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NO_2 CATALYZED CHLORINATION OF ANTHRACENE BY METAL CHLORIDES

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In the presence of nitrogen dioxide, aluminum chloride and some other metal chlorides have been found to be highly selective and regiospecific chlorinating agents for anthracene.

Halogenation of aromatic rings is one of the most thoroughly investigated organic reaction. Nevertheless not many studies have been concerned with the use of metal chlorides as aromatic chlorinating agents. Those that have been frequently employed, include chlorides of copper(II),[1) antimony(V), iron(III), and so on.[2) In other words, metals are limited to those that can change their valences, or are reduced to lower valences during the reaction.

$$\mathrm{ArH} + 2\mathrm{MCl}_n \longrightarrow \mathrm{ArCl} + 2\mathrm{MCl}_{n-1} + \mathrm{HCl} \qquad \text{(I)}$$

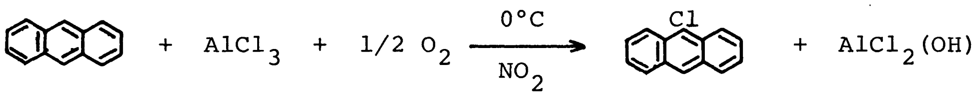
Similar reaction might take place with chlorides of metals that cannot change the valency, provided the reaction system is constructed so as to conjugate with a suitable electron-bridge. Indeed, we have found that aluminum chloride and some other metal chlorides can act as chlorinating agents for anthracene in the presence of catalytic amount of nitrogen dioxide(NO_2). The reaction condition is quite mild and the yield of mono- or dichloroanthracene is satisfactorily high.

Into an ice-cooled solution of 100mg (0.56mmol) of anthracene in 10ml of toluene, was added 78.2mg (0.62mmol) of anhydrous aluminum chloride and 56mg of nitromethane containing 1mg of NO_2. The mixture was stirred for 20 min under an atmosphere of oxygen. An almost quantitative amount of oxygen (6.3ml) was absorbed at the end of the reaction. The reaction mixture was poured into dilute hydrochloric acid and the organic materials were extracted with toluene. The toluene layer was neutralized with sodium hydrogencarbonate and dried over $CaCl_2$.

Anthracene, mono-, and dichloroanthracenes were quantitatively analyzed by gas-chromatography (5% Silicone DC 200, 1m, 210°C). Hydroquinone di-n-heptyl ether was used as an internal standard. The yield of 9-chloroanthracene was 86%. The formation of 1- or 2-chloroanthracene and dichloroanthracenes was not recognized under the present reaction condition. The product was identified by comparing its IR, Mass, and NMR spectra with those of an authentic sample. Mixed melting point, and elemental analyses gave satisfactory results.

Thus, the present chlorination is superior to the conventional methods$^{1)}$ in the selectivity, yield of the product, and reaction condition.

When a commercial-grade nitromethane was used as a solvent, the reaction proceeded without NO_2, whereas carefully purified nitromethane required the addition of NO_2. The irradiation with UV-light to nitromethane prior to the use made it more effective solvent than ordinal commercial-grade reagent.$^{3)}$ No reaction took place under an atmosphere of nitrogen. These facts apparently suggest that, with the aid of atmospheric oxygen, catalytic amount of NO_2 plays an important role in the reaction. The reaction may be formally represented by the equation (II).



(II)

Aluminum chloride can be substituted by other metal chlorides. The results are summarized in Table I.

It is noteworthy that the product is thoroughly determined by the molar ratio of metal chloride/anthracene. The reaction with equimolar amount of aluminum chloride results in the formation of 9-chloroanthracene, whereas that with twice molar affords 9,10-dichloroanthracene. Namely, only one of three chlorine atoms in aluminum chloride can be used for the chlorination. On the other hand, two of four chlorine atoms are effective with titanium(IV) or tin(IV) chloride. Although these metal ions are, generally, able to reduce their valences from four to two, the present reaction proceeds only in the co-existence of NO_2 and oxygen, or the reduction of metal ions do not accompany the reaction. Anthracene was not appreciably chlorinated with silicon tetrachloride. However, when small amount of iron(III) chloride was added to the silicon tetrachloride-anthracene system, 9-chloroanthracene was obtained in a 50% yield. It should be noted that only the reaction shown in eq.I operates for the chlorination of anthracene with iron(III) chloride. That is, the reaction with iron(III) chloride proceeded without absorbing oxygen even in the presence of NO_2. Instead the evolution of hydrogen chloride was recognized. This mixed salts effect indicates that the metal halide plays dual role for the reaction: one for the activation of anthracene and the other for the chlorinating agent.

Table I Reaction with various halides

anthracene: 100mg (0.56mmol), NO_2: 1mg (0.022mmol), toluene: 10ml

chloride (molar ratio of MCl_n/anthracene)	time (min)	temp. (°C)	recovered anthracene (%)	yield of 9-chloro-anthracene (%) a)	absorbed O_2(ml)
$AlCl_3$ (0.55)	30	0	49	46	3.0
$AlCl_3$ (1.1)	20	0	0	86	6.3
$AlCl_3$ (2.2)	10	0	0	0 (52) b)	13.0
$TiCl_4$ (0.55)	30	0	0	91	6.2
$TiCl_4$ (1.1)	30	0	0	0 (91) b)	12.5
$SnCl_4$ (0.55)	30	0	9	75	5.6
$SnCl_4$ (1.1) c)	30	0	0	0 (52) b)	12.0
$SiCl_4$ (1.1)	2 days	30	54	29	5.5
$SiCl_4$ (1.1) $TiCl_4$ (0.2)	180	0	0	94	5.0
$SiCl_4$ (1.1) $FeCl_3$ (0.1)	40	0	27	50	3.9
$FeCl_3$ (1.1)	20	0	71	21	0 d)
$FeCl_3$ (2.2)	60	25	43	40	0 d)
$FeCl_3$ (2.2)	180	25	24	47	0 d)
$CuCl_2$ (1.1)	1 day	25	98	0	0

a) The yields are based on anthracene used. b) The values in parentheses are the yields of dichloroanthracene. c) NO_2(5mg) was added. d) The reaction was accompanied by the evolution of HCl.

The effect of NO_2-concentration on the product distribution has been examined and the result is listed in Table II. The optimum yield of 9-chloroanthracene was achieved with 6 mole percent amount of NO_2. When the concentration of NO_2 is too small ($<$2 mole percent), NO_2 is consumed by some side reactions and the chlorination dose not proceed. With higher concentrations of NO_2 are formed appreciable amount of nitrated products at the sacrifice of chloroanthracene. On the other hand, when the equimolar amount of NO_2 was added dropwise, the reaction under an atmosphere of nitrogen gave chlorinated compound without being accompanied by the nitration. This fact suggests that oxygen serves to reproduce NO_2 from nitrogen monooxide or nitrous acid produced by the reaction. It has been found that the bromination with metal bromides takes place more easily than the chlorination with the corresponding metal chlorides.

Table II Effect of the amount of NO_2

anthracene: 100mg (0.56mmol), toluene: 10ml, temp.: 0°C, $AlCl_3$-CH_3NO_2 soln. (6%) 1.3g

NO_2 mol.%	time (min.)	recovered anthracene(%)	yield of 9-chloroanthracene(%)[a]	absorbed O_2 (ml)
0	30	98	0	0
2	30	12	69	5.0
6	15	0	86	6.3
10	10	0	78	6.5
20	10	0	62	6.5
100	20	0	18	6.5
100[b]	20	0	75	N_2

a) The yield of 9-chloroanthracen was based on anthracene used.

b) NO_2 was added dropwise under an atmosphere of nitrogen.

The scope and the mechanism of the reaction are under investigation.

References and Note

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