

acid was refluxed for forty-eight hours. Formic acid was then removed in a vacuum and the brownish glassy formamido compound (Vf) treated with 10 ml. of phosphorus oxychloride in 100 ml. of toluene in the usual manner. The isoquinoline was purified by repeated distillation under 1 mm. pressure; yield 1.2 g., m. p. 135-136°.

*Anal.* Calcd. for  $C_{12}H_{13}O_2N$ : C, 70.92; H, 6.45. Found: C, 71.21; H, 6.60.

**Hydrochloride.**—Long needles from ethanol-ether, m. p. 237-238°.

**Picrate.**—It is very poorly soluble in hot alcohol, m. p. 270°, and is identical with the picrate obtained from the acid (IVa).

*Anal.* Calcd. for  $C_{18}H_{16}O_9N_4$ : C, 50.5; H, 3.76. Found: C, 50.30; H, 4.02.

**Decarboxylation of IVa.**—Twenty-two mg. of the acid was heated under 1 mm. pressure in a Spaeth tube to 200° and the solid distillate converted into a picrate; crystals from methanol, m. p. 270°. It was identical with the picrate of the crystalline 3-methyl-6,7-dimethoxyisoquinoline, obtained from the formamido compound, as described above.

**Methyl Ester (IVb).**—Five millimoles (123 mg.) of the acid (IVa) was dissolved in 23 ml. of methanol and 3 ml. of an ethereal diazomethane solution added. The solvent was evaporated under reduced pressure, the solid residue (53 mg.) treated with 10 ml. of ether and filtered. The filtrate was shaken with a dilute sodium bicarbonate solution, dried and the ether removed. The residue was 48 mg., m. p. after recrystallization from benzene-petroleum ether, m. p. 151-153°.

*Anal.* Calcd. for  $C_{14}H_{15}O_4N$ : C, 63.70; H, 5.98. Found: C, 63.80; H, 6.03.

**Picrate.**—Yellow needles from methanol, m. p. 168-170°. Pfeiffer recorded for the picrate of the methyl ester of the acid a melting point of 216°.

*Anal.* Calcd. for  $C_{20}H_{18}O_8N_4$ :  $OCH_3$ , 18.94. Found:  $OCH_3$ , 18.67.

**1-Carboethoxy-3-methyl-6,7-dimethoxyisoquinoline (IVc).**—This ester could be isolated by decomposing with absolute ethanol (instead of water) the excess of phosphoryl chloride in the mixture obtained on ring closure of the amide (Ve); yield 2.1 g. from 9.5 g. of ethoxyalylamide (Ve). Repeated distillation from a Spaeth tube under 1 mm. pressure afforded yellowish needles, m. p. 86-87°.

*Anal.* Calcd. for  $C_{16}H_{17}O_4N$ : N, 9.1. Found: N, 9.3.

**Picrate.**—Glistening gold-yellow needles (from 96% ethanol), m. p. 176-177°.

*Anal.* Calcd. for  $C_{21}H_{20}O_{11}N_4$ : C, 50.0; H, 4.0. Found: C, 50.1, 50.1; H, 4.4, 4.45.

**Degradation of 1-Carboxy-3-methyl-6,7-dimethoxyisoquinoline (IVa) to 3,4-Dimethoxyphthalic Acid.**—Two hundred and ten milligrams of potassium permanganate dissolved in 10 ml. of water was added to a solution of 247 mg. of 1-carboxy-3-methyl-6,7-dimethoxyisoquinoline in 40 ml. of dilute sodium hydroxide in fifteen minutes. The residue of evaporation (350 mg.) was extracted as described in previous degradation procedures and 144 mg. of crude crystals was obtained. Purification through the lead salt yielded 27 mg. of metahemipinic acid, m. p. after recrystallization from 0.5 ml. of water 176°, alone and mixed with an authentic specimen. The product was converted in the usual manner into its ethylamide which after sublimation and recrystallization showed m. p. 229° under the microscope.

### Summary

The synthesis of 1-(2'-hydroxy-3',4'-dimethoxyphenyl)-3-methyl-6,7-dimethoxyisoquinoline (IIIa) is described. Its structure has been confirmed by oxidative degradation. It differs from a compound obtained from hematoxyline, incorrectly assigned the same structure in the literature. The synthesis of 3-methyl-6,7-dimethoxyisoquinoline-1-carboxylic acid (IVa) and its methyl ester (IVb) was accomplished in a straightforward manner. They were found to be different from the compounds described earlier.

The recent results proved, in accordance with previous investigations, that the intramolecular condensation of acylamides of type V lead in every case to 6,7-dialkoxy isoquinoline derivatives and in no case to 7,8-dialkoxyisoquinolines, the latter possibility being assumed by earlier investigators.

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## Formation of Bromine Addition Compounds with Some Condensed Ring Hydrocarbons

BY JOHN R. SAMPEY, JESSIE M. COX AND ANNE B. KING

The formation of intermediate addition compounds plays a prominent role in current theories on the mechanism of bromination.<sup>1</sup> Crystalline dibromide addition products of phenanthrene and anthracene have been isolated,<sup>2</sup> while more than fifty years ago Orndorff and Moyer<sup>3</sup> prepared a crystalline naphthalene tetrabromide in 3% yield. In the present study we increased the yield of the latter compound to 30% by photobromination, and we found all the above and other

addition compounds stable when shaken with sodium sulfite solution to remove unreacted bromine, but each readily gave a test for active bromine when treated with an acetone solution of sodium iodide.

### Experimental

**Preparation of Naphthalene Tetrabromide.**—12.8 grams of pure naphthalene in 100 ml. of carbon tetrachloride was brominated under anhydrous conditions at 0° with one mole of bromine in 100 ml. of the same solvent during two hours with a 2" arc at the distance of 2"; the solvent was evaporated and the product extracted with 95% alcohol and crystallized from chloroform; yield 30% of naphthalene tetrabromide, melting 111° and giving four atoms of bromine on a Rosanoff analysis. A sodium

(1) Price, *Chem. Revs.*, **29**, 37-67 (1941); Kharasch, White and Mayo, *J. Org. Chem.*, **2**, 574-576 (1938).

(2) Price, *THIS JOURNAL*, **58**, 1834-1838 (1936).

(3) Orndorff and Moyer, *Am. Chem. J.*, **19**, 262-270 (1897).

iodide analysis<sup>4</sup> gave 72.4% bromine (theory 71.4%), showing all four bromines active.

**Some Factors Influencing the Rate of Formation of Naphthalene Tetrabromide.**—When 0.01 mole of naphthalene in 20.00 ml. of carbon tetrachloride was brominated under anhydrous conditions with 0.01 mole of bromine in 10.00 ml. of the same solvent in a darkened laboratory at room temperature,  $5.1 \pm 1\%$  of the active bromine was found by the sodium iodide analysis. The presence of 0.029 g. of iodine did not change this percentage. Photobromination of 0.01 mole of the hydrocarbon in 20.00 ml. of carbon tetrachloride on a water-bath and under a 6" mercury arc at 3" distance with 10.00 ml. of molar bromine-carbon tetrachloride solution, during three hours, resulted in the formation of  $21.1 \pm 2\%$  of active bromine; cooling the reaction to 0° and using a 2" arc at 2" for seventy minutes gave  $61.0 \pm 5\%$  of active bromine.

With the aid of a Universal Spectrophotometer, Model 14, the effect of wave length on the formation of naphthalene tetrabromide has been determined. When 0.005 mole of naphthalene in 5.00 ml. carbon tetrachloride was brominated for twenty minutes at 41° with 10.00 ml. of half molar bromine solution in the same solvent under anhydrous conditions at 6000, 5250, 3700 Å. and no irradiation, the percentages of active bromine by sodium iodide analyses were respectively,  $23.8 \pm 0.2$ ,  $11.0 \pm 1$ ,  $1.3$  and  $0\%$ .

**Rates of Formation of Bromine Addition Compounds with Other Condensed Ring Hydrocarbons.**—The rates of formation of bromine addition compounds under dark-room conditions were carried out on 0.01 mole quantities of the hydrocarbons in 20.00 ml. carbon tetrachloride at 0° for a period of eighteen hours; 10.00 ml. of bromine-carbon tetrachloride solutions (molar) were added under anhydrous conditions. Sodium iodide analyses yielded the following percentages of active bromine: phenanthrene  $55.2 \pm 3\%$ , naphthalene  $11.2 \pm 0.1\%$  and diphenylmethane  $2.0 \pm 2\%$ . Fluorene, benzene and diphenyl gave no active bromine even though the solu-

tions were kept cold to prevent decomposition of any addition compounds during the treatment with sulfite and evaporation of the carbon tetrachloride. The addition of 0.029 g. iodine to the above reactions did not change by more than 2% the rates of bromine addition.

Since anthracene is insoluble in carbon tetrachloride 0.005 mole of this hydrocarbon was dissolved in 50.00 ml. of carbon disulfide, and the dark room brominations made with 10.00 ml. of half-molar bromine in the same solvent. Naphthalene solutions of the same strength were used for comparison. The results showed the presence of  $13.0 \pm 1.2\%$  bromine with anthracene but none with naphthalene.

The photobrominations were carried out in carbon tetrachloride under anhydrous conditions at 0° with a 2" arc at 2" for sixty minutes; sodium iodide analyses indicated the following active bromine present: phenanthrene  $84.1 \pm 2\%$ , naphthalene  $55.3\%$ , diphenyl 1% and benzene 1%. When 0.005 mole of anthracene and naphthalene were photobrominated in 50.00 ml. of carbon disulfide under similar conditions, they gave  $74.0 \pm 2\%$  and  $69.0\%$  active bromine, respectively. These results demonstrate conclusively that larger amounts of active bromine addition products of the hydrocarbons are formed in photobromination than in dark room bromination.

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### Summary

1. Measurements have been made on the rates of formation of active bromine addition compounds under photo and dark room brominations of some condensed ring hydrocarbons.

2. Naphthalene tetrabromide has been prepared in 30% yield by photobromination.

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(4) Sampey, Blitch and King, *THIS JOURNAL*, **70**, 2606 (1948).

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## The Structure of Diphenylthiocarbazono (Dithizone)<sup>1</sup>

By ALSOPH H. CORWIN AND GEORGE R. JACKSON<sup>2,3</sup>

### Introduction

The compound diphenylthiocarbazono, known as "dithizone," is well known in analytical chemistry because of its colorimetric reactions with traces of metals. A search of the literature will show, however, that no direct attempt has been made to prove the structure arbitrarily assigned to it by Emil Fischer.<sup>4a,b</sup>

Because of increasing interest in dithizone derivatives, it was deemed advisable to attempt a structural determination of diphenylthiocarbazono, from which would follow the structure of its oxidation product, dithizone.

Diphenylthiocarbazono is prepared by the reac-

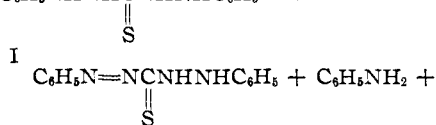
(1) From the doctoral dissertation of G. R. Jackson, The Johns Hopkins University.

(2) Chemical Foundation Fellow, 1942-1943; Standard Oil Company of Indiana Fellow, 1946-1947.

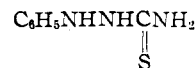
(3) Present address: Chemistry Department, Western Reserve University, Cleveland, Ohio.

(4) (a) E. Fischer, *Ann.*, **190**, 114 (1878); (b) **212**, 320 (1882).

tion of phenylhydrazine with carbon disulfide. In ether or benzene, the phenylhydrazine salt of phenyldithiocarbazono acid precipitates.<sup>5,6</sup> Heating this salt to 90-100° drives off hydrogen sulfide and leaves behind diphenylthiocarbazono. Treating this with alcoholic potassium hydroxide produces dithizone, for which the following equation has been proposed<sup>4a</sup>



II



III

(5) Grummitt and Stickler, *Ind. Eng. Chem., Anal. Ed.*, **14**, 953 (1942).

(6) Billman and Cleland, *THIS JOURNAL*, **65**, 1300 (1943).