hr.; this corresponds to an uptake of 3.06 moles of hydrogen per mole of I. A similar experiment in which the perchloric acid was omitted, resulted in the uptake of 2.79 moles of hydrogen per mole of I during 2 hr. The products were inhomogeneous oils with strong absorption in the infrared at 1700–1710 cm.$^{-1}$

Hydrolysis of I. Two putatively identical hydrolyses were performed. A solution of 1.25 g. (5.0 mmoles) of I, 5.0 ml. of water, and ten drops of concd. perchloric acid in 25 ml. of dioxane was allowed to stand for 3 days. Then 5 ml. of 10% sodium hydroxide solution was added and the mixture heated to reflux for 1 hr. The resulting mixture was poured into ether and water, the water layer acidified, extracted an additional time with ether, and the combined ether layers washed with saturated saline and dried over magnesium sulfate. The ether was removed *in vacuo*, the residue taken up in petroleum ether (60–80°), concentrated, and chromatographed on activated neutral alumina. From the first of the two hydrolyses (done on one-fifth the above scale) two crystalline substances were obtained in about 11 and 6% yields, respectively: A, from the pentane eluates, m.p. 50–60°, a ketone (ν_{max}^{KBr} 1690 cm.$^{-1}$). Vacuum sublimation gave partial separation; the less volatile material formed needles m.p. 69.0–69.5°. Ultraviolet: tail absorption only, $\epsilon_{220}^{95\%\ C_2H_5OH} \sim 670$. A trace of more volatile material was probably compound C, below.

Anal. Calcd. for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.60; H, 9.32.

B, from the 1:1 pentane:ether eluates, m.p. 70–85° Two recrystallizations from petroleum ether gave platelets, m.p. 121–123°, a hydroxy ketone (ν_{max}^{KBr} 3400, 1697 cm.$^{-1}$). Ultraviolet: weak absorption only, $\epsilon_{220}^{95\%\ C_2H_5OH} \sim 530$; $\epsilon_{280}^{95\%\ C_2H_5OH} \sim 45$.

Anal. Calcd. for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.88; H, 9.05.

From the second hydrolysis two different crystalline substances were obtained in roughly 10% yield each:

C, from the 4:1 pentane:ether eluates, m.p. 81–82°. Vacuum sublimation gave well formed rhombs, m.p. 82.0–83.5°, a hydroxy (?) ketone [ν_{max}^{KBr} 1690 cm.$^{-1}$, 3400 (weak-water in potassium bromide ?)]. Ultraviolet: tail absorption only, $\epsilon_{220}^{95\%\ C_2H_5OH} \sim 690$.

Anal. Calcd. for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.86; H, 9.32.

D, from wet ether eluates, m.p. 80–115°. Sixfold crystallization from petroleum ether gave a very poor recovery of thick needles, m.p. 140–141°, an unsaturated hydroxy ketone (ν_{max}^{KBr} 1638, 3400 cm.$^{-1}$). Ultraviolet: $\lambda_{max}^{95\%\ C_2H_5OH}$ 236 mμ (ϵ 9500). The behavior on crystallization made it evident that the crude material contains at least one other substance more soluble in petroleum ether than D which has not been obtained in a pure state.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.92; H, 8.95.

LOS ANGELES 24, CALIF.

[CONTRIBUTION FROM RESEARCH LABORATORY, UNION CARBIDE CONSUMER PRODUCTS CO., DIVISION OF UNION CARBIDE CORP.]

Chlorination of Aromatic Hydrocarbons by Cupric Chloride. I. Anthracene

JUDITH C. WARE AND EARL E. BORCHERT

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A study has been made of the reaction of cupric chloride with anthracene to yield 9-chloro- and 9,10-dichloroanthracenes, cuprous chloride and hydrogen chloride. An analogous reaction occurred with cupric bromide. The available evidence is consistent with a polar mechanism. A comparison is made of the reactivity of cupric chloride with that of other metal chlorides, some of which are known to act as chlorinating agents.

Several metal chlorides, among them ferric chloride,[1] antimony pentachloride,[2] and aluminum chloride,[3] can effect chlorination of aromatic hydrocarbons. Considerable evidence has been adduced[1a] to suggest that the reactions proceed by a polar mechanism wherein the metal halide acts as an electrophile. It has been found that cupric chloride also functions as a chlorinating agent, yielding the products to be expected for electrophilic chlorination:

$$Ar—H + 2\ CuCl_2 \longrightarrow Ar—Cl + 2\ CuCl + 2\ HCl$$

(1) (a) P. Kovacic and N. O. Brace, *J. Am. Chem. Soc.*, **76**, 5491 (1954) and references cited therein; (b) P. Kovacic, R. W. Stewart, and F. J. Donat, Abstracts of Papers, 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957, p. 71-O.

(2) (a) J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. IX, Longmans, Green and Co., New York, N. Y. (1929), p. 489; (b) P. Kovacic and A. K. Sparks, Abstracts of Papers, 136th Meeting of the American Chemical Society, Atlantic City, N. J. (September 1959), p. 23-P.

(3) A. Zinke, F. Funke, and N. Lorber, *Ber.*, **60**, 577 (1927).

The results of a study of the scope and nature of the reaction are presented here.

RESULTS AND DISCUSSION

When a mixture of anthracene and anhydrous cupric chloride was heated at 200°, a yellow solid rapidly sublimed out of the reaction vessel. Hydrogen chloride was evolved as well. Investigation showed the yellow material to consist of a mixture of chloroanthracenes.

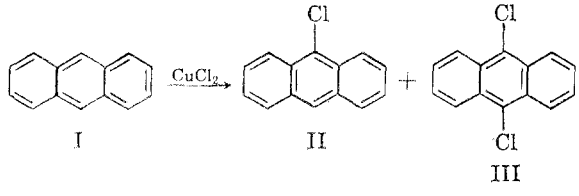
The nature of the reaction was explored by further experiments with anthracene (I), which was selected because its chlorination products were relatively well characterized and easily separated. 9-Chloroanthracene (II) and 9,10-dichloroanthracene (III) were isolated. The reaction product was treated by removing the solvent, if any, by steam distillation, dissolving the salts in hydrochloric acid, and extracting the residue with benzene. Where a single product was obtained, it was purified by recrystallization and, occasionally, chromatography. If a mixture was obtained, its infrared

TABLE I

Moles $CuCl_2$/ Moles (I)	Solvent	Temp.	Time, Hr.	Nature of Product
1.0	None	100	0.17	Mixture containing II and III
1.0	Nitrobenzene	100	1.5	Trace, II
2.0	Nitrobenzene	210	3	Mixture containing 96% II and 4% III
6.4	Nitrobenzene	210	24	III (57% yield)
8.4	Nitrobenzene	210	96	III (69% yield)
8.4	Chlorobenzene	132	72	Mixture containing 18% II and 82% III
8.4	Chlorobenzene	132	96	Mixture containing 13% II and 87% III
8.4	Dimethyl-formamide	153	72	Mixture containing 75% II and 25% III
8.0[a]	Nitrobenzene	210	6	III (57% yield)

[a] 0.004 mole anhydrous aluminum chloride was added to 0.01 mole anthracene.

spectrum was analyzed and results expressed as mole per cent of II and III. The results are presented in Table I.



It was found that limitation of the amount of cupric chloride did not restrict the reaction to monochlorination; rather, a mixture of products was obtained. Nitrobenzene was the preferred solvent, presumably because of its higher boiling point. It may be noted that a reaction took place in dimethylformamide, the only solvent used in which cupric chloride was soluble. The yield of III in this instance was lower than that observed when chlorobenzene was used as a solvent, which could be attributed to reduced activity of the cupric chloride as a result of its interaction with the solvent. Cupric chloride is known to complex with many oxygen- or nitrogen-containing compounds.[4]

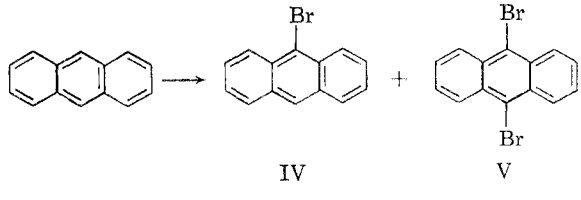
The nature of the products was confirmed by oxidation. When a portion of the chloroanthracene mixture from the solid reaction listed in Table I was treated with chromic oxide in acetic acid, 9,10-anthraquinone was obtained. It would be expected that only I, II, or III could yield this product.

In separate experiments, nitrobenzene was refluxed for several days with both cupric and cuprous chlorides. The nitrobenzene was subsequently distilled unchanged. Its infrared spectrum was also unchanged, suggesting that in neither instance had any reaction occurred between the solvent and copper halide.

The inference that cuprous chloride was formed in the reaction was based upon the fact that when water was added to the crude product of a reaction run without solvent and most of the organic matter extracted with benzene (not all of it would dissolve), a white solid settled out of the aqueous layer. The solid dissolved in concentrated hydrochloric acid. Such behavior is characteristic of cuprous chloride. When a solvent was used, the cuprous chloride, white initially, darkened on standing and gave an analysis too high in copper. It is possible that it suffered photodecomposition in the presence of hydrogen chloride.[5]

The reaction product from a solid reaction was investigated more closely by chromatography in an attempt to discover the nature of any other products. The chloroanthracenes were followed by anthracene when cyclohexane was the eluant. Most of the residual material could then be eluted with increasing proportions of benzene and a small amount of dark-colored, high-melting solid was thus obtained. Its infrared spectrum showed absorption that was in part characteristic of anthraquinone and carbazole, which were known to be trace contaminants in the anthracene used. Nothing else was identified and there was no indication that 9,9′-bianthryl, a possible product of a free radical reaction, had been formed.

It was then demonstrated that under the same conditions, cupric bromide could react with anthracene to yield 9-bromoanthracene (IV) and 9,10-dibromoanthracene (V). The results are found in Table II. Yields were so low that these reactions were not studied further.



It does not seem likely that the cupric chloride underwent preliminary dissociation and that chlorine was the actual halogenating agent. Equilibrium pressure data, listed in Table III, show that the extent of dissociation should not have been significant under the conditions used.

(4) *Gmelins Handbuch der Anorganischen Chemie*, 60B-I, p. 281 ff. (1958).

(5) See ref. (4), p. 222, for a discussion of the light sensitivity of CuCl.

TABLE II

Moles $CuBr_2$/ Mole (I)	Solvent	Temp.	Time, Hr.	Nature of Product
2.0	None	75	0.5	Trace IV and V
4.0	Nitrobenzene	210	75	V (22% yield)
4.0	Nitrobenzene	210	96	V (26% yield)

TABLE III

$CuCl_2$[a]	Temp.	371	411	421	
	P (mm.)	1.2	4.0	7.2	
$CuBr_2$[b]	Temp.	166.0	180.5	203.5	222.8
	P (mm.)	3.1	6.8	22.0	55.4

[a] W. Biltz and W. Fischer, *Z. anorg. u. allgem. Chem.*, **166**, 290 (1927). [b] C. C. Jackson, *J. Chem. Soc.*, **99**, 1066 (1911).

The situation with cupric bromide is not so clear-cut, since it dissociates at lower temperatures. Perhaps the significant amount of bromine present at the temperature of refluxing nitrobenzene accounted for the low yield of V (26% at best) and the difficulty of purifying it. Bromine would have been far more reactive than cupric bromide and might have induced the tar formation which was observed.

Kovacic and Brace[1a] found that aluminum chloride catalyzed the reaction between chlorobenzene and ferric chloride. In the present instance, however, aluminum chloride itself can undergo a vigorous reaction with anthracene in the presence of nitrobenzene. It has been reported[6] that when nitrobenzene is added to a 4:1 mixture of aluminum chloride and anthracene, a carbonaceous material is formed. This finding was confirmed and even under far more moderate conditions, no chlorination would be demonstrated. It was surprising, therefore, to find that when aluminum chloride was added to the warm reaction mixture (anthracene, cupric chloride, nitrobenzene), a vigorous reaction ensued and III was formed more rapidly and in good yield. The catalytic effect of aluminum chloride provides additional evidence in support of a polar mechanism for the reaction.

A cursory investigation of the effect of other metal chlorides on anthracene in nitrobenzene was also undertaken for the sake of comparison. Brief contact with antimony pentachloride at 5° was sufficient to cause extensive reaction, the principal product being III, which was separated chromatographically.[7]

Reaction with ferric chloride was extremely vigorous and only by working at 5° was it possible to obtain trace amounts of the simple chloroanthracenes II and III. Phosphorus pentachloride reacted smoothly at room temperature to form pure III in 60% yield. Mikhailov and Promyslov, working in benzene, obtained only a 54% yield of crude III after six days.[8]

Although the formation of chlorination products by stannic chloride at elevated temperatures could be demonstrated, the product was chiefly an intractable tar. With mercuric chloride, no reaction was observed at 100° and 150°, and at 210° apparently only tar formation occurred.

There is no way of evaluating the reduction potentials of these chlorides under the experimental conditions used. It does not seem valid to compare data obtained in aqueous solution where solvation would play a significant role; at the same time, insufficient data are available to calculate the standard free energy changes in most instances. It is likely also that some of these chlorides interact with the nitrobenzene. Black ferric chloride, for example, dissolves to form an orange solution, a color characteristic of hydrated (*i.e.*, complexed) iron (III).

Finally, from a consideration of reduction potentials[9] in aqueous solution and of standard free energies of formation of phosphorus pentachloride and mercuric chloride and the assumption that large relative differences would still carry over to nonaqueous media, a rough grouping in the order of oxidizing ability is possible.

$$\begin{matrix} Cl_2 & & \\ PCl_5 & & HgCl_2 \\ SbCl_5 & > & CuCl_2 > AlCl_3 \\ FeCl_3 & & SnCl_4 \end{matrix}$$

The reactivity of these metal halides (and chlorine) as aromatic chlorinating agents appears, then, to parallel their oxidizing ability. Activity as a Friedel-Crafts catalyst appears to offer no particular advantage in this instance.

EXPERIMENTAL

Melting points were taken in a heated copper block and are uncorrected. Microanalyses were by Huffman Microanalytical Laboratories, Wheatridge, Colo., or Micro-Tech Laboratories, Skokie, Ill. Infrared spectra were taken by J. Schnell and N. Galer.

Materials. Anhydrous cupric chloride was obtained by heating the dihydrate in an oven at 110° overnight. The brown solid thus obtained was kept in the oven until used. The solvents used were Fisher Reagent chemicals. In initial experiments, the nitrobenzene was distilled, but it was later found that there was no difference in products if it was undistilled. Eastman Kodak white label anthracene was used.

Infrared spectra were taken on a Perkin-Elmer Model 21 double beam instrument. Usually only absorption maxima at wave lengths greater than 10.00 μ are given because they proved most useful for purposes of identification.

Inertness of nitrobenzene to cupric and cuprous chloride. In two separate experiments, 50 ml. of nitrobenzene was refluxed for 72 hr. with 2 g. of cupric or cuprous chloride. The mixtures were protected from moisture but not from air.

(6) R. Scholl and C. Seer, *Ber.*, **55**, 330 (1922).

(7) J. Kommandeur and J. C. Ware, unpublished work.

(8) B. M. Mikhailov and M. Sh. Promyslov, *J. Gen. Chem.* (*U.S.S.R.*), **20**, 338 (1950); *Chem. Abstr.*, **44**, 6408.

(9) N. A. Lange, *Handbook of Chemistry*, Ninth Edition, pp. 1212–1218, 1576–1630 (1956).

After this time, the solid was filtered off and was unchanged in appearance. The infrared spectrum of the nitrobenzene was unchanged in both instances. The solvent from the cupric chloride experiment was distilled unchanged. That from the cuprous chloride experiment was treated with 6*N* hydrochloric acid, but no organic material was extracted.

General procedure for the reaction of cupric halide with an aromatic hydrocarbon. A. No solvent used. The reactants were ground, mixed, and placed in a round-bottom flask which was heated with a mantle. The flask was equipped with an air condenser, thermometer, and drying tube. Air was not excluded. The mixture was stirred from time to time. When the reaction was over, an excess of 6*N* hydrochloric acid was added and the mixture was extracted with benzene. There was always some dark-colored material formed that would dissolve in neither phase. The benzene extract was treated with Norit activated carbon and then the solvent was removed by evaporation. If the product was to be chromatographed, it was dissolved in cyclohexane; the substrate was silica gel. Usually, cyclohexane was used to develop the chromatogram as well. Toward the end, increasing proportions of benzene were sometimes needed. It was found convenient to equip the chromatographic columns with Teflon stopcocks, which require no lubrication.

B. Solvent used. The equipment was the same as in A; a stirrer was used as well. The hydrocarbon was dissolved in the solvent prior to the addition of copper halide. At the end of the reaction, after addition of a few milliliters of concentrated hydrochloric acid, the solvent was removed by steam distillation and the product treated as before.

Action of cupric chloride on anthracene. A. Initial experiments. One gram of anthracene and 10 g. of cupric chloride was mixed without solvent in a beaker and placed on the hot plate (*ca.* 200°). After a few minutes, a yellow solid began to sublime out of the beaker and hydrogen chloride was evolved. After about 10 min., the mixture was cooled and extracted with benzene; the benzene was removed by evaporation and the residual yellow-brown solid chromatographed. First eluted was a yellow solid, m.p. 150–160°. After recrystallization from cyclohexane and then acetone, it melted from 166–186°. The infrared spectrum showed it to consist, in part, of 9,10-dichloroanthracene. Additional absorption at 12.41, 11.88, 11.58, and 10.46 μ remains unexplained; it could not be attributed to anthracene, 9-chloroanthracene, anthraquinone, or bianthryl and is assumed to be caused by a more highly chlorinated anthracene. Later experiments were carried out at lower temperatures in order to reduce the degree of chlorination.

B. 9-Chloroanthracene (II). A mixture of 1.78 g. (0.01 mole) of anthracene and 1.35 g. (0.01 mole) of cupric chloride was heated in 50 ml. of nitrobenzene at 100° for 1.5 hr. This product was chromatographed and the first fraction, m.p. 92–96°, was recrystallized from cyclohexane and then alcohol to give flat yellow plates, m.p. 104.5–105.5° (lit.,[10] m.p. 103°).

Anal. Calcd. for $C_{14}H_9Cl$: C, 79.06; H, 4.26. Found: C, 79.00; H, 4.32.

A portion of the cyclohexane-soluble portion of a similar reaction was oxidized with chromic anhydride in glacial acetic acid.[11] From 0.3 g. of material, 0.21 g. of a quinone, m.p. 286°, was obtained. The melting point was undepressed by admixture with 9,10-anthraquinone.

C. 9,10-Dichloroanthracene (III). A mixture of 1.78 g. (0.01 mole) of anthracene and 11.4 g. (0.084 mole) cupric chloride was refluxed with nitrobenzene for 96 hr. The product was treated with Norit and recrystallized from cyclohexane and then alcohol to yield 1.7 g. (69%) of yellow needles, m.p. 209.5–211° (lit.,[12] m.p. 209°).

Anal. Calcd. for $C_{14}H_8Cl_2$: Cl, 28.7. Found: Cl, 28.1.

Analysis of mixtures II and III was based upon two infrared absorption maxima at 11.44 and 11.98 μ, which were found to be characteristic of II. II possessed additional maxima at 15.03, 13.85, 12.98, 11.27 and 10.65 μ. Absorption maxima for III occurred at 14.37, 13.42, and 10.58 μ.

Examination of the inorganic product. A mixture of 3.56 g. (0.02 mole) of anthracene and 0.50 g. (0.0037 mole) cupric chloride was placed in *ca.* 100 ml. of nitrobenzene and stirred and refluxed. A white solid appeared rapidly in the reaction mixture which, after a few hours, began to darken. When the solid was filtered out after 3 days, it was gray in color.

Anal. Calcd. for CuCl: Cu, 64.2. Found: Cu, 67.8.

Action of cupric bromide on anthracene. A. 9,10-Dibromoanthracene (V). A mixture of 2.23 g. (0.01 mole) of cupric bromide and 1.78 g. (0.01 mole) of anthracene was heated at 75° for 30 min. When the product was chromatographed, the first fraction consisted of bright yellow needles, m.p. 221–223°. They were rechromatographed and the first few fractions recrystallized from alcohol, m.p. 221–222° (lit.,[13] m.p. 226°).

Anal. Calcd. for $C_{14}H_8Br_2$: Br, 47.6. Found: Br, 47.7.

B. 9-Bromoanthracene (IV). When the reaction (A) was repeated without solvent, the chromatographic separation was not satisfactory and the first fraction had the m.p. 190–210°. This was rechromatographed and the second fraction (0.17 g.) consisted of light yellow needles, m.p. 99–100°. After recrystallization from alcohol and cyclohexane, the material melted at 97–101°. The filtrate from the second recrystallization, however, deposited tiny needles, which were collected and washed with petroleum ether, m.p. 101.5–102° (lit.,[10] m.p. 100°).

Anal. Calcd. for $C_{14}H_9Br$: C, 65.39; H, 3.53. Found: C, 65.26; H, 3.57.

Action of aluminum chloride on anthracene. Two grams of anthracene was mixed with 8 g. of aluminum chloride. When 25 ml. of nitrobenzene was added, a vigorous reaction ensued; the mixture became hot and a black, tarry material was formed. After a few minutes, 6*N* hydrochloric acid was added and the nitrobenzene removed by steam distillation. There remained 3.0 g. of black, powdery residue. It did not melt below 400° and burned slowly, leaving no ash.

Anal. Found: C, 78.87; H, 3.87; 0, 2.27; N, 3.22; Cl, 9.50.

Reaction of anthracene with phosphorus pentachloride. A mixture of 1.78 g. (0.01 mole) of anthracene and 17.0 g. (0.082 mole) of phosphorus pentachloride was placed in 50 ml. of nitrobenzene at room temperature. A yellow-orange solution immediately formed. After stirring for 1.5 days, the mixture was hydrolyzed with sodium hydroxide and the solvent removed by steam distillation. A yellow-brown solid remained. After treatment with Norit and recrystallization from cyclohexane, 1.47 g. (60%) of 9,10-dichloroanthracene, m.p. 211°, was obtained.

Anal. Calcd. for $C_{14}H_8Cl_2$: C, 68.04; H, 3.26; Cl, 28.70. Found: C, 68.23; H, 3.25; Cl, 28.67.

Reaction of anthracene with ferric chloride. Only tar was produced when 1.78 g. (0.08 mole) of anthracene was refluxed with 13.04 g. (0.08 mole) of anhydrous ferric chloride in 100 ml. of nitrobenzene for 2 days. The same results were obtained when such a mixture was heated at 100° or when the reaction was run at room temperature. When the components were held at 5° for 45 min., it was possible to extract a small portion of dark brown solid from the product, although it was mostly tar. When the extract was chromatographed, only a small fraction of it could be eluted with cyclohexane. There was insufficient material to be weighed accurately. It was possible to obtain a few infrared spectra, however, and from these, it was evident that initially III was eluted which was followed by mixtures of II and anthracene. The products were not examined further.

(10) A. G. Perkin, *Chem. N.*, **34**, 145 (1876).

(11) C. Marschalk and C. Stumm, *Bull. Soc. chim. France*, **15**, 418 (1948).

(12) C. Graebe and C. Liebermann, *Ann.*, **160**, 137 (1871).

(13) I. M. Heilbron and J. S. Heaton, *Org. Syntheses*, **Coll. Vol. I**, p. 207 (1941).

The action of stannic chloride on anthracene. A. A solution of 1.78 g. (0.01 mole) of anthracene and 20.8 g. (0.08 mole) of stannic chloride in 100 ml. of nitrobenzene was heated at 90° for 3 hr. The mixture turned red-brown as soon as the stannic chloride was added. It was hydrolyzed with sodium hydroxide solution and organic material was removed as well as possible by extraction with benzene. The solvent was removed by a steam distillation, during which some of the solids distilled also. When the nitrobenzene was removed from the distillate by vacuum distillation, 0.12 g. of pale yellow crystals remained. The infrared spectrum showed it to be anthracene plus traces of II and III. The residue consisted of 1.45 g. of dark brown solid in which the infrared spectrum corresponded to that of anthracene and a small amount of II.

B. The reaction was repeated under reflux for 24 hr. When 6*N* sodium hydroxide was added to the dark brown solution, a black tar formed. The mixture did not separate and about half of it was steam distilled. Again, the products distilled as well. A few milligrams of yellow crystals in the condenser was judged to be III on the basis of the infrared spectrum. The residue was an intractable tar which was not examined further.

Reaction of anthracene with mercuric chloride. A mixture of 1.78 g. (0.01 mole) of mercuric chloride was heated in 100 ml. of nitrobenzene at 100° for 24 hr. The solvent was removed by steam distillation, and the residue was found to be unchanged anthracene on the basis of its melting point and infrared spectrum. When the procedure was repeated, heating at 150° for 5 days, the anthracene, except for some tar formation, was unchanged. When the components were heated at reflux for 5 days, only a "tar," a high-melting black solid, was recovered.

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[CONTRIBUTION FROM RESEARCH LABORATORY, UNION CARBIDE CONSUMER PRODUCTS CO., DIVISION OF UNION CARBIDE CORP.]

Chlorination of Aromatic Hydrocarbons by Cupric Chloride. II. Reactivity of Some Polynuclear Compounds

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A study of the products of the reaction of anhydrous cupric chloride with benzene, naphthalene, phenanthrene, anthracene, tetracene, and pyrene has shown them to be consistent with those expected from an electrophilic substitution reaction. Perylene formed products which have not as yet been characterized.

In the first paper of this series,[1] the halogenation of anthracene by anhydrous cupric chloride was investigated. It was of interest to learn whether the reaction would be of preparative value and its scope has been investigated by extension to other aromatic systems.

RESULTS AND DISCUSSION

The procedures were much the same as those described earlier.[1] Reaction of the solids seldom produced much product and so, usually, the hydrocarbon to be investigated was dissolved in nitrobenzene and treated with an excess of cupric chloride. The products were frequently extremely difficult to separate; chromatography was used often and with varying success. Reaction mixtures wherein either naphthalene or phenanthrene was dissolved in nitrobenzene were analyzed by fractional distillation. The results of these studies are presented in Table I.

It is evident that complex mixtures frequently resulted. Such mixtures are often encountered in aromatic halogenations and often only the simpler halogenated derivatives have been characterized. Separations were further complicated by the fact that the chloroaromatics in most cases were more soluble than the parent hydrocarbons and often differed little among themselves in physical properties.

The sealed-tube reactions were particularly useful for the chlorination of the less reactive aromatics. Addition reactions, which often complicate polychlorinations,[2] apparently did not occur, or if they did, they were followed by dehydrohalogenation. The preparation of hexachlorobenzene by this technique is the only single-step synthesis of this compound that has been found. Considerable pressure developed during the reactions, however, and the tubes often broke. Since no suitable bomb was available, the investigation could not be pursued.

When a 2:1 mixture of cupric chloride–perylene was heated in nitrobenzene at 100° for seventy-two hours, a yellow-orange product was obtained which had the proper analysis for dichloroperylene (with increasing proportions of cupric chloride and higher temperatures, even more complex mixtures were obtained). The melting range was usually about 215–245° and on vapor phase chromatography, two very poorly resolved peaks appeared. All attempts to separate the components by crystalli-

(1) J. C. Ware and E. E. Borchert, *J. Org. Chem.*, to be published (1960).

(2) G. S. Badger, *Structures and Reactions of the Aromatic Compounds*, University Press, Cambridge, 1954, p. 257.