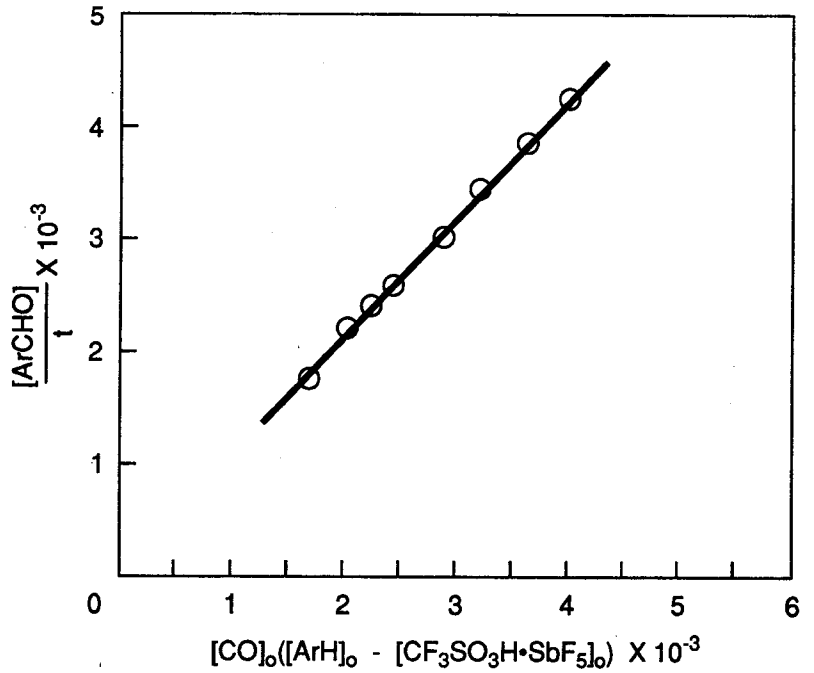


Figure 5. Correlation of $[CO]_o([ArH]_o-[CF_3SO_3H{\bullet}SbF_5]_o)$ with [ArCHO]/t.[a]

a) The SbF_5/*m*-xylene molar ratio was 0~0.6, and the reaction time was 5min.

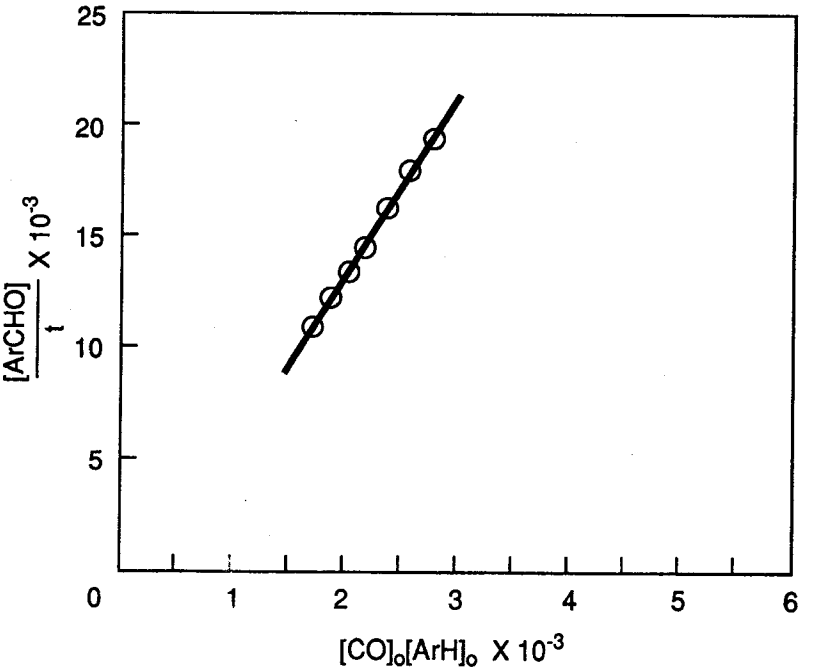


Figure 6. Correlation of $[CO]_o[ArH]_o$ with [ArCHO]/t.[a]

a) The SbF_5/*m*-xylene molar ratio was 7~19, and the reaction time was 1min.

On the other hand, when the SbF_5/*m*-xylene molar ratio was from 2 to 4.5, it was found that the plots of [ArCHO]/t versus $[HCO^+CF_3SO_3^-$

$\bullet SbF_5]=[CO]_o([CF_3SO_3H\bullet SbF_5]_o-[ArH]_o)$ (eq-5) had a good linear relationship as shown in Figure 7.

$$\frac{d[ArCHO]}{dt} = k'[HCO^+CF_3SO_3^-\bullet SbF_5] = k'K_{COSb}[CO]_o([CF_3SO_3H\bullet SbF_5]_o - [ArH]_o) \quad \text{eq-5}$$

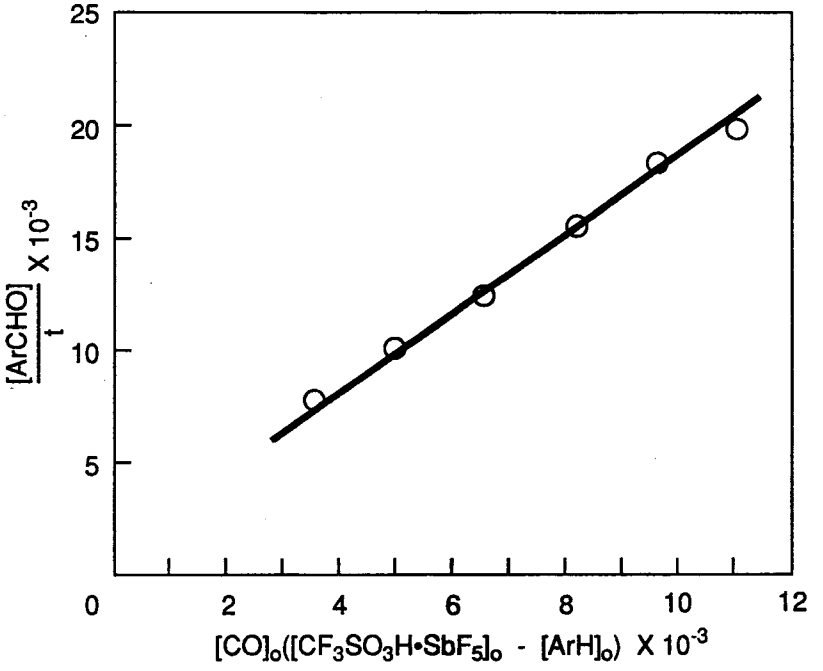


Figure 7. Correlation of $[CO]_o([CF_3SO_3H\bullet SbF_5]_o-[ArH]_o)$ with [ArCHO]/t.[a]

a) The SbF_5/*m*-xylene molar ratio was 2~4.5, and the reaction time was 1min.

This result is coincident with the suggestion from the result of the CO absorption experiment and shows that the formyl cation concentration is low enough to explain the formylation rate as a pseudo first order reaction, although the concentration of *m*-xylene is very low. For example, [ArH] is at most 6.8 mmol/l in a solution of *m*-xylene (10 mmol), CF_3SO_3H (100 mmol), and SbF_5 (30 mmol).

When the SbF_5/*m*-xylene molar ratio is greater than 7, $CF_3SO_3H\bullet SbF_5$ decreases the concentration of *m*-xylene due to the protonation, and results in the formylation rate being seen as a second order reaction. Now, it is interesting that the formylation rate is explained as a second order reaction under these conditions although [ArH] was far greater under conditions when the SbF_5/*m*-xylene molar ratio is smaller than 1. The appearance of the pseudo

first order reaction can be explained by considering that $HCO^+CF_3SO_3^-$ can not directly react with alkylbenzene because $K_{COSb} >> K_{COTf}$ when most of the *m*-xylene is protonated by $CF_3SO_3H \cdot SbF_5$ (eq-6).

$$ArH_2^+CF_3SO_3^- \cdot SbF_5 + HCO^+CF_3SO_3^- \longrightarrow$$
$$ArH + HCO^+CF_3SO_3^- \cdot SbF_5 + CF_3SO_3H \longrightarrow$$
$$ArCHO + CF_3SO_3H \cdot SbF_5 + CF_3SO_3H \qquad \text{eq-6}$$

The range of the pseudo first order reaction where [ArH] is far greater than $[HCO^+CF_3SO_3^- \cdot SbF_5]$ clearly decreases while increasing the value of the protonation equilibrium constant, K_{SbF5}, which is proportional to the basicity of a used alkylbenzene as shown in Figure 8.

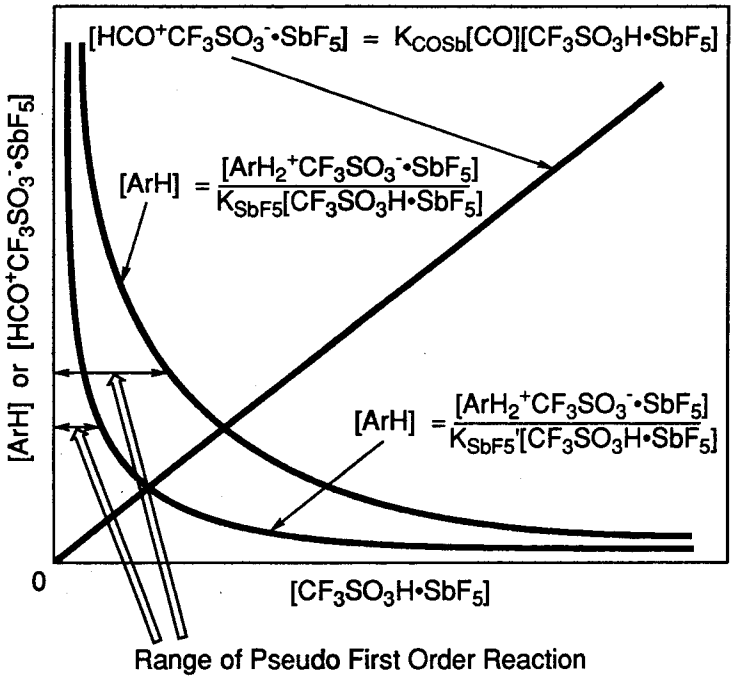


Figure 8. Correlation of $[CF_3SO_3H \cdot SbF_5]$ with [ArH] or $[HCO^+CF_3SO_3^- \cdot SbF_5]$ ($K_{SbF5} < K_{SbF5}'$).

In view of these results, it seems that the apparent relative formylation rate is not proportional to the relative basicity under conditions where the formylation rate is expressed as a second order reaction which involves the term [ArH] that is dependent on protonation. On the contrary, the apparent relative formylation rate is coincident with the relative basicity when the formylation rate is

explained as a pseudo first order reaction.

Apparent Relative Formylation Rate

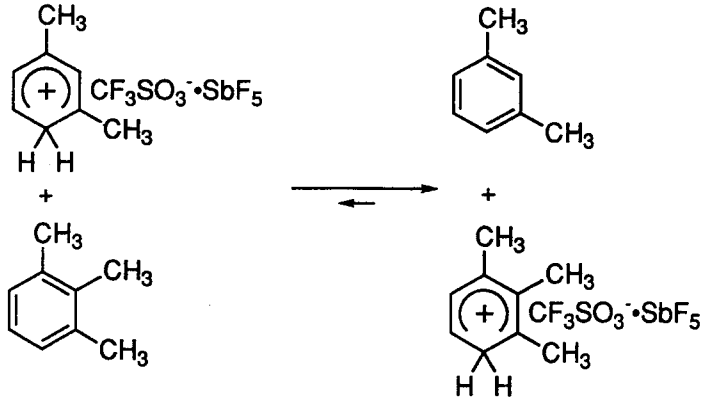
The influence of protonation on the apparent relative formylation rate was studied by the competitive formylation of 1,2,3-trimethylbenzene and *m*-xylene at various SbF_5:alkylbenzene molar ratios in CF_3SO_3H. The results are summarized in Table 1.

Table 1. Apparent Relative Reactivity of 1,2,3-Trimethylbenzene with *m*-Xylene in CF_3SO_3H-SbF_5[a]

SbF_5/alkylbenzenes molar ratio	aldehyde yields(%) from 1,2,3-trimethylbenzene	aldehyde yields(%) from *m*-xylene	product ratio
0.1	18	18	1.0
0.35	16	18	0.9
0.6	12	16	0.8
0.85	9	14	0.6
1.1	10	11	0.9
1.35	24	22	1.1
1.85	44	41	1.1

a) The reaction time was 30min.

Although the reactivity of 1,2,3-trimethylbenzene is greater than that of *m*-xylene in electrophilic substitutions, the apparent formylation rate of *m*-xylene was greater than that of 1,2,3-trimethylbenzene in the presence of SbF_5 when the SbF_5/alkylbenzene molar ratio was less than 1. This result suggests that more 1,2,3-trimethylbenzene than *m*-xylene was protonated by CF_3SO_3H•SbF_5 because the basicity of 1,2,3-trimethylbenzene is greater than that of *m*-xylene (eq-7).



eq-7

The apparent relative formylation rate of various alkylbenzenes was

compared with their relative basicities using *m*-xylene as a standard in CF_3SO_3H in the absence of SbF_5. The results are shown in Table 2. The relative basicity of the alkylbenzenes have been reported in several papers,[10,11] and are listed in Table 2.

Table 2. Apparent Relative Reactivity of Alkylbenzene in CF_3SO_3H[a]

alkylbenzene	aldehyde yields(%) from		product ratio	relative basicity[b]
	alkylbenzene	*m*-xylene		
benzene	0	32	0.0	0.0035
toluene	0	35	0.0	0.024
p-xylene	4	40	0.1	0.038
o-xylene	18	45	0.4	0.042
m-xylene	-	38	1	1
1,2,4-trimethylbenzene	51	30	1.7	2.4
1,2,3-trimethylbenzene	35	30	1.2	2.7
1,2,4,5-tetramethylbenzene	0	24	0.0	5.4
1,2,3,4-tetramethylbenzene	35	24	1.5	15
1,3,5-trimethylbenzene	0	20	0.0	500
1,2,3,5-tetramethylbenzene	0	18	0.0	615

a) The reaction time was 1h. b) The value was cited from ref. 10.

The apparent relative formylation rate increased with an increase in the relative basicity in cases of benzene, toluene, and xylenes. However, 1,2,4-trimethylbenzene showed the greatest apparent formylation rate, and the apparent relative formylation rate decreased with increasing basicity in the case of tri- and tetramethylbenzenes. These results suggest that the more basic alkylbenzenes are protonated more completely and consequently their apparent relative formylation rate is not proportional to their relative basicities.

2-3. Nature of Formyl Cation

Formylation and Acetylation in CF_3SO_3H-SbF_5

In Chapter 2. 2-2, we reported that the protonation equilibrium of *m*-xylene (ArH) should be taken into account to determine the formylation rate in CF_3SO_3H-SbF_5. In this section, the formylation rate showed three aspects which were one pseudo first order reaction, ($k[HCO^+CF_3SO_3^-\cdot SbF_5]$), and two second order reactions, ($k'[HCO^+CF_3SO_3^-][ArH]$ and $k[HCO^+CF_3SO_3^-\cdot SbF_5][ArH]$), which depend on the SbF_5/*m*-xylene molar ratio. The two second order reactions

appeared when the SbF_5/*m*-xylene molar ratio was 0~0.6 and 7~19, respectively. On the other hand, the pseudo first order reaction was observed under conditions where the SbF_5/*m*-xylene molar ratio was 2~4.5. There is a question as to why [$HCO^+CF_3SO_3^-$] does not react with *m*-xylene to produce the pseudo first order reaction under the conditions where most of the *m*-xylene was protonated by $CF_3SO_3H{\bullet}SbF_5$, in other words, when the SbF_5/*m*-xylene molar ratio was greater than 1. As an answer for this question, we suggested that the $CF_3SO_3H{\bullet}SbF_5$ that protonates the *m*-xylene acts as a stronger Brønsted acid than CF_3SO_3H to form [$HCO^+CF_3SO_3^-{\bullet}SbF_5$] from [$HCO^+CF_3SO_3^-$] (eq-1).

$$ArH_2^+CF_3SO_3^-{\bullet}SbF_5 + HCO^+CF_3SO_3^- \longrightarrow$$
$$ArH + HCO^+CF_3SO_3^-{\bullet}SbF_5 + CF_3SO_3H \longrightarrow$$
$$ArCHO + CF_3SO_3H{\bullet}SbF_5 + CF_3SO_3H \qquad \text{eq-1}$$

This suggestion stimulated us to study whether the formyl cation can act as a Brønsted acid or not, because the formyl cation is another species, which is produced by the protonation with superacids in this reaction.

In order to disclose the difference of the formyl cation in nature from typical electrophiles, kinetic studies of the formylation and the acetylation using *m*-xylene were completed in CF_3SO_3H-SbF_5 at 0°C because the acetyl cation, CH_3CO^+, is a typical electrophile which seems not to act as a Brønsted acid under superacidic conditions. These experiments were conducted with two methods, which were the addition of *m*-xylene with CF_3SO_3H-SbF_5 (method A) and neat *m*-xylene (method B) into CF_3SO_3H-SbF_5 with CO or CH_3COF (eq-2).

$$ArH_o \xrightarrow[-\,H^+]{E^+} ArE_B - ArE_A$$
$$\downarrow H^+$$
$$ArH_2^+ \underset{H^+}{\overset{-\,H^+}{\rightleftharpoons}} ArH \xrightarrow[-\,H^+]{E^+} ArE_A$$

Method A:

$$\frac{d[ArE]_A}{dt} = k_{E+}[E^+][ArH]$$

Method B:

$$\frac{d[ArE]_B}{dt} = \frac{d[ArE]_A}{dt} + c\frac{[E^+]_o[ArH]_o}{[E^+]_o + [CF_3SO_3H{\bullet}SbF_5]_o} \qquad \text{eq-2}$$

The reaction rate equation for method A can be explained as an electrophilic

substitution after the dispersion of *m*-xylene is attained in CF_3SO_3H-SbF_5. On the other hand, the reaction rate equation for method B is comprised of two terms which represent the electrophilic substitution in method A and another electrophilic substitution until the dispersion of *m*-xylene is attained in CF_3SO_3H-SbF_5 when the amount of acetylated *m*-xylene and the time during the attainment of the dispersion of *m*-xylene were small and short enough to be considered that the values of $[ArH]_o$ and t in method A and B were the same. The latter term is presented as a competitive reaction of the electrophilic substitution and the protonation to *m*-xylene. If an electrophile has a Brønsted acid nature, it will act as a Brønsted acid to omit the latter term in method B. In these equations, c, [ArH], $[E^+]$, $[ArE]_A$, and $[ArE]_B$ represent the coefficient of the competitive reaction between the electrophile and the proton, the concentration of *m*-xylene, the electrophile, the product in method A, and the product in method B, respectively. These equations were converted using the initial concentration values, which are denoted with the subscript o as mentioned in Chapter 2. 2-2 (eq-3).

Method A:

$$\frac{d[ArE]_A}{dt} = k_{E+}[E^+][ArH] = \frac{k_{E+}}{K}\frac{[E^+]_o[ArH]_o}{[CF_3SO_3H{\cdot}SbF_5]_o - [ArH]_o - [E^+]_o}$$

Method B:

$$\frac{d[ArE]_B}{dt} - \frac{d[ArE]_A}{dt} = c\frac{[E^+]_o[ArH]_o}{[E^+]_o + [CF_3SO_3H{\cdot}SbF_5]_o} \qquad \text{eq-3}$$

In these equations, K is the protonation equilibrium constant of *m*-xylene with $CF_3SO_3H{\cdot}SbF_5$. The reaction was completed under conditions where the SbF_5/*m*-xylene molar ratio was 7~20 at 0°C, therefore, the CH_3COF that was added as an acetylation reagent appeared to completely convert to CH_3CO^+ in CF_3SO_3H-SbF_5.[12] In the case of acetylation, the plots of $[ArCOCH_3]_A/t$ versus $[CH_3CO^+]_o[ArH]_o/([CF_3SO_3H{\cdot}SbF_5]_o-[ArH]_o-[CH_3CO^+]_o)$ in method A gave a good linear relationship as shown Figure 1. Similarly, the graphs of $([ArCOCH_3]_B-[ArCOCH_3]_A)/t$ versus $[CH_3CO^+]_o[ArH]_o/([CH_3CO^+]_o+[CF_3SO_3H{\cdot}SbF_5]_o)$ in method B also showed a good linear relationship as presented in Figure 2.

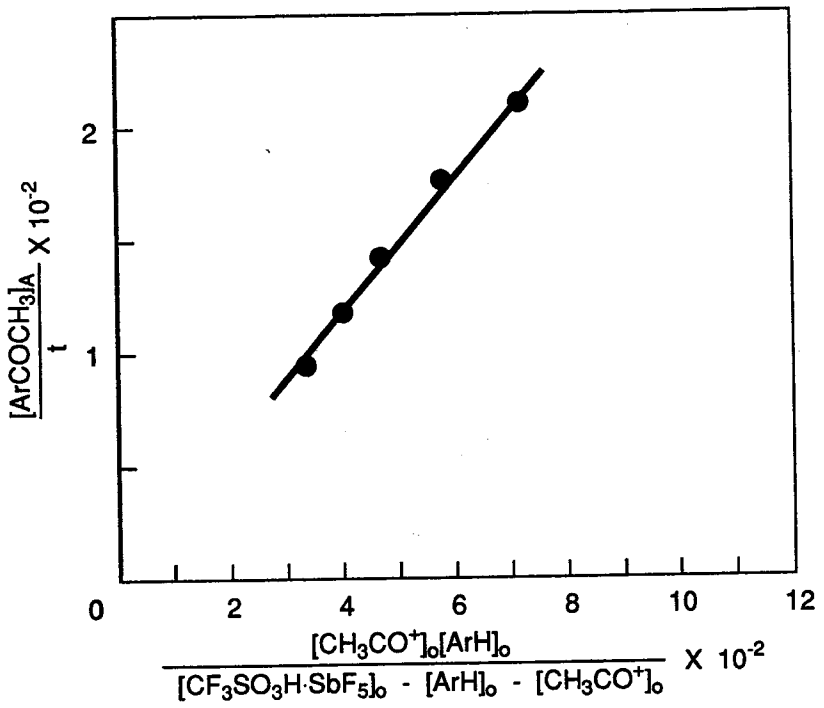


Figure 1. Correlation of $[CH_3CO^+]_o[ArH]_o/([CF_3SO_3H{\bullet}SbF_5]_o-[ArH]_o-[CH_3CO^+]_o)$ with $[ArCOCH_3]_A/t$ (Method A).

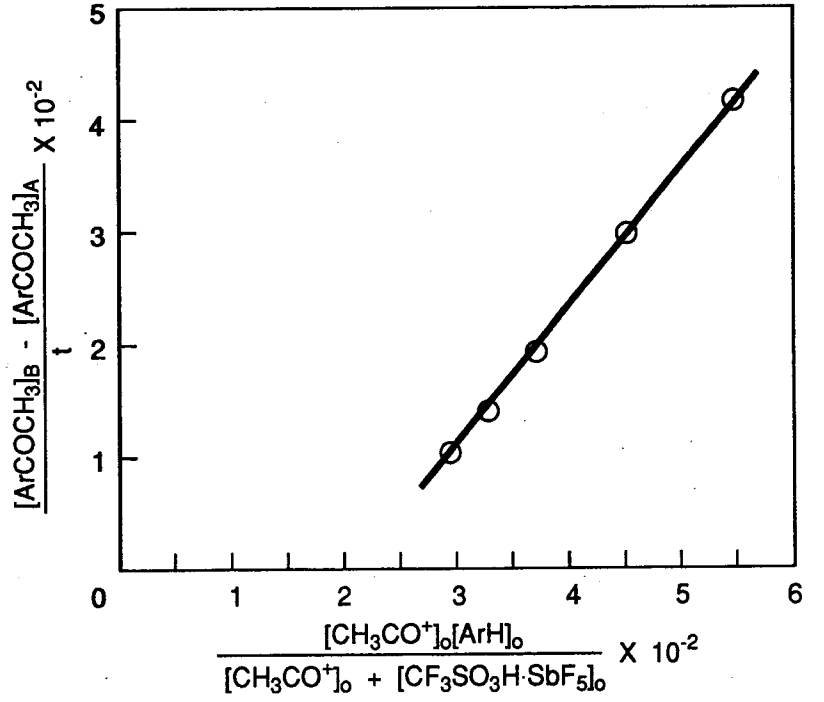


Figure 2. Correlation of $[CH_3CO^+]_o[ArH]_o/([CH_3CO^+]_o+[CF_3SO_3H{\bullet}SbF_5]_o)$ with $([ArCOCH_3]_B-[ArCOCH_3]_A)/t$ (Method B).

These results clearly indicate that the acetyl cation acts as a typical electrophile

because the acetylation proceeded until the dispersion of *m*-xylene was attained. On the contrary, the formylation rate was explained only with the equation in method A regardless of the methods, and the plots of [ArCHO]/t versus $[CO]_o[ArH]_o$ showed a good linear relationship as shown in Figure 3.

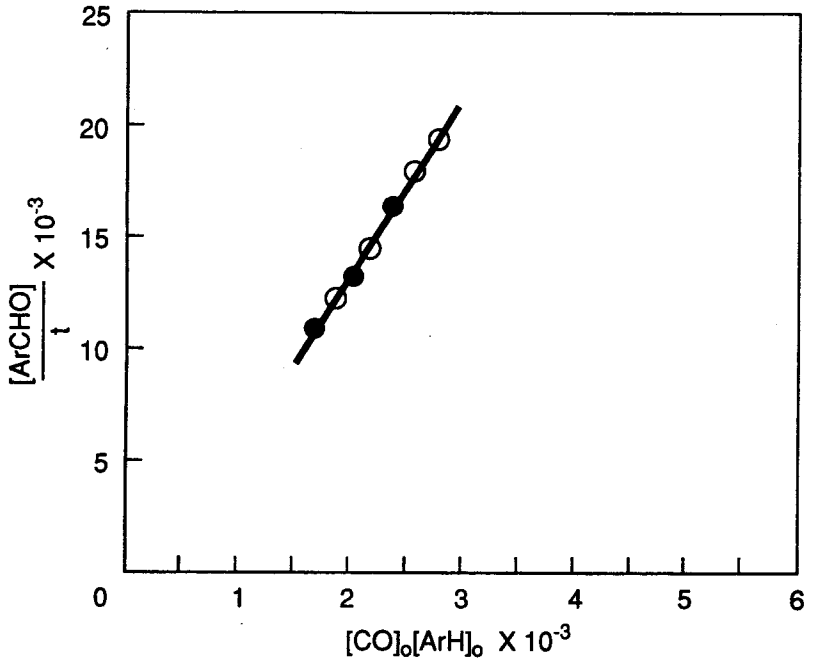


Figure 3. Correlation of $[HCO^+]_o[ArH]_o$ with [ArCHO]/t.[a]

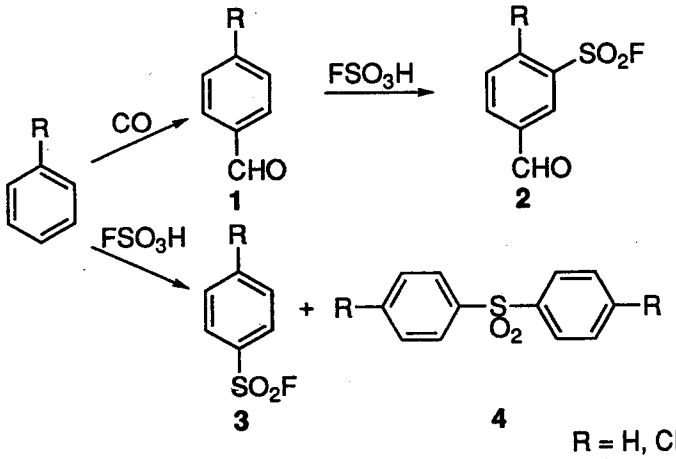
a) ● and ○ present the formylation by method A and method B, respectively.

In control experiments, the formylation and the acetylation were not reversible reactions under these conditions. Therefore, these results clearly show that the formylation did not proceed to omit the latter term of the equation in method B until the dispersion of *m*-xylene was attained and that the formyl cation acted as a Brønsted acid to protonate *m*-xylene. In view of the results of these kinetic studies, a question arose as to how the formylation proceeds in spite of the ability of the formyl cation as a strong Brønsted acid to protonate aromatic compounds.

Formylation and Sulfonation in FSO_3H-SbF_5

In Chapter 1. 1-2, it was found that both formylation and sulfonation take place to give four products from alkylbenzenes in the FSO_3H-SbF_5 system, and the ratio of these products depends on the ratio of FSO_3H and SbF_5 (eq-4).

In order to investigate whether the formyl cation acts as a Brønsted acid in FSO_3H-SbF_5, reactions of highly basic alkylbenzenes such as tri- and tetramethylbenzenes were carried out using various compositions of FSO_3H-SbF_5 under atmospheric CO pressure at 0°C. When alkylbenzenes were slowly added into a mixture of FSO_3H and SbF_5 with vigorous stirring, both formylation and sulfonation took place to give four compounds by a one-pot reaction, and this procedure is equal to method B.



eq-4

In this study, new compounds, formylalkylbenzenesulfonyl fluorides **2**, were obtained from 1,2,3-tri-, 1,3,5-tri-, and 1,2,3,4-tetramethylbenzene when the reaction time was prolonged. The 1,2-shift of the methyl groups occurred, and this phenomenon was also observed in the Friedel-Crafts alkylations.[13] The results are summarized in Table 1. An unreacted substrate was recovered in some experiments, especially in the cases of 1,3,5-trimethylbenzene and 1,2,3,5-tetramethylbenzene. It is clear that this behavior is caused by the protonation, not by the steric hindrance of methyl groups, because the formylation of 1,2,4,5-tetramethylbenzene, which has a higher steric hindrance than 1,3,5-trimethylbenzene, quickly proceeded under the same conditions. When the amount of SbF_5 was small, the sulfonation was the main reaction. The formylation became predominant with the increase in SbF_5 except for 1,3,5-trimethylbenzene and 1,2,3,5-tetramethylbenzene. For these two compounds, the sulfonated compounds were the main products under all conditions. When the formylation of 1,3,5-trimethylbenzene was carried out using more various compositions of FSO_3H-SbF_5, the yield of sulfonated 1,3,5-trimethylbenzene

decreased by the protonation with increasing the SbF_5/1,3,5-trimethylbenzene molar ratio, however, that of the formylated 1,3,5-trimethylbenzene was almost constant as shown in Figure 4. These results reflect that the formyl cation acts as a Brønsted acid more than as an electrophile for these highly basic aromatic compounds.

Table 1. Formylation of Polyalkylbenzenes in FSO_3H-SbF_5[a]

alkylbenzene	SbF_5 (mmol)	product,yields(%)			
		1	2	3	4
1,2,3-tri-methylbenzene	13.8	12(100:0)[c]	0	32(100:0)[c]	0
	69.0	54(89:11)[c]	25[d]	0	0
	138[b]	60(93:7)[c]	11[d]	3(100:0)[c]	0
1,2,4-tri-methylbenzene	13.8	9[e]	0	30[e]	51(91:9)[g]
	69.0	90[e]	1[f]	0	0
	138	78[e]	0	0	0
1,3,5-tri-methylbenzene	13.8	0	0	80	0
	69.0[b]	5	0	27	0
	138[b]	9	0	13	0
1,2,3,4-tetra-methylbenzene	13.8	12(0:0:100)[h]	0	33(18:82)[i]	0
	69.0[b]	84(11:7:82)[h]	0	3(100:0)[i]	0
	138[b]	67(12:19:69)[h]	0	1(0:100)[i]	0
1,2,3,5-tetra-methylbenzene	13.8[b]	0	0	76(100:0)[i]	0
	69.0[b]	5(18:82:0)[h]	0	23(94:6)[i]	0
	138[b]	1(0:0:100)[h]	0	2(100:0)[i]	0
1,2,4,5-tetra-methylbenzene	13.8	4(100:0:0)[h]	0	87(97:3)[i]	0
	69.0[b]	72(97:0:3)[h]	0	3(100:0)[i]	0
	138[b]	75(90:0:10)[h]	0	1(0:100)[i]	0

a) The reaction time was 1h. b) Unreacted alkylbenzene remained. c) Isomer ratio of 2,3,4-trimethylbenzene derivative : 2,4,5-trimethylbenzene derivative. d) The yield of 5-formyl-2,3,4-trimethylbenzenesulfonyl fluoride. e) Products were 2,4,5-trimethylbenzene derivatives. f) The yield of 3-formyl-2,5,6-trimethylbenzenesulfonyl fluoride. g) Isomer ratio of bis(2,4,5-trimethylphenyl) sulfone : 2,2',3',4,5,6'-hexamethyldiphenyl sulfone. h) Isomer ratio of 2,3,5,6-tetramethylbenzaldehyde : 2,3,4,6-tetramethylbenzaldehyde : 2,3,4,5-tetramethylbenzaldehyde. i) Isomer ratio of 2,3,5,6-tetramethylbenzenesulfonyl fluoride and 2,3,4,6-tetramethylbenzenesulfonyl fluoride : 2,3,4,5-tetramethylbenzenesulfonyl fluoride.

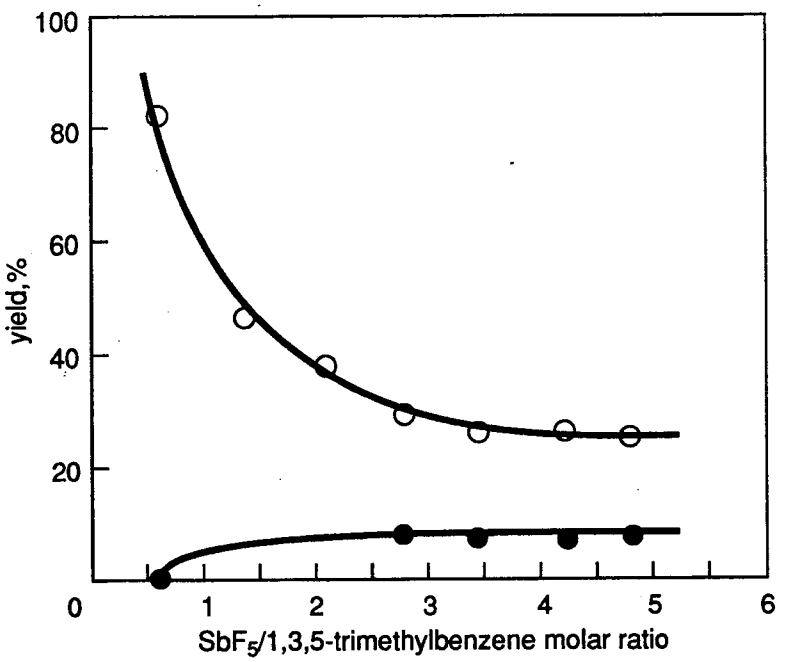


Figure 4. Reaction of 1,3,5-trimethylbenzene in FSO_3H-SbF_5.[a]

a) The reaction time was 1h. ● and ○ present the yields of formylated and sulfonated 1,3,5-trimethylbenzene, respectively.

In order to clarify how to proceed with the formylation under conditions where most of the aromatic compounds are protonated, the time dependence of the product distribution from 1,3,5-tri- and 1,2,3,5-tetramethylbenzene was studied. The results are tabulated in Table 2, and diaryl sulfones **4** were not formed under these conditions.

Table 2. Time Dependence of Product Distribution in FSO_3H-SbF_5[a]

alkylbenzene	time(h)	product,yields(%)		
		1	**2**	**3**
1,3,5-trimethylbenzene	1	9(100:0)[b]	0	13(100:0)[b]
	2	15(63:37)[b]	3(100:0)[c]	14(100:0)[b]
	4	17(40:60)[b]	5(100:0)[c]	9(100:0)[b]
	8	26(18:82)[b]	8(100:0)[c]	9(100:0)[b]
	24	37(5:95)[b]	19(92:8)[c]	10(100:0)[b]
1,2,3,5-tetramethylbenzene	1	1(0:0:100)[d]	0	2(100:0)[f]
	2	3(0:15:85)[d]	0	2(100:0)[f]
	4	17(0:20:80)[d]	0	1(100:0)[f]
	8	48(0:19:81)[d]	2[e]	3(87:13)[f]
	24	41(0:19:81)[d]	15[e]	2(80:20)[f]

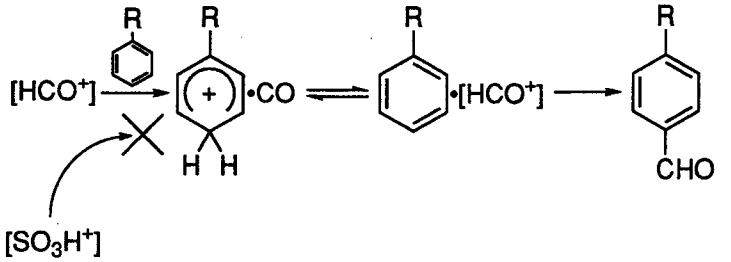
a) The formylation was carried out using 138 mmol of SbF_5. Unreacted alkylbenzene was recovered in all experiments. b) Isomer ratio of 2,4,6-trimethylbenzene derivative : 2,4,5-trimethylbenzene derivative. c) Isomer ratio of 3-formyl-2,4,6-trimethylbenzenesulfonyl fluoride : 3-formyl-2,5,6-trimethylbenzenesulfonyl fluoride. d) Isomer ratio of 2,3,5,6-tetramethylbenzaldehyde : 2,3,4,6-tetramethylbenzaldehyde : 2,3,4,5-tetramethylbenzaldehyde. e) Product was 2-formyl-3,4,5,6-tetramethylbenzenesulfonyl fluoride. f) Isomer ratio of 2,3,5,6-tetramethylbenzenesulfonyl fluoride and 2,3,4,6-tetramethylbenzenesulfonyl fluoride : 2,3,4,5-tetramethylbenzenesulfonyl fluoride.

Although the yields of sulfonyl fluorides **3** were constant, the yields of aldehydes **1** and **2** increased with time. In control experiments, the sulfonation and the formylation were not reversible under these conditions. These results show that the formylation proceeds even after the alkylbenzenes are almost completely protonated, but the sulfonation takes place only until the dispersion of alkylbenzenes is attained in FSO_3H-SbF_5. Because the formyl cation does not react with protonated aromatic compounds,[14] the formylation is clearly one of electrophilic substitutions. Therefore, the priority of the formylation over the sulfonation under strong acidic conditions, where most of the aromatic compounds are protonated, seems to be derived from the reproduction of the formyl cation closer to the aromatic compounds than the other electrophiles by the protonation of CO with not only $FSO_3H{\bullet}SbF_5$ but also protonated aromatic compounds in FSO_3H-SbF_5. This equilibrium among H^+, CO, and ArH is presented in eq-5.

$$\begin{array}{c} H^+ + ArH + CO \\ \swarrow \quad \searrow \\ ArH_2^+ + CO \rightleftharpoons ArH + HCO^+ \longrightarrow ArCHO + H^+ \end{array} \qquad \text{eq-5}$$

During the reproduction of the formyl cation, the reactive species for the sulfonation such as $[SO_3H^+]$[15] are unable to approach to protonated aromatic compounds because of charge repulsion (eq-6). This suggestion can give clear answers to two questions about the formylation which are why the formylation of anisole proceeds using a weaker acid, HF-BF_3,[16] instead of FSO_3H-SbF_5 and HF-SbF_5,[17] and why the formylation of the polynuclear aromatic compounds such

as naphthalene and diphenyl does not occur in FSO_3H-SbF_5.[17] The answer for the former is that the formyl cation, $HCO^+FSO_3^-\cdot SbF_5$ or $HCO^+SbF_6^-$, acts as a stronger Brønsted acid than $HCO^+BF_4^-$ to protonate anisol, and anisol is too basic to reproduce the formyl cation. That for the latter is that the formyl cation acts as a Brønsted acid for polynuclear aromatic compounds, however, the polyprotonation of the polynuclear aromatic compounds is difficult because of their charge repulsion, and the sulfonation takes place at the unprotonated aromatic ring to give sulfonated compounds as the main products.

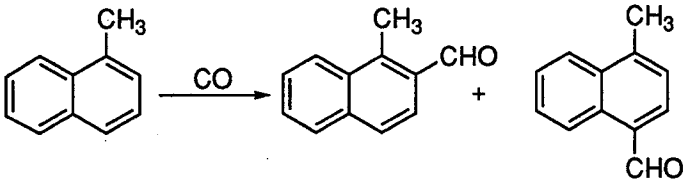


eq-6

3-4. Influence of Protonation on Formylation Regioselectivity

Regioselectivity of 1-Methylnaphthalene Formylation

In order to investigate the reason why methylnaphthalenes showed such a low regioselectivity, the formylation of 1-methylnaphthalene using various compositions of HF-SbF_5 was carried out, and the regioselectivity only for the monoaldehyde was examined because the dialdehyde is a secondary product, and the conditions where the dialdehyde is not formed were adopted. The formylation gave two monoaldehydes which included 1-methyl-2-naphthaldehyde and 1-methyl-4-naphthaldehyde (eq-1).



eq-1

Surprisingly, the regioselectivity drastically changed at the point where the SbF_5/1-methylnaphthalene molar ratio was 1, and the ratio of 1-methyl-2-naphthaldehyde : 1-methyl-4-naphthaldehyde was 0 : 1 or 3 : 7 as shown in Figure 1. In control experiments, the formyl group did not migrate under these conditions. Similarly, the yield of monoaldehyde, which reflects the conversion

of 1-methylnaphthalene, changed when the SbF_5/1-methylnaphthalene molar ratio was greater or less than 1 as shown in Figure 2..

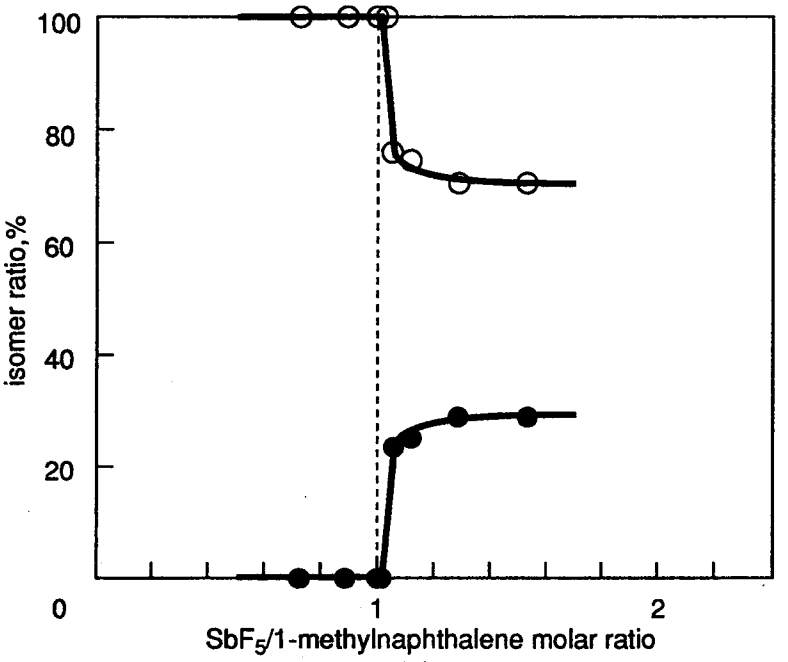


Figure 1. Isomer ratio of monoaldehyde in 1-methylnaphthalene formylation.[a]
a) The formylation was carried out using 500 mmol of HF and 10 mmol of 1-methylnaphthalene at 0°C for 2h under 20 atm of CO pressure. O and ● represent 1-methyl-4- and 1-methyl-2-naphthaldehyde, respectively.

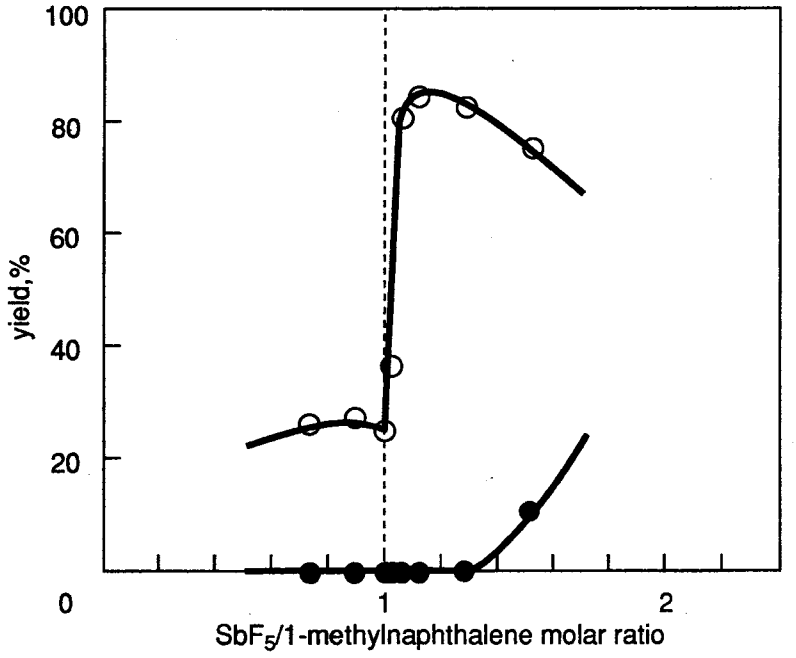
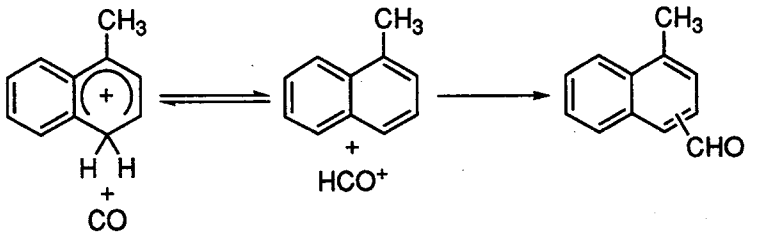


Figure 2. Yield of mono- and dialdehyde in 1-methylnaphthalene formylation.[a]

a) The formylation was carried out using 500 mmol of HF and 10 mmol of 1-methylnaphthalene at 0°C for 2h under 20 atm of CO pressure. O and ● represent monoaldehyde and dialdehyde, respectively.

The change in the yield clearly reflects the influence of the protonation equilibrium of 1-methylnaphthalene with HF•SbF_5 as reported in Chapter 3. 3-2 (eq-2)



eq-2

Factors for Regioselectivity Change

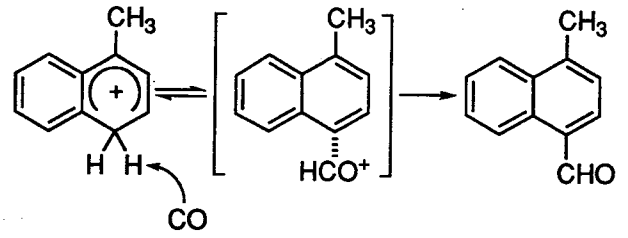
To explain this result, we considered two factors, the nature of formyl cation and the protonation of aromatic compounds, which seems to cause the regioselectivity change. Recently, the existence of a dication as a real electrophile in electrophilic aromatic substitutions is proposed when strong acidity is needed to allow the reactions to occur, namely, under superacidic conditions.[18] Taking into account the protonation equilibrium of aromatic compounds in superacid,[19] the nature of the formyl cation in the HF-SbF_5 system seems to be a monocation when the SbF_5/1-methylnaphthalene molar ratio is less than 1 or a dication under conditions when the SbF_5/1-methylnaphthalene molar ratio is greater than 1 (eq-3).

SbF_5/1-methylnaphthalene≤1 SbF_5/1-methylnaphthalene≥1

$$HCO^+ \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} HCOH^{2+} \qquad \text{eq-3}$$

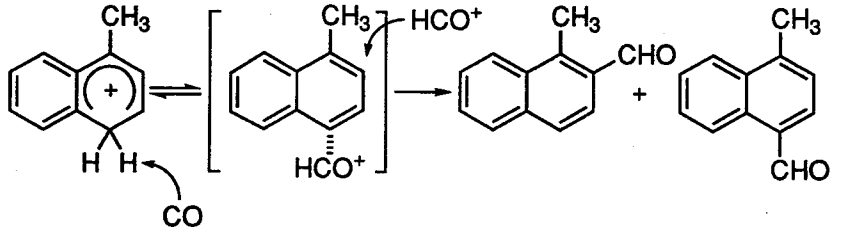
If the regioselectivity change is derived from the difference in the formyl cation nature, i.e., monocation or dication, the regioselectivity at the 4-position of 1-methylnaphthalene should be exclusively high for the monocation, but that should be low for the dication as shown in Figure 1. On the other hand, taking into account the dual reactivity of the formyl cation as an electrophile and as a Brønsted acid,[20] the formation of the σ-complex, which has the ability to produce a formyl cation, seems to influence the regioselectivity when the formylation proceeds through the protonation equilibrium among the aromatic

compound, CO, and superacid, namely, under a solvent-cage-like atmosphere.[21] It is reported that the protonation of 1-methylnaphthalene occurs at the 4-position of 1-methylnaphthalene,[22] therefore, the produced formyl cation due to the protonated 1-methylnaphthalene probably exists close at the 4-position of 1-methylnaphthalene resulting in the high regioselectivity at the 4-position (eq-4).



eq-4

On the other hand, when the formyl cation is formed not only by the σ-complex but also by the superacid, the formylation may show regioselectivity at both the 4-position and the 2-position of 1-methylnaphthalene because the formyl cation produced by the superacid is free from the solvent-cage restriction (eq-5).



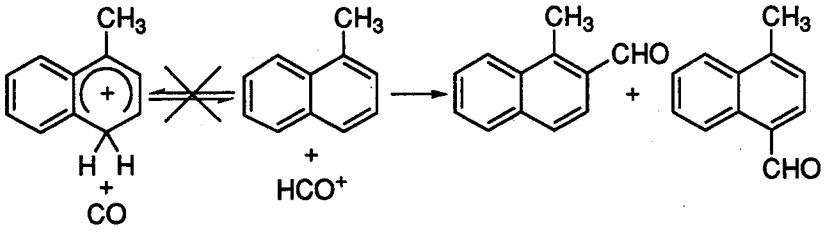
eq-5

According to this hypothesis and the protonation equilibrium, the regioselectivity change can be reasonably explained as follows. In the case of the HF-SbF_5 system, the formylation does not occur in the absence of SbF_5 as mentioned in Chapter 1. 1-3. Therefore, the formyl cation is formed by the σ-complex with HF•SbF_5 to give the high regioselectivity at the 4-position when the SbF_5/1-methylnaphthalene molar ratio is less than 1. On the other hand, the formyl cation is produced by both the σ-complex with HF•SbF_5 and HF•SbF_5 to form 1-methyl-2- and 1-methyl-4-naphthaldehyde under conditions where the SbF_5/1-methylnaphthalene molar ratio is greater than 1.

Regioselectivity of Formylations Using CO and HCOF

In order to clarify which factor, the difference in the formyl cation nature or the protonation of aromatic compounds, causes the regioselectivity

change of the Gattermann-Koch formylation, the formylation of 1-methylnaphthalene in HF-SbF_5 using formyl fluoride, HCOF,[23] instead of CO was carried out, and the regioselectivity of the HCOF formylation was compared with that of the Gattermann-Koch formylation. In control experiments, HCOF was quickly decomposed to HF and CO in HF-SbF_5,[24] and the Gattermann-Koch formylation produced only a trace amount of aldehyde under atmospheric CO pressure. Therefore, the HCOF formylation clearly proceeds without the formation of CO, namely, the formyl cation produced from HCOF immediately reacts with 1-methylnaphthalene without the protonation equilibrium among 1-methylnaphthalene, CO, and superacid (eq-6).[20]



eq-6

These experiments reveal the significant difference in the regioselectivity as shown in Table 1, and in the case of the HCOF formylation, the regioselectivity was constant regardless of the SbF_5/1-methylnaphthalene molar ratio even when the SbF_5/1-methylnaphthalene molar ratio was 2.

Table 1. Formylation of 1-Methylnaphthalene Using HCOF and CO[a]

SbF_5/substrate molar ratio	reagent	temp. (°C)	time	yield of aldehyde(%)	isomer ratio of 2- : 4-aldehyde
1	HCOF	0	1h	15	7:93
1.25	HCOF	0	1h	45	6:94
1.25	HCOF	-40	1h	33	6:94
2	HCOF	-40	1h	50	6:94
1	CO	0	2h	24	0:100
1.25	CO	0	10min	12	32:68
1.25	CO	-40	2h	13	36:64

a) The formylation was carried out using 500 mmol of HF and 10 mmol of 1-methylnaphthalene. HCOF (80 mmol) or CO (20 atm) was used as a formylation reagent. The formation of dialdehyde was not observed in these experiments, and 2- and 4-aldehyde in Table mean 1-methyl-2- and 1-methyl-4-naphthaldehyde, respectively.

Under this condition, the nature of formyl cation seems to be a dication because most of 1-methylnaphthalene are protonated[19] and excess amounts of SbF_5 exist abundantly. Therefore, we concluded that the regioselectivity change is not caused by the difference in the formyl cation nature[25] but by the protonation of aromatic compounds. When the SbF_5/1-methylnaphthalene molar ratio was 1, the HCOF formylation showed regioselectivity not only at the 4-position but also at the 2-position although the Gattermann-Koch formylation showed regioselectivity only at the 4-position of 1-methylnaphthalene. On the contrary, when the SbF_5/1-methylnaphthalene molar ratio was 1.25, the regioselectivity at the 4-position was lower in the Gattermann-Koch formylation than in the HCOF formylation. These results evidently suggest that the protonation of aromatic compounds in the Gattermann-Koch formylation produces two different influences on the regioselectivity which are the increase and the decrease in the regioselectivity at the 4-position of 1-methylnaphthalene depending on the SbF_5/1-methylnaphthalene molar ratio. The former influence may be derived from the dual reactivity of the formyl cation, however, the latter one is expected to appear in other electrophilic aromatic substitutions. On the other hand, the regioselectivity in both formylations was constant regardless of reaction temperature.

3-5. Experimental Section

All aromatic starting materials, SbF_5, CF_3SO_3H, FSO_3H, HF, and CO were of the highest available purity and were used without further purification. CF_3SO_3H contained 5 mol% H_2O for Figure 6 and 7 or 1.5 mol% for others in Chapter 3. 3-2. In Chapter 3. 3-3, CF_3SO_3H contained 5 mol% H_2O in all experiments. H_2O was considered to be converted to $CF_3SO_3H \cdot H_2O$ or $SbF_5 \cdot H_2O$ as an inert additive. The yield determination and the identification of products were performed by GC, IR, MS, and ^1H,^{13}C-NMR.

Formylation Procedures in CF_3SO_3H-SbF_5

The required amount of SbF_5 and CF_3SO_3H (200 mmol, 30 g) were put into a three-necked flask (300 ml) equipped with a CO gas buret under atmospheric pressure. *m*-Xylene (10 mmol, 1.06 g) or a mixture of

alkylbenzene (10 mmol) with *m*-xylene (10 mmol, 1.06 g) was added into CF_3SO_3H-SbF_5 at a time with vigorous stirring at 0°C. The reaction mixture was quenched in ice-water and extracted with benzene. In all experiments, unreacted substrates were recovered. The yields of products were determined by GC, and products were characterized by IR, ^1H,^{13}C-NMR, and MS after the isolation by a vacuum distillation.

Formylation Procedures in HF-SbF_5

HF (500 mmol, 10 g) and SbF_5 (7.5 mmol, 1.63 g) were put into a Hastelloy Taiatsugarasu autoclave (100 ml) equipped with a Hastelloy magnetic stirrer bar with cooling at -78 (using dry ice-acetone-bath) or 0°C (using ice-water-bath). The autoclave was sealed, and CO (20 atm) was introduced. Then, 1-methylnaphthalene-d_{10} (10 mmol, 1.52 g) was added through a syringe into the solution with vigorous stirring under temperature control. After the reaction was over, the autoclave was depressurized and opened after cooling below 0°C. The reaction mixture was quenched in ice-water and extracted with benzene, and the H-D ratio for the formyl group and the aromatic ring of produced aldehyde was determined by ^1H-NMR after isolation.

Extraction Experiment Procedures

The required amount of *m*-xylene, CCl_4 (15 g), and CF_3SO_3H (100 mmol, 15 g) were put into an Erlenmeyer flask with a stopper (30 ml), and the mixture was stirred vigorously at 0°C. After the contents had settled for 3h at 0°C, the CCl_4 layer was separated and the concentration of *m*-xylene was determined by GC.

Similarly, *m*-xylene, 1,1,2-trichlorotrifluoroethane (15 g), CF_3SO_3H (10 mmol, 1.50 g), and SbF_5 (10 mmol, 2.17 g) were poured into the flask, and the 1,1,2-trichlorotrifluoroethane layer was separated after the contents had settled for 5 minutes.

Study of Carbon Monoxide Absorption into CF_3SO_3H-SbF_5 Procedures

A three-necked flask (300 ml) equipped a CO gas buret under atmospheric pressure and a cylinder which contained a mixture of CF_3SO_3H (100 mmol, 15 g) and required amount of SbF_5 (0-30 mmol, 0-6.51 g) was immersed in an ice-water-bath. Water was excluded in all equipments. The mixture was

added into the flask from the cylinder, and the volume of CO absorption was determined with the gas buret.

^{1}H-NMR Study Procedures

All ^{1}H-NMR measurements were carried out at 0°C using a coaxial system. A mixture of *m*-xylene (10 mmol, 1.06 g), SbF_5 (0-15 mmol), and CF_3SO_3H (200 mmol, 30 g) was put into a 5 ø inner glass tube, and $CDCl_3$ with TMS was added into a 10 ø outer glass tube.

Acetylation Procedures of Method A in CF_3SO_3H-SbF_5

A required amount of SbF_5, CF_3SO_3H (92 mmol, 13.82 g), and CH_3COF (20 mmol, 1.24 g) were put into a 300-ml three-necked flask at 0°C. A solution of *m*-xylene (10 mmol, 1.06 g), a required amount of SbF_5, and CF_3SO_3H (108 mmol, 16.18 g) were added into the flask with vigorous stirring at 0°C. The amounts of SbF_5 of the solutions in the flask and the added solutions were controlled to be considered that both solutions have the same SbF_5 concentrations taking into account the consumption of SbF_5 to protonate *m*-xylene and to produce CH_3CO^+. (The *m*-xylene solutions of CF_3SO_3H-SbF_5 gave biaryl derivatives through Scholl reaction, however, the yields of biaryl derivatives were not more than 2%. Therefore, we considered that this influence could be neglected.) After 0.5 min, the reaction mixture was quenched in ice-water and extracted with benzene, and the product yields were determined using GC with an internal standard.

Acetylation Procedures of Method B in CF_3SO_3H-SbF_5

A required amount of SbF_5, CF_3SO_3H (200 mmol, 30.00 g), and CH_3COF (20 mmol, 1,24 g) were put into a 300-ml three-necked flask at 0°C. *m*-Xylene (10 mmol, 1.06 g) was added into the flask with vigorous stirring at 0°C. After 0.5 min, the reaction mixture was quenched in ice-water and extracted with benzene, and the product yields were determined using GC with an internal standard.

Formylation Procedures of Method A in CF_3SO_3H-SbF_5

A required amount of SbF_5 and CF_3SO_3H (110 mmol, 16.60 g) were put into a 300-ml three-necked flask equipped with a CO gas buret under atmospheric pressure at 0°C. A solution of *m*-xylene (10 mmol, 1.06 g), a

required amount of SbF_5, and CF_3SO_3H (90 mmol, 13.40 g) were added into the flask with vigorous stirring at 0°C. The amounts of SbF_5 of the solutions in the flask and the added solutions were controlled to be considered that both solutions have the same SbF_5 concentrations taking into account the consumption of SbF_5 to protonate *m*-xylene. After 1 min, the reaction mixture was quenched in ice-water and extracted with benzene, and the product yields were determined using GC with an internal standard.

Formylation Procedures of Method B in CF_3SO_3H-SbF_5

A required amount of SbF_5 and CF_3SO_3H (200 mmol, 30.00 g) were put into a 300-ml three-necked flask equipped with a CO gas buret under atmospheric pressure at 0°C. *m*-Xylene (10 mmol, 1.06 g) was added into the flask with vigorous stirring at 0°C. After 1 min, the reaction mixture was quenched in ice-water and extracted with benzene, and the product yields were determined using GC with an internal standard.

Reaction Procedures in FSO_3H-SbF_5

A required amount of SbF_5 and FSO_3H (174 mmol, 17.40 g) were put into a 300-ml three-necked flask equipped with a CO gas buret under atmospheric pressure. Alkylbenzene (20 mmol) was added over 30 min into FSO_3H-SbF_5 with vigorous stirring at 0°C. After the addition was complete, the temperature was kept at 0°C for 1h, and the temperature was then increased to room temperature. The reaction mixture was quenched in ice-water and extracted with benzene. The yields of products were determined using GC with an internal standard, and the products were characterized using IR, ^{1}H-NMR, ^{13}C-NMR, mass spectra, and elemental analysis after isolation by a vacuum distillation and recrystallization.

Synthetic Procedures of CH_3COF

HF (0.5 mol, 10.0 g) was placed into a 200-ml Teflon flask at 0°C. $(CH_3CO)_2O$ (0.6 mol, 61.2 g) was slowly added dropwise into the flask with stirring at 0°C. After 3h, the CH_3COF was separated from the reaction mixture in 70% yield by distillation.

HCOF Formylation Procedures

The required amount of SbF_5, 1-methylnaphthalene (10 mmol, 1.42 g),

and HF (500 mmol, 10.0 g) were put into a Teflon round-bottomed flask (300 ml) under temperature control, and then HCOF (80 mmol, 3.84 g), which was prepared from KHF_2, HCOOH, and C_6H_5COCl according to ref. 23-c, was added to the mixture with vigorous stirring. After 1h, the reaction mixtures was quenched with ice-water and extracted with benzene.

Products Properties

3-formyl-2,4,6-trimethylbenzene sulfonyl fluoride: IR(KBr): 1695 (C=O), 1400, 1200 (SO_2F) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.58 (s, 3H), 2.70 (s, 3H), 2.79 (d, 3H, J = 2.4Hz), 7.22 (s, 1H), 10.74 (s, 1H). ^{13}C-NMR($CDCl_3$): δ 17.2, 17.3, 20.6, 23.2, 131.7, 132.1, 134.3, 134.5, 141.9, 143.8, 145.9, 192.7. Anal. Found: C, 51.80; H, 4.76; M^+, 230. Calcd for $C_{10}H_{11}O_3SF$: C, 52.16; H, 4.81; M, 230.

5-formyl-2,3,4-trimethylbenzene sulfonyl fluoride: IR(KBr): 1690 (C=O), 1385, 1205 (SO_2F) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.39 (s, 3H), 2.70 (s, 6H), 8.37 (s, 1H), 10.39 (s, 1H). ^{13}C-NMR($CDCl_3$): δ 15.9, 16.0, 17.9, 131.1, 131.6, 132.5, 141.1, 142.1, 146.6, 190.6. Anal. Found: C, 52.01; H, 4.76; M^+, 230. Calcd for $C_{10}H_{11}O_3SF$: C, 52.16; H, 4.81; M, 230.

2-formyl-3,4,5,6-tetramethylbenzene sulfonyl fluoride: IR(KBr): 1680 (C=O), 1375, 1180 (SO_2F) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.24 (s, 3H), 2.36 (s, 3H), 2.58 (s, 3H), 2.61 (s, 3H), 10.49 (s, 1H). ^{13}C-NMR($CDCl_3$): δ 16.3, 17.2, 17.8, 19.3, 19.4, 132.5, 132.8, 136.2, 136.3, 137.6, 141.2, 142.5, 195.2. Anal. Found: C, 54.01; H, 5.39; M^+, 244. Calcd for $C_{11}H_{13}O_3SF$: C, 54.09; H, 5.36; M, 244.

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(19) The protonation has two roles which are the production of the formyl cation that proceeds the formylation and the formation of the σ-complex to decrease the apparent formylation rate depending on the SbF_5/substrate molar ratio. When the SbF_5/substrate molar ratio is less than 1, SbF_5 protonates the substrate to decrease the apparent formylation rate. Under conditions when the SbF_5/substrate molar ratio is greater than 1, namely in the presence of an excess amount of SbF_5, SbF_5 produces the formyl cation to proceed the formylation. However, when the SbF_5/substrate molar ratio is much greater than 1, the influence of protonation by SbF_5 on the substrate is overwhelming and decreases the apparent formylation rate. The tendency of the protonation to influence the formylation is dependent on the basicity of the substrate. See Chapter 3. 3-2.

(20) The formyl cation is not only an electrophile but also a Brønsted acid for protonating the substrate. Therefore, when the substrate is added to superacid under a CO atmosphere, the formyl cation acts as a Brønsted acid to first protonate the substrate, and then the formyl cation is reproduced by the protonated substrate. The reproduced formyl cation exists close to the substrate, therefore, the formylation has priority over other electrophiles under conditions when the substrate is protonated. See Chapter 3. 3-3.

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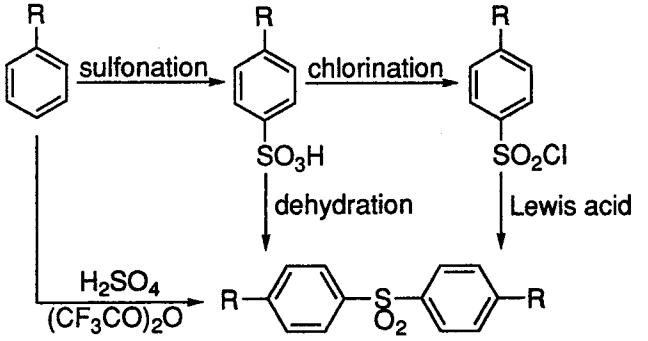
(24) When HCOF was added to HF-SbF_5, the violent CO exhalation was observed. Only a trace amount of aldehyde was obtained when 1-methylnaphthalene was added to the solution.

(25) We could not decide whether the nature of formyl cation was a monocation or a dication in this study.

Chapter 3. Sulfonation of Aromatic Compounds

3-1. Introduction

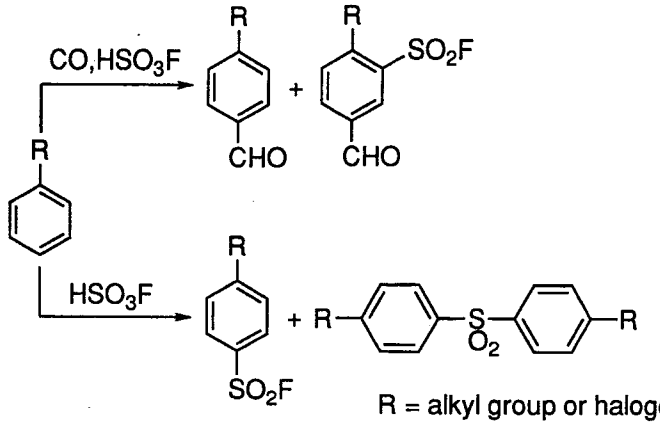
Sulfonyl compounds are useful raw materials for engineering plastics which are clear and thermostable. The synthesis of diaryl sulfones has been extensively studied and reviewed.[1] Generally, diaryl sulfones have been prepared from aromatic compounds by two- or three-step reactions via arylsulfonic acids or sulfonyl chlorides (eq-1).



R = alkyl group or halogen eq-1

The main synthetic methods for preparing diaryl sulfones have been Friedel-Crafts sulfonylations between arylsulfonyl halides and aromatic compounds in the presence of a suitable Lewis acid.[1] Other synthetic methods are the condensation of arylsulfonic acids with aromatic compounds using dehydration reagents[2] such as H_3PO_4 and P_2O_5. A one-pot synthesis of diaryl sulfones from aromatic compounds using H_2SO_4 and $(CF_3CO)_2O$ has been reported.[3]

In Chapter 1. 1-2, it was found that the formylation of aromatic compounds with CO using HSO_3F-SbF_5 produces aromatic aldehydes with unexpected products, namely arylsulfonyl fluorides and diaryl sulfones in a one-pot reaction (eq-2).



R = alkyl group or halogen eq-2

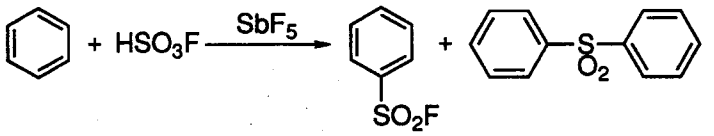
There is of interest to investigate whether the one-pot synthesis of diaryl sulfones can be achieved with the HSO_3F-SbF_5 system in the absence of CO.

In this Chapter, we wish to report a convenient synthesis of diaryl sulfones using HSO_3F-SbF_5.

3-2. Sulfonation of Aromatic Compounds Using HSO_3F-SbF_5

Synthesis of Diaryl Sulfones

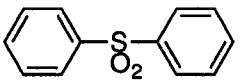
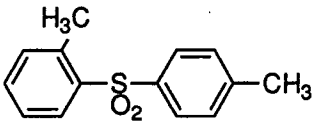
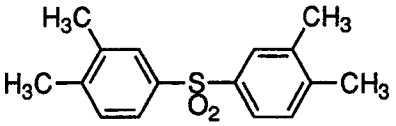
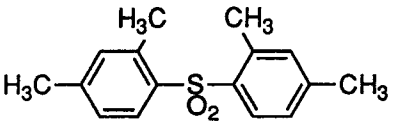
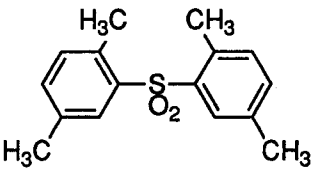
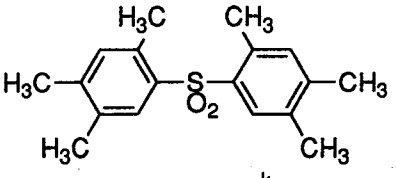
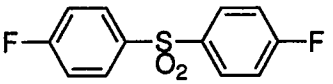
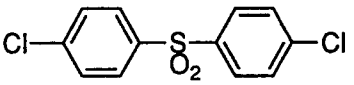
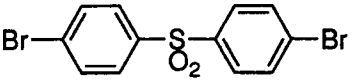
It is reported that aromatic compounds react with HSO_3F to give sulfone compounds.[4] When benzene (20 mmol) was reacted with HSO_3F (174 mmol) in the presence of SbF_5 (27.6 mmol), diphenyl sulfone was obtained in 94% yield with a little amounts of benzenesulfonyl fluoride (in 4% yield) (eq-3).



eq-3

The results of application of this reaction to a variety of aromatic compounds are summarized in Table 1. Diaryl sulfones were obtained in high yield from benzene, toluene, xylenes, 1,2,4-trimethylbenzene, fluoro-, chloro- and bromobenzene by a one-pot reaction, when an excess amount of SbF_5 relative to the substrate was added to HSO_3F. The appropriate amount of SbF_5 depended on the reactivity of the aromatic compounds for the electrophilic substitution, and the required amount of SbF_5 decreased with increasing reactivity of the aromatic compounds. In the case of polyalkylbenzenes such as 1,3,5- and 1,2,3-trimethylbenzene and tetramethylbenzenes, attempts to obtain diaryl sulfones with good yield were unsuccessful, and arylsulfonyl fluorides were formed as the main products. Although the sulfonyl group was mainly introduced to the para position of the substituent, the selectivity was not high. The 1,2-shift of the methyl group occurred in *o*- and *p*-xylene during sulfonation to give *m*-xylene derivatives. This behavior has also been observed in Friedel-Crafts alkylations,[5] and the migration of the methyl group is interpreted to be caused by the formation of the σ-complex in strong acids.

Table 1. Synthesis of Diaryl Sulfones[a]

substrate	temp. (°C)	SbF_5 (mmol)	products,yield(%) sulfonyl fluoride	products,yield(%) diaryl sulfone
benzene	50	27.6	4	 94
toluene	0	27.6	1 (100:0:0)[b]	 95(30:58:4:5:3)[c]
o-xylene	0	27.6	3 (64:16:20)[d]	 92(53:45:2)[e]
m-xylene	0	27.6	4 (87:13)[f]	 83(75:25:0)[g]
p-xylene	25	27.6	2 (100:0)[h]	 83(93:5:2)[i]
1,2,4-trimethylbenzene	0	20.7	20 (55:23:22)[j]	 71(67:24:9)[k]
fluorobenzene	50	69.0	0	 83(80:17:3)[l]
chlorobenzene	50	69.0	0	 94(66:27:7)[l]
bromobenzene	50	69.0	3 (100:0)[m]	 63(67:22:11)[l]

a) The sulfonation was carried out using 174 mmol of HSO_3F and 20 mmol

of aromatic compounds for 1h. The structures of main diaryl sulfone were depicted. b) Isomer ratio of 4-toluenesulfonyl fluoride : 3-toluenesulfonyl fluoride : 2-toluenesulfonyl fluoride. c) Isomer ratio of di(4-methylphenyl) sulfone : 2,4'-dimethyldiphenyl sulfone : di(2-methylphenyl) sulfone : 3,4'-dimethyldiphenyl sulfone : 2,3'-dimethyldiphenyl sulfone. d) Isomer ratio of 3,4-dimethylbenzenesulfonyl fluoride : 2,3-dimethylbenzenesulfonyl fluoride : 2,4-dimethylbenzenesulfonyl fluoride. e) Isomer ratio of bis(3,4-dimethylphenyl) sulfone : 2,3,3',4'-tetramethyldiphenyl sulfone : bis(2,3-dimethylphenyl) sulfone. f) Isomer ratio of 2,4-dimethylbenzenesulfonyl fluoride : 2,6-dimethylbenzenesulfonyl fluoride. g) Isomer ratio of bis(2,4-dimethylphenyl) sulfone : 2,2',4,6'-tetramethyldiphenyl sulfone : bis(2,6-dimethylphenyl) sulfone. h) Isomer ratio of 2,5-dimethylbenzenesulfonyl fluoride : 2,4-dimethylbenzenesulfonyl fluoride. i) Isomer ratio of bis(2,5-dimethylphenyl) sulfone : 2,2',4,5'-tetramethyldiphenyl sulfone : bis(2,4-dimethylphenyl) sulfone. j) Isomer ratio of 2,4,5-trimethylbenzenesulfonyl fluoride : 2,3,6-trimethylbenzenesulfonyl fluoride : 2,3,5-trimethylbenzenesulfonyl fluoride. k) Isomer ratio of di(2,4,5-trimethylphenyl) sulfone : 2,2',3,4',5',6-hexamethyldiphenyl sulfone : 2,2',3,4',5,5'-hexamethyldiphenyl sulfone. l) Isomer ratio of di(4-halophenyl) sulfone : 2,4'-dihalodiphenyl sulfone : di(2-halophenyl) sulfone. m) Isomer ratio of 4-bromobenzenesulfonyl fluoride : 2-bromobenzenesulfonyl fluoride.

Formation Path of Diaryl Sulfones

In order to investigate the formation path of diaryl sulfones, the sulfonation of benzene was carried out in various compositions of HSO_3F-SbF_5. The results are shown in Figure 1. The yield of benzenesulfonyl fluoride decreased with increasing amount of SbF_5. On the other hand, diphenyl sulfone was obtained in the highest yield when the molar ratio of SbF_5 : benzene was 1 : 1.5, and the formation of diphenyl sulfone was also observed even in the absence of SbF_5. This result clearly shows that the formation path of diphenyl sulfone is not only the Friedel-Crafts sulfonylation. It is proposed that arylsulfonyl chlorides and diaryl sulfones are secondary products, and the initial products are arylsulfonic acids in the sulfonation using HSO_3Cl.[6] Similarly, the

formation of benzene sulfonic acid was confirmed in the HSO_3F-SbF_5 system, and furthermore, it was found that HSO_3F acts as not only a sulfonation reagent but also a dehydration reagent to give diaryl sulfones from arylsulfonic acids with aryl compounds in control experiments. Therefore, the formation path of diaryl sulfones consists of two reactions which are the Friedel-Crafts sulfonylation and the dehydration sulfonylation (eq-4).

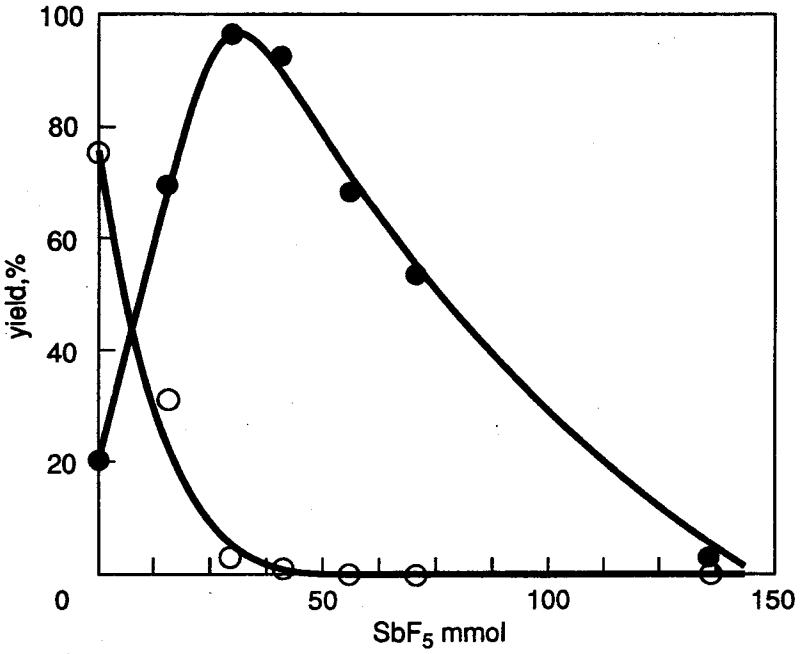
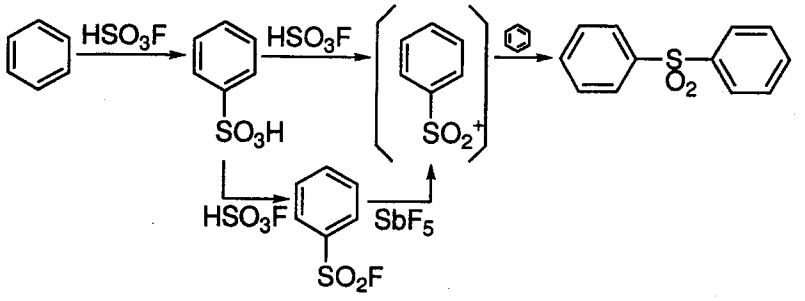


Figure 1. Influence of HSO_3F-SbF_5 compositions.[a]

a) The sulfonation was carried out using 174 mmol of HSO_3F and 20 mmol of benzene at 50°C for 1h. ○ and ● represent benzenesulfonyl fluoride and diphenyl sulfone, respectively.



eq-4

3-3. Experimental Section

All aromatic starting materials, HSO_3F and SbF_5 were of highest available

purity and were used without further purification. The yield determination and the identification of products were performed by GC, IR, MS, and ^{1}H,^{13}C-NMR.

Sulfonation Procedures

The required amount of HSO_3F and SbF_5 were added into a 300 mL three-necked flask under temperature control, and then aromatic compounds were added with vigorous stirring into the mixture of HSO_3F and SbF_5. After the reaction was over, the reaction mixture was quenched in ice-water and extracted by benzene. Products were characterized by IR, ^{1}H,^{13}C-NMR, MS, and elemental analysis, and the yields of them were determined by GC using internal standards. Products isolation was carried out by vacuum distillation or recrystallization in acetone-n-hexane system.

Physical Properties

di(4-methylphenyl)sulfone: IR(KBr): 1300, 1140 (SO_2) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.40 (s, 6H), 7.2-8.1 (m, 8H). ^{13}C-NMR($CDCl_3$): δ 21.5, 127.5, 129.9, 139.2, 143.9. Anal. Found: C, 68.43; H, 5.76; S, 12.94; M^+, 246. Calcd for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73; S, 13.02; M, 246.

bis(3,4-dimethylphenyl)sulfone: IR(KBr): 1305, 1115 (SO_2) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.31 (s, 12H), 7.2-7.8 (m, 6H). ^{13}C-NMR($CDCl_3$): δ 19.8, 19.9, 125.1, 128.3, 130.3, 137.9, 139.4, 142.5. Anal. Found: C, 70.04; H, 6.54; S, 11.82; M^+, 274. Calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61; S, 11.69; M, 274.

bis(2,4-dimethylphenyl)sulfone: IR(KBr): 1290, 1120 (SO_2) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.28 (s, 6H), 2.32 (s, 6H), 7.0-8.2 (m, 6H). ^{13}C-NMR($CDCl_3$): δ 19.9, 21.3, 126.6, 129.8, 133.3, 136.3, 137.5, 144.0. Anal. Found: C, 69.70; H, 6.59; S, 11.65; M^+, 274. Calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61; S, 11.69; M, 274.

bis(2,5-dimethylphenyl)sulfone: IR(KBr): 1295, 1125 (SO_2) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.36 (s, 6H), 2.48 (s, 6H), 7.3-8.4 (m, 6H). ^{13}C-NMR($CDCl_3$): δ 19.5, 20.8, 129.9, 133.0, 133.9, 134.8, 136.1, 138.8. Anal. Found: C, 69.91; H, 6.62; S, 11.64; M^+, 274. Calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61; S, 11.69; M, 274.

di(2,4,5-trimethylphenyl)sulfone: IR(KBr): 1295, 1110 (SO_2) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.57 (s, 18H), 7.01 (s, 2H), 7.98 (s, 2H). ^{13}C-NMR($CDCl_3$): δ 19.2, 19.4, 19.6, 130.5, 133.8, 134.4, 134.7, 136.5, 142.5. Anal. Found: C, 71.13; H, 7.31; S, 10.49; M^+, 303. Calcd for $C_{18}H_{22}O_2S$: C, 71.48; H, 7.33; S,

10.60; M, 303.

3-4. References and Notes

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Chapter 4. Coupling Reaction of Aromatic Compounds

4-1. Introduction

Aromatic radical cations are well-known species in electrochemical and gas phase reactions that produce biaryls through a coupling reaction with aromatic compounds, and the existence of aromatic radical cations in the liquid phase has recently been proposed by spectroscopic studies.[1] Metal salts such as $CuCl_2$,[2] $Tl(OCOCF_3)_3$,[3] and $Mn[CH(COCH_3)_2]_3$[4] and Lewis acids such as $AlCl_3$,[5] $FeCl_3$,[6] and $SbCl_3$[7] are reported to be effective oxidants for aromatic compounds that produce biaryls through the formation of aromatic radical cations. The latter reaction is known as the Scholl reaction.[8] While the formation of biaryls is regarded as conclusive evidence for the formation of aromatic radical cations as reaction intermediates in reaction mechanism studies, there have been few reports about the general synthetic application using the coupling reaction of aromatic radical cations to obtain biaryls because of their high reactivity.

On the other hand, NO^+ is remarkable as a diverse reagent not only for nitrosation[9] and nitration[10] but also for oxidation which produces aromatic radical cations.[11] In our laboratory, the reaction of 1-methylnaphthalene with NO was attempted in CF_3SO_3H-SbF_5 to obtain nitroso compounds. However, only a resin-like black solid was formed, and the formation of nitroso compounds was not observed at all. We considered that this result was caused by the influence of a strong acidic condition through the formation of aromatic radical cations because it is reported that the formation of radical cations tends to be favorable in acidic media.[12] Furthermore, it is proposed that $NOBF_4$ catalytically oxidizes naphthalene derivatives to give binaphthyl derivatives in the presence of O_2 under acidic conditions.[13] These results prompted us to study the coupling reaction of aromatic radical cations to obtain biaryls under acidic conditions.

In this Chapter, we wish to report the coupling reaction of naphthalene derivatives using CF_3SO_3H-$NaNO_2$ or SbF_5.

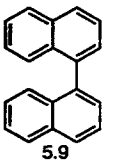
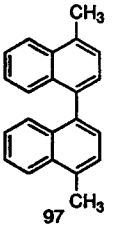
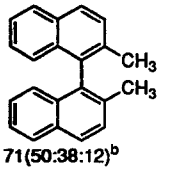
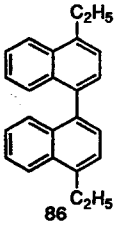
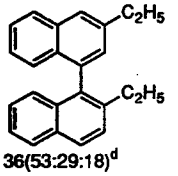
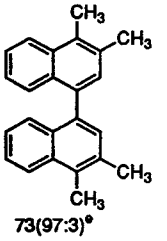
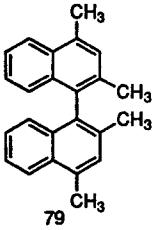
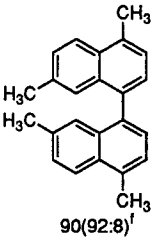
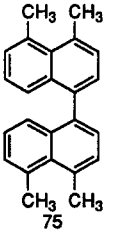
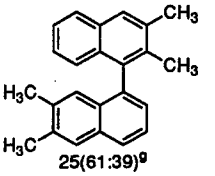
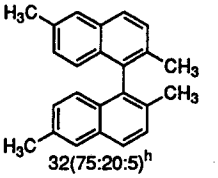
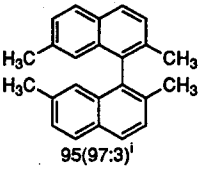
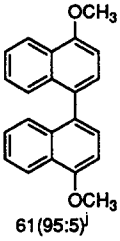
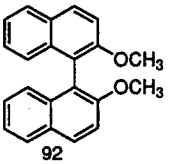
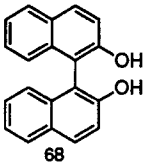
4-2. Coupling Reaction of Naphthalene Derivatives Using CF_3SO_3H-$NaNO_2$

Coupling Reaction of Naphthalene Derivatives

It is well-known that NO^+ is easily produced by treatment of $NaNO_2$

with Brønsted acids. In this study, we chose CF_3SO_3H as the Brønsted acid because a mixture of $NaNO_2$ and CF_3SO_3H in CH_3CN gave a homogeneous solution. When 1-methylnaphthalene (5 mmol) was added to the solution of CH_3CN (50 ml) with $NaNO_2$ (0.5 mmol) and CF_3SO_3H (10 mmol) at 0°C in air, the coupling reaction of 1-methylnaphthalene took place to produce 4,4'-dimethyl-1,1'-binaphthyl in 97% yield. Similarly, other naphthalene derivatives gave the corresponding binaphthyl derivatives as shown in Table 1. Most substrates were converted to give binaphthyl derivatives in good yields with high regioselectivity, however, some substrates showed different tendencies. The low yield of naphthalene was clearly caused by its low reactivity because most of the naphthalene was recovered after the reaction. On the contrary, 1-naphthol was too reactive even at -78°C for the formation of biaryls and resulted only in unidentifiable oily products. On the other hand, the deterioration of the yield and regioselectivity in the case of 2-methyl-, 2-ethyl-, 2,3-, 2,6-dimethylnaphthalene seems to be caused by steric hindrance because 2-methoxynaphthalene, which is more reactive but has a smaller steric hindrance at the 1-position than 2-methylnaphthalene, gave the coupling product in excellent regioselectivity although 2-methylnaphthalene showed low regioselectivity. Furthermore, 1,4- and 1,5-dimethylnaphthalene, which are more reactive than 1-methylnaphthalene, gave only trace amounts of coupling products resulting in the recovery of unreacted substrates. Therefore, steric hindrance is obviously an important factor for controlling the yield and regioselectivity during this reaction. A similar result is reported for the iodination reaction of aromatic compounds using ICl.[14]

Table 1. Coupling Reaction of Naphthalene Derivatives[a]

substrate	temp. (°C)	solvent	products, yield(%)
naphthalene	0	CH_3CN	 5.9
1-methyl-naphthalene	0	CH_3CN	 97
2-methyl-naphthalene	0	CH_3CN	 71(50:38:12)[b]
1-ethyl-naphthalene	0	CH_3CN	 86
2-ethyl-naphthalene[c]	0	CH_3CN	 36(53:29:18)[d]
1,2-dimethyl-naphthalene	-40	CH_3CN	 73(97:3)[e]
1,3-dimethyl-naphthalene	-40	CH_3CN	 79
1,4-dimethyl-naphthalene[c]	-40	CH_3CN	trace
1,5-dimethyl-naphthalene[c]	-40	CH_3CN	trace
1,6-dimethyl-naphthalene	-40	CH_3CN	 90(92:8)[f]
1,8-dimethyl-naphthalene	-40	CH_3CN	 75
2,3-dimethyl-naphthalene[c]	-40	CH_3CN	 25(61:39)[g]
2,6-dimethyl-naphthalene[c]	-40	CH_3CN	 32(75:20:5)[h]
2,7-dimethyl-naphthalene	-40	CH_3CN	 95(97:3)[i]
1-methoxy-naphthalene	-78	CH_3CN-CH_2Cl_2	 61(95:5)[j]
2-methoxy-naphthalene	-78	CH_3CN-CH_2Cl_2	 92
1-naphthol	-78	CH_3CN-CH_2Cl_2	0
2-naphthol	-78	CH_3CN-CH_2Cl_2	 68

a) The reactions were carried out using 0.5 mmol of $NaNO_2$, 10 mmol of CF_3SO_3H, and 5 mmol of substrate in air for 1h. b) Isomer ratio of 2,2'-dimethyl-1,1'-binaphthyl : 2,3'-dimethyl-1,1'-binaphthyl : other isomers. c) Unreacted substrate was recovered. d) Isomer ratio of 2,3'-diethyl-1,1'-binaphthyl : 2,2'-diethyl-1,1'-binaphthyl : other isomers. e) Isomer ratio of 3,3',4,4'-tetramethyl-1,1'-binaphthyl : other isomers. f) Isomer ratio of 4,4',7,7'-tetramethyl-1,1'-binaphthyl : other isomers. g) Isomer ratio of 2,3,6',7'-tetramethyl-1,1'-binaphthyl : 2,2',3,3'-tetramethyl-1,1'-binaphthyl. h) Isomer ratio of 2,2',6,6'-tetramethyl-1,1'-binaphthyl : 2,3',6,7'-tetramethyl-1,1'-binaphthyl : other isomers. i) Isomer ratio of 2,2',7,7'-tetramethyl-1,1'-binaphthyl : other isomers. j) Isomer ratio of 4,4'-dimethoxy-1,1'-binaphthyl : other isomers.

Formation Path of Products

In the reaction of 1-methylnaphthalene with $NaNO_2$ in the presence of CF_3SO_3H, five products, nitro-1-methylnaphthalene **1**, dinitro-1-methylnaphthalene **2**, 4,4'-dimethyl-1,1'-binaphthyl **3**, nitro-4,4'-dimethyl-1,1'-binaphthyl **4**, and dinitro-4,4'-dimethyl-1,1'-binaphthyl **5** were formed, and the product composition was dependent on the combination of reagents. When the amount of $NaNO_2$ was small, the product **3** was produced mainly in the presence of CF_3SO_3H. With an increasing amount of $NaNO_2$, the nitration proceeded to give **1**, **2**, **4**, and **5**. On the other hand, an increase in the CF_3SO_3H amount caused the formation of **3**, **4**, and **5**. However, no nitroso products were obtained, which shows that NO^+ acts only as an oxidant for 1-methylnaphthalene. The identified isomers of **1** were 2-nitro-, 3-nitro-, 4-nitro-, 5-nitro-, and 8-nitro-1-methylnaphthalene. However, in the case of **4**, only one isomer, 2-nitro-4,4'-dimethyl-1,1'-binaphthyl, was identified because of the difficulty in separation. The main isomers of **1** and **4** were 4-nitro-1-methylnaphthalene (about 60% in ratio) and 2-nitro-4,4'-dimethyl-1,1'-binaphthyl (about 80% in ratio), respectively. Isomers of **2** and **5** were not identified because of their difficulty in separation. Products **1** and **3** were clearly formed through the coupling reaction of the 1-methylnaphthalene radical cation with NO_2[15] or 1-methylnaphthalene,[10] respectively. On the other hand, there are two plausible reaction paths for **2**, **4**, and **5**. For

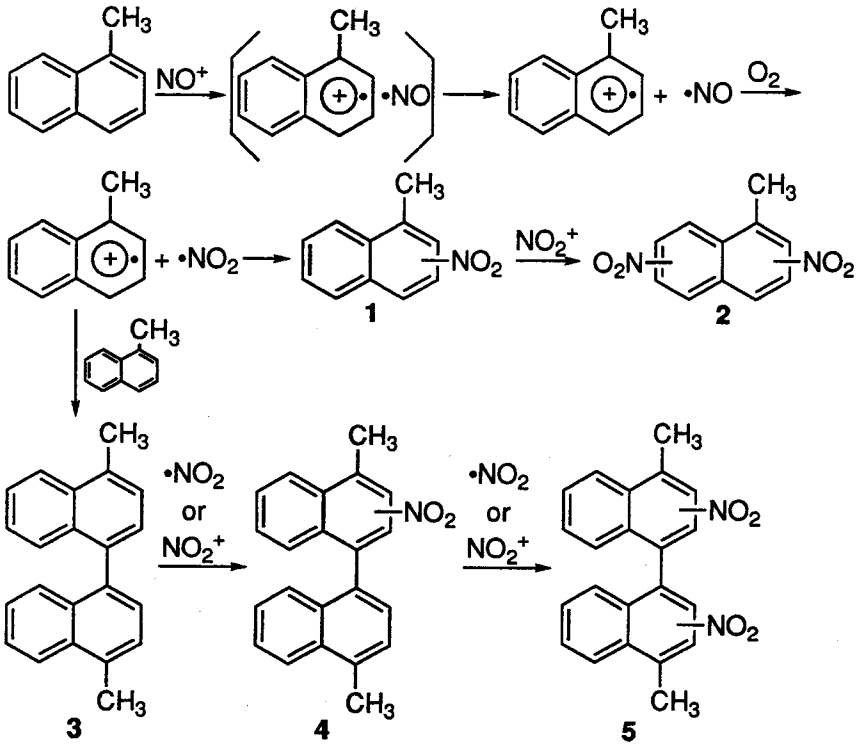
2, the plausible reaction paths are the nitration of **1** with NO_2^+ and the coupling reaction of the **1** radical cation with NO_2. For **4** and **5**, the paths include the nitration (the electrophilic substitution by NO_2^+ and the coupling reaction by NO_2) of **3** or **4** and the coupling reaction of the 1-methylnaphthalene radical cation or the **1** radical cation with **1**, respectively. In order to investigate the formation path of the products, the reactions were carried out using a mixture of 1-methylnaphthalene and **1**, and the results are summarized in Table 2.

Table 2. Reaction Using Nitro-1-methylnaphthalene[a]

substrate composition 1-methylnaphthalene : nitro-1-methylnaphthalene (mmol)	products,yield(%)				
	1	**2**	**3**	**4**	**5**
0 : 0.7	93	0	0	0	0
0.7 : 0.7	46	0	1.9	4.8	19
0.7 : 0	0	1.1	1.4	1.9	15

a) The reactions were carried out using 1 mmol of $NaNO_2$, 10 mmol of CF_3SO_3H, and 50 ml of CH_3CN at 0°C in air for 1h. The yield was determined on the basis of the total amounts of substrates.

When the reaction was conducted using only **1**, no reaction occurred. Therefore, **2** was produced by the nitration of **1** with NO_2^+ because the **1** radical cation was not formed by NO^+. Next, the reaction using equimolar amounts of 1-methylnaphthalene and **1** was carried out to give the same amount of **1** as the former reaction using only **1**, but the reaction using only 1-methylnaphthalene did not give **1** at all. These results show that **1** is inert under these conditions, and **4** and **5** were formed through the nitration of **3** with NO_2^+ or NO_2. Therefore, the formation path of the products can be described as follows (eq-1).



eq-1

Catalytic Cycle of NO^+

In order to investigate the catalytic cycle of NO^+, the reactions of 1-methylnaphthalene were carried out using $NaNO_2$ with CF_3SO_3H under different conditions and using $NOBF_4$, NO_2BF_4, or NO_2SbF_6 instead of $NaNO_2$. The results are tabulated in Table 3.

Table 3. Coupling Reaction of 1-Methylnaphthalene[a]

entry	oxidant	CF_3SO_3H (mmol)	atmosphere	products,yield(%)				
				1	**2**	**3**	**4**	**5**
1	$NaNO_2$	10	air	0	0	97	1.5	0
2	$NaNO_2$	10	N_2	0	0	15	0	0
3	$NOBF_4$	10	air	0	0	90	0	0
4	$NOBF_4$	0	air	5	0	0.8	0	0
5	NO_2BF_4	10	air	0.7	0	86	0	0
6	NO_2SbF_6	10	air	2.3	0	55	0	0

a) The reactions were carried out using 0.5 mmol of an oxidant, 5 mmol of 1-methylnaphthalene, and 50 ml of CH_3CN at 0°C for 1h.

The coupling reaction of 1-methylnaphthalene using $NaNO_2$ with CF_3SO_3H at 0°C in air gave 4,4'-dimethyl-1,1'-binaphthyl **3** and nitro-4,4'-dimethyl-1,1'-binaphthyl **4** in 97% and 1.5% yields, respectively (entry 1). However, when

the reaction using the same amounts of materials was carried out under a N_2 atmosphere (entry 2), the yield of **3** decreased from 97% to 15%, and **4** was not formed. Therefore, the oxidation of NO with O_2 to form NO_2 after the electron transfer of NO^+ with 1-methylnaphthalene is one step of the cycle. Next, the reactions using $NOBF_4$ were conducted in the presence or absence of CF_3SO_3H. In the presence of CF_3SO_3H (entry 3), **3** was obtained in excellent yield similar to the reaction using $NaNO_2$ (entry 1). However, in the absence of CF_3SO_3H, only a small amount of 1-methylnaphthalene was converted to **1** as the main product and **3**, and unreacted substrate was recovered (entry 4). These results show that CF_3SO_3H protonates NO_2, N_2O_4 and $NO^+NO_3^-$ exactly to reproduce NO^+ with the formation of an equal amount of NO_2^+.[16] Recently, it is proposed that NO_2^+ has the ability to function not only as an electrophile but also as an oxidant, which oxidizes NO, to form NO^+.[17] In order to study whether NO_2^+ acts as the oxidant of NO to form NO^+ or as an electrophile to form **1**, the reaction was conducted using NO_2BF_4 and NO_2SbF_6, which is known to always contain a small amount of NO^+ as an impurity, under the same conditions in the presence of CF_3SO_3H (entries 5 and 6). Similar to $NOBF_4$ (entry 3), **3** was formed mainly, but the formation of **1** was observed.[18] These results clearly show that NO_2^+ acted as the electrophile under the conditions when the NO concentration was low, and the formation of **1** was not observed when $NaNO_2$ and $NOBF_4$ were used in the presence of CF_3SO_3H. Therefore, it seems that NO_2^+ acts as the oxidant of NO to produce NO^+ rather than as an electrophile to form **1** in the $NaNO_2$-CF_3SO_3H system. These results suggest the following catalytic cycle of NO^+ (eq-2).[19]

$$NaNO_2 + 2CF_3SO_3H \longrightarrow CF_3SO_3NO + CF_3SO_3Na + H_2O$$

$$2{\bullet}NO + O_2 \longrightarrow 2{\bullet}NO_2$$

$$2{\bullet}NO_2 \rightleftharpoons N_2O_4 \rightleftharpoons NO^+NO_3^-$$

$$NO^+NO_3^- + 2CF_3SO_3H \longrightarrow CF_3SO_3NO + CF_3SO_3NO_2 + H_2O$$

$$\bullet NO + CF_3SO_3NO_2 \longrightarrow CF_3SO_3NO + \bullet NO_2 \qquad \text{eq-2}$$

Role of Acid

In the $NaNO_2$-CF_3SO_3H system, the nitration of 1-methylnaphthalene was almost completely inhibited when $NaNO_2$ was used in a catalytic amount.

Therefore, equimolar amounts of $NaNO_2$ and 1-methylnaphthalene were used with various amounts of CF_3SO_3H to investigate the influence of CF_3SO_3H on the nitration. The results are represented in Figure 1.

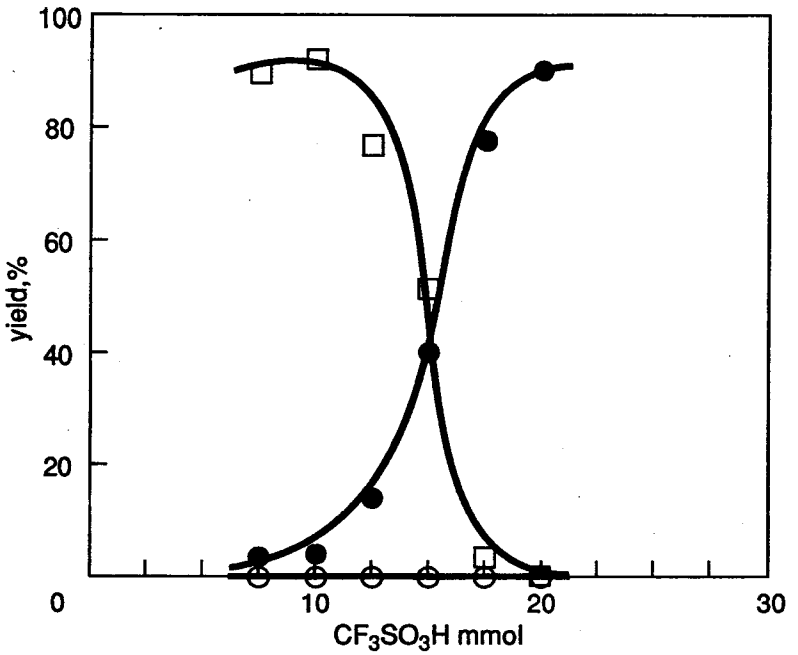


Figure 1. Coupling reaction of 1-methylnaphthalene using 5 mmol of $NaNO_2$.[a] a) The reactions were carried out using 5 mmol of 1-methylnaphthalene at 0°C in air for 1h. The marks of □, ○, and ● represent the yield of **1**, **3**, and **4**, respectively, and **2** and **5** were not formed under these conditions.

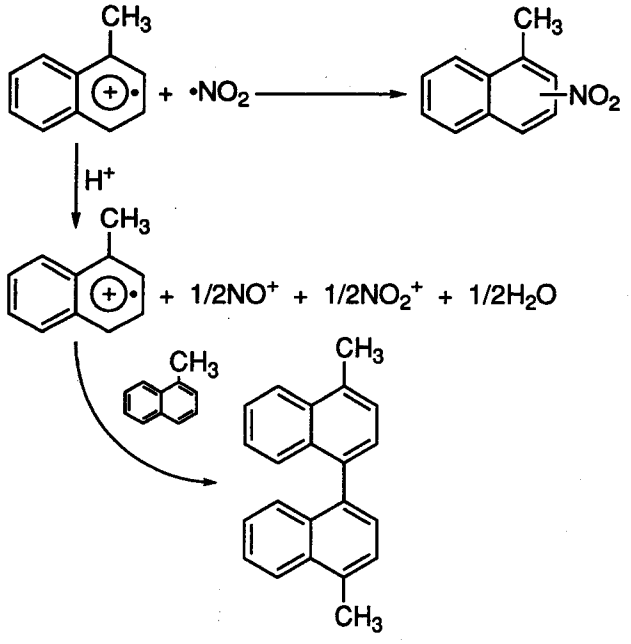
The yield of **1** decreased with an increasing amount of CF_3SO_3H. On the contrary, the yield of **4** increased with an increase in CF_3SO_3H. This result reveals that CF_3SO_3H has the ability to inhibit the nitration of 1-methylnaphthalene with NO_2.[20] The ability of CF_3SO_3H to inhibit the nitration seems to stem from the ability to protonate NO_2 (N_2O_4 and $NO^+NO_3^-$) before the coupling reaction of NO_2 with the 1-methylnaphthalene radical cation.[19] In order to clarify this deduction, the reactions of 1-methylnaphthalene were conducted using several acids such as FSO_3H, CF_3SO_3H, and H_2SO_4 under the same conditions, and the influence of acid strength on the ability to inhibit the nitration was studied. The order of acid strength of these acids is well-known as FSO_3H > CF_3SO_3H > H_2SO_4. The results are shown in Table 4.

Table 4. Influence of Acid Strength[a]

acid	products,yield(%)				
	1	2	3	4	5
FSO_3H	23	0	2.1	64	0
CF_3SO_3H	48	0	0	39	0
H_2SO_4	54	8.3	1.1	1.6	0

a) The reactions were carried out using 5 mmol of $NaNO_2$, 15 mmol of acid, 5 mmol of 1-methylnaphthalene, and 50 ml of CH_3CN at 0°C in air for 1h.

The yield order of coupling products (the sum of **3**, **4**, and **5**) was consistent with the acid strength order. This result evidently shows that acids have two roles in this reaction, which are the production of NO^+ from $NaNO_2$ and the protonation of the formed NO_2 (N_2O_4 and $NO^+NO_3^-$) to inhibit the nitration and to produce NO^+ and NO_2^+. Strong acids give the formation of biaryls an advantage over the formation of nitro compounds (eq-3).



eq-3

Influence of Solvent

We chose CH_3CN as the solvent because the highly polar solvent gave homogeneous solutions of $NaNO_2$-CF_3SO_3H, $NOBF_4$, NO_2BF_4, and NO_2SbF_6. On the contrary, less polar solvents such as CH_2Cl_2, $CHCl_3$, CCl_4, CCl_2FCClF_2, benzene and n-hexane gave heterogeneous solutions of $NaNO_2$-CF_3SO_3H. When 1-methylnaphthalene (5 mmol) was added to the heterogeneous $CHCl_3$ solution

of $NaNO_2$ (5 mmol) with CF_3SO_3H (15 mmol), the coupling reaction proceeded to give only **3** in 73% yield. The result using $CHCl_3$ shows a different tendency from the result using CH_3CN where **1** and **3** were formed in 48% and 39% yields, respectively. The catalytic coupling reaction using $CHCl_3$ also proceeded to give only **3** in 67% yield. Moreover, it was found that H_2SO_4, which did not have sufficient acid strength to inhibit the nitration in CH_3CN, could allow the catalytic coupling reaction to give only **3** in 61% yield. A similar tendency was observed in other solvents such as CH_2Cl_2, CCl_4, CCl_2FCClF_2, benzene, and n-hexane, and no nitro compounds were detected when the heterogeneous solutions of $NaNO_2$-CF_3SO_3H were used. These results are shown in Table 5. In the heterogeneous systems, 1-methylnaphthalene was completely converted, and a resin-like black solid was formed as a by-product which might be produced by polymerization through the radical cation reaction. The tendency of the coupling reaction clearly reflects the polarity of the solvents because the acid strength in solvents is dependent on the polarity of the solvents, and acids can act as stronger acids in low polar solvents, namely, under low solvation conditions. The heterogeneous systems may be useful for industrial applications because the use of inexpensive materials such as H_2SO_4 and $NaNO_2$ is possible.

Table 5. Influence of Solvent[a]

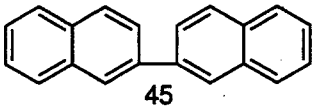
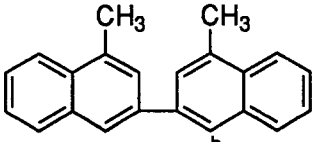
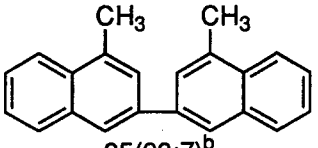
solvent	$NaNO_2$ (mmol)	acid (mmol)	products,yield(%)				
			1	**2**	**3**	**4**	**5**
CH_3CN	5	CF_3SO_3H(15)	48	0	39	0	0
$CHCl_3$	5	CF_3SO_3H(15)	0	0	73	0	0
$CHCl_3$	0.5	CF_3SO_3H(15)	0	0	67	0	0
$CHCl_3$	0.5	H_2SO_4(25)	0	0	61	0	0
CH_2Cl_2	0.5	CF_3SO_3H(15)	0	0	7.9	0	0
CCl_4	0.5	CF_3SO_3H(15)	0	0	39	0	0
CCl_2FCClF_2	0.5	CF_3SO_3H(15)	0	0	36	0	0
benzene	0.5	CF_3SO_3H(15)	0	0	54	0	0
n-hexane	0.5	CF_3SO_3H(15)	0	0	25	0	0

a) The reactions were carried out using 5 mmol of 1-methylnaphthalene and 50 ml of a solvent at 0°C in air for 1h.

Scholl Reaction Using SbF_5

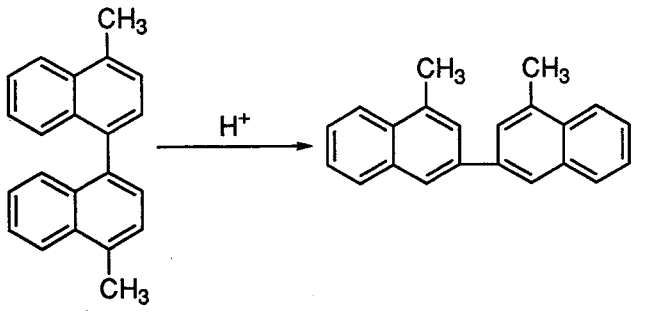
The reaction of naphthalene using $NaNO_2$-CF_3SO_3H did not give good results because of the low reactivity of naphthalene. On the other hand, the coupling reaction of aromatic compounds using Lewis acids as an oxidant is known as the Scholl reaction.[8] Therefore, SbF_5 was used as the oxidant in CCl_2FCClF_2, and the reactions of naphthalene and 1-methylnaphthalene were carried out. The results are summarized in Table 6. The yields of binaphthyl derivatives were not very good, and 1-methylnaphthalene gave better results in the presence of CF_3SO_3H. The reactions gave 2,2'-binaphthyl and 4,4'-dimethyl-2,2'-binaphthyl as the main products from naphthalene and 1-methylnaphthalene, respectively. This observed regioselectivity is quite different from that using NO^+, although both reactions proceed through the formation of radical cations. In a control experiment, it was found that 4,4'-dimethyl-1,1'-binaphthyl was converted to 4,4'-dimethyl-2,2'-binaphthyl in the presence of CF_3SO_3H-SbF_5 in CCl_2FCClF_2, and a similar tendency is reported for Friedel-Crafts alkylations.[21] This result shows that 1,1'-binaphthyl derivatives produced first are converted to more stable 2,2'-binaphthyl derivatives by strong acidic media such as HF-SbF_5 which is formed during the coupling reaction when strong Lewis acids such as SbF_5 are used as an oxidant (eq-4).[22]

Table 6. Scholl Reaction Using SbF_5[a]

substrate	temp. (°C)	additive (mmol)	products,yield(%)
naphthalene	r.t.	–	 45
1-methyl-naphthalene	r.t.	–	 23(81:19)[b]
1-methyl-naphthalene	0	CF_3SO_3H (10)	 35(93:7)[b]

a) The reactions were carried out using 10 mmol of SbF_5, 5 mmol of substrate, and 50 ml of CCl_2FCClF_2 for 1h. b) Isomer ratio of 4,4'-dimethyl-2,2'-

binaphthyl : other isomers.



eq-4

4-3. Experimental Section

All reagents were of the highest available purity and were used without further purification. Dry CH_3CN was used when $NOBF_4$, NO_2BF_4, and NO_2SbF_6 were used. The product yields were determined with GC by the internal standard method, and the separated products were used for the analysis. The product structures were identified by NMR (^{1}H-, ^{13}C-NMR, COSY, NOESY, CHSHF, and COLOC) and mass analysis after isolation by recrystallization or GPC.

Coupling Reaction Procedures Using $NaNO_2$, $NOBF_4$, NO_2BF_4, and NO_2SbF_6

The required amount of oxidant and acid were placed in a three-necked flask (300ml) containing 50 ml of solvent (40 ml for solid substrates such as naphthalene, 1,4-, 1,5-, 1,8-, 2,3-, 2,6-, 2,7-dimethylnaphthalene, 2-methoxynaphthalene, and 2-naphthol), and a substrate was added to the mixture with vigorous stirring in air under temperature control. When the substrate was a solid, the solution of the substrate dissolved in a suitable solvent was added to a mixture (10 ml of CH_3CN for naphthalene, 1,4-, 1,8-, 2,7-dimethylnaphthalene, 20 ml of CH_3CN for 2,3-dimethylnaphthalene, a mixture of CH_3CN (5 ml) and CH_2Cl_2 (5 ml) for 2-methoxynaphthalene and 2-naphthol, and a mixture of CH_3CN (10 ml) and CH_2Cl_2 (10 ml) for 1,5-, 2,6-dimethylnaphthalene). After 1h, the reaction mixture was poured into ice-water and extracted with $CHCl_3$. The product yields and structures were determined according to the general procedures.

Scholl Reaction Procedures Using SbF_5

A substrate (5 mmol) was placed in a three-necked flask (300 ml)

containing CCl_2FCClF_2 (40 ml). The solution of SbF_5 and 10 ml of CCl_2FCClF_2 were added to the flask with vigorous stirring at room temperature. After 1h, the reaction mixture was poured into ice-water and extracted with $CHCl_3$. The product yields and structures were determined according to the general procedures. On the other hand, the mixture of CF_3SO_3H (10 mmol) and SbF_5 (10 mmol) as an oxidant were added to a solution of 1-methylnaphthalene with 50 ml of CCl_2FCClF_2 at 0°C and then stirred vigorously for 1h.

Isomerization Procedure

CF_3SO_3H (10 mmol) and SbF_5 (5 mmol) were placed in a three-necked flask containing CCl_2FCClF_2 (50 ml), and then 4,4'-dimethyl-1,1'-binaphthyl powder (5 mmol) was added into the mixture with vigorous stirring at 0°C. After 1h, the reaction mixture was quenched with ice-water and extracted with $CHCl_3$. The recovery of dimethylbinaphthyls was 69%, and the isomer ratio was 88%, 1%, and 11% for 4,4'-dimethyl-2,2'-binaphthyl, 4,4'-dimethyl-1,1'-binaphthyl, and other isomers, respectively.

4-4. References and Notes

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When the reaction of 1-methylnaphthalene (5 mmol) with $NOBF_4$ (5 mmol) was carried out in the absence of CF_3SO_3H at -45°C in CH_3CN (25 ml) with CH_2Cl_2 (25 ml), five isomers of nitro-1-methylnaphthalenes, 2-nitro-, 3-nitro-, 4-nitro-, 5-nitro-, and 8-nitro-1-methylnaphthalene, were identified, and the isomer distribution was 4:1:84:8:3. This isomer distribution shows fairly agreement with the results of the coupling nitration of 1-methylnaphthalene radical cation salt with NO_2 at -70°C, 8:0:88:1:3 (see ref. 15). Therefore, we concluded that the nitration is a radical reaction.

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It is reported that N_2O_4 which is in the equilibrium with NO_2 dissociates to $NO^+NO_3^-$ in a solvent (see ref. 16). In the presence of a strong acid such as CF_3SO_3H, NO_3^- is evidently converted to NO_2^+ and H_2O.

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The results are very interesting because both yields of **1** (entries 5 and 6) were significantly less than with $NOBF_4$ (entry 4). To explain these results, there are two plausible interpretations, the oxidation of 1-methylnaphthalene by NO_2^+ to produce radical cations and the inhibition of NO_2^+ attack to 1-methylnaphthalene by the protonation. The former has been studied widely, but still controversial (see ref. 12, 15, 18-a). The latter is derived from the fact that the protonation inhibits electrophilic substitutions (see ref. 18 b-d) and means that NO_2^+ attack may be inhibited more strongly than NO^+ attack to 1-methylnaphthalene by the protonation, namely, NO^+ reaction proceeds as the main reaction because NO_2^+ and NO^+ reactions seem to proceed through inner- and outer-sphere reaction, respectively (see ref. 12, 15, 18-a,e). We are now studying about this problem using superacids.

(19) The catalytic cycle in ref. 13 is significantly different from our proposal and is shown as follows.

$$2ArH + 2NO^+ \rightarrow ArAr + 2NO + 2H^+$$

$$2NO + 2H^+ + 0.5O_2 \rightarrow 2NO^+ + H_2O$$

$$NO + NO_2 + 2H^+ \rightarrow 2NO^+ + H_2O$$

Concerning the catalytic cycle of NO^+, it is needed to explain the inhibition of the nitration by superacids, namely, the role of superacids as a NO_2 scavenger. However, in ref. 13, the role of acids is only to produce NO^+, and there is no description about the role of acids to inhibit

the nitration. Therefore, we proposed that superacids can act as a NO_2 scavenger by the protonation of N_2O_4 and $NO^+NO_3^-$, not NO_2. The important concept is that O_2 oxidizes two NO to give two NO_2, therefore, the produced NO_2 by O_2 may exist as N_2O_4 or $NO^+NO_3^-$ first, and then, N_2O_4 and $NO^+NO_3^-$ are converted to NO^+ and NO_2^+ by superacids before the coupling reaction of the radical cation with NO_2 occurs to give nitro compounds.

(20) The catalytic cycle of NO^+ shows that the concentration of NO_2 in the reaction systems is depending on not only the superacid concentration (or the acid strength of superacids) but also the reaction time. According to the catalytic cycle, the concentration of NO_2 in the presence of superacids is low at the initial stage of the reaction and increases with the progress of the reaction by the formation of NO_2 from NO_2^+. Therefore, it is difficult to inhibit the nitration of produced binaphthyl derivatives by the addition of superacids because radical cations of binaphthyl derivatives are a secondary product.

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Conclusions

The new synthetic methods to obtain aromatic aldehydes, diaryl sulfones, and binaphthyl derivatives were found by using superacids, and the investigation about these reaction mechanisms were performed.

In Chapter 1, the formylation of aromatic compounds using HSO_3F-SbF_5 and HF-SbF_5 were examined. In HSO_3F-SbF_5, both formylation and sulfonation take place to give formyl and sulfonyl compounds. The product composition is strongly dependent on the acid strength of the HSO_3F-SbF_5 system, and the formylation becomes predominant with increasing the acidity of the HSO_3F-SbF_5 system. The formylation of aromatic compounds such as benzene, toluene, xylenes, indan, tetralin, fluorobenzene, chlorobenzene, and bromobenzene can be achieved with high yield under atmospheric CO pressure at 0°C. In the case of alkylbenzenes, including toluene, xylenes, 1,3,5-trimethylbenzene and tetralin, formylalkylbenzenesulfonyl fluorides, which are new compounds, are obtained by a one-pot reaction as well as alkylbenzaldehydes. The direct introduction of a formyl and sulfonyl group can be achieved in alkylbenzenes. The formation path of the new compounds is a two-step reaction comprised of the formylation as the first step and the sulfonation as the second step. In HF-SbF_5, the diformylation of polynuclear aromatic compounds such as diphenyl, 4-methyldiphenyl, diphenylmethane, dibenzyl, naphthalene, and methylnaphthalenes occurs to give dialdehydes by a one-pot reaction. Generally, dialdehyde is obtained when the SbF_5/substrate molar ratio is greater than 1.

In Chapter 2, the reaction mechanism of Gattermann-Koch formylation was studied in three aspects, the formylation rate, the nature of the formyl cation, and the regioselectivity of the formylation. The results of the formylation rate investigation shows that the formylation rate of aromatic compounds should be explained by considering their protonation equilibria. The extent of inhibition of the formylation by the protonation is related to the extent of conversion to an inactive σ-complex, and therefore, the apparent relative formylation rate of aromatic compounds is not generally proportional to their relative basicities. The study on the nature of the formyl cation in superacids reveals that the formyl cation has dual reactivity, an electrophile and a Brønsted

acid, and protonated aromatic compounds also act as a Brønsted acid to produce formyl cations. Therefore, the formylation has the priority over other typical electrophilic substitutions under conditions where most aromatic compounds are protonated because the formyl cation is reproduced close to the aromatic compounds by the protonation of CO with not only superacids but also protonated aromatic compounds. The investigation about the regioselectivity of the formylation suggests that the protonation of aromatic compounds influences on the regioselectivity of the formylation under conditions where the formylation proceeds under the solvent-cage-like atmosphere.

In Chapter 3, the sulfonation of aromatic compounds was conducted in the HSO_3F-SbF_5 system. It was shown that the HSO_3F-SbF_5 system is useful for a one-pot synthesis of diaryl sulfones in high yield from aromatic compounds such as benzene, toluene, xylenes, 1,2,4-trimethylbenzene, fluorobenzene, chlorobenzene, and bromobenzene. The formation path of diaryl sulfones consists of two reactions which are the Friedel-Crafts sulfonylation and the dehydration sulfonylation.

In Chapter 4, the coupling reaction of naphthalene derivatives using CF_3SO_3H-$NaNO_2$ or SbF_5 was performed. It was found that the coupling reaction of naphthalene derivatives through the formation of aromatic radical cations using $CF_3SO_3HNaNO_2$ catalytically gives the corresponding 1,1'-binaphthyl derivatives from naphthalene, methyl-, ethyl-, dimethyl-, methoxy-, and hydroxynaphthalenes in air. The acids have two roles in the reaction which are the production of NO^+ and the inhibition of the nitration by the protonation of NO_2 (N_2O_4 and $NO^+NO_3^-$). Therefore, strong acids are necessary to more preferentially produce binaphthyl derivatives than nitro compounds. On the other hand, the Scholl reaction using strong Lewis acids such as SbF_5 produces the secondary products, the 2,2'-binaphthyl derivatives, through the isomerization of the 1,1'-binaphthyl derivatives due to protonation.