filtered and washed with a little benzene. The still gummy material was suspended in cold benzene, the slurry stirred until uniform, and the solid filtered. The more granular product was then digested with boiling benzene. The quite pure product was easily recrystallized from glacial acetic acid (twice) and then digested with boiling benzene. The product was subsequently washed with benzene and hexane, m.p. 242–244°; lit.,[3] m.p. 239–240°. At this stage, microanalyses indicated that the sample was partially solvated with benzene. The sample was desolvated by digestion with boiling hexane and drying at 55° in vacuum for several days.

Anal. Calcd. for $C_{21}H_{18}Cl_2O_3$: C, 64.79; H, 4.66; Cl, 18.22. Found: C, 65.18; H, 4.45; Cl, 18.41.

Another sample was recrystallized from acetic acid. After preliminary drying at 50° for several days the sample was further dried in vacuum at 100° for 24 hr.

Anal. Calcd. for $C_{21}H_{18}Cl_2O_3$: C, 64.79; H, 4.65; Cl, 18.22. Found: C, 64.65; H, 4.87; Cl, 17.84, 17.79.

2,6-Bis(2-hydroxy-5-bromobenzyl)-p-cresol. To a partial solution of 35 g. (large excess) of *p*-bromophenol and 35 ml. of hexane at steam-bath temperature, was added 4.2 g. (0.025 mole) of recrystallized 2,6-dihydroxymethyl-*p*-cresol. The mixture was then treated with 10 drops of concd. hydrochloric acid, whereupon a vigorous exothermic reaction ensued. A dense, semi-solid mass separated from the reaction mixture. The supernatant was decanted and the residue treated with benzene. This treatment promoted rapid crystallization of the product. The product was filtered and washed with benzene. Then it was suspended in cold benzene, filtered, and digested with boiling benzene. Finally, the product was recrystallized from acetic acid (twice) followed by digestion with boiling benzene. The sample was washed with benzene and hexane and dried, m.p. 231–232° dec., with prior sintering and discoloration beginning at 215°. The sample appeared to be partially solvated with benzene. The sample was desolvated by digestion with hexane, followed by drying at 100° in vacuum for 24 hr.

Anal. Calcd. for $C_{21}H_{18}Br_2O_3$: C, 52.74; H, 3.79; Br, 33.43. Found: C, 52.59; H 3.88; Br, 33.24.

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Reactions of Antimony Pentachloride and Ferric Chloride with Deactivated Aromatic Compounds[1]

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Received August 3, 1960

Earlier publications in this series have dealt with the interaction of antimony pentachloride[3] and ferric chloride[4] with simple alkyl- and halobenzenes. This investigation is concerned with the scope of the reaction of these metal halides with deactivated aromatic compounds. Benzotrifluoride, nitrobenzene and benzaldehyde were selected for study.

Benzotrifluoride. Products obtained from antimony pentachloride and benzotrifluoride included *m*-chloro-α,α,α-trifluorotoluene,[5] *m*-benzoyl-α,α,α-trifluorotoluene, benzoic acid and tarry polymer. The compounds derived from side-chain attack might arise from precursors[6–10] such as $C_6H_5CX_2^+$ ($X = F$ or Cl). It is presumed that *m*-benzoyl-α,α,α-trifluorotoluene is formed by hydrolysis[11] of the intermediate *m*-$C_6H_5CX_2C_6H_4CF_3$ ($X = F$ or Cl). Similar condensations of benzotrichloride with itself,[12] phenols[13,14] and benzene[15] have been reported.

On the other hand, ferric chloride reacted exclusively with the trifluoromethyl group of benzotrifluoride, yielding *m*-benzoyl-α,α,α,-trifluorotoluene and benzoic acid as the only isolable products after hydrolysis, in addition to tar.

Nitrobenzene. Antimony pentachloride combined with nitrobenzene at 103–118° to give a 64% yield of chloronitrobenzene (predominantly *meta*).

In contrast, ferric chloride exhibited a quite different mode of reaction. Chloronitrobenzene, *p*-chloroaniline, 2,4,6-trichloroaniline, and chloranil were isolated in low yields. It seems reasonable that the amines rose *via* reduction of nitrobenzene by ferrous chloride. Robertson and Evans have discussed[16] the relationship between the nature of the reducing system and chloroaniline formation in the reduction of nitrobenzene. The generation of chloranil is somewhat reminiscent of conversion of a *p*-aminophenol to a chloroquinone by oxidation with ferric chloride.[17–19] Although the reaction sequences leading to the various products are un-

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(1) Part X of a series on *Reactions of Metal Halides with Organic Compounds;* from the Ph.D. thesis of A. K. Sparks, Case Institute of Technology, 1960.

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known, the following processes might reasonably be involved at one stage or another: oxidation and nuclear chlorination by ferric chloride, rearrangements of the phenylhydroxylamine or Bamberger[20] type.

Quite recently, Miller and White reported[21] the formation of hexachlorobenzene, together with a trace of chloranil, from the reaction of nitrobenzene with excess anhydrous ferric chloride at 190–195°.

Benzaldehyde. The reaction of benzaldehyde with ferric chloride or antimony pentachloride[22] resulted in the formation of dark, polymeric solid accompanied by the evolution of copious quantities of gas containing hydrogen chloride. In the case of ferric chloride, carbon monoxide[23,24] was also detected in the effluent vapor.

EXPERIMENTAL[25]

Antimony pentachloride and benzotrifluoride. Antimony pentachloride (144 g., 0.48 mole) was added slowly to benzotrifluoride (292 g., 2 moles) with stirring under nitrogen at 30–94° during 90 min. After 1 hr. at 90–95°, work-up of the reaction mixture, including refluxing with water, yielded benzoic acid (2 g.) and a liquid (21.2 g.), b.p. 57–58° (40 mm.), identified as chloro-α,α,α-trifluorotoluene (91% *meta*) by infrared analysis (authentic isomers as reference standards) and by hydrolysis[7] to *m*-chlorobenzoic acid, m.p., 152.5–153° from toluene; lit.[26] m.p. 153°.

Anal. Calcd. for $C_7H_5O_2Cl$: Neut. equiv., 156.6 Found: 157.

The liquid, 33.2 g., b.p. 105.5–106.5° (0.6 mm.), turned to a white solid, m.p. 49–50.5°. A mixture melting point with authentic *m*-benzoyl-α,α,α-trifluorotoluene from the ferric chloride-benzotrifluoride reaction showed no depression.

The distillation residue consisted of brown solid (9.1 g.).

Ferric chloride and benzotrifluoride.[27] A mixture of benzotrifluoride (2 moles) and anhydrous ferric chloride (1 mole) was heated under nitrogen at reflux for 4 hr. Work-up, including refluxing with water, yielded benzoic acid (6.6 g.) and *m*-benzoyl-α,α,α-trifluorotoluene, 29.6 g., b.p. 121–123° (1.5 mm.), m.p. 51.5–53° from aqueous methanol.

Anal. Calcd. for $C_{14}H_9F_3O$: C, 67.20; H, 3.62; F, 22.78. Found: C, 67.16; H, 3.77; F,[28] 23.14.

Hydrolysis of a portion of this fraction with sulfuric acid[7] gave a 95% yield (crude) of *m*-benzoylbenzoic acid, m p. 159.5–161° from toluene; lit.[29] m.p. 161°.

Anal. Calcd. for $C_{14}H_{10}O_3$: Neut. equiv., 226. Found: 228.

The distillation residue consisted of dark brown, brittle solid (60 g.).

Antimony pentachloride and nitrobenzene. A mixture of antimony pentachloride (69.9 g., 0.23 mole) and nitrobenzene (111.4 g., 0.91 mole) was heated at 108–118° under nitrogen for 4.5 hr. Chloronitrobenzene, 23.5 g., b.p. 108.5–109.5° (11 mm.) was obtained. The product was a mixture of isomers, predominantly *meta*, as determined by infrared analysis.

Ferric chloride and nitrobenzene. A mixture of ferric chloride (0.5 mole) and nitrobenzene (1 mole) was heated during 4 hr. with stirring under nitrogen to 142° and then at 182–204° for 1 hr.

The reaction mixture was steam distilled and the steam-volatile material was fractionated, yielding a yellow liquid, 1.7 g., b.p. 103–105° (10 mm.), which was identified as a mixture of chloronitrobenzenes by comparison of the infrared spectrum with those of the authentic materials. The brown distillation residue (1.3 g.) was crystallized from toluene to yield 0.71 g. of chloranil, m.p. 289.5–290.5°; lit.[30] m.p. 290°.

Anal. Calcd. for $C_6Cl_4O_2$: C, 29.31; H, 0.00; Cl, 57.68. Found: C, 29.21; H, 0.06; Cl, 57.33.

The pot residue from steam distillation was made basic and the steam distillation continued. A small amount of solid (0.29 g.), m.p. 74.5–76° from dilute ethanol, was collected from the condenser. A mixture melting point with authentic 2,4,6-trichloroaniline showed no depression.

The remaining steam-volatile material was distilled to give a brown oil (0.1 g.), b.p. 64–96° (11 mm.). The infrared spectrum contained all the peaks of *p*-chloraniline, in addition to bands indicative of a nitro compound contaminant. Reaction of a portion of this fraction with benzoyl chloride gave a white solid, m.p. 188–190.5°, which did not depress the melting point of authentic *N*-(*p*-chlorophenyl)benzamide.

Antimony pentachloride and benzaldehyde. Antimony pentachloride (0.15 mole) was added to benzaldehyde (1.22 moles) at 120–156° under nitrogen. After 30 min. at 130–140°, work-up of the reaction mixture yielded black solid as the main product.

Anal. Found: C, 63.43; H, 3.96; Cl, 7.24.

The infrared spectrum of a gas sample collected over water during the early stages of reaction revealed no trace of carbon monoxide.

Ferric chloride and benzaldehyde.[31] A mixture of benzaldehyde (425 g., 4 moles) and ferric chloride (162 g., 1 mole) was heated under nitrogen at 145–160° for 1 hr. A gas sample[23] showed very weak infrared absorption bands of similar intensity at 2120 and 2180 cm.$^{-1}$, characteristic of carbon monoxide; lit.[32] 2135 and 2196 cm.$^{-1}$ (approx.). The reaction mixture yielded insoluble, infusible black solid (30 g.).

Anal. Found: C, 76.26; H, 3.22; Cl, 0.14 Fe, 0.73.

Acknowledgment. We gratefully acknowledge the support of part of this work by the National Science Foundation.

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Reaction of Organophosphorus Acids with Isocyanates[1]

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Received April 29, 1960

In a recent report,[2] it was shown that the tertiary amine salts of phenylphosphinic acid and the cor-