showed the following peaks: 3.3, 3.45, 6.18, 6.35, 6.55, 6.7, 6.95, 7.45, 7.75, 7.9, 8.2, 8.5, 8.7, 9.35, 12.15, 13.05, 13.4, 4.35μ (potassium bromide pellet).

Anal. Calcd. for $C_{50}H_{42}O_6Cu$: C, 71.98; H, 5.07; Cu, 7.62. Found: C, 71.80; H, 5.09; Cu, 7.52.

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The Nitration of 3-Chloro-4-iodonitrobenzene

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Halonitrobenzenes are important intermediates in the synthesis of a variety of compounds such as phenylhydrazine,[2] phenylsemicarbazide,[3] benzotriazole,[4,5] phenoxazine,[6] and anthranil.[7] In a program[8,9,10] on preparation of such compounds, the nitration of 3-chloro-4-iodonitrobenzene was undertaken for detailed investigation. Although it might give a mixture of dinitroisomers, only 1-iodo-2-chloro-4,6-dinitrobenzene[11] was isolated. It reacts with hydrazine hydrate to give 2-chloro-4,6-dinitrophenylhydrazine.[12]

EXPERIMENTAL[13]

Nitration of 3-chloro-4-iodonitrobenzene. To a suspension of 3-chloro-4-iodonitrobenzene (10 g.) in conc. sulfuric acid (42 ml., d., 1.82), fuming nitric acid (14 ml., d., 1.5) was added dropwise with vigorous shaking. When all the nitric acid was added, it was heated on a water bath for an hour and poured on crushed ice. The yellow crystalline solid was filtered and recrystallized successively from acetic acid, methanol, and ethanol to give 1-iodo-2-chloro-4,6-dinitrobenzene (7 g.) in yellow needles, m.p. 118°. Mixed melting point with an authentic sample of 1-iodo-2-chloro-4,6-dinitrobenzene remained undepressed.

Anal. Calcd. for $C_6H_2N_2O_4ClI$: Cl + I, 49.4. Found: Cl + I, 49.2.

2-Chloro-4,6-dinitrophenylhydrazine. To a cooled solution of 1-iodo-2-chloro-4,6-dinitrobenzene (1 g.) in ethanol twice the equivalent quantity of hydrazine hydrate was added. 2-Chloro-4,6-dinitrophenylhydrazine was filtered after an hour, m.p. 175° (lit.[12] m.p., 175°). After two recrystallizations from ethyl acetate, yellow needles (0.5 g.) melting at 190° were obtained.

Anal. Calcd. for $C_6H_5N_4O_4Cl$: Cl, 15.2. Found: Cl, 15.1.

The *acetyl* derivative prepared by the acetic acid–acetic anhydride method crystallized in lemon yellow needles from ethanol, m.p. 189°.

Anal. Calcd. for $C_8H_7N_4O_5Cl$: Cl, 12.9. Found: Cl, 12.7.

The *benzoyl* derivative prepared by the pyridine method crystallized in colorless needles from ethanol, m.p. 208°.

Anal. Calcd. for $C_{13}H_9N_4O_5Cl$: Cl, 10.5. Found: Cl, 10.2.

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[13] All melting points are uncorrected.

Reactions of Nitrohydroxychalcones. Oxidation by Hydrogen Peroxide in Alkaline Medium

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Received September 3, 1959

In earlier publications,[3] we had communicated our observations regarding the isomerization of some nitrohydroxychalcones to flavanones and the conversion of nitrohydroxychalcones to flavones. The behavior of some of these chalcones towards alkaline hydrogen peroxide oxidation is now reported. The chalcones studied were 2′,4′-dihydroxy-3′-nitrochalcone derivatives (type I) and 2′,6′-dihydroxy-3′-nitrochalcone derivatives (type II). The type I chalcones on oxidation yielded the corresponding 3,7-dihydroxy-8-nitroflavone derivatives (type III), while the type II chalcones gave 2-benzylidene-4-hydroxy-7-nitro-3(2H)-benzofuranone derivatives (type IV). The constitutions were fully supported by color tests and analytical values.

The oxidation of type I chalcones gave products that gave a yellow coloration with concentrated sulfuric acid, and with ferric chloride a pale purplish-brown color characteristic of 3-hydroxy flavones. The enhanced halochromism of the 3-hydroxyflavones with *ortho* and *para* alkoxy substitution is shown in Table I.

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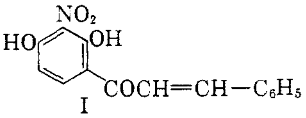
TABLE I

LIST OF CHALCONES OXIDIZED AND THE REACTION PRODUCTS

Chalcone	Product of Oxidation	M.P., °[c]	$FeCl_3$	Conc. H_2SO_4	Formula	Analysis, % Found C	Found H	Calcd. C	Calcd. H
2′,4′-diOH-3′-NO_2	3,7-diOH-8-NO_2 flavone	234[a]	Brownish yellow	Yellow	$C_{15}H_9NO_6$	59.8	2.8	60.2	3.0
2′,4′-diOH-3′-NO_2-2-OCH_3	3,7-diOH-8-NO_2-2′-OCH_3 flavone	249[a]	Brownish yellow	Brownish yellow	$C_{16}H_{11}NO_7$	58.7	3.3	58.4	3.3
2′,4′-diOH-3′-NO_2-3-OCH_3	3,7-diOH-8-NO_2-3′-OCH_3 flavone	208–209[b]	Pinkish violet	Yellow	$C_{16}H_{11}NO_7$	58.4	3.3	58.4	3.3
2′,4′-diOH-3′-NO_2-4-OCH_3	3,7-diOH-8-NO_2-4′-OCH_3 flavone	252[a]	Brownish violet	Orange	$C_{16}H_{11}NO_7$	58.5	3.3	58.4	3.3
2′,4′-diOH-3′-NO_2-3:4-(O_2CH_2)	3,7-diOH-8-NO_2-3′:4′-(O_2CH_2) flavone	259[a]	Pale brown	Deep red	$C_{16}H_9NO_8$	56.4	2.7	56.0	2.6
2′,4′-diOH-3′-NO_2-4-CH_3	3,7-diOH-8-NO_2-4′-CH_3 flavone	223[a]	Violet	Yellow	$C_{16}H_{11}NO_6$	61.0	3.5	61.3	3.5
2′,6′-diOH-3′-NO_2	No product could be isolated	—	—	—	—	—	—	—	—
2′,6′-diOH-3′-NO_2-2-OCH_3	2-(2-OCH_3 benzylidene)-4-OH-7-NO_2-3(2H)-benzofuranone	255[b]	Deep brown	Purple	$C_{16}H_{11}NO_6$	61.3	3.2	61.3	3.5
	Acetate	207[b]	No color	—	$C_{18}H_{13}NO_7$	60.8	3.5	61.0	3.4
2′,6′-diOH-3′-NO_2-3-OCH_3	2-(3-OCH_3 benzylidene)-4-OH-7-NO_2-3(2H)-benzofuranone	225–226[b]	Deep brown	Blood red	$C_{16}H_{11}NO_6$	61.2	3.3	61.3	3.5
	Acetate	173–175[b]	No color	—	$C_{18}H_{13}NO_7$	60.6	3.6	61.0	3.4
2′,6′-diOH-3′-NO_2-4-OCH_3	2-(4-OCH_3 benzylidene)-4-OH-7-NO_2-3(2H)-benzofuranone	254[a]	Deep brown	Purple	$C_{16}H_{11}NO_6$	61.0	3.6	61.3	3.5
	Acetate	191–192[b]	No color	—	$C_{18}H_{13}NO_7$	60.7	3.5	61.0	3.4
2′,6′-diOH-3′-NO_2-3:4-(O_2CH_2)	2-(3:4O_2CH_2 benzylidene)-4-OH-7-NO_2-3(2H)-benzofuranone	278[a]	Deep brown	Purple	$C_{16}H_9NO_7$	58.7	2.7	58.4	2.4
	Acetate	208–210[b]	No color	—	$C_{18}H_{11}NO_8$	58.4	2.9	58.5	3.0

[a] Crystallized from acetic acid. [b] Crystallized from alcohol-acetic acid mixture. [c] The compounds generally underwent considerable decomposition at the melting point.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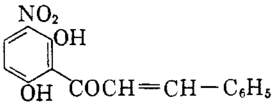
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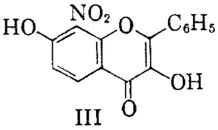
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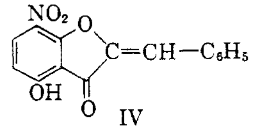
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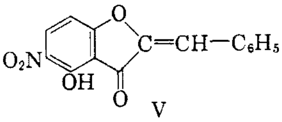
V

The products of oxidation of the type II chalcones, on the other hand, gave deep red colors with concentrated sulfuric acid, the colors being comparable to those given by the original chalcone itself. Because of the 4-hydroxy group they also gave a reddish-brown color with alcoholic ferric chloride. The alternative structure, 2-benzylidene-4-hydroxy-5-nitro-3(2H)-benzofuranone (V), was eliminated from a study of the reactivity of the hydroxyl group. Products could be acetylated even at room temperature by acetic anhydride and pyridine. Structure V contains a hindered hydroxyl group which will not undergo such ready acetylation. The reactivity of 5-hydroxy-8-nitroflavone and the nonreactivity of 5-hydroxy-6-nitroflavone towards acetylation of the hydroxyl group[4] may be cited as an analogous case.

The formation of 3-hydroxyflavones from chalcones of type I was expected as it has been shown that the nitro group does not affect the normal reaction to give 3-hydroxyflavones.[5]

The type II chalcones, however, possess a 6′-hydroxyl group which is chelated. A survey of the literature showed that oxidation of 6′-hydroxyl chalcones had not been carried out so far. On the basis of the mechanism of the abnormal reaction, postulated by Geissman,[6] the 6′-hydroxyl group should be expected to have the same influence as a 6′-methoxy or methyl group. Chalcones with a 6′-hydroxyl group should therefore be expected to give rise to 2-benzylidene-3(2H)-benzofuranones. The formation of the benzylidene benzofuranones shows that the nitro group does not alter the course of the abnormal reaction either.

EXPERIMENTAL

General procedure for oxidation of the chalcines. Sodium hydroxide solution (10 ml.; 10%) was added to the chalcone (0.5 g.). If an insoluble sodium salt formed (as in the case of type I chalcones), sufficient pyridine was added to dissolve it. Hydrogen peroxide solution (15 ml.; 20 vols.) was gradually added to this solution of the chalcone which was kept in ice. After addition, the reaction mixture was left in the refrigerator for 4 days and then for a day at room temperature (about 30°). The reaction mixture was then acidified by dilute hydrochloric acid and the precipitate obtained crystallized from a suitable solvent. Yields: 80 to 100 mg.

In the case of 2′,6′-dihydroxy-3′-nitrochalcone, the reaction mixture on acidifying gave a very small amount of yellowish white material which was very soluble in the usual solvents and could not be crystallized.

The benzylidene benzofuranones obtained from the type II chalcones were acetylated as follows: A 50-mg. sample of the compound was dissolved by heating in acetic anhydride (5 ml.) and a few drops of pyridine. The reaction mixture was then left at room temperature overnight. The solid obtained from the usual work-up was crystallized from a suitable solvent.

The physical and chemical properties of the compounds obtained and their analyses are given in Table I.

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Some Reactions of *N*-Hydroxymethyldodecanamide

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Several years ago we had occasion to prepare the then unknown *N*-hydroxymethyldodecanamide-(Ia) for use as an analytical standard. Its straightforward preparation, elemental analysis, positive Eegriwe test for combined formaldehyde and infrared spectrum left little room for doubt as to its structure. However hydroxyl determinations by the usual method,[2,3] which involve acetylation at steam bath temperature, gave such reproducibly low results that further characterization of (Ia) seemed desirable.

The acetate was prepared and found to decompose at 100°, which makes the low OH values less surprising.

A puzzling phenomenon occurred when (Ia) was heated with 1-naphthyl isocyanate. Instead of the desired urethane derivative a good yield of a dehydration product, $C_{26}H_{52}N_2O_3$, was obtained in the first trial, and nothing but intractable mixtures in later trials. There are two possible simple dehydration products involving the loss of the elements of water between two molecules of Ia;

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