Diformylation of Polynuclear Aromatic Compounds with CO in HF–SbF$_5$

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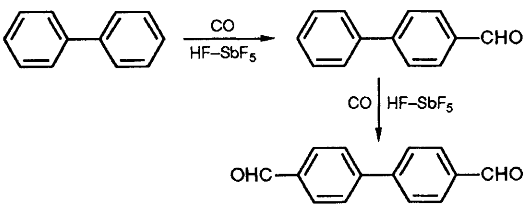
Diformylation of polynuclear aromatic compounds, such as naphthalene, diphenyl, diphenylmethane and dibenzyl with CO was accomplished in a HF–SbF$_5$ system by a one-pot reaction.

Formylation of aromatic compounds with CO is known as the Gattermann–Koch reaction using a mixture of HCl, AlCl$_3$ and a small amount of Cu$_2$Cl$_2$.[1] Other catalyst systems, such as HF–BF$_3$,[2] CF$_3$SO$_3$H[3] and CF$_3$SO$_3$H–SbF$_5$[4] have also been investigated for this reaction, and recently we have reported that the HSO$_3$F–SbF$_5$ system is an effective catalyst for the Gattermann–Koch reaction especially at atmospheric pressure of CO.[5]

The example of diformylation has been reported only with dibenzyl in the HF–BF$_3$ system,[6] and diformylation of polynuclear aromatic compounds linked by a short bond or condensed, such as diphenyl, diphenylmethane and naphthalene has not been known yet. It was of interest to investigate whether diformylation of these polynuclear aromatic compounds could occur by the Gattermann–Koch reaction, and the results of this investigation are now reported.

The HF–SbF$_5$ system, which has been represented to be the strongest superacid,[7] was examined as the diformylation catalyst, since the formylation occurred more easily with increasing acidity of the catalyst systems.[4,8] 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 positional selectivity as shown in eqn. (1). Formylation was carried out using various compositions of HF–SbF$_5$, and the yield of mono- and di-aldehyde depending on the molar ratio of SbF$_5$: diphenyl is shown in Fig. 1. Only monoaldehyde was obtained when the amount of SbF$_5$ was less than that of diphenyl. The formation of dialdehyde was observed when the molar ratio of SbF$_5$: diphenyl was greater than one, and the number of introduced formyl groups was almost parallel with the amount of SbF$_5$.



(1)

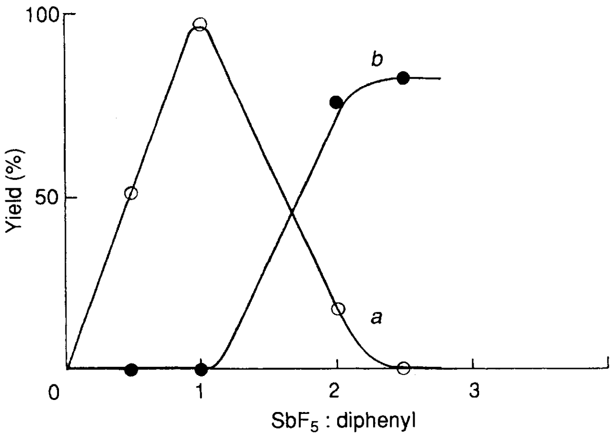
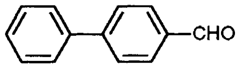
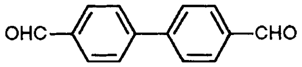
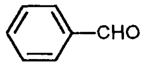
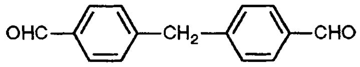
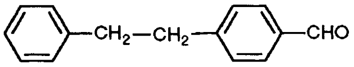
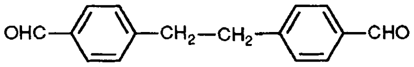
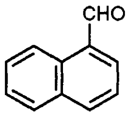
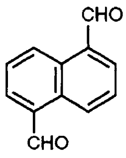


Fig. 1 The composition of mono- and di-aldehyde depending on the molar ratio of SbF$_5$: diphenyl. Formylation was carried out using 10 mmol of diphenyl and 500 mmol of HF under 20 atm of CO pressure at 0 °C for 3 h: (*a*) diphenylaldehyde; (*b*) diphenyldialdehyde.

Table 1 Diformylation of aromatics[a]

Substrate	*t*/h	Product, yield (%)[b]	
Diphenyl	3	 0	 81(93:7:0)[c]
Diphenylmethane	2	 61[d]	 31(91:4:5)[e]
Dibenzyl	2	 0	 98(90:3:7)[f]
Naphthalene[g]	3	 28	 39(71:18:11:0)[h]

[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 structure of main isomer was depicted. [c] Isomer ratio of 4,4′-diphenyldialdehyde : 2,4′-diphenyldialdehyde : 2,2′-diphenyldialdehyde. [d] Diphenylaldehyde 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 60 mmol of SbF$_5$. [h] Isomer ratio of 1,5-naphthalenedialdehyde : 1,6 naphthalenedialdehyde : 1,7-naphthalenedialdehyde : 1,8-naphthalenedialdehyde.

Table 2 Formylation of naphthalene[a]

SbF$_5$ (mmol)	Reaction time/h	CO Pressure /atm	Yield (%) Naphthalenealdehyde[b]	Naphthalenedialdehyde[c]
30	3	20	87 (100 : 0)	6 (39 : 61 : 0 : 0)
40	3	20	88 (97 : 3)	8 (41 : 59 : 0 : 0)
50	3	20	72 (100 : 0)	11 (54 : 46 : 0 : 0)
30	3	60	91 (100 : 0)	7 (36 : 64 : 0 : 0)
40	3	60	78 (100 : 0)	10 (56 : 44 : 0 : 0)
50	3	60	59 (100 : 0)	23 (57 : 28 : 15 : 0)
60	1	20	90 (100 : 0)	4 (31 : 64 : 4 : 0)
60	2	20	84 (100 : 0)	11 (51 : 38 : 11 : 0)
60	4	20	55 (100 : 0)	25 (66 : 19 : 15 : 0)

[a] The formylation was carried out using 10 mmol of naphthalene and 1 mol of HF at 0 °C. [b] Isomer ratio of 1-naphthalenealdehyde : 2-naphthalenealdehyde. [c] Isomer ratio of 1,5-naphthalenedialdehyde : 1,6-naphthalenedialdehyde : 1,7-naphthalenedialdehyde : 1,8-naphthalenedialdehyde.

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$_5$. Attempts to extend this reaction to diphenylmethane, dibenzyl and naphthalene gave dialdehydes, respectively, as summarized in Table 1. Products were characterized by IR, ^{1}H NMR, ^{13}C NMR and mass spectroscopy, and elemental analysis. In the formylation of diphenylmethane, methylene chain cleavage occurred to give benzaldehyde. On the other hand, such behaviour was not observed with diphenyl and dibenzyl. This difference in behaviour is derived from the easy protonation of the methylene chain of diphenylmethane to cause cleavage.[9] In the formylation of naphthalene, an excess of SbF$_5$ was necessary because the formylation rate of naphthalene was slower than that of other aromatics. Formylation of other condensed polynuclear aromatics, such as anthracene, phenanthrene and pyrene in the HF–SbF$_5$ system failed to give aldehydes, and the raw materials were recovered.

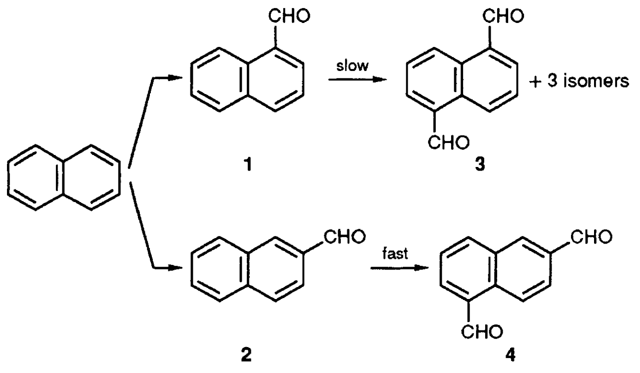
The isomer distribution of products showed high *para* positional selectivity similar to other Gattermann–Kock reactions[8,10] except for naphthalene. The high *para* positional selectivity in the Gattermann–Koch reaction may be due to steric hindrance and stability of the arenium-ion (σ-complex) like intermediate. This formylation is an electrophilic substitution by the formyl cation, protonated CO (HCO^+), and *para* substitution is favoured if the transition state of the highest energy of the reaction is the arenium-ion like intermediate, where a *para* substituent is more stabilizing than an *ortho* or *meta* substituent.[8,10]

The isomer distribution of naphthalenedialdehydes attributed to reaction conditions, acid strength, reaction time and CO pressure is summarized in Table 2. The positional selectivity of naphthalenedialdehydes was lower than that of other dialdehydes, and the isomer distribution varied depending on only the yield of dialdehydes, regardless of acid strength, reaction time and CO pressure. When the dialde-

Table 3 Formylation of 1-naphthalenealdehyde[a]

SbF_5 (mmol)	T/°C	Reaction time/h	Yield (%)	
			Naphthalenealdehyde[b]	Naphthalenedialdehyde[c]
120	−30	24	8 (100 : 0)	82 (51 : 6 : 27 : 16)
80	0	4	0	58 (63 : 8 : 26 : 3)
60	50	1	5 (100 : 0)	43 (80 : 18 : 2 : 0)

[a] The formylation was carried out using 10 mmol of 1-naphthalenealdehyde containing 3% 2-naphthalenealdehyde and 1 mol of HF under 20 atm of CO pressure. [b] Isomer ratio of 1-naphthalenealdehyde : 2-naphthalenealdehyde. [c] Isomer ratio of 1,5-naphthalenedialdehyde : 1,6-naphthalenedialdehyde : 1,7-naphthalenedialdehyde : 1,8-naphthalenedialdehyde.



Scheme 1

hydes yield was low, **4** was the main component, however, **3** became dominant with increasing the dialdehydes yield. This behaviour is explained from the difference in the formylation rate between **1** and **2** as shown in Scheme 1.

In the initial stage of dialdehyde formation, minor product **2** reacted with CO faster than the major product **1** to give **4**, therefore, **4** was the main isomer, and **2** was not observed in most cases as listed in Table 2. It was confirmed that the formylation of **2** was faster than that of **1** to give only **4**, and no formyl-group migration occurred in control experiments.

The isomer distribution by temperature in the formylation of **1** is shown in Table 3. The selectivity to **3** increased with rising temperature. This result clarified that the positional selectivity was controlled by the thermodynamic behaviour.

In summary, diformylation of diphenyl, diphenylmethane, dibenzyl and naphthalene with CO could be achieved in $HF–SbF_5$ system with high positional selectivity, and it was found that the positional selectivity was controlled thermodynamically. Dialdehydes obtained in this work will be useful as raw materials for engineering plastics after conversion to dicarboxylic acids or dialcohols.

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