isomerize partly into its corresponding chalcone when heated above its melting point.

On prolonged reduction with magnesium and hydrochloric acid 7-hydroxy-4′-chloroflavanone develops a deep red color. The rest of the chloro and nitroflavanones, *e.g.*, 7-hydroxy-2′(and 3′)-chloroflavanones and 7-hydroxy-3′-nitroflavanone, however, fail to respond to this color reaction.

All the flavanones described here failed to impart any coloration to ethanolic ferric chloride.

EXPERIMENTAL

All the melting points are uncorrected. The chalcones were prepared according to the procedure of Schraufstätter and Deutsch.[3] The flavanones were secured by the acid isomerization[4] of the appropriate chalcones. The compounds prepared are listed in Tables I–III below.

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Formation of Chloranil During Chlorination of Certain Nitroaromatic Compounds

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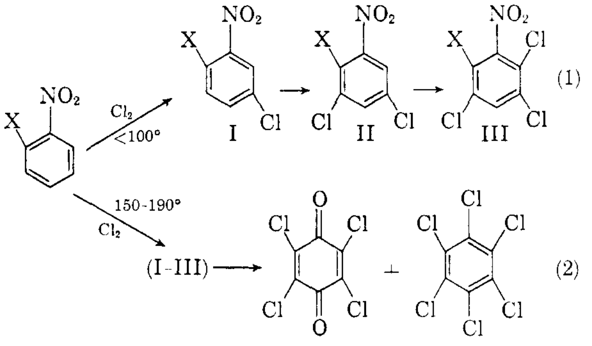
The chlorination of nitrobenzene, *o*-chloronitrobenzene, and *o*-nitrophenol with ferric chloride-chlorine at high temperatures results in the formation of hexachlorobenzene and chloranil together with a variety of chlorinated nitroaromatic derivatives. Hexachlorobenzene has been prepared from nitrobenzene[1] by a ferric chloride-catalyzed chlorination at temperatures above 100°, and from *o*-chloronitrobenzene[2] with antimony pentachloride–chlorine at 120°. The reaction of 1,4-dichloro-2,5-dinitro- or 1,5-dichloro-2,4-dinitrobenzene[3] with ferric chloride and chlorine at 140–180° also yields hexachlorobenzene. However, the formation of chloranil during these reactions was not described.

During the present investigation the conversions of the nitroaromatic compounds to chloranil amounted to 17–29%. Hexachlorobenzene conversion ranged from 7–89%. Although no attempt was made to establish optimum conditions, several observations are pertinent. Denitration of the ring is best accomplished at temperatures of 170–190°. The chlorination reaction is slow—to obtain significant yields of hexachlorobenzene and/or chloranil, a rapid flow rate of chlorine was used over a seven to ten hour period. No direct effects of ferric chloride concentration upon the course of the reaction were observed. Both catalytic and molar quantities of the metallic halide were used with similar results.

The experimental data are recorded in Table I.

Essentially, the formation of chloranil from the chlorination of a nitroaromatic compound represented in the equation below must proceed such that the position *para* to the nitro group is not substituted prior to denitration.



where X=H,OH,Cl.

To establish that denitration of the ring is temperature dependent, the chlorination of *o*-nitrophenol was conducted under mild conditions. Hexachlorobenzene and chloranil were not formed at 72°; 4,6-dichloro-2-nitrophenol (69%) and a mixture of monochloronitrophenols (28%) were the major products. The formation of the 4,6-dichloro isomer from the chlorination of *o*-nitrophenol has been reported earlier.[4] Page[1] has reported the formation of 2,3,5,6-tetrachloronitrobenzene from the chlorination of nitrobenzene below 100°.

While an ionic mechanism for the initial stages of the chlorination reaction would be valid at lower temperatures (Equation 1) complications arise under drastic conditions (130–200°). Thermally-initiated free radical reactions involving chlorination, nitration, denitration and/or oxidation may occur simultaneously. Cohen and Bennett,[5] for example, have reported that chlorination of 2,5-dichloronitrobenzene—the predominant isomer obtained on monochlorination of *o* - chloronitrobenzene[2]— at 130° with antimony pentachloride-chlorine does not give the expected 2,3,5-trichloronitrobenzene, but rather the 2,4,5- isomer.

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TABLE I

CHLORINATION OF NITROAROMATIC COMPOUNDS

X	X-ArNO$_2$, mole	FeCl$_3$, g.	Cl$_2$, c.f.m.	Temp., °	Time, hr.	% Conv.[a] C$_6$Cl$_6$	% Conv.[a] C$_6$Cl$_4$O$_2$
H	0.05	16.2[b]	...	190–195	1	7.1	Trace
o-Cl	0.1	49.0	...	175–193	6	7.0	20.0
o-Cl	0.31	0.1	5	147–170	5	89.5	Trace
				180–196			
o-HO	0.57	0.1	5	150–180	5	17.1	29.6[c]
				190–200	2.5		
o-HO	0.23	0.1	5	72[d]	2.5	...	...[e,f]
o-HO	0.13	0.1	2	60–120	5	....	17.0[g,h]
				150–178	1		

[a] The infrared spectra of hexachlorobenzene and chloranil were identical with reference spectra (4545 and 6634 Sadtler Standard Spectra, respectively). [b] 94.5% of ferric ion converted to ferrous ion during reaction as determined by titration of aqueous washings with 0.05N potassium dichromate. [c] A complex mixture of chlorinated nitrophenols also resulted. [d] Carbon tetrachloride (100 ml.) used as solvent. [e] 4,6-Dichloro-2-nitrophenol (69%), m.p. 124–125°. R. L. Datta and H. Mitter, *J. Am. Chem. Soc.*, **41**, 2035 (1929) give 122–123°. *Anal.* Calcd. for $C_6H_3Cl_2NO_3$: C, 34.56; H, 1.44; Cl, 34.13; N, 6.73. Found: C, 34.91; H, 1.41; Cl, 32.21; N, 6.58. [f] A crude mixture of monochloronitrophenols (28%), m.p. 62–70° also obtained. *Anal.* Calcd. for $C_6H_4ClNO_3$: C, 41.50; H, 2.30; Cl, 20.45. Found: C, 39.59; H, 2.09; Cl, 21.98. [g] *Anal.* Calcd. for $C_6Cl_4O_2$: C, 29.25; Cl, 57.78. Found: C, 29.41, 29.43; Cl, 57.29, 57.28. [h] 4,6-Dichloro-2-nitrophenol (54.6%) also isolated, m.p. 124–126°. Infrared analysis shows absorptions due to hydroxyl, nitro and chloro groups; no adjacent hydrogen atoms on aromatic ring.

In view of the drastic conditions used in the present investigation, it would be difficult to predict the chlorinated intermediates, or the point at which the oxidation reaction occurs. It was shown, however, that the formation of hexachlorobenzene under the present reaction conditions could be derived from the chlorination of chloranil at 155–175°. The formation of hexachlorobenzene from chloranil has previously been reported[6] under somewhat different and even more drastic conditions.

Since nitrogen oxides were evolved during this chlorination reaction of nitroaromatics, the alternate possibility existed that oxidation and/or nitration of hexachlorobenzene may take place. It has been stated[7] that hexachlorobenzene is resistant to substitution by electrophilic reagents, and that when conditions are drastic enough to bring about a reaction with such reagents, it is not one of substitution. Although we were unable to isolate chloranil from the reaction of hexachlorobenzene with nitrogen tetroxide at 150–160°, the quinone has been obtained (21%) from the reaction of hexachlorobenzene with a sulfuric acid-nitric acid mixture at 90°.[8] No nitrated products were isolated.

EXPERIMENTAL

A typical experiment was conducted in the following manner. A cylindrical flask, fitted with a gas inlet tube, stirrer, thermometer, and condenser was charged with 80.0 g. (0.57 mole) of o-nitrophenol and 0.1 g. of anhydrous ferric chloride. The mixture was heated to 150° by means of a silicone oil bath. Chlorine gas was introduced at the rate of 5 c.f.m. After 5 hr. at 150–180°, the gas flow was interrupted, the mixture cooled and weighed. A gain of 45.0 g. had resulted. The mixture was reheated to 190° and chlorine passed through the mixture at 190–200° for an additional 2.5 hr. At this stage sublimation of a yellow solid was observed. The total gain in weight was 86.7 g. The mixture was washed with hot water and then extracted with ether. The ether extracts were discarded. The solids were extracted with chloroform; a yellow solid (41.7 g.) remained insoluble. After two recrystallizations from chloroform, the chloranil melted at 290–291° (sealed tube).

The solvent was removed from the chloroform soluble material (126.0 g.). The solids were extracted with ethanol to give 27.8 g. of insoluble material. This was recrystallized from chloroform to yield hexachlorobenzene, white needles, melting at 230–231°.

Anal. Calcd. for C_6Cl_6: C, 25.28; Cl, 74.80. Found: C, 25.16, 25.20; Cl, 74.36, 74.43.

The ethanol soluble material (73.8 g.) was not further investigated; it is probably a mixture of chlorinated nitrophenols.

Chloranil from hexachlorobenzene. Hexachlorobenzene (10.0 g., 0.03 mole) was placed in a flask and heated to 90° for 8 hr. with 23 ml. of 96% sulfuric acid and 78 ml. of fuming nitric acid. The mixture was cooled, diluted with water, and filtered. The solids were extracted with water and dried. Fractional crystallization of the solids from chloroform gave 1.6 g. (21.6%) of chloranil, yellow needles, m.p. and mixed m.p. 290–291° (sealed tube) (lit.,[9] m.p. 290–291° sealed tube).

Hexachlorobenzene from chloranil. Chloranil, 5.0 g. (0.02 mole) and ferric chloride (0.1 g.) were placed in a test tube and heated to 155–175° while passing chlorine through the mixture for 2.5 hr. at the rate of 5 c.f.m. The cooled mixture was extracted with chloroform to give 1.0 g. (17.5%) of hexachlorobenzene, white needles, m.p., and mixed m.p., 230–232°.

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