1504 © 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 1504—1508 (1982) [Vol. 55, No. 5

The Reaction Involving One Electron Transfer in Key Step. NO_2-Catalyzed Halogenation of Polycyclic Aromatic Compounds with Metal Halides

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(Received July 17, 1981)

In the co-existence of catalytic amount of nitrogen dioxide and oxygen, aluminum halide, titanium(IV) halide, and some other metal halides have been found to be highly selective and regiospecific halogenating agents for polycyclic aromatic compounds, including anthracene, pyrene, benz[*a*]anthracene, chrysene, phenanthrene, naphthalene, triphenylene, fluoranthene, benzo[*b*]thiophene, and dibenzothiophene.

Aromatic nuclei have been halogenated with quite a few methods.[1] The methods could be classified into four groups. They are; (1) reaction of electron-rich aromatic nucleus with a molecular halogen; (2) reaction of less-activated nucleus with a molecular halogen in the presence of a catalyst such as a Lewis acid; (3) reaction of aromatic nucleus with a positive halogen; and (4) halogenation by a metal halide as a halogen-source.[2]

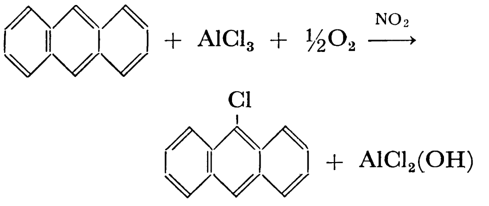
Extensive investigation has been done on the reactions in groups (1), (2), and (3). On the contrary, reactions that belong to the fourth group have received little attention. In many cases, the reaction of aromatic nucleus with a metal halide[3] results in metallation,[4] isomerization,[5] polymerization,[6] or disproportionation[5] rather than halogenation. Therefore, metal halides that have been employed for halogenation have been restricted to halides of copper(II),[7] iron(III),[8] tin(IV),[9] titanium(IV),[2] antimony(V),[10] vanadium(V),[2] and (nonmetallic) phosphorus(V).[9,11] Namely, the reaction with copper(II) chloride is known as Nonhebel's chlorination and has synthetic utility.[12] Side-reactions dominate with other metal halides.

Characteristic of the halogenation with these metal halides are that these metal ions are reduced to their low-valency states during the reaction according to Eq. 1 or 2.

$$\mathrm{ArH} + 2\mathrm{M}^{n+}\mathrm{X}_n^- \longrightarrow \mathrm{ArX} + 2\mathrm{M}^{(n-1)+}\mathrm{X}_{n-1}^- + \mathrm{HX} \quad (1)$$

$$\mathrm{ArH} + \mathrm{M}^{n+}\mathrm{X}_n^- \longrightarrow \mathrm{ArH} + \mathrm{M}^{(n-2)+}\mathrm{X}_{n-2}^- + \mathrm{HX} \quad (2)$$

It is plausible that the halogenation may take place with a metal halide whose metal ion cannot change its valency, provided a suitable electron-source is supplied to the reaction system. Indeed, the author has reported chlorination of anthracene with aluminum (III) chloride in the presence of catalytic amount of nitrogen dioxide under aerobic conditions (Eq. 3).[13]



(3)

This novel chlorination method is superior to conventional ones in intermolecular selectivity, yield of the product, and reaction conditions.

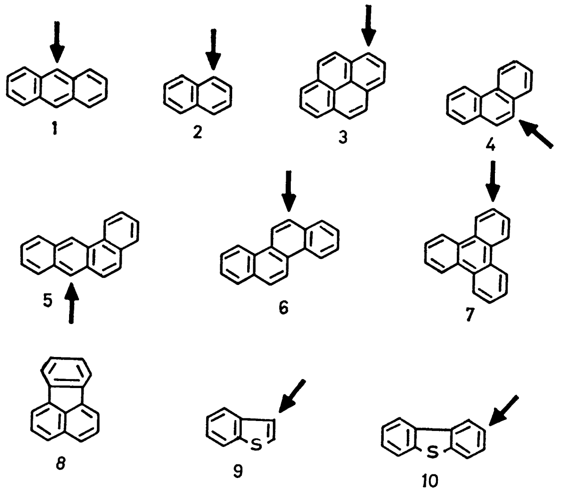
In the present paper, the author wishes to report the scope and limitation of the halogenation which couples with a series of successive electron transfer systems, an electron-bridge.

Results and Discussion

Appropriate amounts of a polycyclic aromatic hydrocarbon and metal halide were allowed to react in toluene or in 1,2-dichloroethane at 0—30 °C. Benzene, nitromethane, acetonitrile, or carbon disulfide could also be used as a solvent. Although toluene was a suitable solvent for most halogenations, the reaction with less reactive aromatics afforded, sometimes, benzylated compounds in this solvent.

The products were isolated and identified by melting points as well as by comparing their spectroscopic properties with those of the corresponding authentic samples. The results are summarized in Table 1 for the chlorination and in Table 2 for the bromination.

The regioselectivity of chlorination is satisfactorily high; GLC-analyses showed that the chlorination of anthracene (**1**) and naphthalene (**2**) afforded 9-chloroanthracene and 1-chloronaphthalene, respectively, as monochlorinated compounds. Other isomeric products were scarcely recognized (2%). Only one monochlorinated product was detected in chlorination of phenanthrene (**4**), benz[*a*]anthracene (**5**), chrysene (**6**), or triphenylene (**7**). The reaction site is indicated in Scheme 1 by an arrow.



Scheme 1. Arrows indicate the position susceptible to monohalogenation. For compound **8**, the position is not identified. For compound **3**, significant amount of the other isomer is formed.

TABLE 1. CHLORINATION OF POLYCYCLIC AROMATICS$^{a)}$

Substrate ArH_2	MX_n	$NO_2$$^{b)}$ (mol%)	Time / min	Consumed ArH_2 (%)	Yield of ArHCl$^{c)}$ / %	Yield of $ArCl_2$$^{c)}$ / %
1$^{d)}$	$AlCl_3$	13	30	100	86	0
	$AlCl_3$$^{e)}$	13	30	51	90	0
	$TiCl_4$	13	30	100	0	91
	$TiCl_4$$^{e)}$	13	30	100	91	Trace
	$SnCl_4$$^{e)}$	13	30	91	82	0
3	$AlCl_3$	13	20	33	79	0
	$TiCl_4$	20	5	100	Trace	92
	$TiCl_4$$^{e)}$	8	10	91	89	Trace
5	$AlCl_3$	13	20	71	65	3
	$TiCl_4$	13	10	98	80	2
6	$TiCl_4$	6	20	95	71	0
4$^{f)}$	$TiCl_4$	22	30	96	52	0
2$^{f)}$	$TiCl_4$	26	1440	95	53	0
7	$TiCl_4$	13	1200	92	67	0
8$^{i)}$	$TiCl_4$	10	120	—$^{g)}$	21$^{h)}$	0
9$^{i)}$	$TiCl_4$	10	120	—$^{g)}$	47$^{h)}$	0
10	$TiCl_4$	10	120	—$^{g)}$	40$^{h)}$	0

a) $MX_n/ArH_2=1.0$. Solvent: toluene. Temp: room temp. b) Mol% is based on substrate used. c) Yield is based on ArH_2 consumed. d) Data from Ref. 13. Temp: 0 °C. e) $MX_n/ArH_2=0.5$. f) Solvent: 1,2-dichloroethane. g) Consumed ArH_2 was not determined. h) Yield is based on ArH_2 used. i) Significant amounts of dimer and trimer were obtained.

Bromination takes place with less selectivity than the chlorination; 5—10% of 2-bromonaphthalene was detected on GLC in addition to the major product, 1-bromonaphthalene. However, the bromination of other substrates gave as good regioselectivity as the chlorination.

It should be noted that the ratio of mono-/dihalogenated product is extremely high in the present reaction, which is a marked contrast to the reaction with, for example, copper(II) chloride.$^{7)}$ Most of the present reactions gave traces of, if any, or no dihalogenated product, when the relative amounts of the reagents were appropriate. On the other hand, dihalogenated compound was obtained as a sole product under appropriate reaction conditions.

Intermolecular selectivity is also seen in competitive chlorination of anthracene, pyrene (**3**), and triphenylene as listed in Table 3.

Further advantage of the present halogenation lies in its reactivity: Whereas it has been reported that a substrate which has ionization potential of less than 7.55 eV is unreactive toward the chlorination with copper(II) chloride,$^{14)}$ in the present halogenation phenanthrene (IP; 8.03),$^{15)}$ naphthalene (IP; 8.10),$^{15)}$ and triphenylene (IP; 8.09)$^{15)}$ are susceptible to the reaction.

It is interesting to point out that the number of halide ion available for the halogenation depends on the reactivities of both metal halide and substrate; as can be seen in Tables 1 and 2, only one of three chlorine atoms in aluminum(III) chloride is available for the chlorination of anthracene, whereas two of three bromine atoms in aluminum(III) bromide react with anthracene. On the other hand, two of four chlorine atoms in titanium(IV) chloride react in the chlorination of reactive substrates such as pyrene and benz[*a*]anthracene, but only one is reactive toward the chlorination of relatively less reactive substrates such as phenanthrene, naphthalene, and triphenylene. Therefore, one can obtain either mono- or dihalogenated compound depending on the substrate/metal halide molar ratio employed for the reaction (*vide supra*). In general, bromides are more reactive than the corresponding chlorides, and a substrate of low ionization potential is more reactive than that of high ionization potential.

Now, the author wishes to demostrate catalytic activity of nitrogen dioxide.$^{13)}$ As listed in Table 4, practically no halogenation takes place with these metal halides when nitrogen dioxide is absent in the reaction system. Even titanium(IV), and tin(IV) bromides require nitrogen dioxide in order to undergo the reaction, though these metal ions have stable lower-valency states. Thus, it is apparent that the reaction with these metal halides is not of the types shown in Eqs. 1 and 2 under the present reaction conditions. Boron tribromide is an exception. Although the effect of catalyst is significant, bromination with boron tribromide proceeds in some extent without the catalyst. Since boron cannot change its valency, the author has no idea on a plausible mechanism.

In the absence of a reactive substrate, toluene is also susceptible to the halogenation and a 1:1 mixture of *ortho*- and *para*-bromotoluenes is obtained in the total yield of 81%.

Benzo[*b*]thiophene (**7**) and dibenzothiophene (**10**) can also be subjected to the halogenation. However, oxygen-containing compounds such as benzofuran and dibenzofuran do not undergo the reaction, probably because lone-pair electrons on the oxygen atom in-

TABLE 2. BROMINATION OF POLYCYCLIC AROMATICS[a)]

Substrate ArH_2	Metal halide MX_n (MX_n/ArH_2)	Time / min	Consumed ArH_2 (%)	Yield of $ArHBr$[b)] / %	Yield of $ArBr_2$[b)] / %
1	$AlBr_3$ (0.5)	60	100	86	3
	$AlBr_3$ (1.0)	1020	100	1	82
	$AlBr_3$ (2.0)[c)]	30	100	2	79
	$TiBr_4$ (0.5)	30	94	92	3
	$TiBr_4$ (1.0)	1020	100	0	87
	BBr_3 (0.5)	1020	100	63	26
	BBr_3 (1.0)	1020	100	1	85
	$CuBr_2$ (1.0)[d)]	1020	100	74	Trace
	$SbBr_3$ (1.0)	1020	100	Trace	55
	$SnBr_4$ (1.0)	1020	100	18	15
	$SnBr_4$ (1.0)	1020	100	13	14
3	$AlBr_3$ (0.5)	30	84	76	5
	$AlBr_3$ (1.0)	30	100	61	6
	$AlBr_3$ (2.0)	30	100	0	69
	$AlBr_3$ (1.0)[e)]	30	86	75	5
	$TiBr_4$ (1.0)	30	100	5	74
	$SnBr_4$ (1.0)	60	81	61	0
5	$AlBr_3$ (0.5)	10	75	92	0
	$AlBr_3$ (1.0)	10	99	94	0
	$TiBr_4$ (1.0)	10	96	96	0
	$SnBr_4$ (1.0)	20	95	75	0
6	$AlBr_3$ (1.0)	180	77	73	Trace
	$AlBr_3$ (2.0)	180	100	45	40
	$AlBr_3$ (1.0)[f)]	180	100	72	28
	$AlBr_3$ (1.0)[f)]	30	80	91	9
	$SnBr_4$ (1.0)	180	98	68	23
4	$AlBr_3$ (0.5)	60	53	47	0
	$AlBr_3$ (1.0)	60	88	64	0
	$AlBr_3$ (2.0)	60	100	69	13
	$TiBr_4$ (1.0)	180	99	69	Trace
	$SnBr_4$ (1.0)	60	59	39	0
	$SnBr_4$ (1.0)	180	100	33	Trace
2	$AlBr_3$ (1.0)[g)]	180	84	56	Trace
	$AlBr_3$ (2.0)	180	100	49	Trace
	$TiBr_4$ (1.0)	180	86	71	Trace
	$SnBr_4$ (1.0)	180	95	63	0

a) Reaction conditions: See the experimental section. Solvent: toluene for **1**, **3**, **5**, and **6**, 1,2-dichloroethane for **4** and **2**. b) Yield is based on ArH_2 consumed. c) Reaction temp: 0 °C. d) Anthraquinone was obtained as a side-product. e) Solvent: acetonitrile. f) Solvent: 1,2-dichloroethane. g) Product: 1-bromonaphthalene/2-bromonaphthalene=93/7.

TABLE 3. COMPETITIVE CHLORINATION

Substrate ArH_2	Yield of $ArHCl$[a)] after 1 min/%	Yield of $ArHCl$[a)] after 3 min/%
Anthracene	20	40
Pyrene	4	10
Triphenylene	—	0

a) Yield is based on substrate used.

teract with positive metal ion decreasing the reactivity of metal halide.

Unfortunately, attempts to iodinate aromatic hydrocarbons were found unsuccessful.

Although detailed mechanism of the reaction is under investigation, nucleophilic character of the halogenation as well as the following evidence allows the author to speculate the formation of an aromatic radical cations as an intermediate of the reaction: It is well known that polycyclic aromatic hydrocarbon forms a charge-transfer complex with Lewis acids.[16)] The aromatic radical cation thus formed may abstract a halide ion. When the reaction is carried out in the presence of trichlorosilane, chlorinated product is obtained.[13)] A hydrogen atom should be abstracted from trichlorosilane, if a free-radical mechanism governed the reaction. In addition, the fact that silicon tetrachloride cannot give the chlorinated products,[13)] suggests the polar nature of the reaction.

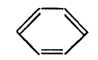
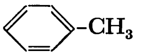
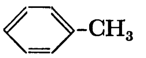
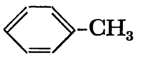
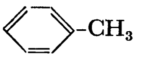
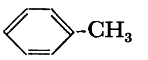
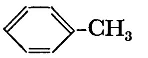
At least a part of catalytic effect of nitrogen dioxide is exerted by the formation of an electron-bridge.

TABLE 4. EFFECT OF NO_2 IN BROMINATION OF ANTHRACENE[a)]

Metal halide MX_n	Solvent	Atmospheric condition	Consumed anthracene ArH_2 (%)	Yield of ArHBr[b)] %	Yield of $ArBr_2$[b)] %
$AlBr_3$[c)]	Toluene	N_2	29	Trace	0
$AlBr_3$[c)]	Toluene	O_2	38	Trace	0
$AlBr_3$[d)]	Toluene	NO_2-O_2	100	88	0
$TiBr_4$	Nitromethane	O_2	4	Trace	0
$TiBr_4$	Nitromethane	NO_2-O_2	100	0	0
BBr_3	Toluene	N_2	12	5	0
BBr_3	Toluene	O_2	52	31	0
BBr_3	Toluene	NO_2-O_2	100	1	86
$SbBr_3$	Acetonitrile	O_2	3	0	0
$SbBr_3$	Acetonitrile	NO_2-O_2	100	Trace	55
$SnBr_4$	Nitromethane	O_2	5	Trace	Trace
$SnBr_4$	Nitromethane	NO_2-O_2	100	18	15

a) Reaction time: 17 h. MX_n/Anthracene = 1.0. Temp: room temp. Anthracene/NO_2 = 1.0/0.13 (mol/mol). NO_2 was used as a 10% solution. b) Yield is based on anthracene used. c) Reaction time: 30 min. d) Reaction time: 5 min. Temp: 0 °C. $AlBr_3$/Anthracene = 0.5.

TABLE 5. EFFECT OF SOLVENT IN BROMINATION OF POLYCYCLIC AROMATICS WITH $AlBr_3$[a)]

Substrate ArH_2	Solvent	Time min	Consumed ArH_2 (%)	Yield of ArHBr[b)] %	Yield of $ArBr_2$[b)] %
1		10	100	79	15
		10	100	65	19
	$ClCH_2CH_2Cl$	10	100	63	23
	CS_2	10	100	75	17
	CH_3CN	10	37	41	0
	CH_3NO_2	10	64	64	0
3		30	84	77	5
	CH_3NO_2	30	99	55	6
5		10	99	94	0
	$ClCH_2CH_2Cl$	10	100	91	0
	CH_3CN	10	25	32	0
6		180	74	77	Trace
	$ClCH_2CH_2Cl$	180	100	72	28
	CH_3CN	180	88	80	21
	CS_2	180	80	88	8
4		30	64	23	0
	$ClCH_2CH_2Cl$	30	84	63	0
	CH_3NO_2	30	23	9	0
2		180	44	55	0
	$ClCH_2CH_2Cl$	180	86	55	0

a) Reaction conditions: See the experimental section. $AlBr_3/ArH_2$ = 1/1. b) Yield is based on ArH_2 consumed.

The halogenation without oxygen proceeds in the presence of equimolar amount of nitrogen dioxide, which implies that oxygen reproduces nitrogen dioxide from its reduced form, nitrogen monoxide. The formation of nitrogen monoxide may couple with the oxidation of aromatic hydrocarbon to its cationic form. Thus, the author prefers to propose that an electron-bridge is constructed in the present reaction, in which an electron migrates from a substrate to nitrogen dioxide and to oxygen molecule.

Experimental

Instruments. The IR, ^1H-NMR, and mass spectra were recorded on a Hitachi EPI-S2, Varian T60, and JEOL JMS-01SG spectrometers, respectively. Analytical GLC was carried out with a Yanaco G-1800 gas chromatograph using a 1.5 m—0.3 cm o.d. stainless column packed with 5% Silicone OV-17 on Chromosorb W. The preparative GLC was carried out with a Varian aerograph model 920 instrument using a 1.0 m—0.45 cm o.d. stainless column packed with 10% Silicone OV-17 on Chromosorb W. The column chromatography was carried out on active alumina Woelm N. Akt. I with solvents of hexane and benzene.

Materials. All the chemicals except for triphenylene were obtained from commercial sources (Nakarai Chemical Co. and Wako Pure Chemical Industries, Ltd.) and used after purification by distillation or column chromatography. Commercial nitrogen dioxide was cooled to liquid in a Dry Ice–acetone bath, weighed, and used as a 5% solvent solution. Triphenylene was prepared from *o*-bromoaniline according to the method of Heaney and Millar[17] mp 198 °C (lit,[17] 199 °C). Found: C, 94.42; H, 5.31%. Calcd for $C_{18}H_{12}$: C, 94.70; H, 5.30%.

Product Analysis. Into a solution (100 ml) or a suspension (100 ml) of 5.0 mmol of an aromatic compound, were added 5.5 mmol of anhydrous metal halide and 460 mg of toluene containing 23 mg of NO_2 (0.5 mmol). The mixture was stirred for appropriate time interval under atmosphere of oxygen at room temperature, and the amount of oxygen absorbed was measured on a gas-buret connected to the reaction vessel. The reaction mixture was poured into dilute hydrochloric acid, and extracted with toluene (3×50 ml). The combined toluene layer was washed with water, neutralized with sodium hydrogencarbonate, dried over $CaCl_2$, and the toluene was removed under reduced pressure. The residue was separated, and purified with column chromatography, and/or with recrystallization. The isolated products were identified by comparing thier IR, ^{1}H-NMR, and mass spectra with those of the corresponding authentic samples. Elemental analyses gave satisfactory results.

Quantitative Analyses. A same experiment as mentioned above was carried out in 1/10 scale. The combined toluene layer was quantitatively analyzed by GLC, after a usual work-up.

Bromination of Toluene. Anhydrous aluminum tribromide (2050 mg, 7.6 mmol) in nitromethane (18.5 g) and nitrogen dioxide (12.5 mg, 0.27 mmol) in nitromethane (250 mg) were added into toluene (25 ml). The mixture was stirred for 24 h under atmosphere of oxygen at room temperature, and poured into dilute hydrochloric acid. Work-up of the mixture by separation of toluene layer, washing with water, drying over $CaCl_2$, and evaporation of toluene yielded a mixture of crude bromotoluenes, which were purified on a preparative gas chromatograph (column temp: 120 °C), and the structure was identified. Quantitative analysis was carried out by GLC (column temp: 120 °C).

Chlorination of Anthracene with Trichlorosilane. Into toluene (10 ml) saturated with BF_3, were added 100 mg (0.56 mmol) of anthracene, toluene (1.4 ml) containing 76 mg (0.56 mmol) of trichlorosilane, and nitromethane (0.15 ml) containing 7.5 mg (0.16 mmol) of NO_2. The mixture was stirred overnight under atmosphere of oxygen at room temperature. After usual work-up, 72 mg (72%) of anthracene and 24.6 mg (74% based on consumed anthracene) of 9-chloroanthracene were obtained on GLC.

Competitive Chlorination. Into a mixture of anthracene (89 mg, 0.5 mmol), pyrene (101 mg, 0.5 mmol) or triphenylene (120 mg, 0.5 mmol), and eicosane (50.8 mg) as an internal standard material for gas chromatographical analysis in dry toluene (10 ml), were added titanium(IV) chloride (142.5 mg, 0.75 mmol) in nitromethane (0.28 ml) at 0 °C, and stirred. After 1 min and 3 min, 1 ml aliquots of the reaction mixture were taken out, respectively. The aliquot was quenched, and after usual work-up, analyzed by GLC.

The author thanks Professor S. Oka and Dr. A. Ohno for useful discussions.

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