Anal. Calcd. for $C_{23}H_{32}O_6$: C, 68.29; H, 7.98. Found: C, 68.06; H, 7.70.

There was a strong depression in m.p. on admixture with the corresponding 11-ketone IV, and the infrared spectra were different.

Oxidation of VI to IV.—The oxidation of 100 mg. of the hydrocortisone acetate rearrangement product VI was carried out with 50 mg. of chromium trioxide in 10 cc. of acetic acid for 10 minutes at room temperature. Isolation with chloroform and crystallization from methanol yielded the triketone IV, m.p. 196–200°, identified with the material (m.p. 199–201°) obtained from cortisone acetate by mixture m.p. determination and infrared comparison.

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Derivatives of 2-Phenylbenzimidazole. II

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As a continuation of work reported earlier[2] all twelve of the 5-nitro-2-monohalophenylbenzimidazoles have been prepared. The data for the derivatives are given in Table I. The method used in the preparation of these compounds was essentially that of Walther and v. Pulawski.[3] The *o*- and *p*-chloro derivatives were prepared also by the method of Weidenhagen[4] using the appropriate halobenzaldehyde, cupric acetate and 4-nitro-*o*-phenylenediamine. The yields were 17 and 45%, respectively.

TABLE I

4-Nitro-*o*-phenylenediamine condensed with, acid	Yield, %	M.p., °C.[a]	Formula	Nitrogen,[b] % Calcd.	Nitrogen,[b] % Found	Halide,[c] % Calcd.	Halide,[c] % Found
o-Fluorobenzoic	21	189	$C_{13}H_8FN_3O_2$	16.33	16.58	7.4	7.4
m-Fluorobenzoic	18	208			16.21		7.2
p-Fluorobenzoic	9	260			16.55		7.7
o-Chlorobenzoic	11	181	$C_{13}H_8ClN_3O_2$	15.38	15.35	13.0	12.7
m-Chlorobenzoic	13	223			15.76		12.5
p-Chlorobenzoic	10	308			15.14		12.7
o-Bromobenzoic	5	173	$C_{13}H_8BrN_3O_2$	13.20	13.55	25.2	24.6
m-Bromobenzoic	10	226			13.62		24.7
p-Bromobenzoic	7	294			13.58		24.7
o-Iodobenzoic	4	208	$C_{13}H_8IN_3O_2$	11.50	11.32	34.8	35.1
m-Iodobenzoic	11	230			11.23		34.9
p-Iodobenzoic	10	264			11.78		34.9

[a] All melting points were determined by means of a Fisher–Johns hot-stage, melting point block. [b] Micro-Dumas nitrogen analyses by C. F. Geiger, 312 Yale St., Ontario, California. [c] Halogen analyses, except fluorine, after fusion in a microperoxide bomb were by Volhard titration. Fluorine analyses after fusion in a peroxide bomb were by the method of Nichols and Olsen.[5]

TABLE II

o-Phenylenediamine condensed with, acid	Yield, %	M.p., °C.[a]	Formula	Nitrogen[a] % Calcd.	Nitrogen[a] % Found	Halide,[a] % Calcd.	Halide,[a] % Found
o-Fluorobenzoic	26	207	$C_{13}H_9FN_2$	13.21	13.14	9.0	9.3
m-Fluorobenzoic	46	258			13.57		9.6
p-Fluorobenzoic	39	257			13.94		8.5

[a] See notes to Table I.

In addition the three 2-monofluorophenylbenzimidazoles were prepared using the same method as previously reported.[1] The data for these compounds are given in Table II.

Experimental

4-Nitro-*o*-phenylenediamine (0.013 mole) and the appropriate halobenzoic acid (0.013 mole) were heated in a Pyrex tube at 210–220° in an oil-bath for one hour. The cooled mass was pulverized, triturated with a saturated solution of sodium bicarbonate, filtered and the residue extracted with hot ethanol. The product was obtained from the alcohol solution by the addition of water. Repeated crystallization from aqueous ethanol using charcoal gave analytically pure samples in the yields indicated in Table I.

The *o*-fluoro-, *o*-chloro- and *o*-bromonitro derivatives were white crystalline substances, while the *o*-iodonitro compound was light yellow. All of the other halonitro derivatives were yellow crystalline substances. The *o*-fluoro- and *o*-chloronitro compounds turned yellow on heating and melted to give a yellow liquid. The *o*-bromo isomer melted to give a yellow liquid while the *o*-iodo isomer turned white on heating but melted to give a yellow liquid. The three 2-fluorophenylbenzimidazoles were white crystalline substances. All of the derivatives were insoluble in water but soluble in acetone, ether, dioxane and alcohol.

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Isomaltose Phenylosazone and Phenylosotriazole

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The phenylosazone of a crude "isomaltose" has been described by Fischer[2] and others.[3] The

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