third and fifth hours. After standing overnight the reaction mixture was heated to boiling and filtered. The filter cake was dissolved in water, made slightly alkaline with dilute sodium hydroxide and acidified with acetic acid to precipitate 3.3 g. (36%) unreacted *p*-dimethylaminobenzoic acid. The xylene filtrate was concentrated and cooled to yield 4.1 g. of crystals, m. p. 147–160°. This material was taken up in chloroform, extracted with sodium bicarbonate solution and dried. Stripping of the solvent followed by recrystallization of the residue from benzene gave 2.6 g. (30%) of *p*-dimethylaminobenzoic anhydride, m. p. 157–159° (cor.).

Anal. Calcd. for $C_{18}H_{20}O_3N_2$: C, 69.3; H, 6.4; N, 9.0. Found: C, 69.6; H, 6.4; N, 8.8.

Method B.—To a solution of 16.0 g. of *p*-dimethylaminobenzoic acid and 60 ml. of triethylamine in 150 ml. of chloroform there was added dropwise 11.7 g. (7.0 ml.) of phosphorus oxychloride. After the initial reaction subsided the solution was heated to reflux for ten minutes and allowed to stand one hour at room temperature. The chloroform solution was extracted with ice-cold dilute sodium hydroxide solution and filtered through anhydrous sodium sulfate. Upon concentration and cooling the chloroform solution deposited 9.6 g. of crystals, m. p. 148–157°. Two recrystallizations of this material from benzene gave 7.5 g. (50%) of *p*-dimethylaminobenzoic anhydride, m. p. 157–159° (cor.), identical with that obtained by method A as evidenced by mixed melting point determination.

Acidification of the alkali extract with acetic acid did not yield any recovery of *p*-dimethylaminobenzoic acid.

Methyl *p*-Dimethylaminobenzoate.—In a sealed tube there was heated for three hours at 100° 0.5 g. of *p*-dimethylaminobenzoic anhydride and 25 ml. of methanol. The reaction mixture was poured into cold dilute sodium hydroxide to dissolve the *p*-dimethylaminobenzoic acid and to precipitate the ester which was collected by filtration. There was thus obtained 0.23 g. (80%) of methyl *p*-dimethylaminobenzoate, m. p. 99–102° (lit. 102°).[3] Acidification of the alkali extract gave 0.18 g. of *p*-dimethylaminobenzoic acid.

***p*-Dimethylaminobenzamide.**—A solution of 0.53 g. of *p*-dimethylaminobenzoic anhydride in 25 ml. of chloroform was saturated with ammonia and then heated in a sealed tube for two hours at 70° and two additional hours at 100°. The chloroform was stripped and the residue recrystallized from water to give 0.21 g. (76%) amide, m. p. 203–206° (lit. 206°).[4]

NATIONAL CANCER INSTITUTE
NATIONAL INSTITUTE OF HEALTH
BETHESDA 14, MARYLAND RECEIVED FEBRUARY 4, 1948

Preparation of 2-Phenylbenzoxazole

BY LUCAS C. GALATIS

The preparation of 2-substituted benzoxazoles by heating appropriately *o*-substituted anilines with an organic acid is a well-known reaction. In the case of benzoxazole, apparently the reaction has been used only for the preparation of the parent compound from *o*-aminophenol and formic acid.[1] It has now been found that 2-phenylbenzoxazole (I) may be prepared by the general method by heating *o*-aminophenol with benzoic acid. Purification of crude I presents difficulty especially because of the persistence of a highly fluorescent by-product which has been commonly encountered when I was prepared by heating aminophenol with various benzoyl derivatives.[2] By choosing ligroin as a solvent, I could be extracted from the reaction product free from other by-products, except traces of the above mentioned fluorescent substance, which were in their turn eliminated by taking advantage of a difference in basicity between I and the latter. The fluorescent matter accumulated in the residue of the ligroin extraction was then easily separated and identified as triphen-dioxazine, an oxidation product of *o*-aminophenol.[3]

Experimental

In a large test-tube an intimate mixture of 10.9 g. of *o*-aminophenol and 15 g. of benzoic acid is melted in an oil-bath at 160°. The tube is then fitted with a stopper carrying a gas inlet tube and an exit tube bent downward. The temperature is raised to 195° while passing carbon dioxide through the tube, at which temperature rapid evolution of water occurs. After two hours the temperature is raised to 200–205° and held at that point for ten hours. Every two or three hours the sublimate is melted down from the walls of the tube. After cooling to 130° the melt is poured with stirring into cold water. The insoluble material is ground in a mortar with 2 *N* sodium hydroxide. The dark colored residue is warmed with 300 ml. of ligroin (b. p. 80–120°) until extraction of 2-phenylbenzoxazole from contaminating black material is complete. After filtering, the solution which is strongly fluorescent, although it does not contain but traces of the fluorescent matter, is shaken with two drops of concd. hydrochloric acid which removes the fluorescent impurity as a violet-blue solution. The ligroin solution is filtered through a dry gravity filter and shaken with 80 ml. of concd. hydrochloric acid which removes the benzoxazole. The acid extract is diluted with stirring with four or five volumes of cold water yielding 14 g. (72%) of 2-phenylbenzoxazole as a white or slightly green powder melting at 101°. A perfectly white product may be obtained by distillation of the material after the sodium hydroxide treatment with superheated steam (180°) followed by the treatment with hydrochloric acid in ligroin.

In order to isolate the main quantity of the fluorescent substance, the black residue from the ligroin extraction is repeatedly extracted with boiling alcohol for removal of a red contaminant, and then with boiling xylene. On cooling, the intensively fluorescent xylene solution deposits small red brown needles with a metallic cast. This shows all the properties of triphen-dioxazine including the characteristic production of green vapor on heating at 300°.

Acknowledgement.—The author is indebted to Mr. Nicholas G. Dovletis for his assistance during this work.

(1) Ladenburg, *Ber.*, **10**, 1124 (1877).
(2) Skraup, *Ann.*, **419**, 76 and 82 (1919).
(3) Seidel, *Ber.*, **23**, 182 (1890).

CHEMICAL LABORATORY
OF THE ADMIRALTY
ATHENS, GREECE RECEIVED SEPTEMBER 3, 1947

Synthesis of 2,3-Diketopiperazine

BY C. E. GOULDING, JR.,[1] AND C. B. POLLARD

Two prior methods for the preparation of 2,3-diketopiperazine by the reaction between diethyl oxalate and 1,2-ethanediamine[2,3] have been reinvestigated in this Laboratory and found to afford yields of only about 1 and 10%, respectively. A new method involving the reaction of oxamide and 1,2-ethanediamine in 1,4-dioxane was therefore

(1) Present address: Caracas, Venezuela.
(2) Hofmann, *Ber.*, **5**, 247 (1872).
(3) Van Alphen, *Rec. trav. chim.*, **54**, 937 (1935).