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

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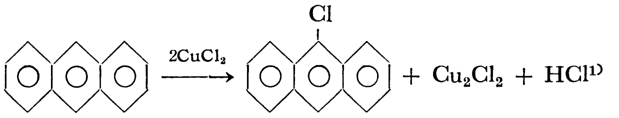
Anthracene is selectively chlorinated with solid copper(II) chloride to give a quantitative yield of 9-chloroanthracene. The tentative reaction mechanisms so far proposed fail to explain the nonreactivity of some other hydrocarbon homologues, *e.g.* naphthalene and phenanthrene, toward copper(II) chloride. The present study revealed that the oxidative half-wave potentials ($E_{1/2\text{ox}}$) 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,[2)] 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[3)] or ligand transfer[4)] 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 ($E_{1/2\text{ox}}$), 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 (5×10^{-4} mol) was refluxed with pulverized copper(II) chloride (1×10^{-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 $E_{1/2\text{ox}}$ values.

TABLE 1. CHLORINATION BY COPPER(II) CHLORIDE

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

Solvent: a) benzene, b) chlorobenzene. Molar ratio (CuCl$_2$: 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.

Voltammetric Measurement of $E_{1/2\text{ox}}$ of Aromatic Hydrocarbons. To investigate a correlation between $E_{1/2\text{ox}}$ and the reactivity of hydrocarbons toward solid copper(II) chloride, $E_{1/2\text{ox}}$ 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 $E_{1/2\text{ox}}$ 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 $E_{1/2\text{ox}}$ below *ca.* 1.26 V were reactive toward solid copper(II) chloride. $E_{1/2\text{ox}}$ correlates linearly with the ionization potential (IP) of aromatic hydrocarbons as proposed by Pysh and co-workers,[5)] and $E_{1/2\text{ox}}$ 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).[6)] This fact suggests that initial one electron transfer from aromatic π-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$_4$ groups.[7)] In the binary phase chlorination performed in a non-

Table 2. Oxidative half-wave potentials ($E_{1/2\mathrm{ox}}$/V *vs.* SCE[a]) and reactivities in the chlorination of hydrocarbons by copper(II) chloride

Compound	$E_{1/2\mathrm{ox}}$/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[*a,h*]anthracene	1.41	no
Benz[*a*]anthracene	1.36	no
7-Methylbenz[*a*]anthracene	1.26	no
Anthracene	1.26	yes
Pyrene	1.23	yes
1-Methylanthracene	1.23	yes
12-Methylbenz[*a*]anthracene	1.22	no
2-Methylanthracene	1.21	yes
Benz[*a*]pyrene	1.18	yes
1,5-Dimethylanthracene	1.18	yes
1,4-Dimethylanthracene	1.17	yes
9-Methylanthracene	1.15	yes
1,4,5-Trimethylanthracene	1.04	yes
Perylene	1.00	yes
Naphthacene	0.94	yes
Azulene	0.88	yes

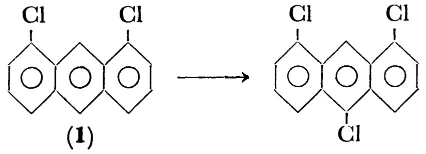
a) Solvent: acetonitrile. Supporting electrolyte : 0.1 M tetraethylammoniumperchlorate. Working electrode: rotatory platinum disk electrode (2000 rpm). Voltage sweep rate: 0.2 V/min.

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 $E_{1/2\mathrm{ox}}$ 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.

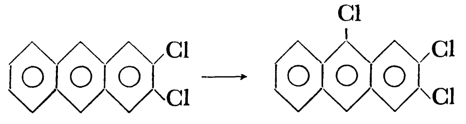
Competitive halogenation of anthracene gives us a further insight of the reacting aspect. Halogenation of anthracene (3.8×10^{-4} mol) by solid copper(II) bromide (7.6×10^{-4} mol) in the presence of tetraethylammonium chloride (3.8×10^{-4} mol) dissolved in chlorobenzene (30 ml) afforded 9-bromoanthracene 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 ^{1}H-NMR data are summarized in Table 3 and 4.

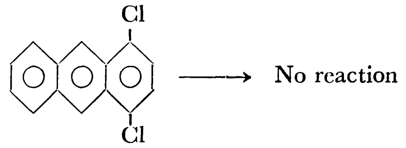
From the results of chlorination of substituted anthracenes it is concluded that the rate of chlorination is enhanced by methyl substituent, but in contrary, chloro substituent retarded it. Since the electron-donating substituents lower the oxidation potential of aromatic hydrocarbons, the observation supports the view mentioned above that the reaction is initiated by an electron transfer. In addition, steric effect of the substituents controlls 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 $E_{1/2\mathrm{ox}}$ 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 indicates that chlorine atom occupying peri position against 9- or 10-position of anthracene affects a strong steric inhibition on the chlorination.



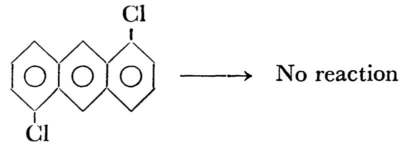
(**1**)



(**2**)



(**3**)



(**4**)

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 CCl_4 δ(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	—	≈7.9	—
2-Cl	8.28	8.36	≈7.9	≈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	—	≈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-)[a]	H(1-)[a]	H(8-)[a]	H(Me-)[a]	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-)	≈7.85	≈7.85	—	2,10-diCl
	—	8.48	≈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)[a]
	—	—	≈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)[a]
1,4-Dimethyl	8.26(10-)	—	8.45	2.70 (4-Me), 3.14 (1-Me)	9-Cl-1,4-diMe
1,5-Dimethy	8.18(10-)	—	8.32	2.70 (5-Me), 3.14 (1-Me)	9-Cl-1,5-diMe
	—	—	≈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[a]	1,10-dichloroanthracene	75	126—127
	4[b]	1,10-dichloroanthracene	90	
2-Chloro	1[a]	2,10-dichloroanthracene	90	115—116
	10[b]	2,9,10-trichloroanthracene	90	181—182
1,8-Dichloro	6[a]	1,8,10-trichloroanthracene	90	191—192
	10[b]	1,8,10-trichloroanthracene	100	
2,3-Dichloro	48[a]	2,3,9-trichloroanthracene	90	172—173
	23[b]	2,3,9-trichloroanthracene	90[c]	
1,4-Dichloro	10[a,b]	no reaction		
1,5-Dichloro	10[a,b]	no reaction		
1-Methyl	0.5[a]	9-chloro-4-methylanthracene	90	66—68
	8[b]	9,10-dichloro-1-methylanthracene	5	132—134
9-Methyl	0.5[a,b]	9-chloro-10-methylanthracene	90	177—178
1,4-Dimethyl	30[a]	9-chloro-1,4-dimethylanthracene	80[c]	41.5—44
1,5-Dimethyl	8[a]	9-chloro-1,5-dimethylanthracene	60	111—114
	40[b]	9,10-dichloro-1,5-dimethylanthracene	10	154—156
1,4,5-Trimethyl	26[a]	9-chloro-1,4,5-trimethylanthracene	40	120—122

Reaction conditions: solvent; chlorobenzene, reaction temp; 132 °C, molar ratio ($CuCl_2$: 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.

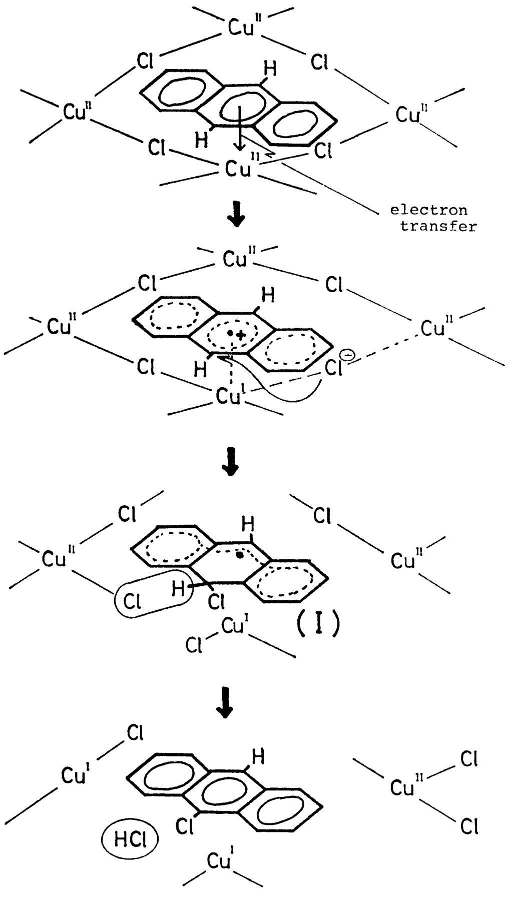
Table 5. Hydrogen abstraction by copper(II) chloride

Compound	Recovery/%
1,2-Dihydronaphthalene[a]	10[c]
9,10-Dihydroanthracene[a]	35[d]
1,2,3,4-Tetrahydronaphthalene[b]	95
Xanthene[b]	98
Cumene[b]	90
Diphenylmethane[b]	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: 2.5×10^{-3} mol; $CuCl_2$: 5×10^{-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).



Reaction scheme.

Experimental

Melting points were measured on a micro hot-stage manufactured by Mitamura Riken Kogyo Inc. and were uncorrected. ^{1}H-NMR spectra were recorded on a JEOL MH-100 spectrometer with Me_4Si 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:[8] Mp 85 °C (lit, mp 86 °C); NMR (CCl_4) δ=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:[8] Mp 73—74 °C (lit, mp 74 °C); NMR (CCl_4) δ=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:[9] Mp 84—85 °C (lit, mp 81—82 °C); NMR (CCl_4) δ=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:[9] Mp 223 °C (lit, mp[10] 223 °C); NMR (CCl_4) δ=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:[11] Mp 179—181 °C (lit, mp 180 °C); NMR (CCl_4) δ=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:[9] Mp 181—182 °C (lit, mp 185 °C); NMR (CCl_4) δ=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:[9] Mp 151—153 °C (lit, mp 156 °C); NMR (CCl_4) δ=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:[11] Mp 265—265.5 °C (lit, mp 261 °C); NMR (CCl_4) δ=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:*[12] Mp 138.5—139.5 °C (lit, mp[13]

140.5—141.5 °C).

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

1,5-Dimethyl- (5) and 1,4,5-Trimethylanthracene (6): Synthesis of **6** was performed as follows. 3,6-Dimethylphthalic anhydride (**7**) was obtained from maleic anhydride and 2,5-dimethylfuran.[14] 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.[15] By the heating of **8** and concentrated sulfuric acid for 1.5 h in a steam bath, 1,4,5-trimethylanthraquinone (**9**) (mp 142—147 °C, lit, mp[16] 143 °C) was obtained. The reduction of **9** by zinc dust and aqueous ammonia afforded **6**. 1,5-Dimethylanthracene was prepared by a similar method. **5**: mp 139—140 °C (lit, mp[17] 139—140 °C); NMR (CCl_4) $\delta=2.84$ (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_4) $\delta=2.82$ (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+, 220. Calcd for $C_{17}H_{16}$: 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[18] 105.2—107 °C); NMR (CCl_4) $\delta=7.3$—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[19] 209 °C) NMR (CCl_4) $\delta=7.5$ (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-Chloropyrene: Mp 116—118 °C (lit, mp[20] 119 °C). (Found: C, 80.71; H, 3.69%; M+ 236).

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

Chloroperylene: Mp 243—246 °C. (Found: C, 80.96; H, 3.65%. Calcd for $C_{20}H_{11}Cl$: C, 83.77; H, 3.87%).

Dichloroperylene: Mp 222—226 °C.[22] (Found: C, 73.97; H, 3.04%. Calcd for $C_{20}H_{10}Cl_2$: C, 74.74; H, 3.14%).

5,11-Dichloronaphthacene: Mp 227—228 °C (lit, mp[23] 220 °C); NMR ($CDCl_3$) $\delta=7.4$—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_4) $\delta=7.13$ (5- and 7-H, t, $J=10$ Hz). Found: C, 61.02; H, 2.95%; M+, 197. Calcd for $C_{10}H_6Cl_2$: C, 60.95; H, 3.07%; M, 197.

1,10-Dichloroanthracene: Mp 126—127 °C (lit, mp[24] 127—128 °C has been reported as the mp of 1,9- or 1,10-dichloroanthracene); NMR (CCl_4) $\delta=7.32$—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+, 246. Calcd for $C_{14}H_8Cl_2$: C, 68.04; H, 3.26 %; M, 246.

2,10-Dichloroanthracene: Mp 115—116 °C; NMR (CCl_4) $\delta=7.3$—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+, 246. Calcd for $C_{14}H_8Cl_2$: C, 68.04; H, 3.26%; M, 246.

2,9,10-Trichloroanthracene: Mp 181—182 °C (lit, mp[24] 178 °C); NMR (CCl_4) $\delta=7.5$—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[25] 194 °C); NMR (CCl_4) $\delta=7.4$—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_4) $\delta=7.4$—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+, 281. Calcd for $C_{14}H_7Cl_3$: C, 59.72; H, 2.51%; M, 281.

9-Chloro-10-methylanthracene: Mp 177—178 °C; NMR (CCl_4) $\delta=3.06$ (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+, 226. Calcd for $C_{15}H_{11}Cl$: C, 79.47; H, 4.89%; M, 226.

9-Chloro-4-methylanthracene: Mp 66—68 °C; NMR (CCl_4 $\delta=2.81$ (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+, 226. Calcd for $C_{15}H_{11}Cl$: C, 79.47; H, 4.89 %; M, 226.

9,10-Dichloro-1-methylanthracene: Mp 132—134 °C; NMR (CCl_4) $\delta=3.22$ (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+, 260. Calcd for $C_{15}H_{10}Cl_2$: C, 68.99; H, 3.86%; M, 260.

9-Chloro-1,4-dimethylanthracene: Mp 41.5—44.0 °C; NMR (CCl_4) $\delta=2.70$ (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+, 240. Calcd for $C_{16}H_{13}Cl$: C, 79.83; H, 5.44%; M, 240.

9-Chloro-1,5-dimethylanthracene: Mp 111—114 °C; NMR (CCl_4) $\delta=2.70$ (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+, 240. Calcd for $C_{16}H_{13}Cl$: C, 79.83; H, 5.44%; M, 240.

9,10-Dichloro-1,5-dimethylanthracene: Mp 154—156 °C; NMR (CCl_4) $\delta=3.14$ (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+, 274. Calcd for $C_{16}H_{12}Cl_2$: C, 69.84; H, 4.40%; M, 274.

9-Chloro-1,4,5-trimethylanthracene: Mp 120—122 °C; NMR (CCl_4) $\delta=2.76$ (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+, 254. Calcd for $C_{17}H_{15}Cl$: C, 80.15; H, 5.94%; M, 254.

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