

## Binary Phase Chlorination of Aromatic Hydrocarbons with Solid Copper(II) Chloride: Reaction Mechanism

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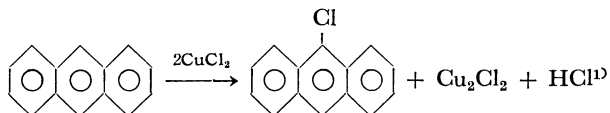
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(Received April 6, 1979)

Anthracene is selectively chlorinated with solid copper(II) chloride to give a quantitative yield of 9-chloroanthracene. The tentative reaction mechanisms so far proposed fail to explain the nonreactivity of some other hydrocarbon homologues, *e.g.* naphthalene and phenanthrene, toward copper(II) chloride. The present study revealed that the oxidative half-wave potentials ( $E_{1/2ox}$ ) of all reactive hydrocarbon homologues were less than 1.26 V. On the basis of this finding we postulate a reaction mechanism involving one electron transfer from hydrocarbon to copper(II) chloride.

Solid copper(II) chloride has been used to regio- and chemospecific synthesis of 9-chloroanthracene from anthracene. This binary phase chlorination which is performed under heterogeneous conditions gives a high yield of the regiospecific product:



While solid copper(II) chloride is effective also for chlorination of pyrene,<sup>2)</sup> the reagent was found to be entirely nonreactive toward some of other homologous hydrocarbons, *e.g.* naphthalene and phenanthrene. Furthermore, a solution of copper(II) chloride in acetone or in acetonitrile failed to react with those hydrocarbons which react under the binary phase conditions. Such an outstanding contrast has not been fully explained by tentatively proposed mechanisms, *e.g.* ionic<sup>3)</sup> or ligand transfer<sup>4)</sup> mechanisms.

The present work deals with the binary phase chlorination of a wide variety of aromatic hydrocarbons by solid copper(II) chloride. The results evidently showed that their reactivities were closely related with their oxidative half-wave potentials ( $E_{1/2ox}$ ), but for some substituted anthracenes steric effects were a dominant factor controlling the reactivity.

### Results and Discussion

**Reactivities of Aromatic Hydrocarbons toward Solid Copper(II) Chloride.** In a typical procedure, aromatic hydrocarbon ( $5 \times 10^{-4}$  mol) was refluxed with pulverized copper(II) chloride ( $1 \times 10^{-3}$  mol) in chlorobenzene. The reaction proceeds under heterogeneous binary phase conditions. The chlorination was followed by means of gas chromatograph and the products were identified by elemental analysis, MS and NMR. The chlorination products obtained are summarized in Table 1. In general, single product was obtained in a high yield under the conditions. Active and inactive hydrocarbons toward solid copper(II) chloride are tabulated in Table 2 together with their  $E_{1/2ox}$  values.

**Voltammetric Measurement of  $E_{1/2ox}$  of Aromatic Hydrocarbons.** To investigate a correlation between  $E_{1/2ox}$  and the reactivity of hydrocarbons toward solid copper-

TABLE 1. CHLORINATION BY COPPER(II) CHLORIDE

| Compound                      | Reaction time/h | Product                                | Yield % |
|-------------------------------|-----------------|----------------------------------------|---------|
| Anthracene <sup>a,c)</sup>    | 2               | 9-Chloroanthracene                     | 80      |
| Anthracene <sup>a,d)</sup>    | 8               | 9-Chloroanthracene                     | 88      |
|                               |                 | 9,10-Dichloroanthracene                | 12      |
| Anthracene <sup>b,d)</sup>    | 4               | 9,10-Dichloroanthracene                | 87      |
| Pyrene <sup>b,c)</sup>        | 3               | 1-Chloropyrene                         | 90      |
| Benz[a]pyrene <sup>a,c)</sup> | 8               | 6-Chlorobenz[a]pyrene                  | 90      |
| Perylene <sup>a,c)</sup>      | 7               | Chloroperylene <sup>c)</sup>           | 90      |
| Perylene <sup>a,d)</sup>      | 7               | Dichloroperylene <sup>c)</sup>         | 90      |
| Naphthacene <sup>b,d)</sup>   | 1.5             | 5,11-Dichloronaphthacene <sup>f)</sup> | 75      |
| Azulene <sup>b,d)</sup>       | 0.5             | 1,3-Dichloroazulene <sup>f)</sup>      | 95      |

Solvent: a) benzene, b) chlorobenzene. Molar ratio (CuCl<sub>2</sub>: compound): c) 2:1, d) 4:1. e) Product was the mixture of isomers. f) Mono chlorides of naphthacene and azulene could not be isolated in pure state.

(II) chloride,  $E_{1/2ox}$  measurements of aromatic hydrocarbons were carried out in an acetonitrile solution containing tetraethylammonium perchlorate (TEAP), using a rotatory platinum disk electrode (2000 rpm). The voltage sweep rate was 0.2 V/min. The data are summarized in Table 2. The correlation between  $E_{1/2ox}$  and the reactivity of an aromatic hydrocarbon for solid copper(II) chloride, if any, is not immediately clear, but it should be emphasized that of the aromatic hydrocarbons examined only those with  $E_{1/2ox}$  below *ca.* 1.26 V were reactive toward solid copper(II) chloride.  $E_{1/2ox}$  correlates linearly with the ionization potential (IP) of aromatic hydrocarbons as proposed by Pysh and co-workers,<sup>5)</sup> and  $E_{1/2ox}$  value of 1.26 V corresponds to 7.68 eV of IP value, which is in a close agreement with that obtained by photoelectroscopy (*ca.* 7.5 eV).<sup>6)</sup> This fact suggests that initial one electron transfer from aromatic  $\pi$ -system to solid copper(II) chloride is a key step required for the initiation of the reaction. The electron transfer may trigger off the reaction. The oxidation potential is obviously lowered by the introduction of electron-donating methyl group to aromatic ring.

It is known that anhydrous solid copper(II) chloride is in covalent state and consists of planar CuCl<sub>4</sub> groups.<sup>7)</sup> In the binary phase chlorination performed in a non-

TABLE 2. OXIDATIVE HALF-WAVE POTENTIALS ( $E_{1/2ox}/V$  vs. SCE<sup>a</sup>) AND REACTIVITIES IN THE CHLORINATION OF HYDROCARBONS BY COPPER(II) CHLORIDE

| Compound                            | $E_{1/2ox}/V$ | Reactivity |
|-------------------------------------|---------------|------------|
| Benzene                             | 2.43          | no         |
| Biphenyl                            | 1.86          | no         |
| Naphthalene                         | 1.72          | no         |
| Triphenylene                        | 1.72          | no         |
| Phenanthrene                        | 1.67          | no         |
| Acenaphthylene                      | 1.62          | no         |
| Chrysene                            | 1.54          | no         |
| Dibenz[ <i>a,h</i> ]anthracene      | 1.41          | no         |
| Benz[ <i>a</i> ]anthracene          | 1.36          | no         |
| 7-Methylbenz[ <i>a</i> ]anthracene  | 1.26          | no         |
| Anthracene                          | 1.26          | yes        |
| Pyrene                              | 1.23          | yes        |
| 1-Methylantracene                   | 1.23          | yes        |
| 12-Methylbenz[ <i>a</i> ]anthracene | 1.22          | no         |
| 2-Methylantracene                   | 1.21          | yes        |
| Benz[ <i>a</i> ]pyrene              | 1.18          | yes        |
| 1,5-Dimethylantracene               | 1.18          | yes        |
| 1,4-Dimethylantracene               | 1.17          | yes        |
| 9-Methylantracene                   | 1.15          | yes        |
| 1,4,5-Trimethylantracene            | 1.04          | yes        |
| Perylene                            | 1.00          | yes        |
| Naphthacene                         | 0.94          | yes        |
| Azulene                             | 0.88          | yes        |

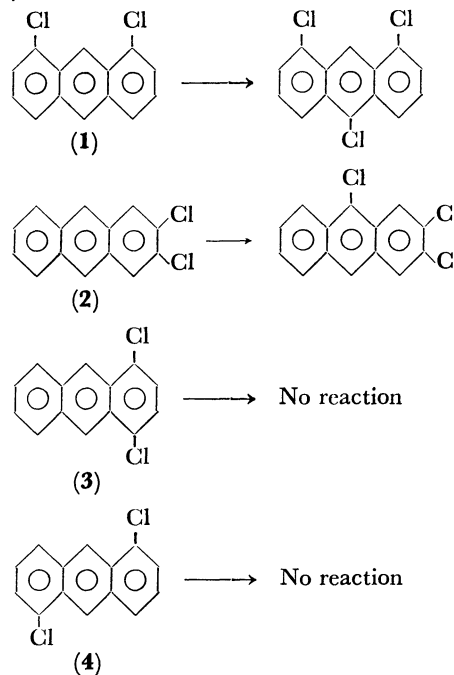
a) Solvent: acetonitrile. Supporting electrolyte : 0.1 M tetraethylammoniumperchlorate. Working electrode: rotatory platinum disk electrode (2000 rpm). Voltage sweep rate: 0.2 V/min.

polar solvent, the planar chloro ligands of anhydrous copper(II) chloride presumably occupies a favorable position for one electron transfer from hydrocarbons to copper(II) clusters. The plane of aromatic ring could approach to solid copper(II) chloride in the fashion parallel with the  $CuCl_4$  surface, and the electron transfer from the approaching hydrocarbon could occur at a critical distance where the aromatic ring plane would come in a close contact with the acceptor orbital of copper(II) chloride. Although  $E_{1/2ox}$  of 7- and 12-methylbenz[*a*]anthracene were 1.26 and 1.22 V (vs. SCE), respectively, they were hardly reactive toward solid copper(II) chloride. Presumably, steric repulsion due to rotating methyl group could prevent the molecule from closely approaching to copper(II) chloride surface in the transition state.

Competitive halogenation of anthracene gives us a further insight of the reacting aspect. Halogenation of anthracene ( $3.8 \times 10^{-4}$  mol) by solid copper(II) bromide ( $7.6 \times 10^{-4}$  mol) in the presence of tetraethylammonium chloride ( $3.8 \times 10^{-4}$  mol) dissolved in chlorobenzene (30 ml) afforded 9-bromoanthracene nearly as a sole product, whereas the halogenation using an equimolar mixture of solid copper(II) chloride and bromide gave a higher yield of 9-chloroanthracene than 9-bromoanthracene (11:1). These facts will readily suggest that the binary phase halogenation proceeds in a closely contacted state of reacting substrate with the surface of solid copper(II) halide.

Chlorination of substituted anthracenes with methyl or chloro groups by solid copper(II) chloride in chlorobenzene resulted in the formation of chlorinated products. The yields and structures of the products together with their  $^1H$ -NMR data are summarized in Table 3 and 4.

From the results of chlorination of substituted anthracenes it is concluded that the rate of chlorination is enhanced by methyl substituent, but in contrary, chloro substituent retarded it. Since the electron-donating substituents lower the oxidation potential of aromatic hydrocarbons, the observation supports the view mentioned above that the reaction is initiated by an electron transfer. In addition, steric effect of the substituents controls the product. Though the monochlorination of substituted anthracenes occurs at 9- or 10-position, less hindered position is more favorable for the chlorination; *e.g.* 1-methyl or 1-chloroanthracene was chlorinated at 10-position. Chlorination of dichloroanthracenes provides a good example to show both steric and electronic effects are operating together. Since  $E_{1/2ox}$  values of 1,8- (1.48 V) (1), 2,3- (1.40 V)



(2), 1,4- (1.48 V) (3), and 1,5-dichloroanthracene (1.40 V) (4) were comparable, they are expected to be similarly reactive toward solid copper(II) chloride. However, 1 and 2 were reactive, but 3 and 4 were not. These results clearly indicate that chlorine atom occupying peri position against 9- or 10-position of anthracene affects a strong steric inhibition on the chlorination.

#### Hydrogen Abstraction by Solid Copper(II) Chloride.

Diphenylmethane, xanthene, tetrahydronaphthalene, and cumene were recovered after refluxing for 14 h with solid copper(II) chloride in cyclohexane, whereas anthracene was chlorinated under the same reaction conditions (Table 5). It is noteworthy that under the present reaction conditions no hydrogen abstraction occurred with those hydrocarbons which allow, in general, an easy hydrogen abstraction by a radical,

TABLE 3. PROTON CHEMICAL SHIFT IN  $\text{CCl}_4$   $\delta$ (ppm from TMS).

## (A) Substituted anthracenes

| Substituent     | H(9-) | H(10-) | H(1-)         | H(8-)         | H(Me-)                              |
|-----------------|-------|--------|---------------|---------------|-------------------------------------|
| —               | 8.31  | 8.31   | 7.88          | 7.88          | —                                   |
| 1-Cl            | 8.77  | 8.32   | —             | $\approx 7.9$ | —                                   |
| 2-Cl            | 8.28  | 8.36   | $\approx 7.9$ | $\approx 7.9$ | —                                   |
| 9-Cl            | —     | 8.24   | 8.38          | 8.38          | —                                   |
| 1,4-Dichloro    | 8.81  | 8.81   | —             | 8.04          | —                                   |
| 1,5-Dichloro    | 8.76  | 8.76   | —             | 7.93          | —                                   |
| 1,8-Dichloro    | 9.24  | 8.38   | —             | —             | —                                   |
| 2,3-Dichloro    | 8.25  | 8.25   | 8.06          | 7.94          | —                                   |
| 1-Me            | 8.39  | 8.28   | —             | $\approx 7.8$ | 2.80                                |
| 9-Me            | —     | 8.15   | 8.08          | 8.08          | 3.07                                |
| 1,4-Dimethyl    | 8.34  | 8.34   | —             | 7.85          | 2.79 (2Me)                          |
| 1,5-Dimethyl    | 8.38  | 8.38   | —             | 7.78          | 2.84 (2Me)                          |
| 1,4,5-Trimethyl | 8.37  | 8.46   | —             | 7.76          | 2.82 (1-Me), 2.82 (1Me), 2.85 (1Me) |

## (B) Chlorination products of substituted anthracenes

| Substituent     | H(9- or 10-) <sup>a)</sup> | H(1-) <sup>a)</sup> | H(8-) <sup>a)</sup> | H(Me-) <sup>a)</sup>              | Substituents in product               |
|-----------------|----------------------------|---------------------|---------------------|-----------------------------------|---------------------------------------|
| —               | 8.24 (10-)                 | 8.38                | 8.38                | —                                 | 9-Cl                                  |
| 1-Cl            | 8.76 (9-)                  | —                   | 8.02                | —                                 | 1,10-diCl                             |
| 2-Cl            | 8.22 (9-)                  | $\approx 7.85$      | $\approx 7.85$      | —                                 | 2,10-diCl                             |
|                 | —                          | 8.48                | $\approx 8.44$      | —                                 | 2,9,10-triCl                          |
| 9-Cl            | —                          | 8.41                | 8.41                | —                                 | 9,10-diCl                             |
| 1,8-Dichloro    | 9.24 (9-)                  | —                   | —                   | —                                 | 1,8,10-triCl                          |
| 2,3-Dichloro    | 8.08 (10-)                 | 8.48                | 8.36                | —                                 | 2,3,9-triCl                           |
| 1-Me            | 8.46 (9-)                  | —                   | 7.96                | 2.81                              | 9-Cl-4-Me (10-Cl-1-Me) <sup>a)</sup>  |
|                 | —                          | —                   | $\approx 8.45$      | 3.22                              | 9,10-diCl-1-Me                        |
| 9-Me            | —                          | 8.42                | 8.42                | 3.06                              | 9-Cl-10-Me (10-Cl-9-Me) <sup>a)</sup> |
| 1,4-Dimethyl    | 8.26 (10-)                 | —                   | 8.45                | 2.70 (4-Me), 3.14 (1-Me)          | 9-Cl-1,4-diMe                         |
| 1,5-Dimethyl    | 8.18 (10-)                 | —                   | 8.32                | 2.70 (5-Me), 3.14 (1-Me)          | 9-Cl-1,5-diMe                         |
|                 | —                          | —                   | $\approx 8.4$       | 3.14 (1- and 5-Me)                | 9,10-diCl-1,5-diMe                    |
| 1,4,5-Trimethyl | 8.46 (10-)                 | —                   | 8.4                 | 2.76 (1Me), 2.82(1Me), 3.16(1-Me) | 9-Cl-1,4,5-triMe                      |

a) Position is numbered after substituted anthracene before chlorination.

TABLE 4. CHLORINATION OF SUBSTITUTED ANTHRACENES BY COPPER(II) CHLORIDE

| Anthracene      | Reaction time/h      | Product                              | Yield/%          | Mp/°C   |
|-----------------|----------------------|--------------------------------------|------------------|---------|
| 1-Chloro        | 16 <sup>a)</sup>     | 1,10-dichloroanthracene              | 75               | 126—127 |
|                 | 4 <sup>b)</sup>      | 1,10-dichloroanthracene              | 90               |         |
| 2-Chloro        | 1 <sup>a)</sup>      | 2,10-dichloroanthracene              | 90               | 115—116 |
|                 | 10 <sup>b)</sup>     | 2,9,10-trichloroanthracene           | 90               | 181—182 |
| 1,8-Dichloro    | 6 <sup>a)</sup>      | 1,8,10-trichloroanthracene           | 90               | 191—192 |
|                 | 10 <sup>b)</sup>     | 1,8,10-trichloroanthracene           | 100              |         |
| 2,3-Dichloro    | 48 <sup>a)</sup>     | 2,3,9-trichloroanthracene            | 90               | 172—173 |
|                 | 23 <sup>b)</sup>     | 2,3,9-trichloroanthracene            | 90 <sup>c)</sup> |         |
| 1,4-Dichloro    | 10 <sup>a, b)</sup>  | no reaction                          |                  |         |
| 1,5-Dichloro    | 10 <sup>a, b)</sup>  | no reaction                          |                  |         |
| 1-Methyl        | 0.5 <sup>a)</sup>    | 9-chloro-4-methylanthracene          | 90               | 66—68   |
|                 | 8 <sup>b)</sup>      | 9,10-dichloro-1-methylanthracene     | 5                | 132—134 |
| 9-Methyl        | 0.5 <sup>a, b)</sup> | 9-chloro-10-methylanthracene         | 90               | 177—178 |
| 1,4-Dimethyl    | 30 <sup>a)</sup>     | 9-chloro-1,4-dimethylanthracene      | 80 <sup>c)</sup> | 41.5—44 |
| 1,5-Dimethyl    | 8 <sup>a)</sup>      | 9-chloro-1,5-dimethylanthracene      | 60               | 111—114 |
|                 | 40 <sup>b)</sup>     | 9,10-dichloro-1,5-dimethylanthracene | 10               | 154—156 |
| 1,4,5-Trimethyl | 26 <sup>a)</sup>     | 9-chloro-1,4,5-trimethylanthracene   | 40               | 120—122 |

Reaction conditions: solvent; chlorobenzene, reaction temp; 132 °C, molar ratio ( $\text{CuCl}_2$ : anthracene); a) 2:1 b) 4:1. c) A product produced by the further chlorination was detected by GLC, but could not be isolated for its low yield.

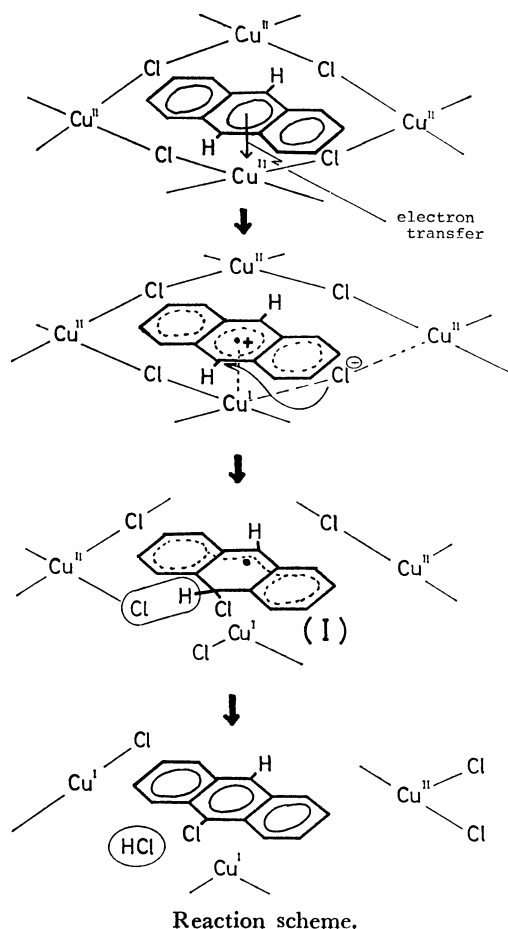
TABLE 5. HYDROGEN ABSTRACTION BY COPPER(II) CHLORIDE

| Compound                                    | Recovery/%       |
|---------------------------------------------|------------------|
| 1,2-Dihydronaphthalene <sup>a)</sup>        | 10 <sup>c)</sup> |
| 9,10-Dihydroanthracene <sup>a)</sup>        | 35 <sup>d)</sup> |
| 1,2,3,4-Tetrahydronaphthalene <sup>b)</sup> | 95               |
| Xanthene <sup>b)</sup>                      | 98               |
| Cumene <sup>b)</sup>                        | 90               |
| Diphenylmethane <sup>b)</sup>               | 100              |

Reaction time: a) 10 min, b) 14 h. Product: c) naphthalene (yield 90%), d) anthracene (yield 65%). Solvent: cyclohexane 10 ml; reaction temp: 80 °C; compound:  $2.5 \times 10^{-3}$  mol;  $\text{CuCl}_2$ :  $5 \times 10^{-3}$  mol.

although 1,2-dihydronaphthalene or 9,10-dihydroanthracene reacted under the same conditions, yielding naphthalene or anthracene together with evolution of hydrogen chloride.

**Reaction Scheme.** As has been shown above, hydrocarbons with IP value lower than *ca.* 7.5 eV were reactive for solid copper(II) chloride chlorination. 7- and 12-Methylbenz[*a*]anthracene, both nonreactive, may be the borderline case, where spatial repulsive effect due to the methyl group presumably inhibits the initial electron transfer from the hydrocarbons to copper(II) chloride. The electron transfer will trigger the chlorination. This is strongly supported by the above-mentioned electronic effect of methyl and chloro substituents. Once an electron is transferred to copper(II) chloride from a hydrocarbon, the resulting cation



radical of the aromatic hydrocarbon could be immediately attacked by chloride anion at the less hindered, but the highest positively charged position to give (I). Although copper(II) chloride is a typical ligand-transfer oxidation reagent toward a radical, under the present reaction conditions the reagent may abstract a hydrogen atom from the radical (I) and convert it into the stable chlorinated aromatic molecule (see Reaction scheme).

## Experimental

Melting points were measured on a micro hot-stage manufactured by Mitamura Riken Kogyo Inc. and were uncorrected. <sup>1</sup>H-NMR spectra were recorded on a JEOL MH-100 spectrometer with Me<sub>4</sub>Si as an internal standard. GLC analyses were carried out on a JEOL Model JGC-1100 using a 1 m column packed with Apiezone L grease 3 wt % on Celite 545 NAW. HPLC analyses were performed on a Shimadzu liquid chromatograph Model LC-2F equipped with a Shimadzu-Du Pont Permaphase ODS column. Voltammetry was carried out in an acetonitrile solution on a Yanagimoto Model P-8 polarograph. The working electrode was a rotatory platinum disk electrode (2000 rpm). An aqueous saturated calomel electrode (SCE) and a platinum electrode were used as a reference and a counter electrode, respectively. Voltage sweep rate was 0.2 V/min. Tetraethylammonium perchlorate (Eastman) was used as supporting electrolyte (0.1 M).

**Materials.** Anhydrous copper(II) chloride was prepared by heating copper(II) chloride dihydrate in an oven at 110 °C for 20 h. 1,2-Dihydronaphthalene (Aldrich) was used without further purification.

The following substrates were prepared according to the procedure described in literature.

**1-Methylanthracene:**<sup>8)</sup> Mp 85 °C (lit, mp 86 °C); NMR ( $\text{CCl}_4$ )  $\delta$ =2.80 (3H, s, 1-Me), 7.20–7.50 (2-, 3-, 6-, and 7-H, m), 7.6–8.1 (4-, 5-, and 8-H, m), 8.28 (10-H, s) and 8.39 (9-H, s).

**1,4-Dimethylanthracene:**<sup>8)</sup> Mp 73–74 °C (lit, mp 74 °C); NMR ( $\text{CCl}_4$ )  $\delta$ =2.79 (6H, s, 1- and 4-Me), 7.03 (2- and 3-H, s), 7.30 (6- and 7-H, dd, *J*=8 and 2 Hz), 7.85 (5- and 8-H, dd, *J*=8 and 2 Hz) and 8.34 (9- and 10-H, s).

**1-Chloroanthracene:**<sup>9)</sup> Mp 84–85 °C (lit, mp 81–82 °C); NMR ( $\text{CCl}_4$ )  $\delta$ =7.18–7.58 (2-, 3-, 6-, and 7-H, m), 7.76–8.12 (4-, 5-, and 8-H, m), 8.32 (10-H, s) and 8.77 (9-H, s).

**2-Chloroanthracene:**<sup>9)</sup> Mp 223 °C (lit, mp<sup>10)</sup> 223 °C); NMR ( $\text{CCl}_4$ )  $\delta$ =7.28–7.60 (3-, 6-, and 7-H, m), 7.80–8.05 (1-, 4-, 5-, and 8-H, m), 8.28 (9-H, s) and 8.36 (10-H, s).

**1,4-Dichloroanthracene:**<sup>11)</sup> Mp 179–181 °C (lit, mp 180 °C); NMR ( $\text{CCl}_4$ )  $\delta$ =7.44 (2- and 3-H, s), 7.50 (6- and 7-H, dd, *J*=8 and 2 Hz), 8.04 (5- and 8-H, dd, *J*=8 and 2 Hz) and 8.81 (9- and 10-H, s).

**1,5-Dichloroanthracene:**<sup>9)</sup> Mp 181–182 °C (lit, mp 185 °C); NMR ( $\text{CCl}_4$ )  $\delta$ =7.32 (3- and 7-H, t, *J*=8 Hz), 7.55 (2- and 6-H, d, *J*=8 Hz), 7.93 (4- and 8-H, d, *J*=8 Hz) and 8.76 (9- and 10-H, s).

**1,8-Dichloroanthracene:**<sup>9)</sup> Mp 151–153 °C (lit, mp 156 °C); NMR ( $\text{CCl}_4$ )  $\delta$ =7.35 (3- and 6-H, t, *J*=8 Hz), 7.59 (2- and 7-H, d, *J*=8 Hz), 7.87 (4- and 5-H, d, *J*=8 Hz), 8.38 (10-H, s) and 9.24 (9-H, s).

**2,3-Dichloroanthracene:**<sup>12)</sup> Mp 265–265.5 °C (lit, mp 261 °C); NMR ( $\text{CCl}_4$ )  $\delta$ =7.3–7.58 (6- and 7-H, m), 7.94 (5- and 8-H, dd, *J*=8 and 2 Hz), 8.06 (1- and 4-H, s) and 8.25 (9- and 10-H, s).

**7-Methylbenz[*a*]anthracene:**<sup>12)</sup> Mp 138.5–139.5 °C (lit, mp<sup>13)</sup>

140.5—141.5 °C).

*12-Methylbenz[a]anthracene*:<sup>12</sup> Mp 136—137 °C (lit, mp 138—139 °C).

*1,5-Dimethyl- (5) and 1,4,5-Trimethylantracene (6)*: Synthesis of **6** was performed as follows. 3,6-Dimethylphthalic anhydride (**7**) was obtained from maleic anhydride and 2,5-dimethylfuran.<sup>14</sup> The reaction of **7** and 2-methylphenylmagnesium bromide afforded 2-(2-methylbenzoyl)-3,6-dimethylbenzoic acid (**8**) by a similar procedure described for 2-benzoyl-3-methylbenzoic acid.<sup>15</sup> By the heating of **8** and concentrated sulfuric acid for 1.5 h in a steam bath, 1,4,5-trimethylantracene (**9**) (mp 142—147 °C, lit, mp<sup>16</sup> 143 °C) was obtained. The reduction of **9** by zinc dust and aqueous ammonia afforded **6**. 1,5-Dimethylantracene was prepared by a similar method. **5**: mp 139—140 °C (lit, mp<sup>17</sup> 139—140 °C); NMR (CCl<sub>4</sub>)  $\delta$ =2.84 (6H, s, 2Me), 7.12—7.30 (2-, 3-, 6-, and 7-H, m), 7.78 (4- and 8-H, dd,  $J$ =8 and 2 Hz) and 8.38 (9- and 10-H, s). **6**: mp 107.5—108.5 °C; NMR (CCl<sub>4</sub>)  $\delta$ =2.82 (6H, s, 2Me), 2.85 (3H, s, 1Me), 7.07 (2- and 3-H, s), 7.18—7.32 (6- and 7-H, m), 7.76 (8-H, dd,  $J$ =8 and 2 Hz), 8.37 (9-H, s) and 8.46 (10-H, s). Found: C, 92.83; H, 7.38%; M<sup>+</sup>, 220. Calcd for C<sub>17</sub>H<sub>16</sub>: C, 92.68; H, 7.32%; M 220.

**General Reaction Procedures.** Anhydrous copper(II) chloride (2.2 or 4.4 mmol) and aromatic hydrocarbons (1 mmol) was refluxed with stirring in 10 ml of chlorobenzene for appropriate reaction time. The reaction was stopped when the yield of product, which was followed by GLC, reached to a maximum. The reaction of azulene was followed by HPLC, in which methanol–water was used as the eluent at a rate of 1 ml/min. After usual work-up the crude product was dissolved in benzene and eluted by petroleum ether on a Florisil column.

**Identification of Products.** *9-Chloroanthracene*: Mp 103 °C (lit, mp<sup>18</sup> 105.2—107 °C); NMR (CCl<sub>4</sub>)  $\delta$ =7.3—7.6 (2-, 3-, 6-, and 7-H, m), 7.87 (4- and 5-H, dd,  $J$ =8 and 2 Hz), 8.24 (10-H, s) and 8.38 (1- and 8-H, dd,  $J$ =8 and 2 Hz). (Found: C, 79.20; H, 4.32%).

*9,10-Dichloroanthracene*: Mp 210 °C (lit, mp<sup>19</sup> 209 °C) NMR (CCl<sub>4</sub>)  $\delta$ =7.5 (2-, 3-, 6-, and 7-H, dd,  $J$ =8 and 2 Hz) and 8.41 (1-, 4-, 5-, and 8-H, dd,  $J$ =8 and 2 Hz). (Found: C, 67.88; H, 3.11%).

*1-Chlorophyrene*: Mp 116—118 °C (lit, mp<sup>20</sup> 119 °C). (Found: C, 80.71; H, 3.69%; M<sup>+</sup> 236).

*6-Chlorobenz[a]pyrene*: Mp 212 °C (lit, mp<sup>21</sup> 210 °C). (Found: C, 83.17; H, 3.71%; M<sup>+</sup> 286).

*Chloroperylene*: Mp 243—246 °C. (Found: C, 80.96; H, 3.65%. Calcd for C<sub>20</sub>H<sub>11</sub>Cl: C, 83.77; H, 3.87%).

*Dichloroperylene*: Mp 222—226 °C.<sup>22</sup> (Found: C, 73.97; H, 3.04%. Calcd for C<sub>20</sub>H<sub>10</sub>Cl<sub>2</sub>: C, 74.74; H, 3.14%).

*5,11-Dichloronaphthacene*: Mp 227—228 °C (lit, mp<sup>23</sup> 220 °C); NMR (CDCl<sub>3</sub>)  $\delta$ =7.4—7.7 (2-, 3-, 8- and 9-H, m), 8.10 (1- and 7-H, d,  $J$ =8 Hz), 8.50 (4- and 10-H, d,  $J$ =8 Hz) and 9.12 (6- and 12-H, s). (Found: C, 72.70; H, 3.25%).

*1,3-Dichloroazulene*: Mp 93—94 °C; NMR (CCl<sub>4</sub>)  $\delta$ =7.13 (5- and 7-H, t,  $J$ =10 Hz). Found: C, 61.02; H, 2.95%; M<sup>+</sup>, 197. Calcd for C<sub>10</sub>H<sub>6</sub>Cl<sub>2</sub>: C, 60.95; H, 3.07%; M, 197.

*1,10-Dichloroanthracene*: Mp 126—127 °C (lit, mp<sup>24</sup> 127—128 °C has been reported as the mp of 1,9- or 1,10-dichloroanthracene); NMR (CCl<sub>4</sub>)  $\delta$ =7.32—7.68 (2-, 3-, 6-, and 7-H, m), 8.02 (8-H, dd,  $J$ =8 and 2 Hz), 8.42 (4- and 5-H, dd,  $J$ =8 and 2 Hz) and 8.76 (9-H, s). Found: C, 68.20; H, 3.29%; M<sup>+</sup>, 246. Calcd for C<sub>14</sub>H<sub>8</sub>Cl<sub>2</sub>: C, 68.04; H, 3.26%; M, 246.

*2,10-Dichloroanthracene*: Mp 115—116 °C; NMR (CCl<sub>4</sub>)  $\delta$ =7.3—7.7 (3-, 6- and 7-H, m), 7.78—7.96 (1- and 8-H,

m), 8.22 (9-H, s), 8.3—8.5 (4- and 5-H, m). Close examination of NMR data showed that the sharp peak due to 1-H at  $\delta$ =ca. 8.5 was characteristic of 2,9-dichloro substituted anthracenes. Accordingly, the lack of this peak necessarily indicates that the present product is 2,10-dichloroanthracene. Found: C, 68.24; H, 3.33%; M<sup>+</sup>, 246. Calcd for C<sub>14</sub>H<sub>8</sub>Cl<sub>2</sub>: C, 68.04; H, 3.26%; M, 246.

*2,9,10-Trichloroanthracene*: Mp 181—182 °C (lit, mp<sup>24</sup> 178 °C); NMR (CCl<sub>4</sub>)  $\delta$ =7.5—7.7 (3-, 6-, and 7-H, m), 8.4—8.55 (4-, 5-, and 8-H, m) and 8.48 (1-H, s).

*1,8,10-Trichloroanthracene*: Mp 191—192 °C (lit, mp<sup>25</sup> 194 °C); NMR (CCl<sub>4</sub>)  $\delta$ =7.4—7.7 (2-, 3-, 6-, and 7-H, m), 8.40 (4- and 5-H, d,  $J$ =8 Hz) and 9.24 (9-H, s).

*2,3,9-Trichloroanthracene*: Mp 172—173 °C; NMR (CCl<sub>4</sub>)  $\delta$ =7.4—7.7 (6- and 7-H, m), 7.86 (5-H, dd,  $J$ =8 and 2 Hz), 7.95 (4-H, s), 8.08 (10-H, s), 8.36 (8-H, dd,  $J$ =8 and 2 Hz) and 8.48 (1-H, s). Found: C, 59.84; H, 2.52%; M<sup>+</sup>, 281. Calcd for C<sub>14</sub>H<sub>7</sub>Cl<sub>3</sub>: C, 59.72; H, 2.51%; M, 281.

*9-Chloro-10-methylantracene*: Mp 177—178 °C; NMR (CCl<sub>4</sub>)  $\delta$ =3.06 (3H, s, 10-Me), 7.3—7.6 (2-, 3-, 6-, and 7-H, m), 8.15 (4- and 5-H, dd,  $J$ =8 and 2 Hz) and 8.42 (1- and 8-H, dd,  $J$ =8 and 2 Hz). Found: C, 79.20; H, 5.12%; M<sup>+</sup>, 226. Calcd for C<sub>15</sub>H<sub>11</sub>Cl: C, 79.47; H, 4.89%; M, 226.

*9-Chloro-4-methylantracene*: Mp 66—68 °C; NMR (CCl<sub>4</sub>)  $\delta$ =2.81 (3H, s, 4-Me), 7.15—7.60 (2-, 3-, 6-, and 7-H, m), 7.96 (5-H, dd,  $J$ =8 and 2 Hz), 8.32 and 8.50 (1- and 8-H, dd,  $J$ =8 and 2 Hz) and 8.46 (10-H, s). Found: C, 79.25; H, 5.08%; M<sup>+</sup>, 226. Calcd for C<sub>15</sub>H<sub>11</sub>Cl: C, 79.47; H, 4.89%; M, 226.

*9,10-Dichloro-1-methylantracene*: Mp 132—134 °C; NMR (CCl<sub>4</sub>)  $\delta$ =3.22 (3H, s, 1-Me), 7.2—7.64 (2-, 3-, 6-, and 7-H, m) and 8.3—8.6 (4-, 5-, and 8-H, m). Found: C, 69.89; H, 3.70%; M<sup>+</sup>, 260. Calcd for C<sub>15</sub>H<sub>10</sub>Cl<sub>2</sub>: C, 68.99; H, 3.86%; M, 260.

*9-Chloro-1,4-dimethylantracene*: Mp 41.5—44.0 °C; NMR (CCl<sub>4</sub>)  $\delta$ =2.70 (3H, s, 4-Me), 3.14 (3H, s, 1-Me), 7.04 (2- and 3-H, s), 7.3—7.56 (6- and 7-H, m), 7.8 (5-H, dd,  $J$ =8 and 2 Hz), 8.26 (10-H, s) and 8.45 (8-H, d,  $J$ =8 Hz). Found: C, 79.45; H, 5.40%; M<sup>+</sup>, 240. Calcd for C<sub>16</sub>H<sub>13</sub>Cl: C, 79.83; H, 5.44%; M, 240.

*9-Chloro-1,5-dimethylantracene*: Mp 111—114 °C; NMR (CCl<sub>4</sub>)  $\delta$ =2.70 (3H, s, 5-Me), 3.14 (3H, s, 1-Me), 7.1—7.4 (2-, 3-, 6-, and 7-H, m), 7.5—7.7 (4-H, m), 8.18 (10-H, s) and 8.32 (8-H, d,  $J$ =8 Hz). Found: C, 80.12; H, 5.48%; M<sup>+</sup>, 240. Calcd for C<sub>16</sub>H<sub>13</sub>Cl: C, 79.83; H, 5.44%; M, 240.

*9,10-Dichloro-1,5-dimethylantracene*: Mp 154—156 °C; NMR (CCl<sub>4</sub>)  $\delta$ =3.14 (6H, s, 1- and 5-Me), 7.2—7.40 (2-, 3-, 6-, and 7-H, m) and 8.3—8.5 (4- and 8-H, m). Found: C, 70.18; H, 4.63%; M<sup>+</sup>, 274. Calcd for C<sub>16</sub>H<sub>12</sub>Cl<sub>2</sub>: C, 69.84; H, 4.40%; M, 274.

*9-Chloro-1,4,5-trimethylantracene*: Mp 120—122 °C; NMR (CCl<sub>4</sub>)  $\delta$ =2.76 (3H, s, Me), 2.82 (3H, s, Me), 3.16 (3H, s, 1-Me), 7.1 (2- and 3-H, s), 7.1—7.5 (6- and 7-H, m), 8.4 (8-H, d,  $J$ =8 Hz) and 8.46 (10-H, s). Found: C, 80.40; H, 6.10%; M<sup>+</sup>, 254. Calcd for C<sub>17</sub>H<sub>15</sub>Cl: C, 80.15; H, 5.94%; M, 254.

The present work was partially supported by a Research Grant from Kyoto Women's University.

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