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Synthesis of Polynuclear Aromatic Dialdehyde in HF–SbF_5

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The reaction of aromatic compounds with CO in acid catalysts resulting in aldehyde is known as the Gattermann–Koch formylation.[1,2] After Gattermann and Koch reported their original work on the synthesis of *p*-tolualdehyde from toluene and CO in the HCl-$AlCl_3$-Cu_2Cl_2 system,[1] various acid catalyst systems such as HF–BF_3,[3] HF-CF_3SO_3H-BF_3,[4] and CF_3SO_3H[4,5] have also been investigated for this reaction. Recently, we reported that the HSO_3F–SbF_5 system is an effective medium for Gattermann-Koch formylation.[6] In spite of extensive studies in various superacid systems, only one precident for dialdehyde formation from bibenzyl in HF–BF_3 is known.[7] It is of interest to investigate whether or not diformylation of polynuclear aromatic compounds such as naphthalene and biphenyl can be achieved by the Gattermann-Koch formylation. In a previous paper,[8] we reported that the diformylation of these polynuclear aromatic compounds could be achieved using the HF–SbF_5 system.

In this paper, we wish to report on the progress of our study, including dialdehyde formation from methylnaphthalenes and 4-methyldiphenyl and the role of SbF_5.

We found that HSO_3F–SbF_5 is an effective formylation catalyst system, and both formylation and sulfonation took place to give alkylbenzaldehyde, formylalkylbenzenesulfonyl fluoride, alkylbenzenesulfonyl fluoride, and bis(alkylphenyl)sulfone from alkylbenzene.[6,9] Therefore, the formylation of naphthalene and diphenyl was carried out under high CO pressure (60 atm) in HSO_3F–SbF_5. Although aldehyde was obtained from alkylbenzene in good yield even under atmospheric CO pressure,[6] sulfonation by HSO_3F was the main reaction and only a trace of aldehyde was obtained in the case of naphthalene and biphenyl. Therefore, the HF–SbF_5 system which was comprised of HF instead of HSO_3F was used as a formylation catalyst. When naphthalene was added into a mixture of HF and SbF_5 under CO pressure, at first naphthaldehyde was formed, and then the formyl group introduction to naphthaldehyde occurred to yield 1,5-naphthalenedialdehyde mainly.

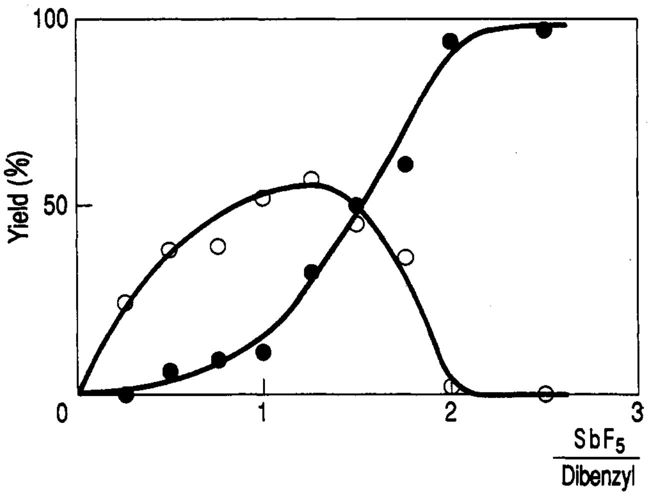
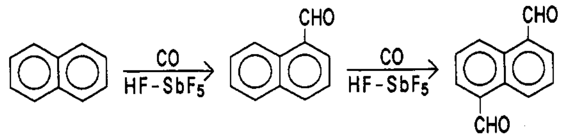


Figure 1. The composition of monoaldehyde and dialdehyde depending on the molar ratio of SbF_5/dibenzyl. The formylation was carried out using 10 mmol of bibenzyl and 500 mmol of HF under 20 atm of CO pressure at 0 °C for 2h: (1) bibenzylaldehyde; (2) bibenzyldialdehyde.



Dialdehyde synthesis from polynuclear aromatic compounds is summarized and the structures of the main products are depicted in Table I. Biphenyl and bibenzyl gave dialdehydes with excellent yields. The yield of dialdehyde from 4-methylbiphenyl 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. 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.

In our previous work,[8] 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 the bibenzyl formylation showed a different tendency as shown in Figure 1. In the case of bibenzyl, dialdehyde was produced even under conditions where the SbF_5/bibenzyl molar ratio was less than 1. It was suggested that the aromatic rings of bibenzyl are chemically independent because of the ethylene chain between them. These results show that the first introduced formyl group strongly inactivates the substrate; therefore, a strong acid catalyst such as the HF–SbF_5 system, which is known as the strongest superacid,[10] and an excess amount of SbF_5 are necessary to obtain dialdehyde. The role of SbF_5 in HF is to produce formyl cation by the protonation of CO because no formylation occurred in the absence of SbF_5.

On the other hand, the formylation of 1-methylnaphthalene proceeded more slowly with the increase of the

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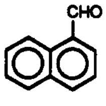
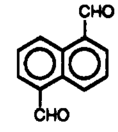
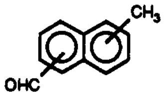
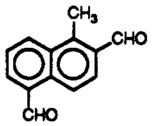
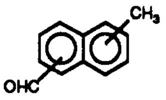
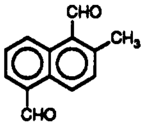
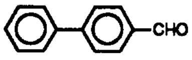
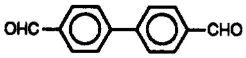
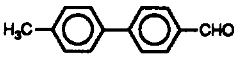
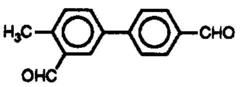
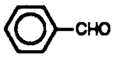
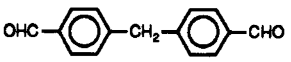
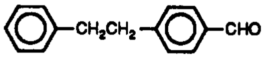
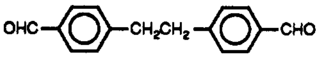
Table I. Diformylation of Polynuclear Aromatic Compounds[a]

substrate	time (h)	product, yield (%)	
naphthalene[b]	2	 0	 53 (73:18:9:0)[c]
1-methylnaphthalene	6	 44[d]	 47 (66:34)[c]
2-methylnaphthalene	6	 29[d]	 44 (36:64)[f]
biphenyl	3	 0	 81 (93:7:0)[g]
4-methylbiphenyl	2	 0	 27 (97:3)[h]
diphenylmethane	2	 61[i]	 31 (91:4:5)[j]
bibenzyl	2	 0	 98 (90:3:7)[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] 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. [c] Isomer ratio of 1,5-naphthalenedialdehyde:1,6-naphthalenedialdehyde:1,7-naphthalenedialdehyde:1,8-naphthalenedialdehyde. [d] Isomer ratio could not be determined. [e] Isomer ratio of 1-methyl-2,5-naphthalenedialdehyde:methylnaphthalenedialdehydes. [f] Isomer ratio of 2-methyl-1,5-naphthalenedialdehyde:methylnaphthalenedialdehydes. [g] Isomer ratio of 4,4′-biphenyldialdehyde:2,4′-biphenyldialdehyde:2,2′-biphenyldialdehyde. [h] Isomer ratio of 4-methyl-3,4′-biphenyldialdehyde:4-methylbiphenyldialdehydes. [i] Diphenylmethanealdehyde was not obtained. [j] Isomer ratio of 4,4′-diphenylmethanedialdehyde:2,4′-diphenylmethanedialdehyde:2,2′-diphenylmethanedialdehyde. [k] Isomer ratio of 4,4′-bibenzyldialdehyde:2,4′-bibenzyldialdehyde:2,2′-bibenzyldialdehyde.

SbF_5/1-methylnaphthalene molar ratio although most formylations readily occurred with increasing acid/substrate molar ratio.[4] The result is shown in Figure 2. 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.[6] These phenomena suggested that the proton produced by SbF_5 had two roles, which are the protonation of a CO and a substrate. Therefore, highly 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 arenium ion complex which is formed by protonation in strong acids.[11]

The isomer distribution of products from biphenyl, 4-methylbiphenyl, diphenylmethane, and bibenzyl showed high para positional selectivity similar to other Gattermann–Koch formylations.[12] However, naphthalenes showed a low positional selectivity. In our previous work,[8] it has been clarified that the positional selectivity of formyl group is controlled by its thermodynamic behavior.

In conclusion, the diformylation of polynuclear aromatic compounds with CO was achieved in the HF–SbF_5 system. In the formylation of highly basic aromatic compounds, the rate of formylation was slower because of protonation of the substrate when the acidity of HF–SbF_5 was increased. The proton produced by SbF_5 had two roles, which are the protonation of a CO and a substrate.

Experimental Section

All aromatic starting materials, HF, HSO_3F (Moritakagaku), SbF_5 (Aldrich), and CO (Nihonsanso) were of highest available purity and were used without further purification. Yanagimoto G-3800 and G-6800 gas chromatographs equipped with an online automatic integrator were used for GC analysis. A 25-m capillary column (OV-1701) was used for isomer separation, whereas a 1.5-m packed column (OV-17) was utilized for yield

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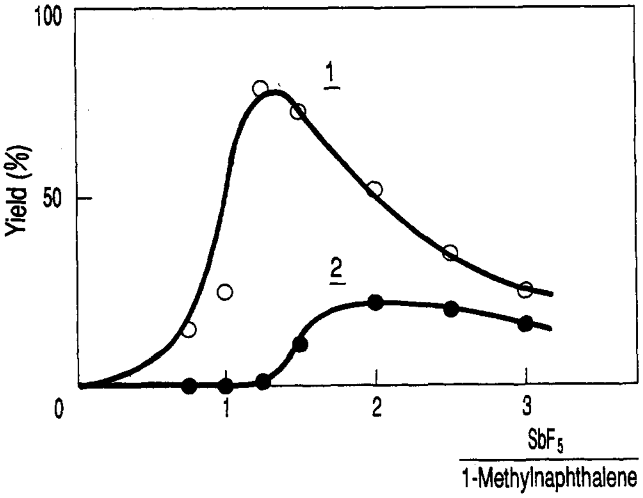

Figure 2. The composition of monoaldehyde and dialdehyde depending on the molar ratio of SbF_5/1-methylnaphthalene. The formylation was carried out using 10 mmol of 1-methylnaphthalene and 500 mmol of HF under 20 atm of CO pressure at 0 °C for 2 h: (1) methylnaphthaldehyde; (2) methylnaphthalenedialdehyde.

determination. MS analysis (GC–MS) was performed on a Hitachi M-2000 fitted with a 50-m capillary column (OV-1701). ^{1}H-NMR spectra were recorded on a Hitachi R-24B, and ^{13}C-NMR spectra were recorded on a Nihondenshi FX-200. Infrared analysis was accomplished on a Nihonbunko IRA-1.

Formylation Procedures in HF–SbF_5. The required amounts of HF, SbF_5, and aromatic compounds were put into a 100-mL Hastelloy Taiatsugarasu 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 by GC and characterized by IR, ^{1}H-NMR, ^{13}C-NMR, elemental analysis, and mass spectra after isolation by vacuum distillation or recrystallization in an acetone–*n*-hexane system.

Formylation Procedures in HSO_3F–SbF_5. The mixture of 87 mmol of HSO_3F and 69 mmol of SbF_5 was poured into a 100-mL autoclave with cooling at 0 °C, and the autoclave was sealed. After 60 atm of CO was introduced into it, 5 mmol of naphthalene or biphenyl was added and reacted with vigorous stirring for 1 h at 0 °C. After the reaction was over, the reaction mixture was quenched in ice–water, extracted by benzene, and analyzed similar to formylation procedures.

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Supplementary Material Available: Spectral data for dialdehydes (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.