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.

Acknowledgment. The authors wish to thank J. O. Koehler for advice and encouragement during the course of this work.

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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

JUDITH C. WARE AND EARL E. BORCHERT

Received July 1, 1960

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-

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

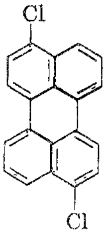
[2] G. S. Badger, *Structures and Reactions of the Aromatic Compounds*, University Press, Cambridge, 1954, p. 257.

TABLE I

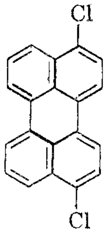
Hydrocarbon	Moles $CuCl_2$ / Moles Hydrocarbon	Solvent	Temp.	Time, Hr.	Nature of Product
Benzene	12.0	None—sealed tube	300	72	Mixture: 1,2,4,5- and 1,2,3,5-tetrachlorobenzenes
Benzene	12.0	None—sealed tube	400	72	Hexachlorobenzene
Naphthalene	7.0	None	100	0.5	None
Naphthalene	6.4	Nitrobenzene	210	72	1-Chloronaphthalene and 1,4-dichloronaphthalene[a]
Naphthalene	12.0	None—sealed tube	300	72	Unidentified yellow crystals, m.p. 118–128°; analysis approximated that for a tetrachloronaphthalene[b]
Anthracene	8.4	Nitrobenzene	210	72	9,10-Dichloroanthracene[c]
Phenanthrene	8.4	Chlorobenzene	132	96	None
Phenanthrene	4.1	Nitrobenzene	210	168	Some 9,10-dichlorophenanthrene[d]
Pyrene	1.0	None	100	0.5	Small amount of 3-chloropyrene
Pyrene	16.5	Nitrobenzene	210	72	Mixture: 3,8- and 3,10-dichloropyrenes, small amount of 3,5,10-trichloropyrene[e]
Tetracene	2.0	None	100	1	Some 5,11-dichlorotetracene[d]
Tetracene	8.4	Chlorobenzene	132	168	Some 5,11-dichlorotetracene[d]
Perylene	2.0	Nitrobenzene	100	72	Dichloroperylene

[a] Separation from solvent was incomplete. [b] The tip of the tube broke and the crystals remaining within the tube were examined. [c] From ref. 1. [d] Part of product was unidentified. [e] The products were not completely separated—the (only) separation (see ref. 13) of these isomers required over 400 melting point determinations.

zation, column chromatography, and sublimation have failed. The usual dichlorination product of perylene is the 3,9-derivative (A), m.p. 291°.[3] A small amount of impure 3,10-dichloroperylene (B), m.p. *ca.* 180°, has also been isolated.[4]



A



B

It is likely that in the present instance, the same products have been obtained although in different proportions. The problem is still under investigation.

With the possible exception of perylene, the hydrocarbons investigated have yielded the same products as those to be expected from an electrophilic chlorination[5] (under controlled conditions, in the case of reactive hydrocarbons). No evidence has been obtained for an addition-elimination reaction path. As well as can be judged, the reactivities of the aromatic hydrocarbons (perylene, pyrene, tetracene > anthracene, phenanthrene > naphthalene, benzene) fell in the order which might have been anticipated for an electrophilic substitution.[6] The action of cupric chloride is less vigorous than that of chlorine or of the other metal chlorides, known to cause nuclear halogenation, which have been studied.[7] Cupric chloride is easy to handle and stoichiometry is easily controlled. For that reason, it might be of utility for the chlorination of sensitive compounds provided that suitable conditions could be found.

EXPERIMENTAL

All melting points were taken in a heated copper block and are uncorrected. Microanalyses were by Micro-Tech Laboratories, Skokie, Ill., and Huffman Microanalytical Laboratories, Denver, Colo. Infrared spectra were determined by J. Schnell and N. E. Galer.

Action of cupric chloride on benzene. A. 1,2,4,5- and 1,2,3,5-Tetrachlorobenzenes. A mixture of 1.56 g. (0.02 mole) of benzene and 32.3 g. (0.24 mole) of cupric chloride was placed in a heavy-walled tube[1](1/2″ I.D. × 11″ with wall thickness 3 mm.). The tube was cooled in liquid nitrogen, evacuated, and sealed. An iron pipe with perforated caps screwed on each end was used as a shield. The tube was placed in an oven at 300° for 72 hr. When it was opened, a considerable amount of hydrogen chloride was evolved. The solid, then tan colored, was extracted with benzene in a Soxhlet extractor for 2 days. When the benzene had evaporated from the extract, white crystals remained, some of which were lost by sublimation. These were recrystallized from alcohol-water, m.p. 122–138° (lit., m.p. of 1,2,4,5-tetrachlorobenzene, 138°,[8] and m.p. of 1,2,3,5-tetrachlorobenzene, 51°[9]). The infrared spectrum of the crystals contained maxima at 6.79, 8.16, and 8.95 μ, characteristic of 1,2,4,5-tetrachlorobenzene, and one at 14.43 μ, characteristic of 1,2,3,5-tetrachlorobenzene.[9]

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[3] A. Zinke, K. Funke, and N. Lorbes, *Ber.*, **60**, 577 (1927).

[4] A. Zinke, A. Pongratz, and K. Funke, *Ber.*, **58**, 330 (1925).

[5] The Monograph by E. Clar, *Aromatische Kohlenwasserstoffe*, Second Edition, Springer-Verlag, Berlin (1952), contains sections on all of the polynuclear hydrocarbons studied and describes their chlorination products.

[6] See reference (2), p. 242.

[7] *Cf.* P. Kovacic and N. O. Brace, *J. Am. Chem. Soc.*, **76**, 5491 (1954).

[8] A. F. Holleman, *Rec. trav. chim.*, **39**, 736 (1920).

[9] E. K. Plyler, H. C. Allen, Jr., and E. D. Tidwell, *J. Research Natl. Bur. Stds.*, **58**, 255 (1957).

B. Hexachlorobenzene. The same quantities of materials contained in a sealed tube ($^1/_2$" I.D. × 22$^1/_2$" and wall thickness 3 mm.) were heated at 400° for 72 hr. White needles had sublimed onto the walls above the grayish mass of cuprous-cupric chloride. The material was extracted as before and on evaporation of the benzene, 4.50 g. of a light yellow solid remained. It was treated with Norit and recrystallized from cyclohexane to yield white needles, m.p. 221–222° (lit.,[10] m.p. of hexachlorobenzene, 226–227°). The yield was 80% and the infrared spectrum agreed with that of hexachlorobenzene.[9]

Anal. Calcd. for C_6Cl_6: C, 25.30; Cl, 74.70. Found: C, 24.88; H, 0.40; Cl, 74.55.

The inorganic product was dried and analyzed. Calcd. for CuCl: Cu, 64.2. Found: Cu, 63.0.

Action of cupric chloride on naphthalene. A. 1-Chloronaphthalene. A mixture of 3.85 g. (0.03 mole) of naphthalene and 32.3 g. (0.24 mole) of cupric chloride was heated in refluxing nitrobenzene for 1 week. The nitrobenzene could not be removed by steam distillation because the products distilled as well and so the former was removed by distillation through a two-foot, helix-packed column. The residue (*ca.* 10 ml.) was then distilled in a spinning band column.

Boiling Range	Pressure, Mm.	Weight, G.
59.2	0.6	1.73
44.2–44.5	0.15	2.14
44.5–66.0	0.15	0.31

All of the fractions contained 1-chloronaphthalene contaminated with nitrobenzene, according to their infrared spectra. The 66° distillate contained, in addition, another component which absorbed at 10.15, 7.40, and 6.54 μ. When 1,4-dichloronaphthalene was added to a portion of the latter and the infrared spectrum retaken, there were no new peaks observed and the heights of the peaks mentioned were enhanced. For the analysis, it was estimated that 1,4-dichloronaphthalene constituted one-third of the fraction by weight. A quantitative estimate of the amount of 1-chloronaphthalene present in the three fractions, based upon infrared peak height ratios at 2.99 and 9.77 μ, was 2.78 g. The minimum yield then was 57%.

B. A mixture of 1.28 g. (0.01 mole) of naphthalene and 10.75 g. (0.08 mole) of cupric chloride was heated in a sealed tube (22$^1/_2$" × $^1/_2$" I.D.) at 300° for 72 hr. The tip broke off the tube sometime during this period, but a quantity of yellow crystalline material as well as tan solid remained in the tube. The whole was extracted as before with benzene and the extract treated with Norit and recrystallized from cyclohexane. Yellow crystals, m.p. 118–128°, were obtained.

Anal. Calcd. for $C_{10}H_4Cl_4$: C, 45.16; H, 1.52; Cl, 53.32. Found: C, 43.99; H, 1.91; Cl, 54.17.

The action of cupric chloride on phenanthrene. A mixture of 5.34 g. (0.03 mole) of phenanthrene and 16.70 g. (0.124 mole) of cupric chloride was refluxed in 100 ml. of nitrobenzene for 1 week. Since previous experiments had shown that steam distillation did not separate the solvent from the products, the copper salts were filtered off and the filtrate distilled. Most of nitrobenzene was removed at 10 mm. through a two-foot, helix-packed column and the residue was distilled at 0.6 mm. in a spinning band column. Initial fractions consisted mostly of nitrobenzene which also contaminated the first product fraction.

No.	Boiling Range	Weight, g.	Nature of Distillate
1	161–164	1.5	Red oil containing some white solid
2	164–186	2.1	Yellow-orange solid
3	186	0.8	Orange solid
4	(Benzene-soluble residue)	0.6	Dark orange solid

When solid from No. 1 was crystallized from alcohol, white crystals, m.p. 135–150°, were obtained. Neither chromatography nor further recrystallization would separate the mixture.

Anal. Calcd. for $C_{14}H_9Cl$: C, 79.06; H, 4.27; Cl, 16.67, $C_{14}H_8Cl_2$: C, 68.04; H, 3.26; Cl, 28.70. Found: Cl, 24.38.

Fractions 2 and 3 were combined and chromatographed after recrystallization failed to achieve separation. First, about 1.5 g. of crystals, m.p. 130–150°, were obtained. They were recrystallized from cyclohexane and then from alcohol, yielding white needles, m.p. 158–160° (lit.,[11] m.p. of 9,10-dichlorophenanthrene, 160–161°). The infrared absorption spectrum had long wave-length maxima at 14.01, 13.42, 11.10 and 10.27 μ.

Anal. Found: C, 67.66; H, 3.51; Cl, 28.92.

Later fractions, again, consisted of oils and solids with broad, low melting ranges. Fraction 4 could not be separated by recrystallization or chromatography either. The infrared spectra of all four fractions contained absorption maxima characteristic of 9,10-dichlorophenanthrene.

Action of cupric chloride on pyrene. A. 3-Chloropyrene. A mixture of 2.02 g. (0.01 mole) of pyrene and 1.35 g. (0.01 mole) of cupric chloride was heated without solvent at 100° for 0.5 hr. When the product was chromatographed, it was found to be principally unchanged pyrene. The leading fractions, however, contained other materials. The first, m.p. 115–120°, was rechromatographed and after some higher melting material had been eluted, a quantity of crystals, m.p. 119–120°, was obtained. The material was assumed to be 3-chloropyrene (lit.,[12] m.p. 119°, m.p. of red picrate, 177–178°). Recrystallization of the material served only to widen its melting range; it gave a red picrate, m.p. 150–178°.

Anal. Calcd. for $C_{16}H_9Cl$: C, 81.19; H, 3.83. Found: C, 80.60; H, 3.98.

B. 3,5,8-Trichloropyrene; 3,8- and 3,10-dichloropyrenes. A mixture of 2.02 g. (0.01 mole) of pyrene and 22.3 g. (0.165 mole) of cupric chloride was refluxed in 50 ml. of nitrobenzene for 3 days. The tarry residue of the steam distillation was extracted with benzene. After treatment with Norit and successive recrystallizations from benzene (m.p. 175–200°), acetic acid (m.p. 197–250°), and toluene, 0.1 g. of buff-colored needles, m.p. 247–251°, remained (lit.,[13] m.p. of 3,5,10-trichloropyrene, 256–257°). No further purification of this material was attempted.

Anal. Calcd. for $C_{16}H_7Cl_3$: C, 62.9; H, 2.3; Cl, 34.8. Found: C, 64.2; H, 2.6; Cl, 33.1.

The rest of the material, about 1.0 g., was recrystallized from acetic acid, m.p. 162–170°, and the remainder then from toluene, m.p. 154–160° (lit.,[13] m.p. of 3,8-dichloropyrene, 194–196°; m.p. of 3,10-dichloropyrene, 154–156°). A separation of isomers was not attempted since it was found to be exceedingly difficult and time-consuming. The crystals obtained from acetic acid were analyzed.

Anal. Calcd. for $C_{16}H_8Cl_2$: C, 70.87; H, 2.98; Cl, 26.15. Found: C, 70.54; H, 3.23; Cl, 25.69.

Action of cupric chloride on tetracene. 5,11-Dichlorotetracene. A mixture of 1.14 g. (0.005 mole) of tetracene and 1.35 g. (0.01 mole) of cupric chloride was heated without solvent at 100° for 1 hr. Good contact with the tetracene could not be achieved because the flaky crystals were not easily broken up. When the product was chromatographed, it moved very

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(10) C. Willgerodt and K. Wilcke, *Ber.*, **46**, 2752 (1910).

(11) J. Schmidt and G. Ladner, *Ber.*, **37**, 4402 (1904).

(12) H. Vollman, H. Becker, M. Corell, and H. Streech, *Ann.*, **531**, 1 (1937).

(13) G. Goldschmiedt and R. Wegscheider, *Monat.*, **4**, 666 (1883).

slowly; the first material to be eluted consisted of red-orange crystals, m.p. 217–221°. Recrystallization twice from methyl ethyl ketone afforded brick-red needles, m.p. 218–220° (lit.,[14] m.p. of 5,11-dichlorotetracene, 220°). When the reaction was repeated in refluxing chlorobenzene, an inseparable mixture of chlorinated products was obtained.

Anal. Calcd. for $C_{18}H_{10}Cl_2$: Cl, 23.87. Found: Cl, 24.04.

Action of cupric chloride on perylene. A mixture of 1.26 g. (0.005 mole) of perylene and 1.35 g. (0.01 mole) of cupric chloride was heated in 25 ml. of nitrobenzene at 100° for 3 days. A black precipitate which formed during the course of the reaction was removed by filtration. It disappeared on hydrolysis, yielding a yellow-orange organic product and, presumably, copper salts. A small portion of the product, dissolved in the solvent, had an infrared spectrum essentially the same as that obtained from the black precipitate and so the two were combined. No purification could be achieved by recrystallization from cyclohexane, benzene, acetone, or ethyl alcohol. When purification with Norit was attempted, the product could not be desorbed even by boiling chlorobenzene and the reaction had to be repeated. The melting range was generally about 215–245°. If the material was chromatographed on alumina with cyclohexane, it moved very slowly, but finally yellow-orange crystals could be obtained in which the melting range was about the same as before. Infrared absorption maxima occurred at 10.20, 11.37, 12.15, 12.47, 12.75, 13.15, and 14.53 μ. Later fractions contained perylene contamination as well. There was obtained 1.29 g. of the yellow-orange material. A portion of the latter was recrystallized from cyclohexane, m.p. 218–245°.

Anal. Calcd. for $C_{20}H_{10}Cl_2$: C, 74.78; H, 3.14; Cl, 22.08. Found: C, 74.84; H, 3.26; Cl, 22.21.

If dichloroperylene had been formed, then 1 mole of cupric chloride introduced 1 mole of chlorine instead of 0.5 mole as experienced previously. On this basis, the yield of dichloroperylene was 80%. Oxidation by sulfuric acid yielded no distinct product.

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[14] C. Marschalk and C. Stumm, *Bull. Soc. Chem. France*, **15**, 418 (1948).

[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION]

Conversion of Trichloromethyl Groups into Dichloromethyl Groups[1]

EHRENFRIED KOBER[2]

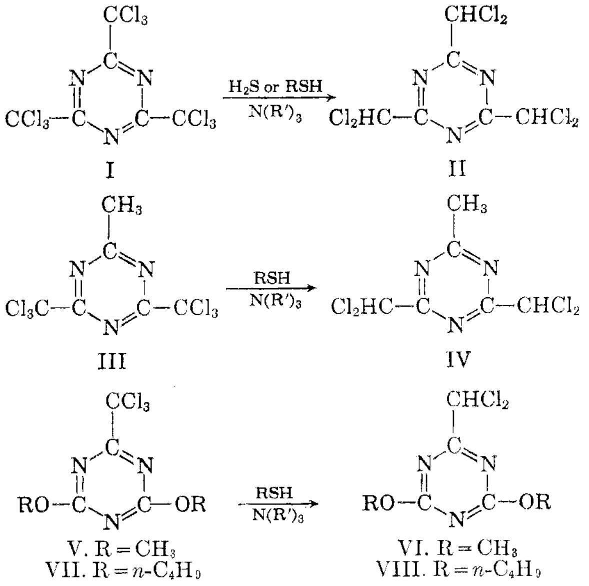
Received October 28, 1960

Trichloromethyl-*s*-triazines and derivatives of trichloroacetic acid can be converted into the corresponding dichloromethyl compounds by means of mercaptans in the presence of tertiary amines; mercaptals are formed as by-products.

In connection with a study on the reactivity of trichloromethyl groups attached to the *s*-triazine nucleus we had found that the reaction of trichloromethyl-*s*-triazines with alcohols in the presence of certain tertiary amines led, depending on the reaction conditions, to the stepwise replacement of trichloromethyl groups by alkoxy groups.[3] Furthermore, we reported that the reaction of 2,4,6-tris(trichloromethyl)-*s*-triazine (I) with water and certain tertiary amines resulted in the formation of tertiary amine salts of 2-hydroxy-4,6-bis(trichloromethyl)-*s*-triazine.[3]

It was of interest to know whether the reaction of trichloromethyl-*s*-triazines with mercaptans instead of alcohols would proceed in the presence of tertiary amines correspondingly and result in the formation of alkylthio-*s*-triazines. It also appeared desirable to determine whether the reaction of I with hydrogen sulfide instead of water would lead in the presence of tertiary amines, in an analogous fashion, to the formation of tertiary amine salts of 2-mercapto-4,6-bis(trichloromethyl)-*s*-triazine.

It was surprisingly found that 2,4,6-tris(trichloromethyl)-*s*-triazine (I) reacted with either ethanethiol or 1-butanethiol in the presence of triethylamine to give 2,4,6-tris(dichloromethyl)-*s*-triazine (II). This result indicated that the reaction of compound I with mercaptans in the presence of triethylamine took an entirely different course as compared with the reaction of compound I with alcohols; instead of being replaced by alkylthio groups, the trichloromethyl groups were converted into dichloromethyl groups.



I

II

III

IV

V. R = CH_3
VII. R = n-C_4H_9

VI. R = CH_3
VIII. R = n-C_4H_9

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[2] Olin Mathieson Chemical Corporation, Organics Division, New Haven, Conn.

[3] E. Kober, *J. Org. Chem.*, **25**, 1728 (1960).