acid was added in 10-ml. increments. The oily upper layer was then separated, dried with calcium chloride and fractionated under reduced pressure. The main fraction, b.p. 65–67.5°/5 mm., consisted of 15.7 g. (49%) of a pale yellow liquid. Refractionation gave a colorless analytical sample, b.p. 68–70°/7 mm., n_D^{25} 1.5148, f.p. −4 to −6.5°.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.3; H, 8.5. Found: C, 72.6; H, 8.4.

1-Ethyl-2,5-dimethoxy-4-nitrobenzene. 1-Ethyl-2,5-dimethoxybenzene (8.0 g.) was nitrated by the procedure used in *Run D* for 2′,5′-dimethoxyacetophenone with the exception that the mixture was quenched immediately after completion of the acid addition. The reaction was considerably more vigorous than in the case of 2′,5′-dimethoxyacetophenone. The yield was 9.2 g. (92%) of yellow needles, m.p. 79–80°. Recrystallization from either methanol or benzene-petroleum ether did not raise the melting point.

Anal. Calcd. for $C_{10}H_{13}O_4N$: N, 6.6. Found: N, 6.7.

Attempts at nitration with concd. nitric acid at −18° and −35° resulted in the formation of dark tars.

Determination of structure of the nitro compounds. The structure of 1-ethyl-2,5-dimethoxy-4-nitrobenzene was established by its oxidation to 2,5-dimethoxy-4-nitrobenzoic acid followed by demethylation of the latter to 2,5-dihydroxy-4-nitrobenzoic acid, a known compound.[12] The structure of 2′,5′-dimethoxy-4′-nitroacetophenone was determined by its conversion to 2,5-dimethoxy-4-nitrobenzoic acid; that of 2′,5′-dimethoxy-6′-nitroacetophenone by its conversion to 2,5-dimethoxy-6-nitrobenzoic acid, a compound also obtained from 2-bromo-2′,5′-dimethoxy-6′-nitroacetophenone.[13] The position of the nitro group in the latter compound has been established by its conversion to 4,4′,7,7′-tetramethoxyindigotin by treatment with ammonium sulfide.[13]

1-Ethyl-2,5-dimethoxy-4-nitrobenzene (3.0 g.) was refluxed for 6 hr. with a solution of 9.0 g. of potassium permanganate and 34.5 ml. of 5% sodium hydroxide in 500 ml. of water. Following removal of manganese dioxide by filtration, the solution was extracted with ether, then acidified to *p*H 1 with 10% sulfuric acid. The material thus precipitated was recrystallized from hot water, yielding orange-red crystals of 2,5-dimethoxy-4-nitrobenzoic acid, m.p. 192–193° dec.

Anal. Calcd. for $C_9H_9O_6N$: N, 6.2; neut. equiv., 227. Found: N, 6.3; neut. equiv., 231.

A mixture of 0.23 g. of 2,5-dimethoxy-4-nitrobenzoic acid, 0.20 ml. of glacial acetic acid and 1.49 ml. of 49% hydrobromic acid was heated at 125–160° for 18 hr. The acetic acid was then removed under reduced pressure and the residue extracted with ether. The solid obtained on evaporation of the ether was recrystallized from hot water, yielding orange-red needles of 2,5-dihydroxy-4-nitrobenzoic acid, m.p. 244–245 dec. (no depression on mixing with an authentic sample prepared by an independent, unambiguous procedure[12,14]; identical ultraviolet and visible absorption spectra with maxima at 278 mμ and 425 mμ in benzene; deep violet color with alkali[12]).

2′,5′-Dimethoxy-4′-nitroacetophenone was isolated as yellow needles, m.p. 122–123°, from the fractional crystallization of the crude nitration product from *Run A*.

Anal. Calcd. for $C_{10}H_{11}O_5N$: C, 53.3; H, 4.9; N, 6.2. Found: C, 53.4; H, 5.1; N, 6.2.

Treatment of this material with hypohalite yielded 2,5-dimethoxy-4-nitrobenzoic acid, m.p. 192–193° dec. (no depression on mixing with a sample of the product obtained from the oxidation of 1-ethyl-2,5-dimethoxybenzene; identical ultraviolet absorption spectra with maxima at 277 mμ and 360 mμ in benzene).

2′,5′-Dimethoxy-6′-nitroacetophenone was also isolated from the fractional crystallization as pale yellow needles, m.p. 72–73°.

Anal. Calcd. for $C_{10}H_{11}O_5N$: C, 53.3; H, 4.9; N, 6.2. Found: C, 53.0; H, 4.9; N, 6.3.

Treatment of this material with hypohalite yielded 2,5-dimethoxy-6-nitrobenzoic acid, m.p. 192–193° dec. (no depression on mixing with a sample prepared from 2-bromo-2′,5′-dimethoxy-6′-nitroacetophenone by the haloform reaction[13]; identical ultraviolet absorption spectra with maxima at 325 mμ in benzene; large depression in melting point on mixing with a sample of 2,5-dimethoxy-4-nitrobenzoic acid).

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Chalcones. IV. Synthesis of Chloro- and Nitrochalcones

DURGA NATH DHAR[1a]

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Syntheses of some methylchalcones have been reported.[1b,2] The present communication records the synthesis of isomeric chloro- and nitro- substituted chalcones obtained by the Claisen-Schmidt condensation of resacetophenone, resacetophenone dimethyl ether, and *o*-hydroxyacetophenone with isomeric chlorobenzaldehydes and of resacetophenone and *o*-hydroxyacetophenone with *m*-nitrobenzaldehyde.

Condensation of *o*-chlorobenzaldehyde with resacetophenone, taken in stoichiometric proportion, at room temperature for eight days, gave the 2′,4′-dihydroxy-2-chlorochalcone in a good yield (58.7%) and without the formation of any resinous products. The same condensation could also be effected by heating at 60° for three hours, and subsequently leaving the reaction mixture at room temperature for twenty-two hours to give the above chalcone in 55% yield.

In the synthesis of 2′,4′-dihydroxy-3-chlorochalcone the yield was found to increase from 18–33% by using four times the stoichiometric amount of *m*-chlorobenzaldehyde. But a considerable amount of *m*-chlorobenzoic acid was formed in this condensation.

It is interesting to find that the isomeric 2′,4′-dihydroxy-4-chlorochalcone is pyrochromatic—becomes orange on heating and yellow on cooling.

Condensation of isomeric chlorobenzaldehydes with resacetophenone, under similar experimental conditions, gave significant differences in the yields

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TABLE I

CHALCONES

Chalcone	Color and Crystalline Shape	Solvent for Crystallization	M.P.°	Formula	Analysis Calcd. C	Analysis Calcd. H	Analysis Found C	Analysis Found H
2',4'-Dihydroxy-2-chloro	Yellow micro-needles	Chloroform	166–167	$C_{15}H_{11}O_3Cl$	65.57	4.0	65.52	3.98
2',4'-Dihydroxy-3-chloro-	Yellow micro-needles	Aqueous methanol	161–162	$C_{15}H_{11}O_3Cl$	65.57	4.0	65.70	3.84
2',4'-Dihydroxy-4-chloro-	Yellow lozenge shaped plates	Acetone	190–191	$C_{15}H_{11}O_3Cl$	65.57	4.0	65.20	4.24
					Cl		Cl	
2',4'-Dimethoxy-2-chloro-	Pale yellow silky needles	Ethanol	107–107.5	$C_{17}H_{15}O_3Cl$	11.7		11.6	
2',4',-Dimethoxy-4-chloro-	Pale yellow silky needles	Ethanol	117.5	$C_{17}H_{15}O_3Cl$	11.7		11.8	
					N		N	
2',4'-Dihydroxy-3-nitro-	Lemon yellow micro-needles	Ethanol–acetic acid	214–215	$C_{15}H_{11}O_5N$	4.91		5.09	
2'-Hydroxy-3-nitro-	Yellow micro-crystalline powder	Ethanol	153–154	$C_{15}H_{11}O_4N$	5.20		5.5	

TABLE II

FLAVANONES

Flavanone	Color and Crystalline Shape	Solvent	M.P.,°	Formula	Calcd. C	Calcd. H	Found C	Found H
7-Hydroxy-2'-chloro-	Pinkish white plates	Benzene–petroleum ether	208–209	$C_{15}H_{11}O_3Cl$	65.57	4.0	65.32	4.2
7-Hydroxy-3'-chloro-	Colorless flat micro-needles	Benzene	184–185	$C_{15}H_{11}O_3Cl$	65.57	4.0	65.42	4.28
7-Hydroxy-4'-chloro-	Colorless hexagonal prisms	Acetone	209–210	$C_{15}H_{11}O_3Cl$	65.57	4.0	65.07	4.31
					N		N	
7-Hydroxy-3'-nitro-	Yellowish white micro-plates	Ethanol	240–241	$C_{15}H_{11}O_5N$	4.91		5.21	

TABLE III

CHALCONE 2,4-DINITROPHENYLHYDRAZONES

	Color and Crystalline Shape	Solvent	M.P.,°	Formula		
					N	N
2',4',-Dihydroxy-2-chloro-	Orange-red micro-needles	Ethyl acetate	253–254.5	$C_{21}H_{15}O_6ClN_4$	12.32	12.48
2',4',-Dihydroxy-3-chloro-	Red micro-needles	Ethyl acetate	263° dec.	$C_{21}H_{15}O_6ClN_4$	12.32	12.39
2',4',-Dihydroxy-4-chloro-	Deep red micro-needles	Ethanol	245–247	$C_{21}H_{15}O_6ClN_4$	12.32	12.13

of isomeric chlorochalcones, *e.g.*, 2',4'-dihydroxy-2-chlorochalcone (64%) and 2',4'-dihydroxy-3 (and 4)-chlorochalcones (17.8% and 19.4%). The high yield of 2',4'-dihydroxy-2-chlorochalcone may be explained on the basis of combined inductive and direct effects (I+D) of the chloro substituent in the aldehyde component which makes the latter more electropositive and hence facilitates the condensation.

It has been found that in the condensation of resacetophenone with isomeric nitrobenzaldehydes, the presence of high concentration of alkali causes much resinification of the latter. No chalcone could be secured from either *o*- or *p*-nitrobenzaldehyde. Condensation with *m*-nitrobenzaldehyde, at 60° for forty-five minutes, however, gave 2',4'-dihydroxy-3-nitrochalcone in 14% yield by the use of a larger quantity of the solvent as a diluent. The reaction is clean although resinification ensues on prolonged condensation.

On acid isomerization, the chloro- and nitrochalcones readily yield their corresponding flavanones. In the isomerization of 2',4'-dihydroxy-4-chlorochalcone a large quantity of red coloring matter was produced with the 7-hydroxy-4'-chloroflavanone. This flavanone was found to 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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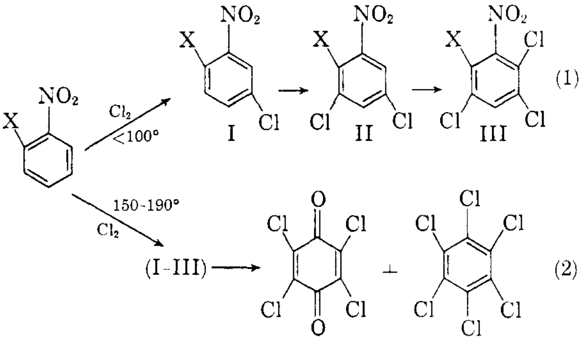
The chlorination of nitrobenzene, *o*-chloronitrobenzene, and *o*-nitrophenol with ferric chloride-chlorine at high temperatures results in the formation of hexachlorobenzene and chloranil together with a variety of chlorinated nitroaromatic derivatives. Hexachlorobenzene has been prepared from nitrobenzene[1] 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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