N-Benzylbenzenesulfonhydroxamic Acid.—Hydrolysis of 0.60 g. (2.3 mmoles) of N-benzyl O-tetrahydropyran-2-ylbenzenesulfonhydroxamate by refluxing with 10 ml. of 2% hydrogen chloride in 50% aqueous ethanol for 2 hours, cooling the mixture and diluting the water gave 0.39 g. (85.5%) of N-benzylbenzenesulfonhydroxamic acid, m.p. 87–91° after recrystallization from benzene, undepressed by mixture with an authentic sample. The analysis corresponded to the presence of a half-mole of benzene of crystallization, in agreement with Piloty's original report[11] of this compound obtained from benzenesulfonyl chloride and N-benzylhydroxylamine.

*Anal.* Calcd. for $C_{13}H_{13}O_3NS \cdot {}^1/_2C_6H_6$: C, 63.55; H, 5.33; N, 4.63. Found: C, 63.89; H, 5.42; N, 4.29, 4.40.

N-Hydrocinnamyl O-Tetrahydropyran-2-ylbenzenesulfon-hydroxamate.—Refluxing 1.60 g. (6.2 mmoles) of O-tetra-

hydropyran-2-ylbenzenesulfonhydroxamic acid with 1.23 g. (5.0 mmoles) of hydrocinnamyl iodide and 1.5 ml. of 20% sodium hydroxide solution in 10 ml. of 95% ethanol gave 1.24 g. (70%) of product, m.p. 80.5–82°. Five recrystallizations from ethanol gave an analytical sample, m.p. 81.5–83°.

*Anal.* Calcd. for $C_{20}H_{25}NO_4S$: C, 63.98; H, 6.71; N, 3.73. Found: C, 63.95; H, 6.84; N, 3.66.

Hydrolysis of 0.85 g. (2.3 mmoles) of the foregoing compound by refluxing in 50% aqueous ethanol for 2 hours followed by dilution with water gave an oil which could not be crystallized. The oil was refluxed for 0.5 hour in dilute ethanolic sodium hydroxide, and the cooled solution was then diluted with water and extracted with ether. Neutralization of the aqueous layer with carbon dioxide gave 120 mg. (35%) of hydrocinnamaldoxime, m.p. 83–87°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY, CLEVELAND 6, OHIO]

# Chlorination of Aromatic Compounds by Antimony Pentachloride[1,2]

BY PETER KOVACIC AND ALLEN K. SPARKS[3]

Investigation of the reaction of antimony pentachloride with halobenzenes and toluene indicates that chlorination proceeds by electrophilic substitution involving an attacking species of low activity, as evidenced by the almost exclusive *ortho–para* orientation. Preliminary dissociation of the metal chloride is deemed unlikely, since the *ortho/para* ratio produced by chlorination of chlorobenzene or toluene by antimony pentachloride is substantially lower than that obtained from catalytic chlorination with chlorine gas. The reactions with mesitylene and pentamethylbenzene were also studied. Theoretical aspects of the chlorination reaction are discussed.

## Introduction

Since the appearance, in 1862, of the first report[4] on the chlorination of aromatic compounds by antimony pentachloride, the reaction has received relatively little attention, except as a route to polychlorinated compounds. Thus, Steiner[5] isolated decachlorobenzophenone, hexachlorobenzene and pentachlorobenzoic acid from the reaction of benzophenone with an excess of the pentachloride at elevated temperatures. It was not until recently, however, that a study, preliminary in nature, of the mechanism of aromatic chlorination by antimony pentachloride was reported.[6]

The purpose of the present work was to elucidate the mechanism of aromatic chlorination by antimony pentachloride. Included in this study were the halobenzenes, toluene, mesitylene and pentamethylbenzene.

## Results and Discussion

Early work[7] established the general equation for chlorination by antimony pentachloride. On the

$$ArH + SbCl_5 \rightarrow ArCl + SbCl_3 + HCl$$
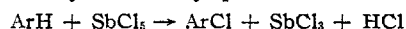
basis of our investigations, the reaction is considered to proceed by electrophilic substitution, as evidenced by the predominant *ortho–para* orientation in the halobenzene series and with toluene.

(1) Part IV of a series on "Reactions of Metal Halides with Organic Compounds"; presented in part at the 136th Meeting of the American Chemical Society in Atlantic City, N. J., September, 1959, Abstracts of Papers, p. 23P.

(2) From the Ph.D. thesis of Allen K. Sparks, Case Institute of Technology, 1960.

(3) Allied Chemical Corp. Fellow, 1958–1960.

(4) H. Müller, *J. Chem. Soc.*, **15**, 41 (1862).

(5) K. Steiner, *Monatsh.*, **36**, 825 (1915); *C. A.*, **10**, 181 (1916).

(6) P. Kovacic and N. O. Brace, THIS JOURNAL, **76**, 5491 (1954).

(7) A. Rosenheim and W. Stellman, *Ber.*, **34**, 3377 (1901).

### TABLE I

ANTIMONY PENTACHLORIDE AND AROMATIC COMPOUNDS

| $C_6H_5X$,[a] $X =$ | Temp., °C. | Time, hr. | B.p., °C. | Yield | o | m | p |
|---|---|---|---|---|---|---|---|
| F[b] | 43–49 | 2 | 127–128 | 83[c] | 4 | <1[d] | 96[e] |
| Cl | 41–59 | 2 | 170–172 | 82 | 15 | 1 | 84 |
| Br | 31–56 | 1 | 192–194 | 83 | 25 | 1 | 74 |
| I | 4–17 | 1 | 129–135[f] | 36[g] | 50[e] | <1[d] | 50 |
| CH₃ | 18–31 | 2.5 | 156 | 87[h] | 47 | 2 | 51 |

Header spanning columns: $ClC_6H_4X$ — %

[a] $C_6H_5X$ (2 moles) and $SbCl_5$ (0.5 mole). [b] Run at half scale; reaction mixture was distilled directly. [c] Calcd. for $C_6H_4ClF$: C, 55.20; H, 3.09. Found: C, 55.41; H, 3.45. [d] No detectable *m*-isomer. [e] By difference. [f] At 55 mm. [g] See Experimental section for other products. [h] Plus 1.1 g. of distillation residue consisting of chlorotoluene and dichlorotoluene by infrared analysis.

In addition, this interpretation is consistent with the order of reactivity of the aromatic component (toluene > benzene > chlorobenzene), based on a comparison of "initiation temperatures," as well as on kinetic evidence.[8] The increasing amount of *ortho* substitution as the atomic number of the halogen increases has been encountered with other electrophilic reagents,[6,9] and is explained on the basis of the inductive effect of the substituent.

It has been assumed that antimony pentachloride acts by preliminary dissociation to free chlorine which then functions as the actual chlorinating agent.[4,10]

$$SbCl_5 \rightleftharpoons SbCl_3 + Cl_2$$

$$ArH + Cl_2 \xrightarrow{SbCl_3} ArCl + HCl$$
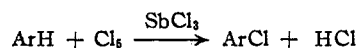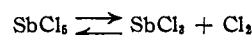
(8) A. K. Sparks and P. Kovacic, forthcoming publication.

(9) E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 242.

(10) A. W. Hofmann, *Ann.*, **115**, 264 (1860).

TABLE II

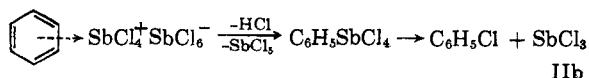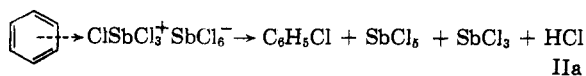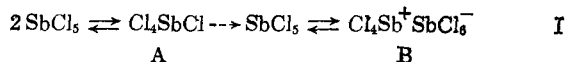ISOMER DISTRIBUTION BY VARIOUS HALOGENATING METHODS[a]

| Conditions | o | m | p |
|---|---|---|---|
| **Chlorobenzene** | | | |
| SbCl₅ (41–59°) | 15 | 1 | 84 |
| SbCl₅ (38–53°)[6] | 18 | | 82 |
| FeCl₃ (125–140°)[6] | 11 | 1 | 88 |
| Cl₂ (40–50°, SbCl₅ cat.) | 34 | 1 | 65 |
| Cl₂ (40–55°, FeCl₃ cat.) | 40 | 3 | 57 |
| Cl₂ (60–65°, FeCl₃ cat.)[b] | 39 | 5 | 56 |
| Br₂ (60–65°, Fe cat.)[b] | 11 | 2 | 87 |
| **Toluene** | | | |
| SbCl₅ (18–31°) | 47 | 2 | 51 |
| SbCl₅ (30–40°)[6] | 45 | 4 | 51 |
| FeCl₃ (50–60°)[6] | 13 | <1 | 87 |
| Cl₂ (25–30°, SbCl₅ cat.) | 72 | 2 | 26 |
| Cl₂ (r.t., SbCl₅ cat.)[c] | 58 | | 42 |
| Cl₂ (25–35°, FeCl₃ cat.) | 64 | 4 | 32 |
| Cl₂ (10–15°, Fe cat.)[d] | 58 | | 42 |
| Cl₂ (25°, HOAc solv.)[e] | 60 | <1 | 40 |
| HOCl (25°, HClO₄ cat.)[f] | 75 | 2 | 23 |
| Br₂ (50°, FeBr₃ cat.)[g] | 37 | | 63 |

[a] See J. S. Reese, *Chem. Revs.*, **14**, 55 (1934). [b] A. F. Holleman and T. van der Linden, *Rec. trav. chim.*, **30**, 305 (1911). [c] E. Wertyporoch, *Ann.*, **493**, 153 (1932); discrepancy between these and our data might be due to the chemical method of analysis, involving oxidation to the acids, used by Wertyporoch. [d] A. Wahl, G. Normand and G. Vermeylen, *Bull. soc. chim.*, **31**, 570 (1922). [e] H. C. Brown and L. M. Stock, THIS JOURNAL, **79**, 5175 (1957). [f] P. B. D. de la Mare, J. T. Harvey, M. Hassan and S. Varma, *J. Chem. Soc.*, 2756 (1958). [g] F. van der Laan, *Rec. trav. chim.*, **26**, 1 (1907).

However, the large difference in isomer distribution between chlorination with antimony pentachloride and with chlorine gas in the presence of a catalyst indicates that this assumption cannot be applied to the present investigation.

The dissimilarity involves the *ortho–para* distribution, with antimony pentachloride producing a considerably lower *ortho–para* ratio. Additional evidence against participation by free chlorine is found in the report by Braune and Tiedje[11] that dissociation of antimony pentachloride is very slow at temperatures below 120°. In this work, chlorinations with the metal chloride were carried out below 60°. However, since decomposition is known to occur slightly even at room temperature,[12] chlorine gas may take part to a minor extent. At high temperatures, chlorination by generated chlorine may assume increased importance.

On the basis of these and other considerations, several plausible reaction schemes are proposed for aromatic chlorination by antimony pentachloride.

$$2\,SbCl_5 \rightleftarrows Cl_4SbCl \dashrightarrow SbCl_5 \rightleftarrows Cl_4Sb^+SbCl_6^-    I$$

$$\quad\quad\quad A \quad\quad\quad\quad\quad\quad\quad\quad B$$



IIa



IIb

(11) H. Braune and W. Tiedje, Z. anorg. u. allgem. Chem., **152**, 39 (1926).

(12) P. Fireman and E. G. Portner, J. Phys. Chem., **8**, 500 (1904).

Furthermore, antimony pentachloride may participate[8] in the form of a complex with antimony trichloride, SbCl₄⁺SbCl₄⁻. Initial complex formation involving antimony pentachloride and the aromatic compound followed by coördination with an additional molecule of metal halide is a reasonable alternative route leading to the transition states in IIa and IIb. Strong Lewis acids, such as aluminum bromide, are known[13] to form complexes with aromatic compounds, and antimony pentachloride and aluminum bromide both dissolve readily in aromatic solvents to form colored solutions.

Various lines of evidence support these basic concepts. The comparatively low *ortho/para* ratio points to an attacking species which possesses a relatively large steric factor, whereas the formation of small amounts of *m*-isomer suggests a weak electrophile.[13] The positive charge on the cation presumably can be distributed by resonance.[14] The transition state for IIa is thus envisioned to involve a concerted transfer of a positive chlorine from SbCl₄⁺ to the aromatic compound. It is
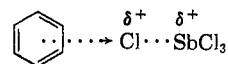


significant that the isomer distribution in catalyzed bromination (Table II) more closely resembles the antimony pentachloride reaction than does catalyzed chlorination.

The contention that the complexes SbCl₄⁺SbCl₆⁻ and SbCl₄⁺SbCl₄⁻ (from antimony trichloride formed *in situ*) may be involved in the substitution step is consistent with the kinetic data.[8] Spectral studies[15] on the structure of solid and fused antimony pentachloride indicate that the molecule exists in an unsymmetrical trigonal bipyramidal configuration with one ionic and four covalent antimony–chlorine bonds, which accounts for the observed dipole moment[16] as well as the conductivity of its solutions in liquid sulfur dioxide.[15] Pertinent to the discussion are reports of the existence of the SbCl₄⁺ ion (presumably as part of an ion pair) in the systems SbCl₄F–AsF₃[14] and SbCl₅–SbCl₃.[17] In addition, A and B are comparable to the coördinative and ionic structures which have been proposed for complexes of antimony pentachloride with inorganic halides such as thionyl chloride,[18] nitrosyl chloride[19] and phosphorus oxychloride.[20]

Analogy for the postulated metalation reaction IIb can be cited in the processes of mercuration[21–23]

(13) K. L. Nelson and H. C. Brown in "The Chemistry of Petroleum Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1955, Vol. 3, p. 503.

(14) L. Kolditz, Z. anorg. u. allgem. Chem., **289**, 128 (1957).

(15) H. Moureu, P. Süe and M. Magat, Contrib. etude structure mol., Vol. commem. Victor Henri, 125 (1947/48); C. A., **43**, 2513 (1949).

(16) E. Bergmann and L. Engel, Z. physik. Chem., Abt. B, **13**, 232 (1931).

(17) M. I. Usanovich, T. N. Sumarokova and M. B. Beketov, Izvest. Akad. Nauk. Kasakh. S. S. R. No. 123, Ser. Khim., No. 7, 3 (1953); C. A., **48**, 5703 (1954).

(18) H. Spandau and E. Brunneck, Z. anorg. u. allgem. Chem., **278**, 197 (1955).

(19) F. Seel, Z. anorg. Chem., **252**, 24 (1944).

(20) V. Gutmann, Z. anorg. u. allgem. Chem., **270**, 179 (1952).

(21) H. Gilman and G. F. Wright, THIS JOURNAL, **55**, 3302 (1933).

(22) W. J. Klapproth and F. H. Westheimer, ibid., **72**, 4461 (1950).

and telluration.[24] In a study of the reaction of antimony pentachloride with diphenyldichlorosilane[25] leading to phenyltrichlorosilane, chlorobenzene and antimony trichloride, Yakubovich and Motsarev demonstrated that phenylantimony tetrachloride functions as a precursor of chlorobenzene and antimony trichloride. Our attempts to isolate intermediates of the type $ArSbCl_4$ (or the corresponding stibonic acids) in the reaction of antimony pentachloride with benzene, chlorobenzene and toluene at $-20$ to $-30°$ have failed.

In endeavoring to ascertain the mechanism, it is instructive to compare antimony pentachloride with ferric chloride in their reactions with aromatic compounds. Both metal halides[6,26] effect nuclear chlorination, and with simple alkylbenzenes yield diphenylmethane-type hydrocarbons and products from disproportionation.

On the other hand, marked dissimilarities are also evident. Antimony pentachloride is a more active chlorinating agent than ferric chloride toward benzene and chlorobenzene. Various lines of evidence indicate that the attacking species in the case of antimony pentachloride possesses a smaller steric factor than that of the ferric chloride reaction. For example, with antimony pentachloride, the product from chlorobenzene exhibited a slightly higher *ortho/para* ratio, and drastically higher for the product from toluene. The isomer distributions from the toluene reactions point to a smaller steric factor for chlorination with antimony pentachloride, and a larger one with ferric chloride, in reference to bromination with bromine (Table II). In the reactions with pentamethylbenzene, antimony pentachloride accomplished nuclear chlorination, whereas only side-chain attack leading to 2,2',3,3',4,4',5,5',6-nonamethyldiphenylmethane was observed[27] with ferric chloride. Antimony pentachloride and mesitylene yielded mono-, di- and trichloromesitylene, but ferric chloride[27] differed in that bimesityl was formed in addition to chloromesitylene.

Chlorination and biaryl formation with ferric chloride have been supposed[6,26,27] to proceed through a labile organo-iron intermediate. If an analogous organo-antimony intermediate (IIb) were formed, one would not expect hindered aromatic compounds such as mesitylene and pentamethylbenzene to react as readily, if at all, because of the larger steric factor associated with $-SbCl_4$ in comparison with $-FeCl_2$, just as one would expect less *o*-substitution in monosubstituted benzenes with antimony pentachloride. This argument is supported by the work[28] of Nesmeyanov and co-workers on formation of arylantimony tetrachlorides from aryldiazonium chlorides and antimony pentachloride. With 2-methyl-4,6-dibromobenzenediazonium chloride, the desired organo-

antimony product was not obtained, presumably due to steric factors introduced by the two *o*-substituents. On the other hand, the steric factors associated with antimony pentachloride might be offset to some extent by its greater chlorinating ability *vis-à-vis* ferric chloride. In addition, a favorable "*ortho*-effect" may be operative in the case of antimony pentachloride.

All factors taken into consideration, scheme IIa is somewhat favored for the chlorination reaction.

## Experimental[29]

**Materials.**—Unless otherwise specified, the aromatic compounds (Matheson, Coleman and Bell) were reagent grade chemicals which were used directly after being dried over magnesium sulfate. Commercial toluene was distilled b.p. 109.4–109.6°, through a 60-cm. vacuum-jacketed, helix-packed column immediately prior to use. Fluorobenzene (Eastman Kodak Co., white label grade) was dried and used without further purification. Eastman Kodak Co. chemicals (white label) were distilled and used for infrared standards. Antimony pentachloride was from the Baker Chemical Co.

**Antimony Pentachloride and Aromatic Compounds. Small Scale Procedure.**—The aromatic compound (0.20 mole) was cooled in liquid nitrogen, and antimony pentachloride (0.05 mole) was added. The reaction mixture was allowed to warm slowly (external heating required with chlorobenzene) with stirring. The temperature at which hydrogen chloride was first detected in the trap, followed by steady evolution, was taken as the "initiation temperature." About 30 min. elapsed between addition and hydrogen chloride evolution. The following "initiation temperatures" were observed: toluene, $-12°$; benzene, 18°; chlorobenzene, 40°.

**Antimony Pentachloride and Chlorobenzene. General Procedure.**—(a) Chlorobenzene (225 g., 2 moles) was placed in a flask connected through a safety trap to a gas dispersion tube immersed in a phenolphthalein indicator solution (which was titrated with standard 2 N sodium hydroxide as hydrogen chloride was evolved). With rapid stirring, antimony pentachloride (149.5 g., 0.5 mole) was added in small portions at 9–59° during 1 hr. while a slow stream of dry nitrogen was passed through the apparatus. The red-orange reaction mixture gradually darkened, and at 41° hydrogen chloride was evolved at a fairly rapid rate. The reaction proceeded at good velocity for about 90 min. at 46–59°, with very little gas evolution during an additional 15 min. A total of 111% of the theoretical amount (based on antimony pentachloride) of standard alkali was required.

The organic portion of the distillate from subsequent steam distillation was salted out, extracted with ether, dried, and distilled through an 8-in. helix-packed column with variable take-off head. The fraction, b.p. 170–172°, 59.5 g. (81% yield), was shown by infrared analysis to be a mixture of dichlorobenzenes (83.5% *para*, 15.4% *ortho*, and 1.1% *meta*). A m.p.–f.p. determination indicated a composition of 83.5% *para* and 16.5% *ortho–meta*.

The residue from steam distillation was filtered, washed thoroughly with 6 N hydrochloric acid until all antimony salts were removed, and then dried. Less than 0.5 g. of a black, ether-soluble solid remained.

(b) In a similar experiment at 39–51° for 30 min., the reaction was intentionally terminated at the 61% yield point for dichlorobenzene ($o/m/p = 16/1/83$).

**Antimony Pentachloride and Iodobenzene.**—The reaction conditions are recorded in Table I. The distillate from steam distillation was extracted with ether and distilled, yielding fractions contaminated with small amounts of iodine even at reduced pressure. After separation of a forerun, b.p. 68–133°, 6.2 g., which contained benzene and chlorobenzene as indicated by the infrared spectrum

(23) R. M. Schramm, W. J. Klapproth and F. H. Westheimer, *J. Phys. Colloid Chem.*, **55**, 843 (1951).

(24) G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 2307 (1925).

(25) A. Yakubovich and G. V. Motsarev, *J. Gen. Chem. (U.S.S.R.)*, **23**, 1414 (1953).

(26) P. Kovacic, C. Wu and R. W. Stewart, THIS JOURNAL, **82**, 1917 (1960).

(27) P. Kovacic and C. Wu, unpublished work.

(28) A. N. Nesmeyanov, O. Reutov and P. G. Knol, *Bull. acad. sci. U.S.S.R., Div. chem. sci.*, 347 (1954); *C. A.*, **49**, 9651 (1955).

(29) Melting points and boiling points are uncorrected. Elemental analyses were performed by Drs. Weiler and Strauss, Oxford, Eng., and Geller Laboratories, Bardonia, N. Y.

(benzene band at 14.6–14.9 μ), 324 g. of iodobenzene, b.p. 102–104° at 55 mm., was recovered. Following isolation of the desired product, chloroiodobenzene, $n^{20}$D 1.5262, an additional fraction, b.p. 132–135° at 15 mm., 5.1 g., was obtained consisting mainly of dichloroiodobenzene.

**Antimony Pentachloride and Mesitylene.**—Antimony pentachloride (0.5 mole) was slowly added to mesitylene (2 moles) during 3 hr. at 3–10°. After addition was complete, the reaction mixture was heated to 70°, cooled, and then allowed to stand for 48 hr. The liquid was decanted from a black solid (35.3 g.) which appeared to consist of polymeric material mixed with a small amount (1.9 g.) of trichloromesitylene. The liquid was washed thoroughly, first with 6 N hydrochloric acid and then with water, dried, and distilled. After removal of the unchanged mesitylene, 8.3 g. of chloromesitylene was collected at 124–129° (56 mm.), $n^{20}$D 1.5262. The dinitro derivative melted at 175–176° and the mixture melting point with authentic material was not depressed.

*Anal.* Calcd. for $C_9H_9ClN_2O_4$: Cl, 14.49; N, 11.45. Found: Cl, 14.65; N, 11.30.

Dichloromesitylene (2.7 g.) which was collected at 151–153° (56 mm.) melted at 59–69° after crystallization from ethanol. A mixture melting point with authetic material showed no depression.

The distillation residue contained solid material which was separated, wt. 24.4 g., including 2 g. of alcohol-insoluble, polymeric solid. Crystallization of the soluble portion from ethanol gave white needles, m.p. 204–204.5°. The mixture melting point with authentic trichloromesitylene showed no depression.

*Anal.* Calcd. for $C_9H_9Cl_3$: C, 48.36; H, 4.05; Cl, 47.58. Found: C, 48.43; H, 4.08; Cl, 47.70.

**Antimony Pentachloride and Pentamethylbenzene.**—Antimony pentachloride (37 g., 0.12 mole) was added to pentamethylbenzene (74 g., 0.5 mole) at 70–76° during 20 min. After completion of reaction, the cooled mixture was washed thoroughly with 6 N hydrochloric acid, diluted with ether, and filtered to remove black solid (0.9 g.). Distillation of the filtrate to remove ether and unchanged pentamethylbenzene gave a solid residue which was extracted with ethanol leaving a dark brown solid (7.8 g.). The solid was treated with hot cyclohexane, filtered, and the filtrate on evaporation yielded only a small amount (less than 0.5 g.) of sticky, non-crystalline material.

Crude chloropentamethylbenzene (16.2 g., 71%), recovered from the alcohol extract, was recrystallized from alcohol to a constant melting point of 152–153.5°, lit.[30] m.p. 155°.

**Attempted Isolation of Arylantimony Tetrachloride. General Procedure.**—To the aromatic compound (benzene, chlorobenzene or toluene, 25 g.) at −20 to −30°, antimony pentachloride (5 g.) was added slowly with shaking. After standing at this temperature for 30 min., the mixture was stirred thoroughly with 6 N hydrochloric acid (15 ml.). Attempts to precipitate the arylantimony tetrachloride as the ammonium salt (by addition of solid ammonium chloride) or the corresponding stibonic acid (by addition of 6 N sodium hydroxide) were unsuccessful.

**Chlorine and Mesitylene.**—Mesitylene (100 g., 0.83 mole) was treated with dry chlorine gas at 0–10° essentially according to the procedure of Fittig and Hoogewerff.[31]

After 7 hr., addition of chlorine was discontinued upon separation of a solid product. The insoluble trichloromesitylene was removed by filtration and crystallized from ethanol as white needles, m.p. 204–205°, lit. m.p. 204–205°. The filtrate from the reaction mixture was distilled yielding mesitylene, wt. 16.1 g., b.p. 158–159°; chloromesitylene, wt. 24.9 g., b.p. 122–125° (56 mm.), $n^{20}$D 1.5260 (dinitro derivative, m.p. 176–177° from dilute ethanol, lit. m.p. 178–179°); and dichloromesitylene, wt. 52.3 g., b.p. 155–156° (56 mm.), m.p. 57.5–58.5° from dilute ethanol, lit. m.p. 59°. The distillation residue appeared to consist mainly of crude trichloromesitylene.

**Chlorination with Chlorine Gas. General Procedure. Chlorobenzene (SbCl₅ Catalyst).**—Chlorobenzene (2 moles) was chlorinated with chlorine gas at 40–50° during 3 hr. in the presence of antimony pentachloride (0.05 mole). Distillation of the reaction mixture yielded 43.7 g. of dichlorobenzene (b.p. 170.5–171°), shown by infrared analysis to contain 33.6% o-, 1.5% m- and 64.8% p-isomer (o–m/p = 36/64 by m.p.-f.p. determination). There was less than 3 g. of distillation residue. Other experiments in this category are listed in Table III.

TABLE III

CATALYTIC CHLORINATION WITH CHLORINE GAS[a]

| Catalyst | Mole | Temp., °C. | Time, hr. | Yield, mole | $ClC_6H_4X$ o | m | p |
|---|---|---|---|---|---|---|---|
| | | | Chlorobenzene (X = Cl) | | | | |
| SbCl₅ | 0.5 | 10–24 | 0.5 | 0.3 | 29 | 1 | 70 |
| SbCl₅ | .05 | 40–50 | 3.0 | .3 | 34 | 1 | 65 |
| FeCl₃ | .05 | 40–55 | 3.5 | .7 | 40 | 3 | 57 |
| | | | Toluene (X = CH₃) | | | | |
| SbCl₅ | 0.05 | 25–30 | 4.0 | 0.4 | 72 | 2 | 26 |
| FeCl₃ | .05 | 25–30 | 2.3 | .1[b] | 64 | 4 | 32 |
| SbCl₅ | .025 | 22–30 | 1.5 | .1 | 70 | 2 | 28 |

[a] Two moles of aromatic compound.   [b] Plus about 10 g. of tar.

**Analytical Methods.**—The infrared spectra of the following compounds were obtained in cyclohexane solution, and plots of concentration vs. log $I_0/I$ were made, using the base line method, at the indicated wave lengths (μ): o-dichlorobenzene (13.38), p-dichlorobenzene (12.23), m-dichlorobenzene (12.78), o-chlorotoluene (13.41), p-chlorotoluene (12.43), m-chlorotoluene (12.98), o-chlorobromobenzene (13.40), p-chlorobromobenzene (12.28), p-chloroiodobenzene (12.34), and o-chlorofluorobenzene (13.34). m-Isomer determinations were made by the differential method, using mixtures of the o- and p-isomers in the reference cell. Comparisons with the spectra of known mixtures showed the average error for the o- and p-isomers to be 1.0–1.5%. For the m-isomer, present in much smaller amounts, the average error was 10–20%. A Perkin–Elmer infrared spectrophotometer model 21 was used in this work.

In the case of the dichlorobenzenes and the bromochlorobenzenes, isomer ratios determined by the m.p.-f.p. method were found to differ from the infrared analyses by no more than 1% for the p-isomer. Use was made of the curves reported by Holleman and van der Linden.[32]

(30) A. Tohl, Ber., 25, 1521 (1892).

(31) R. Fittig and S. Hoogewerff, Ann., 150, 323 (1869).

(32) A. F. Holleman and T. van der Linden, Rec. trav. chim., 30, 305 (1911).