column (100 g., activity II), using freshly distilled hexane as eluent. The triphenylethylene-C^{14} was finally purified by recrystallization from absolute methanol, m.p. 66.5–67.5° in agreement with the literature.[26]

Oxidative Degradation of Triphenylethylene-C^{14}.—The above triphenylethylene-C^{14} was oxidized to benzoic acid in benzophenone using potassium permanganate dissolved in aqueous acetone, adapting the procedure of Bonner and Collins.[16–20] Yields of the oxidation products were quantitative. The benzoic acid was purified by recrystallization from water, followed by sublimation, m.p. 122.4–123.2°. The benzophenone product was converted in the usual way into its 2,4-dinitrophenylhydrazone, which was purified by successive recrystallizations from ethyl acetate, m.p. 240.6–241.6°. Duplicate radioactivity assays of these products and their precursors were performed in the usual way[27,28] by wet combustion followed by counting with the aid of a Cary Model 31 vibrating-reed electrometer. The radioactivity data are summarized in Table I.

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Reactions of Molybdenum Pentachloride and Vanadium Tetrachloride with Alkyl- and Halobenzenes[1]

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Isomer distributions were determined for the chlorination of toluene and halobenzenes by molybdenum pentachloride and vanadium tetrachloride. Polymeric material was the principal product from the toluene–molybdenum pentachloride reaction. With mesitylene, these metal halides yielded a mixture of bimesityl and chloromesitylene. Halogenation proceeded smoothly on treatment of benzene with vanadium tetrachloride or antimony pentachloride. The theoretical aspects are discussed.

Certain metal halides are known to effect direct halogenation of aromatic compounds.[3] Antimony pentachloride, ferric chloride, and cupric halides have received the most attention. Depending upon the metal halide, aromatic reactant, and reaction conditions other types of transformations may occur, such as nuclear coupling, side-chain attack in alkylbenzenes, and disproportionation.

The objective of the present study was to investigate the behavior of molybdenum pentachloride and vanadium tetrachloride toward simple aromatic compounds. In addition to ascertaining the nature of the products formed, we were particularly interested in orientation effects, mechanistic aspects, and comparisons with other metal halides. Although the chlorinating action of molybdenum pentachloride was noted many years ago,[4] there appears to be no specific data relative to the aromatic series. With the exception of this early cursory observation and recent reports from our laboratory dealing with molybdenum pentachloride,[5,6] there is no highly pertinent, prior literature concerning these two salts.

Results and Discussion

Most of our attention was devoted to halobenzenes (fluoro-, chloro-, and bromobenzene) and alkylbenzenes (toluene and mesitylene). In addition, studies were carried out with benzene, and with antimony pentachloride–benzene. Yields are based on the metal halide according to the pertinent stoichiometry.

Benzene.—Molybdenum pentachloride[5] and ferric chloride[7] convert benzene to *p*-polyphenyl[8] under mild conditions. The system aluminum chloride–cupric chloride is a particularly effective one for the oxidative cationic polymerization of benzene.[9,10] In all of these cases, only minor amounts of nuclear chlorination were observed.

On the other hand, halogenation was the favored route with vanadium tetrachloride which produced chlorobenzene in 66% yield. Only a negligible amount of nuclear coupling, leading to 4,4′-dichlorobiphenyl, took place. Since water functions as a cocatalyst in the polymerization of benzene by ferric chloride,[11] the influence of this Brønsted acid was investigated. At a 2:1 ratio of VCl$_4$:water, the yield of chlorobenzene, still the predominant product, was decreased. In addition, a small amount of solid was obtained whose infrared spectrum was very similar to that of *p*-polyphenyl. It is known that vanadium tetrachloride is rapidly converted to the oxychloride on exposure to water.[12a] A possible stoichiometric relationship for the chlorination reaction is indicated. However,

$$2\mathrm{VCl_4} + \mathrm{C_6H_6} \longrightarrow \mathrm{C_6H_5Cl} + 2\mathrm{VCl_3} + \mathrm{HCl} \qquad (1)$$

there is no direct evidence for the terminal stage of the vanadium reduction.

The antimony pentachloride–benzene reaction proceeded very smoothly with formation of chlorobenzene in 74% yield. Nuclear halogenation accounts for essentially all of the metal halide consumed. Unless conditions are carefully controlled, polychlorination occurs quite readily.[13]

$$\mathrm{SbCl_5} + \mathrm{ArH} \longrightarrow \mathrm{ArCl} + \mathrm{SbCl_3} + \mathrm{HCl} \qquad (2)$$

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[1] Paper XIV, Reactions of Metal Halides with Organic Compounds.

[2] National Science Foundation Fellow, 1963–1964.

[3] P. Kovacic, "Friedel-Crafts and Related Reactions," Vol. IV, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, Chapter 48.

[4] A. G. Page, *Ann.*, **225**, 196 (1884); B. Aronheim, *Ber.*, **8**, 1400 (1875).

[5] P. Kovacic and R. M. Lange, *J. Org. Chem.*, **28**, 968 (1963).

[6] P. Kovacic and R. M. Lange, *ibid.*, **29**, 2416 (1964).

[7] P. Kovacic and F. W. Koch, *ibid.*, **28**, 1864 (1963).

[8] Therefore, it is unlikely that molybdenum pentachloride is the substituting entity in the chlorination of benzene with chlorine gas and molybdenum chloride catalyst (see ref. 4).

[9] P. Kovacic and J. Oziomek, *J. Org. Chem.*, **29**, 100 (1964).

[10] P. Kovacic and A. Kyriakis, *J. Am. Chem. Soc.*, **85**, 454 (1963).

[11] P. Kovacic, F. W. Koch, and C. E. Stephan, *J. Polymer Sci.*, **A2**, 1193 (1964); P. Kovacic and C. Wu, *ibid.*, **47**, 45 (1960).

[12] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1929: (a) Vol. IX, p. 805; (b) Vol. XI, p. 624.

[13] H. Müller, *J. Chem. Soc.*, **15**, 41 (1862).

Halobenzenes.—In previous work, nuclear chlorination was found to be the favored route when halobenzenes are treated with ferric chloride[14] or antimony pentachloride.[15] Competing processes are negligible.

A similar situation pertained in the case of molybdenum pentachloride (Table I) and vanadium tetrachloride (Table II). With chlorobenzene, molybdenum pentachloride at 85–87° yielded dichlorobenzene possessing the distribution *ortho/meta/para* = 12:1:87. At 105–110° the *ortho/para* ratio was slightly lower. At 118–121° the vanadium tetrachloride reaction provided an orientation of *ortho/meta/para* = 17:3:80.

$$MoCl_5 + ArH \longrightarrow ArCl + MoCl_3 + HCl \qquad (3)$$

Table I

Chlorination of Halobenzenes with Molybdenum Pentachloride[a]

			Chlorohalobenzene			
$MoCl_5$, mole	Halobenzene (moles)	Temp., °C.	Yield, %	*ortho*	*meta*	*para*
0.25	C_6H_5F (1)	84	25	8	1	91
0.5	C_6H_5Cl (2.5)	105–110	31	12	1	87
0.5	C_6H_5Cl (2)	85–87	31	15	1	84
0.47	C_6H_5Br (1.7)	120–154	36	21	3	76
0.47	C_6H_5Br (2)	94–108	33	13	1	86

[a] 2.5 hr.

Table II

Chlorination of Aromatic Compounds with Vanadium Tetrachloride[a]

			Chloro aromatic			
VCl_4, mole	Aromatic (moles)	Temp., °C.	Yield, %	*ortho*	*meta*	*para*
0.52	C_6H_5Cl (2.1)	118–121	70	17	3	80
0.33	$C_6H_5CH_3$ (1)	7–25	40	15	1	84

[a] 2.5 hr.

Orientation studies with molybdenum pentachloride were extended to bromo- and fluorobenzene (Table I). The *ortho/para* ratio decreased with change in the nuclear halogen as indicated, Br ≅ Cl > F. The decrease in the *ortho/para* ratio with decrease in the atomic number of the nuclear halogen, also observed in chlorination with ferric chloride[14] or antimony pentachloride[15] and in nitration,[16] has been attributed to the inductive[17] influence of the substituent.

We wish to point out that decreased reactivity of the halobenzenes necessitated reaction temperatures in the vicinity of 100°. Although an increase in temperature favors rearrangement, the very small amount of *meta* isomer present indicates that isomerization is negligible. Control experiments also supported this contention. Treatment with molybdenum pentachloride–hydrogen chloride at 110° demonstrated the stability of *o*-dichlorobenzene to isomerization. Under conditions which effected rearrangement of *o*-bromochlorobenzene in this same system, only the *meta* isomer was formed. Since the metal halide is being consumed during halogenation, the situation is less favorable for isomerization. The rearrangement characteristics of these dihalobenzenes have been ascertained in detail by Olah and co-workers. In the presence of aluminum chloride–water, equilibrium mixtures were obtained of the compositions, 4–8% *ortho*, 60–64% *meta*, and 32–33% *para*.[18]

Alkylbenzenes.—In earlier investigations with toluene, antimony pentachloride gave nuclear chlorination exclusively.[15] Although ferric chloride also favored the halogenation pathway, much polymeric material resulted, in addition to a small amount of phenyltolylmethane.[19]

Toluene was readily attacked by vanadium tetrachloride at low temperatures yielding chlorotoluenes, *ortho/meta/para* = 15:1:84 (Table II). Isomerization appears to be negligible since catalytically induced rearrangement results in an equilibrium distribution of 31% *ortho*, 44% *meta*, and 25% *para*.[20] There was no evidence of nuclear coupling or side-chain attack.

In the case of molybdenum pentachloride, the picture was much more complex. Only an intractable brown solid was obtained. However, the presence of aluminum chloride catalyst modified the reaction course somewhat. Although polymeric material remained the predominant product, small amounts of chlorotoluene and phenyltolylmethane were isolated. The evidence for side-chain attack suggests that the higher molecular weight material may contain diarylmethane structures. On the other hand, nuclear coupling should also be considered.

Analysis of the chlorotoluene fraction provided the isomer distribution, *ortho/meta/para* = 32:2:65. The usefulness of the orientation data is impaired by our ignorance of the precursors involved in formation of the principal product.

Several types of transformations have been noted in prior investigations of mesitylene and metal halides. In addition to uncharacterized polymer, antimony pentachloride produced chlorinated mesitylenes.[15] With ferric chloride, chloromesitylene and bimesityl were obtained.[21] The metal halides in the present study resemble ferric chloride. Molybdenum pentachloride gave rise to bimesityl (34%) and chloromesitylene (5%). With vanadium tetrachloride the yields were 30 and 21%, respectively.

Let us now consider the mechanistic aspects of the various reaction categories for these metal halides in comparison with those previously investigated.

Chlorination.—Orientation data from toluene and chlorobenzene indicate that halogenation by molybdenum pentachloride and vanadium tetrachloride entails electrophilic attack by a species of low activity. Appreciable bulkiness is associated with the attacking entities as evidenced by the comparatively low *ortho/para* ratios. Since the isomer distributions are quite different from those reported in the case of chlorine–catalyst,[14,15] it is clear that substitution *via* chlorine arising from dissociation is of no more than minor im-

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(14) P. Kovacic and N. O. Brace, *J. Am. Chem. Soc.*, **76**, 5491 (1954).

(15) P. Kovacic and A. K. Sparks, *ibid.*, **82**, 5740 (1960).

(16) A. Lapworth and R. Robinson, *Mem. Proc. Manchester Lit. Phil. Soc.*, **72**, 43 (1927).

(17) An alternative interpretation consists of specific *para* activation through resonance, which would be favored in the order, F > Cl > Br. This is the counterpart of the Ingold hypothesis involving specific *para* deactivation which was advanced to rationalize the high *ortho/para* ratios obtained in nitration of nitrobenzene and benzaldehyde: C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 262.

(18) G. A. Olah, W. S. Tolgyesi, and R. E. A. Dear, *J. Org. Chem.*, **27**, 3449, 3455 (1962).

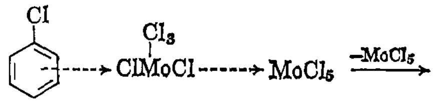
(19) P. Kovacic, C. Wu, and R. W. Stewart, *J. Am. Chem. Soc.*, **82**, 1917 (1960).

(20) G. A. Olah and M. W. Meyer, *J. Org. Chem.*, **27**, 3464 (1962).

(21) P. Kovacic and C. Wu, *ibid.*, **26**, 759 (1961).

portance. Vanadium tetrachloride is reported to decompose slowly into the trichloride and chlorine at room temperature and more quickly at the boiling point (148°).[12a] In contrast, molybdenum pentachloride is much more resistant to thermal degradation.[12b]

Various mechanistic pathways have been suggested, including direct attack by a polarized dimer complex[3,22] (illustrated with molybdenum pentachloride).



$C_6H_4Cl_2 + MoCl_3 + HCl$ (4)

Radical intermediates have also been postulated.[14,23] If this scheme is correct, then a radical-cation species, formed by transfer of an electron from the aromatic to the metal halide, appears to be the most plausible.[7,21,23,24] Similar theoretical considerations apparently pertain in the case of ferric chloride and antimony pentachloride.[3]

It has been noted that metal halides which possess halogenating properties are characterized by the dual properties of coordinative ability and a favorable reduction potential.[14] Presumably, a similar correlation pertains to nuclear coupling and side-chain involvement. Both molybdenum pentachloride and vanadium tetrachloride show considerable Lewis acid catalyst activity.[25] The oxidation-reduction potentials of the couples of greatest interest are listed in Table III.

TABLE III

OXIDATION-REDUCTION POTENTIALS IN ACID SOLUTIONS[a]

Couple	$E°$
$Fe^{+3} + e = Fe^{+2}$	0.77
$H_3SbO_4 + 2H^+ + 2e = H_3SbO_3 + H_2O$	0.75[b]
$Cu^{+2} + Br^- + e = CuBr$	0.64
$Sb_2O_5 + 6H^+ + 4e = 2SbO^+ + 3H_2O$	0.58
$VO^{+2} + 2H^+ + e = V^{+3} + H_2O$	0.36
$Mo^{+5} + 2e = Mo^{+3}$	0.11

[a] W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, pp. 253, 342, 343. [b] "Handbook of Chemistry and Physics," C. D. Hodgman, Ed., 39th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1957-1958, p. 1637.

It should be borne in mind that these data pertain to acid solutions, whereas the metal halide-aromatic reactions were carried out in nonaqueous systems. Furthermore, the nature of the anion is important. Therefore, the recorded $E°$ values should be considered as approximate indications relative to the present study.

Considering the over-all data, the indicated order defines the proclivity for nuclear halogenation *vs.* competing processes in the benzene and toluene systems, $SbCl_5 \geq VCl_4 > FeCl_3 \geq MoCl_5$.

Nuclear Coupling and Side-Chain Attack.—When halogenation decreases in importance, competing processes, such as nuclear coupling or side-chain attack, may assume greater significance. It should be emphasized that factors other than the nature of the aromatic and metal halide also play vital roles in determining the reaction course. Thus, catalytic or cocatalytic influences, *e.g.*, involving water, have been reported for the systems, benzene-ferric chloride,[11] xylenes-ferric chloride,[23] cumene-antimony pentachloride,[26] and alkylbenzenes-cupric bromide.[27]

The interpretive aspects associated with these reaction categories have been treated previously.[3,19,21,26-29] In addition, the physical nature of the reaction mixtures may well have an important bearing. Antimony pentachloride and vanadium tetrachloride possess generally good solubility in the investigated aromatic systems, whereas molybdenum pentachloride, ferric chloride, and cupric bromide are usually less soluble.

Experimental Section[30]

Materials.—Molybdenum pentachloride (Climax Molybdenum Co.), antimony pentachloride, and vanadium tetrachloride (Stauffer Chemical Co., weighed and transferred under dry nitrogen) were used directly. Chlorobenzene, bromobenzene, and fluorobenzene were distilled from calcium hydride. Benzene, toluene, and mesitylene were distilled from sodium.

Analytical Procedures.—Elemental analyses were performed by Drs. Weiler and Strauss, Oxford, England.

Isomer distributions were determined by infrared analysis as described previously.[15] In most cases, the results were confirmed by melting point-freezing point determinations.[31]

Metal Halides and Aromatics. General Procedure.—After slow addition of the metal halide to the aromatic reactant with vigorous stirring at approximately 0°, the mixture was heated to the desired temperature. The reaction was followed by titration of the evolved acid gas with standard base. The mixture was then stirred with 18% hydrochloric acid. The organic layer was extracted three times with dilute hydrochloric acid, washed with dilute sodium hydroxide, then with water, dried over anhydrous sodium sulfate, and fractionally distilled through an 18-in. spinning-band column (a Minilab apparatus was used in the case of mesitylene).

Molybdenum Pentachloride and Toluene.—Reaction of molybdenum pentachloride (0.1 mole) with toluene (0.8 mole) at 25-27° for 2.5 hr. gave 4 g. of brown polymeric solid as the principal product. No chlorotoluene was detected.

With aluminum chloride (0.01 mole) as catalyst, molybdenum pentachloride (0.5 mole) and toluene (2 moles) were allowed to react at 50-55° for 0.8 hr. After treatment with dilute acid, filtration of the reaction mixture gave 6.5 g. of dark solid material, as well as a red-brown organic phase. Work-up gave 1.2 g. of chlorotoluene, b.p. 160-161°. Infrared analysis provided the isomer distribution, *ortho/meta/para* = 33:2:65.

Continued fractional distillation gave 1.1 g. of straw-colored viscous liquid, b.p. 280° (744 mm.). The infrared spectrum resembled that of a mixture of methyldiphenylmethanes. Values reported[32] for authentic methyldiphenylmethanes are for the 2 isomer, b.p. 280.5°; for the 3 isomer, b.p. 279°; and for the 4 isomer, b.p. 282°. The distillation residue consisted of 2.5 g. of black, solid material.

The solid residue from filtration was triturated with concentrated hydrochloric acid until a colorless filtrate was obtained, then washed with boiling water until the filtrate gave a negative

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[22] H. P. Braendlin and E. T. McBee, "Friedel-Crafts and Related Reactions," Vol. III, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p. 1558.

[23] A. C. Akkerman-Faber, Ph.D. Thesis, University of Amsterdam, 1964.

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[26] P. Kovacic and A. K. Sparks, *J. Org. Chem.*, **28**, 972 (1963).

[27] P. Kovacic and K. E. Davis, *J. Am. Chem. Soc.*, **86**, 427 (1964).

[28] P. Kovacic and C. Wu, *J. Org. Chem.*, **26**, 762 (1961); P. Kovacic, S. T. Morneweck, and H. C. Volz, *ibid.*, **28**, 2551 (1963).

[29] A. Streitwieser, Jr., and L. Reif, *J. Am. Chem. Soc.*, **86**, 1988 (1964).

[30] Melting points and boiling points are uncorrected.

[31] A. F. Holleman and T. van der Linden, *Rec. trav. chim.*, **30**, 305 (1911).

[32] J. H. Lamneck, Jr., H. F. Hipsher, and V. O. Fenn, National Advisory Committee for Aeronautics, Technical Note No. 3154, 1954, p. 9.

silver nitrate test for chloride ion. The solid was then dried and extracted with petroleum ether (b.p. 60–90°) to give 5 g. of light brown, soluble material and 1.5 g. of dark brown, insoluble polymer.

Molybdenum Pentachloride and Mesitylene.—Molybdenum pentachloride (0.25 mole) was allowed to interact with mesitylene (1 mole) at 23–25° for 2.5 hr. Work-up gave 1.8 g. of colorless liquid, b.p. 65–67° (4 mm.), n^{24}_{D} 1.5250. The infrared spectrum was identical with that of an authentic sample of chloromesitylene.

Bimesityl, 20 g. (34% yield), was obtained as white crystals on continued vacuum distillation, b.p. 135–145° (3 mm.), m.p. 100.5–101.5° (from ethanol), the mixture melting point with authentic bimesityl was undepressed. A small amount of viscous, yellow oil, 0.5 g., b.p. 180–205° (3 mm.), was also collected. The residue comprised 1.9 g. of black, glassy solid.

Vanadium Tetrachloride and Benzene. 1.—Reaction of vanadium tetrachloride (0.42 mole) with benzene (1.6 moles) of 80° for 2.5 hr. gave chlorobenzene, b.p. 127–131°, 15.6 g. (66% yield), as the principal product. The infrared spectrum proved to be identical with that of authentic material. A small amount of dichlorobenzene, b.p. 170–176°, 0.5 g., having an isomer distribution predominantly *ortho–para*, was also obtained. Fractional distillation of the residue (about 0.1 ml.) through a short-path, semimicro apparatus, yielded a small quantity of white crystalline condensate (0.05 g.), m.p. 144–146°. The infrared spectrum was identical with that of 4,4′-dichlorobiphenyl. The ultraviolet spectrum and mixture melting point confirmed the identification.

2.—In the presence of water (0.1 mole), vanadium tetrachloride (0.2 mole) and benzene (0.8 mole) at 80° for 2.5 hr. gave 1.3 g. (12% yield) of chlorobenzene, b.p. 130–131°. Filtration of the reaction mixture, after addition of dilute acid, afforded 0.2 g. of yellow-brown solid whose infrared spectrum was very similar to that of *p*-polyphenyl (principal bands at 767, 807 (major), 1000, 1400, and 1483 cm.$^{-1}$).

Vanadium Tetrachloride and Mesitylene.—Vanadium tetrachloride (0.2 mole) and mesitylene (0.8 mole) at 25° for 2.5 hr. provided 3.2 g. (21% yield) of chloromesitylene, b.p. 51–56° (1.8 mm.), identified by comparison with authentic material. Bimesityl, 7.2 g. (30% yield), distilled at 136–165° (1.8 mm.), colorless crystals, m.p. 100–101° (from ethanol). Residual material weighed 0.8 g. (black solid).

Antimony Pentachloride and Benzene.—Reaction of antimony pentachloride (0.25 mole) and benzene (1 mole) at 80° for 2.5 hr. gave 20.9 g. (74% yield) of chlorobenzene, b.p. 130–131°, identified by comparison (infrared spectrum) with authentic material. A second fraction, 0.9 g., (4.9% yield), b.p. 170–176°, was identified (infrared analysis) as a mixture of dichlorobenzenes.

Isomerization of *o*-Bromochlorobenzene in the Presence of Molybdenum Pentachloride–Hydrogen Chloride.—A mixture of *o*-bromochlorobenzene (28.8 g., 0.15 mole) and molybdenum pentachloride (13.65 g., 0.05 mole) was heated at 108–110° for 2.5 hr. with good stirring while hydrogen chloride was passed into the mixture. The cooled reaction mixture was stirred with 18% hydrochloric acid and then extracted with methylene chloride. The organic portion, after being washed, was freed of solvent. The red-brown liquid residue, 28 g., was examined by gas chromatography (Aerograph 202, 40 cc./min. of helium, 185°, 5 ft. of SE-30 or FFAP on Chromosorb W). G.l.p.c. and infrared analyses indicated the presence of *o*- and *m*-bromochlorobenzene, but no *para* isomer. There were minor amounts of two higher molecular weight materials, presumably formed from chlorination or disproportionation.

Attempted Isomerization of *o*-Dichlorobenzene in the Presence of Molybdenum Pentachloride–Hydrogen Chloride.—A mixture of *o*-dichlorobenzene (45 g., 0.3 mole, g.l.p.c. pure) and molybdenum pentachloride (27.3 g., 0.1 mole) was heated with stirring at 110° for 2.5 hr. while hydrogen chloride was introduced below the surface. After treatment with 18% hydrochloric acid, the organic phase was washed with water and dried. Infrared and g.l.p.c. analyses of the recovered dichlorobenzene demonstrated the presence of only the *ortho* isomer. These analytical procedures revealed that 1,2,4-trichlorobenzene was formed in 12% yield.

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Structure and Reactivity of Methoxy-Substituted Benzenediazonium Cations

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A systematic relationship between the molecular structure of methoxy-substituted benzenediazonium salts and the N–N stretching frequency has been observed. This is useful in the identification and classification of these molecules. Resultant substituent constants, σ^+, for multiple substituted derivatives were assigned on the basis of their observed N–N frequencies and a Hammett ρ–σ correlation of the rate constants for the coupling reaction with 6-naphthol-2-sulfonate produced a ρ of 3.05.

Previous workers have shown that there is a correlation between molecular structure and reactivity in substituted benzenediazonium cations. Kazitsyna, Kikot′, and Ashkinadze[1] reported that a linear relationship exists between the N–N stretching frequency and the Hammett substituent constant, σ, for singly substituted benzenediazonium cations and they explained this structural effect in terms of resonance theory. Increased resonance interaction between the benzene ring and the diazonium group will lower the N–N bond order,[2] and the bond-order frequency dependence is well known in other systems. Berthier, Pullman, and Pontis[3] report a linear correlation between bond order and the carbonyl stretching frequency. The same dependence is found in the P–O system.[4] A carbonyl stretching frequency and Hammett σ constant relationships have been reported by Flett[5] and Jones[6] and other frequency *vs.* σ constant correlations are summarized by Jaffé.[7]

Therefore, we can expect to determine the effective σ constant for multiple substituted derivatives by this direct measurement. Furthermore, since Zollinger[8] has shown that the coupling rate constants of single substituted benzenediazonium salts with 6-naphthol-2-sulfonate can be correlated by a Hammett ρ–σ treatment, we can check the consistency of these independent assignments by a similar correlation. Eleven

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