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The chloromethylation of biphenyls catalyzed by group 3 and 4 metal triflates

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Abstract

Some group 3 and 4 metal triflates, such as $Sc(OTf)_3$, $Yb(OTf)_3$, $Sm(OTf)_3$, $In(OTf)_3$ and $Hf(OTf)_4$, worked as highly effective catalysts for the chloromethylation of biphenyl (BP) and 9,10-dihydrophenanthrene (DHP) with hydrochloric acid and trioxane under heterogeneous organic and aqueous biphasic conditions. The catalytic activity decreased in the order: $Sc(OTf)_3 > Yb(OTf)_3 > Sm(OTf)_3 \gg In(OTf)_3 > Hf(OTf)_4$. $Sc(OTf)_3$ had the highest activity among them. They were stable under reaction conditions and active enough at less than 5% against biphenyls. The chloromethylation of BP catalyzed by the triflates gave a mixture of 4-chloromethylbiphenyl (**Ia**), 2-chloromethylbiphenyl (**Ib**), 4,4′-bis(chloromethyl)biphenyl (**IIa**) and 2,4′-bis(chloromethyl)biphenyl (**IIb**). The selectivity for **IIa** among the isomers was around 70% for all triflates. The addition of small amount of acetic acid and formic acid enhanced the chloromethylation of **Ia** to **IIa**. DHP also gave 2,7-bis(chloromethyl)-9,10-dihydrophenanthrene (**IV**) in high yield by the triflate catalyzed chloromethylation with hydrochloric acid and trioxane.

The catalysis by triflates occurred in heterogeneous mixture of hydrocarbon, trioxane and triflate in aqueous hydrochloric acid. Since the triflate stayed in aqueous phase, the catalyst was easily separated from the products and recycled for new reaction without significant loss of the catalytic activity.

Keywords: Chloromethylation; Group 3 and 4 metal triflate; $Sc(OTf)_3$; Biphenyl; 9,10-Dihydrophenanthrene; 4,4′-Bis(chloromethyl)biphenyl; Trioxane; Bi-phase catalysis

1. Introduction

Chloromethylated aromatic hydrocarbons are promising key intermediates for fine-chemicals, pharmaceuticals, polymers, etc., because of their easy transformation to many chemicals. The chloromethylation of aromatic hydrocarbons has been well documented in the papers [1–6]. The reaction of aromatic hydrocarbons with hydrochloric acid and trioxane or paraformaldehyde as formaldehyde precursor sometimes gave the chloromethylated products without catalyst [5,6]; however, the rate was low and not enough for the practical chemical processes. Lewis acids such as zinc chloride, stannic chloride and born trifluoride are well known catalysts for the chloromethylation; among these acids, zinc chloride is an effective catalyst in hydrochloric acid solution [1,2]; however, stoichiometric amount of a catalyst to substrate is required and makes work up procedure tedious. These catalysts, in general, suffer from the inherent problem of corrosiveness, high susceptibility to water, difficulty in catalyst recovery, environmental hazards, waste control after the reaction, etc. Another drawback using these catalysts is the formation of carcinogenic chloromethylethers and the chlorine contamination of aromatic rings. It is important to replace the catalysts with environment conscious catalysts, which are active under mild conditions and can be easily recovered after the reactions and reused for the new reactions [7]. Recently, transition-metal triflates, particularly rare earth metal triflates, act as Lewis acid; they are stable in aqueous medium and active for the catalysis in organic synthesis [8–12].

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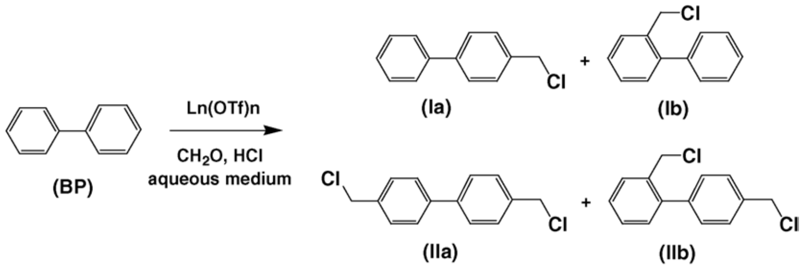
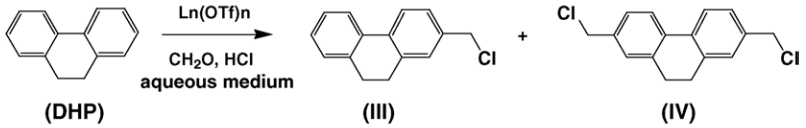


Scheme 1.



Scheme 2.

In previous paper, we applied group some 3 and 4 metal triflates, such as $Sc(OTf)_3$, $Yb(OTf)_3$, $Sm(OTf)_3$, $In(OTf)_3$ and $Hf(OTf)_4$ for the catalysts of the chloromethylation of mononuclear aromatic hydrocarbons and found that $Sc(OTf)_3$ was the most active among them under heterogeneous organic and aqueous biphasic conditions [13]. For examples, $Sc(OTf)_3$ catalyzed chloromethylation of *m*- and *p*-xylenes afforded effectively bis(choloromethyl)xylenes with substitution at 1,2,4,5-positions by methyl and chloromethyl groups, which are key chemicals for the production of pyromellitic dianhydride.

The chloromethylation of biphenyls is also a promising way of their functionalization for advanced materials. There were several patents described the effective synthesis of 4,4′-bis(chloromethyl)biphenyl by the chloromethylation of biphenyl. Some of recent examples were carried out using paraformaldehyde, gaseous hydrogen chloride and thionyl chloride with $ZnCl_2$ [14] in strong organic acids, such as trifluroacetic acid and trichloroacetic acid without or with $ZnCl_2$ [15,16], or formaldehyde and hydrochloric acid with sulfuric acid and phase transfer catalysts [17]. However, these examples involve the similar tedious procedures, such as separation of product and catalyst, recovery of catalysts and/or waste treatment and the possibility for the formation of chloromethyl methyl ether and bis(chloromethyl)ether as by-products, chlorine contamination of aromatic rings, etc. In this paper, we describe the chloromethylation of biphenyl (BP) and 9,10-dihydrophenanthrene (DHP) with some group 3 and 4 metal triflates in aqueous medium to elucidate key factors for environmentally conscious catalyses.

2. Experimental

2.1. Reagents

Scandium, ytterbium, samarium, hafnium and indium triflates and triflic acid were purchased from Tokyo Kasei Chem. Ind., Co. Ltd., Tokyo, Japan. Zinc chloride and trioxane were obtained from Kishida Chemicals Co. Ltd., Osaka, Japan. BP and DHP were obtained from Aldrich Japan.

2.2. Reaction procedures

Typical procedures for the chloromethylation are shown in the case of BP as follows: a mixture of BP (1.5 g, 9.7 mmol), trioxane (6.6 g, 73.3 mmol), 36% aqueous hydrochloric acid (16.4 g, 157 mmol) and $Sc(OTf)_3$ (0.2 g, 0.5 mmol) were stirred in 30 ml round flask for 22 h at 80 °C. After cooling, the organic products were extracted with chloroform and dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo, and organic residue was again resolved in chloroform and analyzed by HLPC using Finepack SIL C-18-5 $\varphi 4.6 \times 250$ mm (JASCO, Tokyo, Japan). The mixture of 4-chloromethylbiphenyl (**Ia**), 2-chloromethylbiphenyl (**Ib**), 4,4′-bis(chloromethyl)biphenyl (**IIa**) and 2,4′-bis(chloromethyl)biphenyl (**IIb**) obtained as the products. Each product was separated by silica gel column chromatography using hexane–chloroform (3/1 then 1/1) as eluent. All compounds obtained had satisfactory analytical data by ^{1}H and ^{13}C NMR, IR and elemental analysis. The PCB contents in the products were less than the limit of detection (0.03 wt. ppm) by GC–MS analysis done by Shinnikka Environmental Eng. Co. Ltd.

Analytical data of the chloromethylation of 9,10-dihydrophenanthrene are as follows:

*2-(Chloromethyl)-9,10-dihydrophenanthrene (**III**)*

m.p. 47–48 °C. IR(KBr): 688.5 cm^{-1} (C–Cl). ^{1}H NMR (500 MHz, δ in ppm from TMS in $CDCl_3$): 2.84 (s, 4H, Ar–CH_2–Ar), 4.56(s, 2H, CH_2), 7.21–7.29(m, 5H, ArH), 7.69–7.71(m, 2H, ArH), ^{13}C NMR(125 MHz, δ in ppm from TMS in $CDCl_3$): 28.83, 46.22, 123.76, 124.02, 126.98, 127.20, 127.66, 128.14, 128.36, 133.87, 134.72, 136.34, 137.36, 137.81. Elemental analysis: C, 78.77%, H, 5.73% calculated from $C_{15}H_{13}Cl$. observed: C, 78.85%, H, 5.81%.

*2,7-Bis(chloromethyl)-9,10-dihydrophenanthrene (**IV**)*

m.p. 150.8–154.2 °C. IR(KBr): 694 cm^{-1} (C–Cl). ^{1}H NMR (500 MHz, δ in ppm from TMS in $CDCl_3$): 2.86 (s, 4H, Ar–CH_2–Ar), 4.60 (s, 4H, CH_2), 7.25–7.34 (m, 4H, ArH), 7.74–7.75 (m, 2H, ArH). ^{13}C NMR (500 MHz, δ in ppm from

TMS in $CDCl_3$): 28.81, 46.17, 124.17, 127.30, 128.45, 134.19, 136.71, 137.89. Elemental analysis: C, 69.33%, H, 5.09% calculated from $C_{16}H_{14}Cl_2$. observed: C, 69.24%, H, 5.12%.

The conversion of BP was based on the consumed amount of BP and the selectivity for **IIa** was calculated from combined amounts of **IIa** and **IIb**, and the selectivity for **Ia** was similarly calculated from amounts of **Ia** and **Ib**.

2.3. Recycle of catalyst

The reaction catalyzed by $Sc(OTf)_3$ was carried out in the same manner as in previous section. After the separation of organic layer, the aqueous catalytic solution was saturated with HCl by bubbling of dry hydrogen chloride gas and subjected to the further reaction. The reaction was carried out by the addition of BP (1.5 g, 8.3 mmol) and trioxane (5.6 g, 62.2 mmol) for 22 h at 80 °C. The analysis of products was carried out as described previously.

3. Results and discussion

3.1. The chloromethylation of biphenyl

The chloromethylation of BP was examined with hydrochloric acid and trioxane as formaldehyde precursor by using some group 3 and 4 metal triflates as catalyst. Typical results are shown in Fig. 1. The triflates such as $Sc(OTf)_3$, $Yb(OTf)_3$, $Sm(OTf)_3$, $In(OTf)_3$ and $Hf(OTf)_4$ are the excellent catalysts for the chloromethylation of BP. BP gave a mixture of **Ia** and **Ib**, **IIa** and **IIb**. The triflates were enough active for the chloromethylation in catalytic amounts and the conversions were more than 90% for all triflates under our reaction conditions. The yield for the chloromethylated biphenyls was excellent to almost quantitative for consumed BP and decreased in the order: $Sc(OTf)_3 > Yb(OTf)_3 > Sm(OTf)_3 \gg In(OTf)_3 > Hf(OTf)_4$, and the yields of **IIa** and **IIb** were also increased in the order. The selectivities for **IIa** among its isomers were around 70% for all triflates; however, the yield of **IIa** and **IIb** was lower than **Ia** and **Ib** under the conditions shown in Fig. 1. From these results, all triflates are active for the chloromethylation of BP, and $Sc(OTf)_3$ has the highest activity among them.

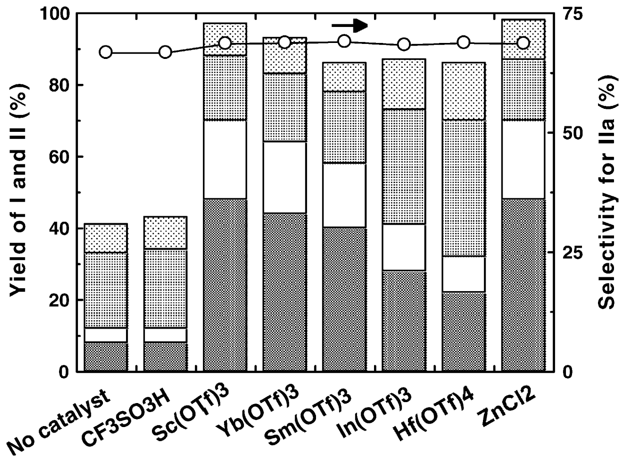


Fig. 1. Influences of type of triflates on the chloromethylation of BP. Reaction conditions: BP, 1.5 g (9.7 mmol); catalyst, 0.5 mmol (triflate), 9.7 mmol ($ZnCl_2$); trioxane, 6.6 g (72.7 mmol); conc. HCl, 16.4 g (157 mmol); temperature, 80 °C; period, 22 h. Legend: ▩, **IIa**; □, **IIb**; ▦, **Ia**; ▨, **Ib**.

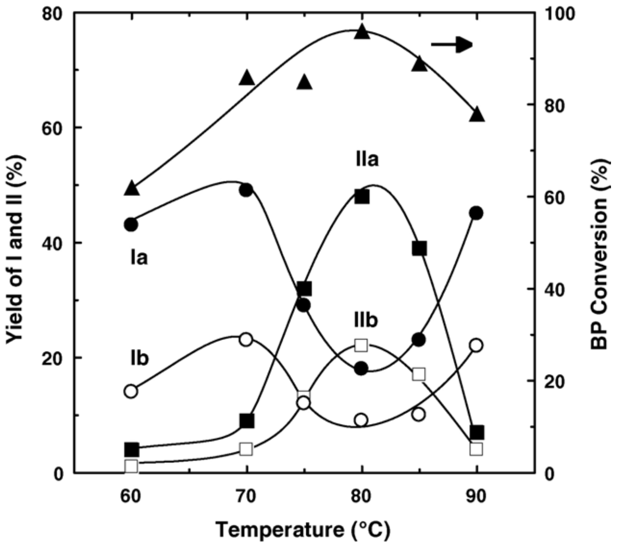


Fig. 2. Influences of temperature on the chloromethylation of BP. Reaction conditions: BP, 1.5 g (9.7 mmol); $Sc(OTf)_3$, 0.24 g (0.5 mmol); trioxane, 6.6 g (72.7 mmol); conc. HCl, 16.4 g (157 mmol); period, 22 h.

The chloromethylation proceeded without the catalyst under our conditions: yield of the products was as high as 40%, and the combined yield of **IIa** and **IIb** was less than 15%. The activity for triflic acid was almost the same level as the reaction without the catalyst. These results show that the activities of the chloromethylation in Fig. 1 are due to the triflates and not to triflic acid liberated from the triflate during the reaction. From the results discussed above, we chose $Sc(OTf)_3$ as the catalyst to elucidate the factor to control the catalysis, because it had the highest activity for **IIa** among the triflates. $ZnCl_2$ gave the products in almost the same level as $Sc(OTf)_3$; however, it was necessary to use an approximately stoichiometric amount for corresponding yields.

Fig. 2 shows the influences of reaction temperature on the chloromethylation. The catalytic activity increased with the temperature to 80 °C; however, the conversion was decreased at 90 °C. The yields of **Ia** and **Ib** were 40–50% at 60–70 °C and decreased with the increase in the temperature. The yields reached minimum at 80 °C and again increased at 90 °C. On the other hand, the yields of **IIa** and **IIb** reached the maximum at 80 °C and then, decreased at 80–90 °C. The selectivity for **IIa** among its isomers was unchanged by raising the temperature. These results show that the moderate temperature, such as 80 °C enhanced the consecutive formation of **IIa** and **IIb** via **Ia** and **Ib**. The decrease of the yield of **IIa** and **IIb** at higher temperature is due to the decrease of HCl concentration in the reaction mixtures.

The influences of the concentration of hydrochloric acid at 80 °C are shown in Fig. 3. No reaction occurred in the absence of hydrochloric acid, and the increase in the concentration of

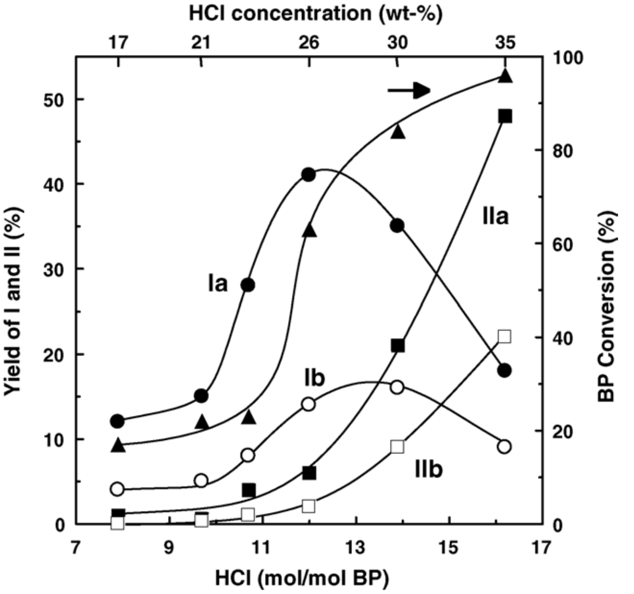


Fig. 3. Influences of amounts of HCl on the chloromethylation of BP. Reaction conditions: BP, 1.5 g (9.7 mmol); $Sc(OTf)_3$, 0.24 g (0.5 mmol); trioxane, 6.6 g (72.7 mmol); temperature, 80 °C; period, 22 h.

hydrochloric acid enhanced the catalysis. The yields of **Ia** and **Ib** reached maximum at the 26% hydrochloric acid (HCl/BP = 12); however, they decreased with further increase in the amount of HCl. On the other hand, the yields of **IIa** and **IIb** increased with the increase in the concentration of hydrochloric acid.

Fig. 4 shows the influences of the ratio of trioxane and BP at 80 °C. The conversion of BP increased with the ratio of CH_2O/BP and reached maximum at 20 of the ratio. The yields of **Ia** and **Ib** were predominant at the ratios lower than 15. However, the yield of **IIa** increased rapidly at the ratio higher than 15 and reached maximum at the ratio of around 20–25. These results show that the high CH_2O/BP ratio enhanced the formation of **IIa** and **IIb**. However, further addition of formaldehyde resulted in the decrease of the yield of **IIa**. This is due to the formation of poly(chloromethyl)biphenyls, which were observed in LC chromatogram and confirmed by GC–MS although we did not identify their structures.

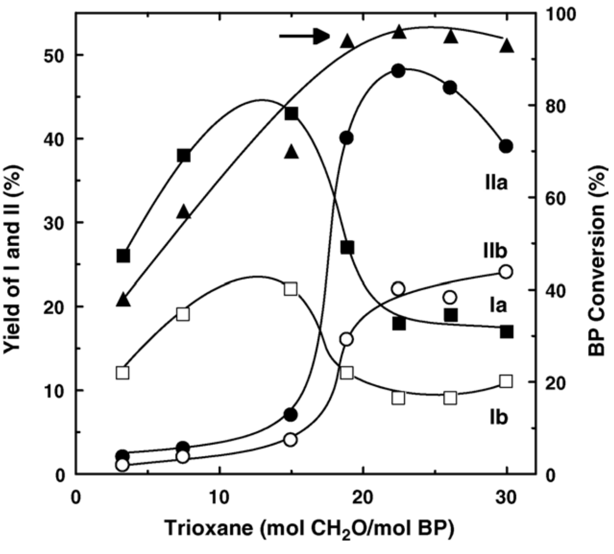


Fig. 4. Influences of amount of trioxane on the chloromethylation of BP. Reaction conditions: BP, 1.5 g (9.7 mmol); $Sc(OTf)_3$, 0.24 g (0.5 mmol); conc. HCl, 16.4 g (157 mmol); temperature, 80 °C; period, 22 h.

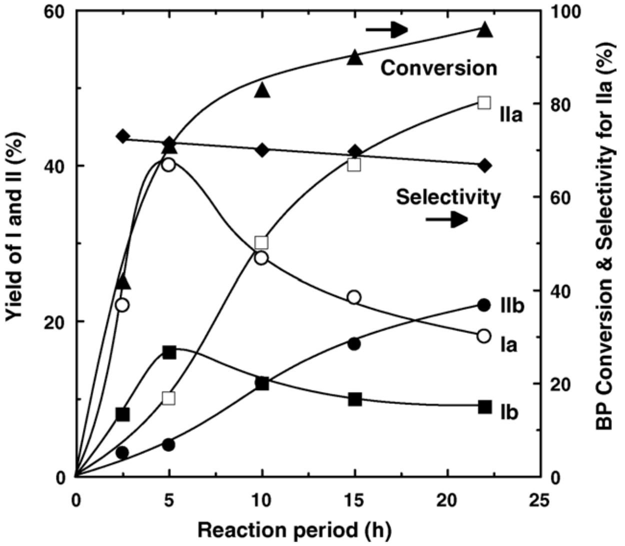


Fig. 5. Reaction profile of the chloromethylation of BP. Reaction conditions: BP, 1.5 g (9.7 mmol); $Sc(OTf)_3$, 0.24 g (0.5 mmol); trioxane, 6.6 g (72.7 mmol); conc. HCl, 16.4 g (157 mmol); temperature, 80 °C.

The reaction profile of chloromethylation of BP at 80 °C is shown in Fig. 5. **Ia** and **Ib** yielded in the early stages, and subsequently, they converted consecutively to **IIa** and **IIb**. The selectivity for **IIa** among bis(chloromethyl)biphenyls was about 70% during the reaction. However, the formation of 2,2′-bis(chloromethyl)biphenyl (**IIc**) was not found in the detectable amounts during the reaction. The chloromethylation of **Ia** and **Ib** was examined under the same conditions to know the reaction path to the formation of **IIa** and **IIb**: a mixture of **IIa** and **IIb** was obtained by the chloromethylation of **Ia**, and the selectivity for **IIa** was 87% as shown in Table 1. However, the chloromethylation of **Ib** yielded only **IIb**, and **IIc** was not detected in the reaction mixture. The selectivity for **IIa** from **Ia** was higher than the case of **Ia** from BP. These results show that the chloromethylation of BP gave a mixture of **Ia** and **Ib** in the first step. **IIa** was formed from **Ia** and **IIb** was yielded from **Ia** and **Ib** in the second step.

These catalyses occurred under heterogeneous organic and aqueous biphasic conditions. The catalytic solution was easily

Table 1
The chloromethylation of 2- and 4-chloromethylbiphenyls with $Sc(OTf)_3$

Substrate	Conversion (%)	Yield (%)			Selectivity for **IIa** (%)
		IIa	**IIb**	**IIc**	
Ia	90	77	12	–	87
Ib	85	–	85	–	0

Reaction conditions: **Ia** or **Ib**, 1.5 g (7.40 mmol); $Sc(OTf)_3$, 0.24 g (0.48 mmol); trioxane, 6.55 g (72.7 mmol); conc. HCl, 16.4 g (157 mmol); temperature, 80 °C; period, 22 h.

Table 2
Recycle of catalytic solution in the chloromethylation of BP with Sc(OTf)$_3$

Catalytic cycle	Conversion (%)	Yield (%)			
		Ia	**Ib**	**IIa**	**IIb**
1	96	18	9	48	22
2[a]	93	20	9	44	19
3[a]	94	19	8	45	21

BP, 1.5 g (9.7 mmol); catalyst 0.5 mmol Sc(OTf)$_3$ trioxane 6.6 g (72.7 mmol); conc. HCl, 16.4 g (157 mmol); temperature, 80 °C; period, 22 h.

[a] After the separation of products, the catalyst solution was saturated with dry hydrogen chloride and the reaction was carried out with addition of trioxane 6.6 g (72.7 mmol), at 80 °C for 22 h.

separated from the reaction mixtures after the reaction, and the catalyst stayed in aqueous phase.

We examined the recovery and recycle of Sc(OTf)$_3$ from aqueous catalytic solution in two methods. First, Sc(OTf)$_3$ is recovered from evaporation of catalytic solution and can be used as fresh catalyst. This result show the triflate is stable during the catalysis. Secondly, we examined the aqueous catalytic solution was recycled and reused for further reaction. After catalytic solution was separated from reaction mixture and saturated with HCl gas, the solution was subjected to the new batch of reaction by the addition of BP and trioxane. The yield of products in catalyst recycle was shown in Table 2. The yield of products kept in the similar conversion and yield by two times recycles of the catalytic solution.

The influences of the addition of organic additives are shown in Fig. 6. The addition of small amounts of formic and acetic acids enhanced the yield of **IIa** and **IIb**; however, dioxane retarded the catalysis. Fig. 7 shows the influences of amount of acetic acid. The formation of **IIa** was enhanced by the addition of small amount of acetic acid; however, the yield of **IIb** remained unchanged. The influences of the addition of acetic acid (1 ml) on the chloromethylation were shown in Fig. 8. The formation of **IIa** and **IIb** in the second step was accelerated significantly by the addition of acetic acid as compared to Fig. 5.

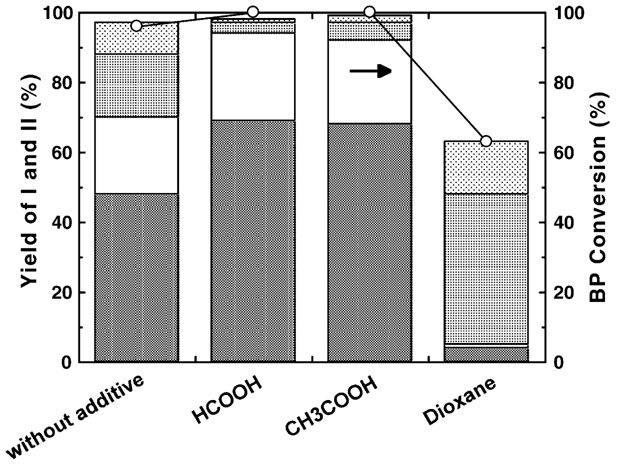


Fig. 6. Influences of type of additive on the chloromethylation of BP. Reaction conditions: BP, 1.5 g (9.7 mmol); Sc(OTf)$_3$, 0.24 g (0.5 mmol); trioxane, 6.6 g (72.7 mmol); conc. HCl, 16.4 g (157 mmol); organic additive, 4 ml; temperature, 80 °C; period, 22 h. Legend: ▩, **IIa**; □, **IIb**; ▤, **Ia**; ▨, **Ib**.

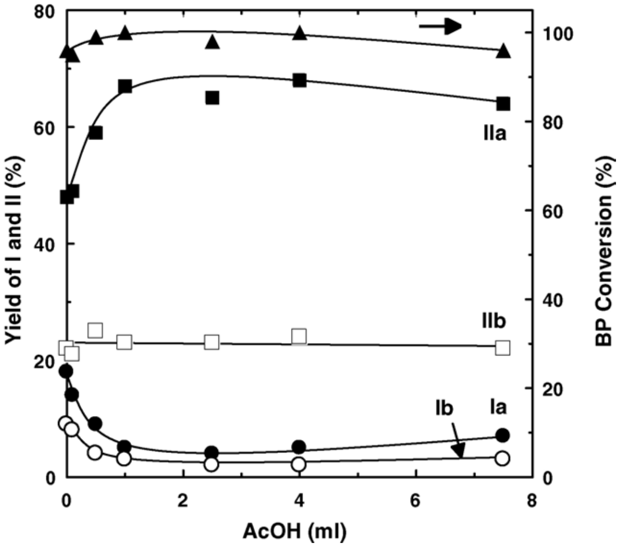


Fig. 7. Influences of addition of acetic acid on the chloromethylation of BP. Reaction conditions: BP, 1.5 g (9.7 mmol); Sc(OTf)$_3$, 0.24 g (0.5 mmol); trioxane, 6.6 g (72.7 mmol); conc. HCl, 16.4 g (157 mmol); temperature, 80 °C; period, 22 h.

One possibility for the role of acetic acid may be due to the enhancement of solubility to prompt the contact of triflate with BP by the solvation; however, further studies are necessary for the clarification of the mechanism.

The rate of the chloromethylation of BP using group 3 and 4 metal triflates as catalyst is much lower than the case of mononuclear aromatic hydrocarbons, such as benzene, toluene, *m*- and *p*-xylenes previously described in our pervious paper [13]. Large amounts of formaldehyde and hydrochloric acid and long reaction time are necessary for the high yield of **IIa** as discussed above.

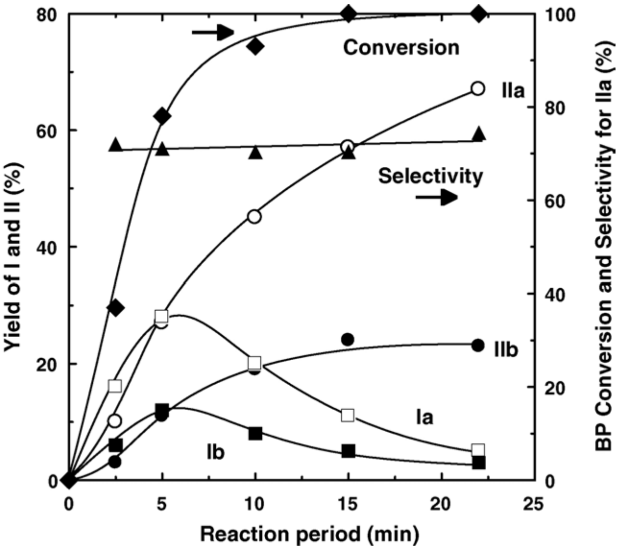


Fig. 8. Influences of the addition of acetic acid on reaction period in the chloromethylation of BP. Reaction conditions: BP, 1.5 g (9.7 mmol); Sc(OTf)$_3$, 0.24 g (0.5 mmol); trioxane, 6.6 g (72.7 mmol); conc. HCl, 16.4 g (157 mmol); acetic acid, 1 ml; temperature, 80 °C.

The formation of carcinogenic chloromethyl methyl ether and/or bis(chloromethyl)ether has been suspicious during the chloromethylation with the catalysis by $ZnCl_2$ and/or in acid solution such as acetic acid. However, the possibilities for the formation of these ethers are low during the chloromethylation of BP with $Sc(OTf)_3$ because the hydrolysis of these chloromethylethers are predominated over their formation. Actually, we could not find any proof on the formation of these ethers by the analysis of gas phase. The contents of PCB in the products were less than the limit of detection (0.03 wt. ppm): this result means that no chlorine contamination in aromatic rings occurs during the chloromethylation of BP with $Sc(OTf)_3$. These merits come from the catalysis in aqueous medium under mild reaction conditions.

3.2. The chloromethylation of 9,10-dihydrophenanthrene

The influences of type of triflates on the chloromethylation of DHP are shown in Fig. 9. DHP gave 2-choloromethyl-9,10-dihydrophenanthrene (**III**) and 2,7-bis(chloromethyl)-9,10-dihydrophenanthrene (**IV**) in high to excellent yield. Triflates were enough active for the chloromethylation in catalytic amounts. The conversions were more than 80% for all triflates under our reaction conditions. The combined yield of **III** and **IV** decreased in the order: $Sc(OTf)_3 > Yb(OTf)_3 > Sm(OTf)_3 \gg Hf(OTf)_4 > In(OTf)_3$. This order is the similar to the cases of BP and *m*-xylene except the cases of $Hf(OTf)_4$ and $In(OTf)_3$ [13]. These catalyses occurred in heterogeneous organic and aqueous biphasic conditions, and **IV** appeared sometimes as solid crystals during the reactions. The catalysts were easily separated from the reaction mixtures after the reaction.

The chloromethylation occurred without the catalyst; however, combined yield of the products was as high as 40%. Hereafter, we chose $Sc(OTf)_3$ as the catalyst to elucidate the factor to control the catalyses, because it had the highest activity for **IV** among the triflates. The chloromethylation by using $ZnCl_2$ gave the products in the almost same level as $Sc(OTf)_3$ as a catalyst; however, it was necessary to use an approximately stoichiometric amount for corresponding yields.

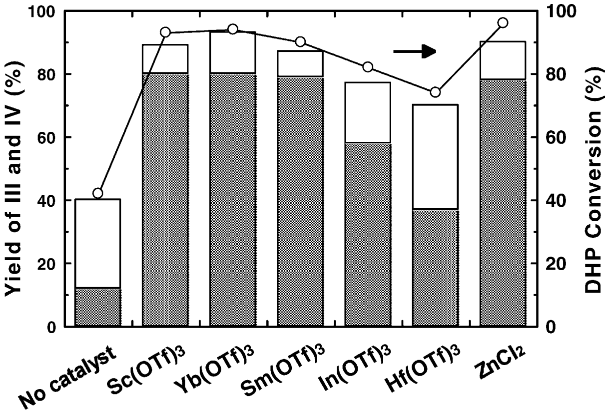


Fig. 9. Effects of type of triflates on the chloromethylation of DHP. Reaction conditions: DHP, 1.5 g (8.3 mmol); catalyst, 0.4 mmol(triflates), 8.3 mmol($ZnCl_2$); trioxane, 5.6 g (62.2 mmol); conc. HCl, 14.0 g (134 mmol); temperature, 80 °C; period, 22 h. Legend: ▩, **IV**; ☐, **III**.

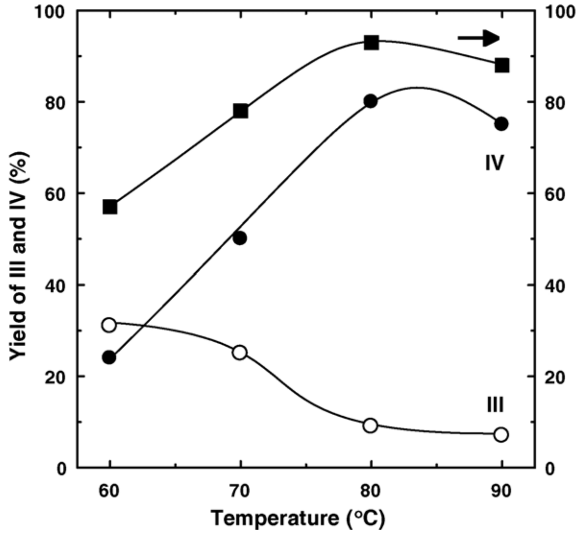


Fig. 10. Effects of temperature on the chloromethylation of DHP. Reaction conditions: DHP, 1.5 g (8.3 mmol); $Sc(OTf)_3$, 0.21 g (0.4 mmol); trioxane, 5.6 g (62.2 mmol); conc. HCl, 14.0 g (134 mmol); period, 22 h.

The influences of reaction temperature on the chloromethylation are shown in Fig. 10. The catalytic activity increased with the increase in reaction temperature to 80 °C; however, the conversion was decreased at 90 °C. The yield of **IV** reached the maximum at 80 °C and then, decreased at 90 °C. However, the yield of **III** was decreased with the reaction temperature. These results show that the high temperature enhanced the consecutive formation of **IV** via **III**, and the decrease of the yield of **IV** at high temperature is due to decrease of HCl concentration in the reaction mixtures as discussed above.

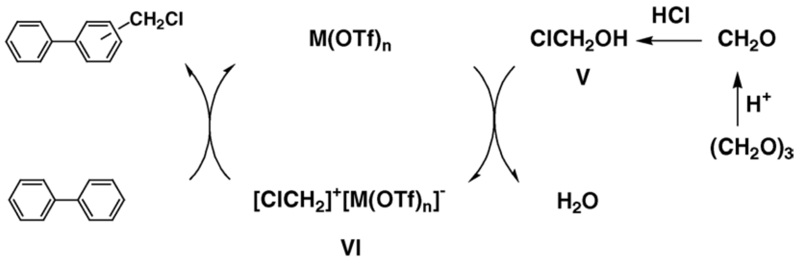
Fig. 11 shows that the influences of the concentration of hydrochloric acid at 80 °C. No reaction occurred in the absence of hydrochloric acid. The activity and the yields of **IV** increased with the increase in the concentration of hydrochloric acid; however, the yield of **III** reached maximum at ca. 28% hydrochloric acid (HCl/DHP = 13). The similar results were obtained in the chloromethylation of BP as discussed above.

Fig. 12 shows the influences of the amount of trioxane in the chloromethylation. The conversion of DHP increased with the ratio of CH_2O/DHP and saturated at the ratio higher than 25. The yields of **IV** were also increased with the ratio and saturated at 20–25 of the ratio. However, **III** was decreased linearly with the ratio.

The influences of the addition of acids were also examined in the chloromethylation of DHP; however, the significant enhancement of the yield **IV** could not be observed by the addition of formic and acetic acids.

3.3. Mechanistic aspects of the catalysis

The catalysis is considered to proceed by a similar mechanism as proposed for mononuclear aromatic hydrocarbons [1,2,13]. Group 3 and 4 metal triflates work as Lewis acids stable in aqueous medium and catalyze many organic transformations



Scheme 3. A possible reaction mechanism.

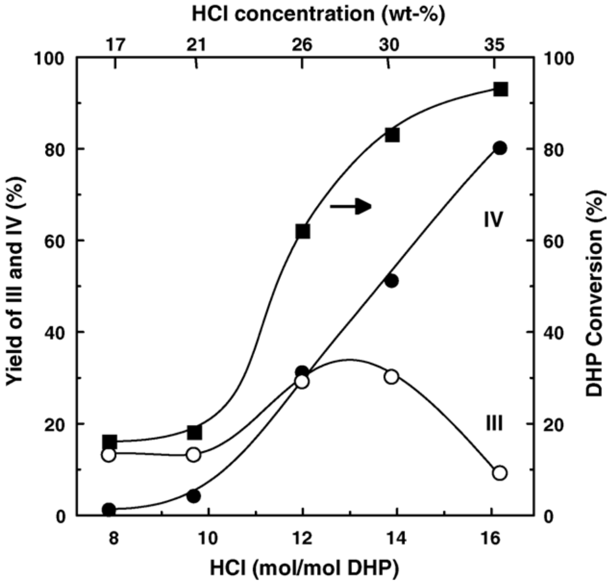


Fig. 11. Effects of amounts of HCl on the chloromethylation of DHP. Reaction conditions: DHP, 1.5 g (8.3 mmol); $Sc(OTf)_3$, 0.21 g (0.42 mmol); trioxane, 5.6 g (62.2 mmol); temperature, 80 °C; period, 22 h.

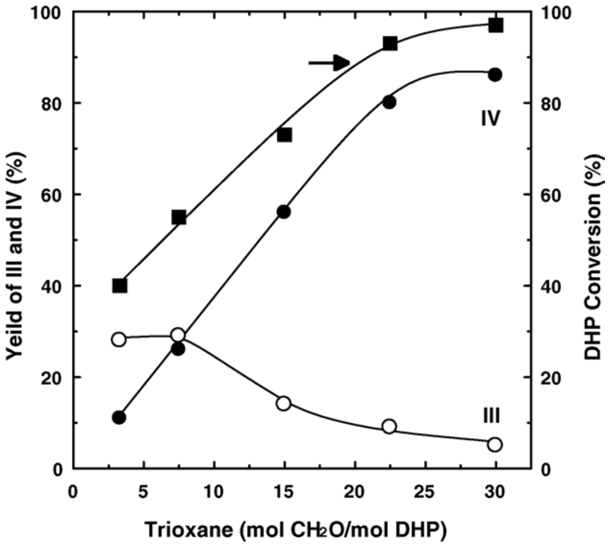


Fig. 12. Effects of amount of trioxane on the chloromethylation of DHP. Reaction conditions: DHP, 1.5 g (8.3 mmol); $Sc(OTf)_3$, 0.21 g (0.4 mmol); conc. HCl, 14.0 g (134 mmol); temperature, 80 °C; period, 22 h.

[8,9]. Scheme 3 shows a plausible mechanism for the catalysis based on the triflate ($M(OTf)_n$) as a Lewis acid. First, trioxane is hydrolyzed to formaldehyde by acid catalysis. Formaldehyde reacts with HCl to form chloral (**V**) and then, **V** reacts with the triflate to yield a chloromethyl triflate complex (**VI**). The formation of **VI** should be plausible because no reaction occurs in the absence of hydrochloric acid. The complex **VI** reacts with aromatic hydrocarbon to yield chloromethylated product and the triflate. The choloromethylation of aromatic hydrocarbons to the complex **VI** occurs via a nucleophillic addition-elimination substitution reaction [18].

The chloromethylation of BP predominantly occurs at *ortho*- and *para*- positions in the aromatic ring to afford **Ia** and **Ib** in the first step. The substitution at 4-position is predominated over 2-position because of steric restriction of phenyl group and of electronic situation of BP. In the second step, a mixture of **IIa** and **IIb** was obtained from **Ia** with 87% selectivity for **IIa**. Only **IIb** was observed in the chloromethylation of **Ib**; however, **IIc** could not be found in detectable amounts. The selectivity for **IIa** from **Ia** in the second step was higher than the case from BP. These differences are due to the simultaneous formation of **IIb** from **Ia** and **Ib**. No observation of **IIc** in the chloromethylation of BP may be due to the severe steric repulsion at the transition-state from **Ib**.

The chloromethylation of DHP occurs selectively at 2-position in a similar manner for BP and there was no detectable formation of 3- and 4-chloromethyl-9,10-dihydrophenanthrenes. The attack to 4-position is retarded because of steric repulsion by the opposite phenyl group. The substitution at 3-position is disfavored due to higher electron density at 3-position than at 2-position because of mesomeric resonance by planar character of DHP.

4. Conclusions

Some group 3 and 4 metal triflates are highly active for the chloromethylation of biphenyl (BP) and 9,10-dihydrophenanthrene (DHP). The catalytic activity decreased in the order: $Sc(OTf)_3 > Yb(OTf)_3 > Sm(OTf)_3 \gg In(OTf)_3 > Hf(OTf)_4$. $Sc(OTf)_3$ had the highest activity among them. The catalysts were stable under the reaction conditions, and catalytic amount of triflates was effective for the chloromethylation of BP and DHP. BP yielded a mixture of 4-chloromethylbiphenyl (**Ia**), 2-chloromethylbiphenyl (**Ib**), 4,4′-bis(chloromethyl)biphenyl (**IIa**) and 2,4′-bis(chloromethyl)biphenyl (**IIb**). The selectivity for **IIa** was around 70% among its isomers for all triflates. The catalysis by triflates occurs in heterogeneous mixture of hydrocarbon, trioxane and the triflate in aqueous hydrochloric acid. Since the triflate stayed in aqueous phase during the reaction, the catalyst solution was easily separated from the products and recycled for a new reaction. The addition of small amount of formic acid and acetic acid enhanced the chloromethylation of **Ia** to increase the yield of **IIa**. DHP gave a mixture of 2-chloromethyl-9,10-dihydrophenanthrene (**III**) and 2,7-bis(chloromethyl)-9,10-dihydrophenanthrene (**IV**) in high yield.

From environmental point of view, there are merits of the catalysis in aqueous medium for the chloromethylation: the prevention of carcinogenic chloromethyl ethers and no chlorine contamination of aromatic rings of the products. The group 3 and 4 metal triflates are active enough for the green chloromethylation of biphenyl, 9,10-dihydrophenanthrene and other aromatic hydrocarbons.

Further aspects of the catalysis and the application to organic syntheses and practical chemical processes are under investigation.

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