Polymerization of Benzene to *p*-Polyphenyl by Molybdenum Pentachloride[1]

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Benzene is polymerized by molybdenum pentachloride under mild conditions to *p*-polyphenyl. The polymer, which contained a small amount of chlorine, was identified by elemental analyses, infrared spectrum, X-ray diffraction pattern, pyrolysis products, oxidative degradation, insolubility, and thermal stability. The low molecular weight organic product, present in trace amounts, contained 4,4′-dichlorobiphenyl, dichlorobenzene, and chlorobenzene. Facile dehydrogenation of 1,4-cyclohexadiene to benzene by molybdenum pentachloride lends support to the proposal that the reaction proceeds by oxidative cationic polymerization. The polymer formed under more drastic conditions possessed a darker color and a higher C/(H + Cl) atomic ratio.

This paper is concerned with the polymerization of benzene to *p*-polyphenyl by molybdenum pentachloride. Apparently, a novel polymerization method is involved similar to the recently reported preparation of *p*-polyphenyl in the system, benzene–aluminum chloride–cupric chloride.[2] Earlier work revealed that uncharacterized higher molecular weight products are obtained on treatment of benzene with aluminum chloride under drastic conditions.[3] For the benzene–ferric chloride polymerization, evidence indicated the presence of polynuclear structures in the polymer.[4]

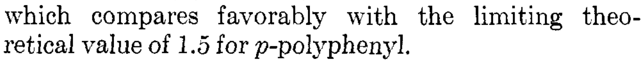
Of pertinence are the reports concerning the involvement of benzene in free radical polymerizations, *e.g.*, the copolymerization of benzene with vinyl acetate,[5] and the formation of tetrahydroquaterphenyls from the decomposition of benzoyl peroxide in benzene.[6]

Previous attempts to prepare high molecular weight *p*-polyphenyl have been unsuccessful, except for the recent synthesis[7] of impure *p*-polyphenyl by dehydrogenation of poly-1,3-cyclohexadiene. Other investigators have used mainly the Fittig, Ullmann, or Grignard methods. For example, condensation of *p*-dichlorobenzene with sodium-potassium alloy yielded a polyphenyl possessing an estimated thirty-four rings.[8] The properties of the product indicated isomerization and considerable branching. In all cases, there was no evidence for an all-*para* structure.[8,9] Methyl and halogen substituted polyphenyls have been similarly prepared.[10] Synthesis of low molecular weight *p*-polyphenyls, through septiphenyl, has been accomplished by the classical methods,[11] and by the catalytic reduction of *p*-dibromobenzene in the presence of methanol.[12]

Incompletely characterized polymers presumed to be polyphenyls have been reported from the dehydrogenation of aromatic hydrocarbon mixtures by sulfur,[13] the reaction of heavy metal halides with dilithium benzene,[14,15] and electrolysis of phenylmagnesium bromide.[16] A polymeric product possessing both polyphenyl and azo units resulted from the action of cuprous ion on 4,4′-bisdiazobiphenyl.[17]

Results and Discussion

Benzene was found to polymerize under the influence of molybdenum pentachloride yielding *p*-polyphenyl which contained a small amount of chlorine. In most cases, the reaction was carried out in the presence of water added as a potential cocatalyst. The light brown polymer was produced under surprisingly mild conditions, 0.5 hour at 50–55° (Table I). Reaction apparently proceeds according to the equation,



Both acid gas and molybdenum trichloride were shown to be among the reaction products. The structural designation is derived primarily from the elemental analyses, infrared spectrum, X-ray diffraction pattern, and thermal and oxidative degradation.

At reaction temperatures of 40–55°, the polymer possessed a C/(H + Cl) atomic ratio of 1.45–1.57 which compares favorably with the limiting theoretical value of 1.5 for *p*-polyphenyl.

Crystallinity of the organic solid was established by the X-ray diffraction pattern which gave d-spacings of 4.48, 3.83, and 3.14 Å. in decreasing order of intensity. In comparison, *p*-quaterphenyl revealed a very similar pattern with d-spacings of 4.49, 3.83, 3.40, and 3.14 Å. The most intense d-spacing, 4.48 Å., corresponds closely to the value of about 4.5 Å. which has been reported as the length of a phenyl unit.[7,18] The relative simplicity of the transmission pattern is an indication of a predominantly *para* structure for the polymer.[7]

In the infrared spectrum, an absorption maximum occurred at 807 cm.$^{-1}$ characteristic of *para* substitution. A moderately strong band at 1001 cm.$^{-1}$ also

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[1] Paper III in the series, "*Polymerization of Aromatic Nuclei*," from the forthcoming Ph.D. thesis of R. M. Lange.

[2] P. Kovacic and A. Kyriakis, *Tetrahedron Letters*, 467 (1962).

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[4] P. Kovacic and C. Wu, *J. Polymer Sci.*, **47**, 45 (1960).

[5] W. H. Stockmayer and L. H. Peebles, Jr., *J. Am. Chem. Soc.*, **75**, 2278 (1953). NOTE ADDED IN PROOF.—However, see G. A. Mortimer and L. C. Arnold, *ibid.*, **84**, 4986 (1962).

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[7] C. S. Marvel and G. E. Hartzell, *ibid.*, **81**, 448 (1959).

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TABLE I

POLYMERIZATION OF BENZENE TO *p*-POLYPHENYL BY MOLYBDENUM PENTACHLORIDE

				p-Polyphenyl					
						%			
Cocatalyst	Cocatalyst, mole	Time, hr.	Temp., °C.	Yield, g./mole $MoCl_5$	Color	C	H	Cl	C/(H+Cl), atomic
H_2O	0.25	0.5	50–55	4.4	Yel.-br.	91.71	5.28	2.72	1.45
H_2O	0.25	1.7	50–55	8.9	Br.	89.25	4.66	4.66	1.56
H_2O	0.25	5.0	50–55	9.9	Br.-blk.	89.63	4.74	4.16	1.55
H_2O	0.25	1.7	40–43	8.5	Lt. Br.	91.14	4.76	3.04	1.57
H_2O	0.25	1.7	80	9.6	Br.-blk.	85.41	3.94	9.07	1.71
$TiCl_4$	0.01	1.7	80	21.2	Br.-blk.	85.16	3.83	9.98	1.74
...[a]	...	2.0	80	13.0	Br.-blk.	76.43	2.63	19.74	2.00

[a] C_6H_6, 2 moles.

indicates a *para* configuration. Other absorption maxima were situated at 967 cm.$^{-1}$ (monosubstitution), 1400 cm.$^{-1}$, and 1483 cm.$^{-1}$ (C=C skeletal in-plane vibrations). The paucity of fine structure in the spectrum and the location of the principal *para* band at a relatively high wave length support the contention that the *p*-polyphenyl is of comparatively high molecular weight.[19]

Analysis of the benzene filtrate from the reaction mixture demonstrated the presence of small amounts of chlorobenzene, dichlorobenzene, and 4,4′-dichlorobiphenyl. Molybdenum pentachloride is known to effect nuclear chlorination of aromatic compounds.[20] The 4,4′-dichlorobiphenyl would represent the dimer stage of polymerization. The essential absence of low molecular weight polyphenyls was further evidenced by extraction studies involving 1-methylnaphthalene, dichloronaphthalene, and 1,2,4-trichlorobenzene. Unfortunately, the high insolubility of the polymer prevents molecular weight determination by the common solution techniques.

Additional evidence pertinent to the structure was obtained from thermal decomposition of the polymer. Pyrolysis–gas chromatography revealed that benzene was a component of the effluent gas. Degradation *in vacuo* at 750–800° gave a sublimate and residual material. The sublimed product contained biphenyl, *p*-terphenyl, *p*-quaterphenyl, and *p*-quinquephenyl. Identification was accomplished by comparison of the melting points, and the infrared and ultraviolet spectra with those of authentic materials. It is significant that gas chromatographic analysis of the unpurified *p*-terphenyl revealed only small amounts of a second component, apparently *m*-terphenyl. This suggests the occurrence of rearrangement to a minor degree during pyrolysis, or, alternatively, the presence of a limited number of branches or cross-links in the polymer. On the basis of the elemental analyses and infrared data, the existence of polynuclear structures in the pyrolysis residue is indicated.

Chromic acid oxidation of the polymer in aqueous acetic acid yielded terephthalic acid and 4,4′-biphenyl dicarboxylic acid, identified as their methyl esters, and *p*-chlorobenzoic acid. One may conclude that the terephthalic acid is derived from *p*-terphenyl moieties in the polymer chains, and the 4,4′-biphenyldicarboxylic acid from *p*-quaterphenyl units. The absence of isomeric benzenedicarboxylic acids was established by gas chromatographic examination of the unpurified dimethylterephthalate. The *p*-chlorobenzoic acid is undoubtedly formed by oxidation of the terminal structure of the polymer.

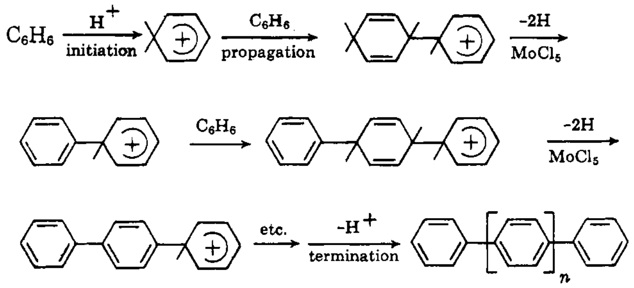
Experiments concerned with the thermal and oxidative stability in air revealed only minor destruction below about 450°. The thermal stability, extreme insolubility, and high melting point of *p*-polyphenyls have attracted a considerable amount of attention.[7,17]

It is reasonable to conclude, on the basis of the infrared spectrum, X-ray data, pyrolysis studies, oxidative degradation, insolubility, and absence of a melting point, that the polymer possesses a structure which is predominantly *para*. Also, one would expect on steric grounds that the growing chain would be reluctant to assume an *ortho* configuration during polymerization.

The data indicate that the *p*-polyphenyl derived from benzene-molybdenum pentachloride is essentially identical to the polymer recently reported[2,19] from benzene–aluminum chloride–cupric chloride, and to the *p*-polyphenyl obtained in impure form by Marvel and Hartzell[7] from the dehydrogenation of poly-1,3-cyclohexadiene.

The formation of *p*-polyphenyl can logically be explained by a mechanism involving oxidative cationic polymerization.

$$MoCl_5 + H_2O \rightleftharpoons H_2O \dashrightarrow MoCl_5 \rightleftharpoons H^+MoCl_5(OH)^-$$



The similarity of certain aspects of the proposed sequence to the well established mechanism for the cationic polymerization of olefins has been pointed out.[19] Apparently, molybdenum pentachloride assumes the dual function of catalyst and oxidizing agent. As noted earlier, evidence derived from potentiometric titration pointed to the presence of reduced molybdenum ($MoCl_3$) in the reaction mixture. The hypothesis that the metal halide acts in part by dehydrogenation of cyclohexadiene units to aromatic structures was tested with a model compound. On treatment with molybdenum pentachloride, 1,4-cyclohexadiene was converted smoothly to benzene under very mild conditions. The exothermic reaction proceeded with vigorous gas evolution.

The chlorine content of the polymer and the evidence from oxidation studies for the presence of *p*-chloro-

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(19) P. Kovacic and A. Kyriakis, *J. Am. Chem. Soc.* in press.

(20) P. Kovacic and R. M. Lange, unpublished work.

phenyl end groups can be rationalized in several ways: reaction of the growing carbonium ion with chloride, or chlorination of the polymer by molybdenum pentachloride.

In investigations of cocatalysis, experiments were performed with no added water and with molybdenum pentachloride which had been heated to remove water. Although polymerization proceeded readily, this does not conclusively eliminate the operation of a cocatalytic effect since trace amounts of Brønsted acid were probably still present. The introduction of hydrogen chloride resulted in no observable change in the end result. A cocatalytic influence by Brønsted acids has been noted in the polymerization of benzene by ferric chloride.[4]

Several reaction variables were studied (Table I) in relation to the effect on yield, chlorine content, color, and C/(H + Cl) atomic ratio. At 50–55°, based on hydrogen chloride evolution, the reaction appeared to be essentially complete at the end of one hour. Nuclear chlorination is rather insensitive to time variation at these same temperatures, increasing by a factor of only 1.5 for a tenfold increase in reaction time. For some unknown reason, the addition of a small amount of titanium tetrachloride to the benzene–molybdenum pentachloride system produced a large increase in the polymer yield. Concerning the temperature dependence, an increase of 30° in reaction temperature resulted in a yield increase of only 12%.

At higher temperatures, particularly in the absence of added water, the generated polymer possessed a higher C/(H + Cl) atomic ratio (1.7–2.0) and an increased chlorine content (9.1–19.7%). In addition, there was a darkening in the color to brown-black. These data suggest a conversion, under more drastic conditions, of *p*-polyphenyl to a product containing polynuclear structures. Polynuclear material possesses greater chromophoric power than polyphenyls, and also should undergo substitution with greater facility. It may well be that small amounts of polynuclear structure are present in the polymer formed under mild conditions.

Although the exact nature of the subsequent transformation involving *p*-polyphenyl is unknown, several plausible interpretations come to mind: (1) cross-linking of the individual polymer chains, (2) reaction with benzene–molybdenum pentachloride leading to polynuclear structures. The latter interpretation is preferred on the basis of evidence from studies with the analogous *p*-polyphenyl–benzene–ferric chloride system.[21] In addition, we were unable to cross-link *p*-polyphenyl by treatment with molybdenum pentachloride in either titanium tetrachloride or 1,2,4-trichlorobenzene. In both media the extent of chlorination increased markedly, but the C/(H + Cl) atomic ratio remained essentially unchanged.

Experimental[22]

Materials.—Benzene, Mallinckrodt reagent grade, dried by distillation from sodium; molybdenum pentachloride, Climax Molybdenum Co., weighed under dry nitrogen; titanium tetrachloride, reagent grade, Matheson Coleman and Bell; terephthalic acid, biphenyl, *m*-and *p*-terphenyl, and 1,2,4-trichlorobenzene(distilled from calcium hydride), Eastman Organic Chemicals; biphenyl-4,4′-dicarboxylic acid and 1,4-cyclohexadiene, Aldrich Chemical Co.; *p*-quaterphenyl and *p*-quinquephenyl (recrystallized from pyridine), K and K Laboratories.

Instruments.—Beckman DK-2 ultraviolet spectrophotometer (cyclohexane solution); Perkin–Elmer, Model 237, Infracord (pyrolysis products in potassium bromide pellets); Perkin–Elmer 137 Infracord (oxidation products in potassium bromide pellets); X-ray diffraction apparatus, 114.7-mm. "Norelco" powder camera, copper K_α radiation, $\lambda = 1.539$ Å.; F and M Model 500 Programmed Gas Chromatograph, 6 ft., 20% silicone rubber on firebrick, 225–340° at 11°/min., helium flow rate 30 ml./min.

Polymerization of Benzene to *p*-Polyphenyl by Molybdenum Pentachloride. (A) General Procedure.—Water (4.5 g., 0.25 mole) was added slowly with efficient stirring to a mixture of molybdenum pentachloride (136 g., 0.5 mole) and benzene (195 g., 2.5 moles) at 6° under nitrogen. The reaction mixture was heated at 40–43° for 1.7 hr. Standard base was used to follow hydrogen chloride evolution which began at 7–8°.

The viscous reaction mixture was cooled rapidly, mixed with cold 1:1 hydrochloric acid and filtered. After several extractions of the solid with benzene, the polymer was purified by trituration with hot concentrated hydrochloric acid until the extracts remained colorless. The polymer was then boiled with 10% sodium hydroxide, filtered, treated with hot concentrated hydrochloric acid until colorless washings were obtained, then washed with boiling water until no chloride could be detected in the washings (silver nitrate), and dried overnight at 120°; yield 4.5 g. This treatment gave no residue on ignition of the polymer. Care was taken to avoid contamination of the polymer.

(B) Low Molecular Weight By-products.—The benzene from the filtrate and washings was distilled leaving a red-brown residue, wt. 0.7 g. Chlorobenzene, isolated by gas chromatography of the residue and identified by comparison of its ultraviolet and infrared spectra with those of authentic material, was shown to be the major component. Also present were dichlorobenzene, identified by comparison of its retention volume to that of authentic material, and 4,4′-dichlorobiphenyl, identified by melting point (144–146°), mixture melting point (144–145°), and comparison of the ultraviolet (λ_{max} 258 mμ) and infrared (absorption maximum at 820 cm.$^{-1}$) spectra with those of authentic 4,4′-dichlorobiphenyl (lit.,[23] m.p. 144–145°).

Investigations of Cocatalysis. (A).—Hydrogen chloride, dried by passage through sulfuric acid, was passed during 10 min. into a stirred mixture of molybdenum pentachloride (136 g., 0.5 mole) and benzene (195 g., 2.5 moles) at 6°. A second sulfuric acid trap was installed near the gas outlet of the reaction flask. The mixture was then heated for 20 min. at 80°, and processed in the usual manner. The yield of brown-black polymer was 6.4 g.

In a control experiment identical quantities of reagents were allowed to react in the same manner but with no added hydrogen chloride. The yield of brown-black polymer was 6.8 g.

(B).—Molybdenum pentachloride was heated for 2 hr. at 100° under vacuum (18 mm.). Green-black crystals on the upper walls of the flask turned bright green, indicating that water was being released by the main body of the salt. The green crystals are probably molybdenum oxytrichloride, $MoOCl_3$, the expected product when molybdenum pentachloride reacts with very small amounts of water.

A mixture of molybdenum pentachloride (68 g., 0.25 mole) from the main body of green-black crystals and benzene (98 g., 1.25 moles) was heated at 80° for 20 min.; yield 3.5 g. of brown-black polymer.

Characterization of the *p*-Polyphenyl. (A) Infrared Analysis.—The potassium bromide pellet technique was used. The spectrum taken on a Beckman IR-7 spectrophotometer exhibited peaks at 767 (vw), 807 (vs), 1001 (m), 1125 (w). 1400 (w), and 1483 (m) cm.$^{-1}$. A polystyrene standard was used for calibration.

(B) X-Ray Analysis.—The X-ray diffraction pattern possessed three major lines corresponding to d-spacings of 4.48, 3.83, and 3.14 Å., in decreasing order of intensity.

(C) Pyrolysis.—The pyrolysis apparatus consisted of a Vycor tube joined by means of a ball joint to a tube 30 cm. in length and bent at a 110° angle, then to two consecutive traps, the first immersed in Dry Ice–acetone, the second in liquid nitrogen, leading, in turn, to a manometer and vacuum pump. The polymer (10.2 g.) was pyrolyzed in 0.6 g. portions at 750–800° ("Labasco" gas burner)/1–2 mm. for 30 min. The black residue after each pyrol-

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[21] P. Kovacic and F. W. Koch, unpublished work.

[22] Elemental analyses were performed by Drs. Weiler and Strauss, Oxford, England. Melting points are uncorrected.

[23] H. Meyer and A. Hoffmann, *Monatsh.*, **38**, 141 (1917).

ysis was removed before the next portion of polymer was introduced, total wt., 8.46 g. Elemental analysis gave a C/H ratio of 4.10 for the residue (no chlorine). The liquid nitrogen trap was found to contain a liquid which was completely vaporized at room temperature. The solid sublimate in the cold traps and the tube was repeatedly extracted with boiling ether. Gas chromatography of the extract showed two major peaks, corresponding to biphenyl and *p*-terphenyl. A small shoulder was noted on the *p*-terphenyl peak, having a retention volume identical with that of *m*-terphenyl. By means of mixtures of authentic *m*- and *p*-terphenyl, it was determined that the minor component was present to the extent of less than 2%. The infrared spectrum of the unpurified *p*-terphenyl was essentially identical with that of authentic material. Evaporation of the ethereal solution gave an off-white residue which was treated with 95% ethanol at room temperature to selectively dissolve biphenyl. The ethanol solution was evaporated to a volume of about 5 ml., and 20 ml. of water was added to precipitate the crude biphenyl (98 mg., m.p. 60–63°). Purification by fractional sublimation at 60–70°/1–2 mm. for 40 min. gave 93 mg. of white crystals; m.p. 69–70° (lit.,[11] m.p. 70°), m.m.p. with authentic biphenyl, 69–70°. The infrared and ultraviolet spectra (λ_{max} 248 mμ) were identical with those of authentic biphenyl. The residue from the ethanol treatment (45 mg., m.p. 190–193°) was fractionally sublimed at 130–150°/2 mm. to give 34 mg. of *p*-terphenyl, m.p. 204–206°. Purification of the crude product by vapor phase chromatography yielded pure *p*-terphenyl, m.p. 209–210° (lit.,[11] m.p. 210°), m.m.p. with authentic material, 209–210.5°. The infrared and ultraviolet spectra (λ_{max} 275 mμ) matched those of authentic *p*-terphenyl.

The white residue, insoluble in ether and ethanol, was placed in a small-scale sublimation apparatus consisting of a vertical sealed Vycor tube joined by a $^{10}/_{38}$ joint to a tube 150 mm. in length possessing a 90° bend at its midpoint, leading to two Dry Ice–acetone traps and thence to a manometer and vacuum pump. Sublimation of the residue at 500–550° (Tirell burner)/1 mm. gave rather indistinct bands of sublimate which varied in color from off-white through pale yellow to light yellow-brown near the mouth of the sublimation vessel. The indistinct bands were separated as well as possible, and the pale yellow one (25 mg., m.p. 298–300°) was fractionally sublimed to yield 15 mg. of white, crystalline *p*-quaterphenyl, m.p. 304–305°, authentic *p*-quaterphenyl, m.p. 306–308°, m.m.p. with authentic material, 304–306° (lit.,[11] m.p. 302°). The infrared and ultraviolet spectra ($\lambda_{max}^{CHCl_3}$ 300 mμ) were identical with those of authentic *p*-quaterphenyl. The light yellow-brown band was purified by removal of lower molecular weight polyphenyls by sublimation (280–290°/0.15 mm.) and recrystallization of the residue from pyridine, yield 8 mg., pale yellow-green crystals, m.p. 382–388°, authentic *p*-quinquephenyl, m.p. 381–384°, m.m.p. with authentic material, 381–385° (block) (lit.,[11] m.p. 395°). The infrared and ultraviolet spectra ($\lambda_{max}^{CHCl_3}$ 309 mμ) were identical with those of authentic *p*-quinquephenyl.

Pyrolysis-gas chromatography yielded three peaks, the major one being benzene (1.9% yield).[24]

(D) **Oxidation.**—A solution of chromic anhydride (150 g.) in 40% acetic acid (150 ml.) was added to *p*-polyphenyl (15 g.) suspended in glacial acetic acid (850 ml.). The mixture was stirred at reflux for 10 hr., cooled, and diluted with 200 ml. of 1:2 hydrochloric acid. The precipitated acids were filtered, washed with 5% hydrochloric acid, and suction-dried; yield 9.5 g. The crude acid (3 g.) was esterified by heating at reflux for 6 hr. with 100 ml. of hydrogen chloride-saturated methanol containing 6 ml. of concentrated sulfuric acid. After the addition of water (50 ml.), the mixture was cooled to 10°, and filtered. Treatment of the solid with ether revealed the presence of soluble and insoluble fractions. The ether layer was extracted with three portions of 10% sodium hydroxide, washed once with water, and dried over anhydrous sodium sulfate. After distillation of the ether, the residue (2.46 g.) was exhaustively steam distilled. The distillate contained dimethyl terephthalate, m.p. 139–140°, authentic material, m.p. 139–140°, m.m.p. with authentic ester, 139–140° (lit.,[25] m.p. 140°). The infrared and ultraviolet spectra (λ_{max} 241 mμ) were identical with those of authentic dimethyl terephthalate. The gas chromatograph of the unpurified ester indicated the absence of the *ortho* and *meta* isomers.

The solid residue from steam distillation consisted of dimethyl-4,4′-biphenyldicarboxylate, m.p. 211–212° (lit.,[26] m.p. 212–213°). The infrared and ultraviolet spectra (λ_{max} 278 mμ) were identical with those of the authentic ester.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.99; H, 5.24.

The combined filtrates and washings of the oxidation product were extracted with three 300-ml. portions of ligroin (30–60°). After the extract was dried over anhydrous sodium sulfate, evaporation yielded 0.12 g. of white crystals (m.p. 230–234°, soft. 210°). Recrystallization of 25 mg. from methanol yielded 18 mg. of 4-chlorobenzoic acid, m.p. 241–242° (lit.,[27] m.p. 241.5°), m.m.p. with authentic acid, 242–243°. The infrared and ultraviolet spectra (λ_{max} 242 mμ) were identical with those of the authentic acid. Treatment of the acid, first with phosphorus pentachloride and then with ammonia, yielded 4-chlorobenzamide, m.p. 174–175° from 10% ethanol (lit.,[28] m.p. 175°), m.m.p. with authentic amide, 174–175°.

(E) **Extraction**—Extraction of the polymer with boiling xylene until colorless filtrates were obtained gave 0.5 to 0.6% of soluble material. Extraction of 4 g. of *p*-polyphenyl with two 200-ml. portions of 1-methylnaphthalene, dichloronaphthalene, and 1,2,4-trichlorobenzene at reflux for 30 min. under nitrogen gave 0.12 g., 0.10 g., and 0.06 g. of black, gummy residue, respectively.

(F) **Thermal and Oxidative Stability.**—The polymer (1 g.) was placed in each of two porcelain vessels, one of which was equipped with a lid. The vessels were heated for 30 min. in a muffle furnace at temperatures which were increased by 50° increments in the 400–700° range. The polymer in the covered vessel was converted to a black solid at 700° amounting to 56% of the original sample weight. Uncovered vessel; temp., % wt. loss; 400°, 10.3; 450°, 81; 500°, 99.6. Covered vessel; 400°, 3.4; 450°, 8.9; 500°, 15.7; 550°, 25.2; 600°, 32.9; 650°, 39.6; 700°, 44.3.

Dehydrogenation of 1,4-Cyclohexadiene to Benzene by Molybdenum Pentachloride.—Known mixtures containing 12.2, 21.5, 48.4, and 55.8 mole % benzene in 1,4-cyclohexadiene were analyzed by gas chromatography. The ratio of the area of the benzene peak to that of the 1,4-cyclohexadiene peak for each sample (obtained by use of a planimeter) was plotted against mole per cent benzene. The resultant curve was linear over the range 10 to 60 mole % benzene, but the linearity was apparently not preserved at concentrations lower than 10 mole %.

The chromatogram of the pure 1,4-cyclohexadiene showed that it contained approximately 1% of benzene as an impurity. This value was estimated from the ratio of the peak areas.

Molybdenum pentachloride (0.5190 g., 1.9 mmoles) was added slowly with shaking to 1,4-cyclohexadiene (1.004 g., 12.5 mmoles) at 10–15°. Gas was evolved during the exothermic reaction. The light blue liquid phase was decanted from the black solid and immediately subjected to gas chromatography. Analysis revealed the presence of 31 mole % benzene in the reaction mixture.

Attempted Cross-linking of *p*-Polyphenyl. **(A) In 1,2,4-Trichlorobenzene.**—A mixture of *p*-polyphenyl (4 g.), C/(H + Cl) (atomic) = 1.57, molybdenum pentachloride (0.25 mole), and 1,2,4-trichlorobenzene (1 mole) was heated at 80° with vigorous stirring under nitrogen for 13 hr. Work-up gave 4.5 g. of brown-black polymer.

Anal. C, 62.54; H, 2.65; Cl, 32.50; C/(H + Cl) (atomic) = 1.47.

In addition there was obtained 1.05 g. of black, crystalline solid, soluble in 1,2,4-trichlorobenzene, but insoluble in petroleum ether.

Anal. C, 53.80; H, 1.67; Cl, 42.15; residue, 1.08.

(B) In Titanium Tetrachloride.—A mixture of *p*-polyphenyl (4 g.), C/(H + Cl) (atomic) = 1.57, titanium tetrachloride (190 g., 1 mole) and molybdenum pentachloride (68 g., 0.25 mole) was stirred vigorously under nitrogen at 80° for 10.5 hr. The black mixture slowly evolved 68 mmoles of hydrogen chloride. Work-up yielded brown-black polymer.

Anal. C, 61.44; H, 2.85; Cl, 26.95; C/(H + Cl) (atomic) = 1.43.

Analysis of the Molybdenum Pentachloride–Benzene Product Mixture for Mo^{+3}.—A mixture of molybdenum pentachloride

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[24] Pyrolyzed at 1150°/20 sec., Aerograph A-600B, 5-ft. column, 15% Hallcomid M-18 on Chromosorb W 60/80, 75°, flow rate 25 ml./min. We are grateful to Wilkens Instrument and Research, Inc., for this analysis.

[25] H. Schwanert, *Ann.*, **132**, 259 (1864).

[26] M. Weiler, *Ber.*, **32**, 1056 (1899).

[27] N. V. Sidgewick and E. K. Enbank, *J. Chem. Soc.*, 979 (1921).

[28] M. L. van Scherpenzeel, *Rec. trav. chim.*, **16**, 113 (1897).

(54.5 g., 0.2 mole) and benzene (78 g., 1 mole) was heated at 80° for 1 hr., and stirred with 100 ml. of 3 *N* hydrochloric acid under nitrogen. After removal of the polymer by filtration under nitrogen, the aqueous phase was separated and kept under nitrogen. The dark red-brown solution (5 ml.) was added to 50 ml. of 3 *N* hydrochloric acid and titrated potentiometrically with 0.1 *N* ceric ammonium nitrate (Beckman pH meter, saturated calomel reference, and platinum indicator electrode). The curve obtained matched closely that of a known mixture of molybdenum trichloride and molybdenum pentachloride in 3 *N* hydrochloric acid. Three points of inflection were obtained, the first two corresponding to the oxidation of Mo^{+3} to Mo^{+5}, and Mo^{+5} to Mo^{+6}, respectively. The third inflection corresponded to the potential derived from the presence of Ce^{+3} and excess Ce^{+4} in solution.

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Reaction of Antimony Pentachloride with Monoalkylbenzenes[1]

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The products formed from antimony pentachloride and monoalkylbenzenes included chloroalkylbenzenes, diarylmethane type hydrocarbons, disproportionation products, and polymeric material. Ethylbenzene yielded chloroethylbenzene, 1-(ethylphenyl)-1-phenylethane, and polymer. Cumene gave chlorocumene, benzene, diisopropylbenzene, 2-(isopropylphenyl)-2-phenylpropane, and polymer. Evidence was found for a cocatalytic effect in the cumene–antimony pentachloride reaction involving side-chain attack.

The major portion of the previous work concerning the behavior of antimony pentachloride toward aromatic compounds has dealt with nuclear chlorination.[3] We have recently reported evidence indicating that the halogenation proceeds by electrophilic substitution effected by an attacking species of low activity.[4] Furthermore, preliminary dissociation of the metal halide was deemed unlikely. In the present study, our aim was to elucidate the nature of the antimony pentachloride–monoalkylbenzene reaction by product identification and by an investigation of cocatalysis.

The products formed were found to include chloroalkylbenzenes, diarylmethane type hydrocarbons, disproportionation products, and polymeric material (Table I). Bear in mind that the reactions proceed with evolution of hydrogen chloride and reduction of Sb^{+5} to Sb^{+3}. These results then closely parallel those published a few years ago for the ferric chloride–alkylbenzene systems.[5,6]

TABLE I

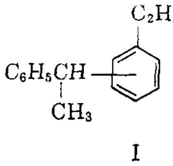
ANTIMONY PENTACHLORIDE AND MONOALKYLBENZENES[a]

C_6H_5R, R =	Time, hr.	Temp., °C	Products ClC_6H_4R, %	Diarylmethane type, %	Polymer, g.
CH_3[b]	2.5	18–31	87	..	..
CH_3CH_2	2.1	17–33	78	2	3.7
$(CH_3)_2CH$	3	8–40	14	20	20.6

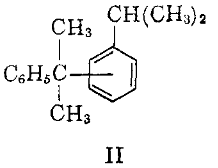
[a] Monoalkylbenzene (2 moles), antimony pentachloride (0.5 mole). [b] Ref. 4a.

Nuclear chlorination occurred with all of the alkylbenzenes, decreasing in the order, $C_6H_5CH_3 > C_6H_5C_2H_5 > C_6H_5CH(CH_3)_2$. Quantitative data for the isomer distribution of the chlorotoluene have already been reported.[4a] Results from the infrared analysis pointed to the presence of isomeric mixtures in the case of the chloroethylbenzenes and chlorocumenes. *p*-Chlorobenzoic acid was formed from the oxidation of both chlorinated products. From the accumulated evidence, it was concluded that the chlorocumene fraction also contained diisopropylbenzene.

With the presence of *sec*- and *tert*-α-hydrogens in the alkyl group, the side-chain became susceptible to attack. Ethylbenzene yielded 1-(ethylphenyl)-1-phenylethane (I), and cumene gave 2-(isopropylphenyl)-2-phenylpropane (II).



I



II

The evidence in support of the structural assignment for I is quite convincing, based partly upon elemental analysis, molecular weight, and chromic acid oxidation to *p*-benzoylbenzoic acid. The infrared spectrum indicated the presence of isomeric 1-(ethylphenyl)-1-phenylethanes, and was very similar, except for the relative intensities of various bands, to that of material prepared from ethylbenzene and styrene by the Friedel–Crafts method. I has also been reported as a product of the ethylbenzene–ferric chloride reaction.[5] Supporting evidence was provided by the studies of Corson and co-workers[7] on the dimerization of styrene in ethylbenzene. They demonstrated the presence of 1-(*p*-ethylphenyl)-1-phenylethane spectrometrically and also by oxidation to *p*-acetylbenzophenone and *p*-benzoylbenzoic acid. In addition, these investigators synthesized the authentic 1-(*o*- and *p*-ethylphenyl)-1-phenylethanes by unequivocal methods. All bands present in the infrared spectra of the authentic ortho and para isomers were also observed in the spectrum of the ethylbenzene–antimony pentachloride product.

Identification of the corresponding hydrocarbon (II) from cumene proved to be a more arduous task, since

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[1] Part XI in the series on "Reactions of Metal Halides with Organic Compounds," from the Ph.D. thesis of A. K. Sparks, Case Institute of Technology, 1960.

[2] Allied Chemical Corp. Fellow, 1958–1960.

[3] For a review, see A. K. Sparks, Ph.D. thesis, Case Institute of Technology, 1960.

[4] (a) P. Kovacic and A. K. Sparks, *J. Am. Chem. Soc.*, **82**, 5740 (1960); (b) *J. Org. Chem.*, **26**, 1310 (1961); (c) 2541 (1961).

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[6] P. Kovacic and C. Wu, *J. Org. Chem.*, **26**, 762 (1961).

[7] B. B. Corson, J. Dorsky, J. E. Nickels, W. M. Kutz, and H. I. Thayer *ibid.*, **19**, 17 (1954).