Each tube contained 7 g. of pure sulfur mixed separately with 0.3 g. and 1.0 g. of CoF_3; 0.3 g. and 1.0 g. of HgF; 0.5 g. and 1.0 g. of AgF. At the end of the experiments, all tubes were under fairly high pressure indicating formation of the gases had taken place. Only after prolonged heating (about forty-eight hours at 180–440°) was a slight reduction of the viscosity noted.

These experiments lead to the opinion that the observed failure of the sulfur fluorides to greatly affect the viscosity of sulfur is just one more instance of the abnormal behavior of fluorine and its compounds when viewed in comparison with the other halogens.

TEXAS GULF SULFUR CO., INC.
NEW YORK 17, N. Y.
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The Melting Point of Mustard Gas

BY W. A. FELSING, C. A. HUNTING AND S. D. FELL

Recently du Vigneaud and Stevens[1] reported a study of the preparation and purification of mustard gas (*bis*-(β-chloroethyl) sulfide) and its action on yeast. They purified the mustard by three recrystallizations from absolute ethanol and once from petroleum ether; the product had a melting point of 14.5°. The authors also cite references to other reliable melting point determinations found in relatively recent literature (*i. e.*, 14.4° and 14.5°).

In Chemical Laboratory Report No. 369, Edgewood Arsenal, Edgewood, Md., dated November 29, 1918, the authors of this note reported the purification and the melting point of mustard gas. Crude Levinstein mustard gas, melting at 8–9°, was distilled at 10 mm. pressure, yielding a distillate melting at 13.6°. This material was thrice distilled at pressures below 10 mm. and subjected to partial freezing. It was collected on a Buchner filter and the adhering liquid was removed rapidly by suction. The collected crystals were melted and again the resulting liquid was partially re-frozen and the crystals collected as before. In all, the crystals were partially frozen, drained and remelted seven times. The final product weighed about 750 g. (original volume of distilled mustard gas was about 1 gallon).

The melting point of the purified mustard gas was determined by the usual procedure of taking temperature readings every thirty seconds until every trace of the crystals had disappeared. The melting point was determined graphically from a time–temperature plot. The melting point apparatus and the thermometer were kindly loaned by the Physical Chemistry Division of Johns Hopkins University. The short-range thermometer, whose ice-point was carefully checked and which was calibrated by the Physikalische Technische Reichsanstalt (P.R.T. No. 26260) was calibrated in 0.1° and temperatures could be estimated to 0.02° by the aid of a magnifier. Two series of determinations yielded a melting point of 14.45° and one of 14.44°.

Both of these values agree markedly well with the values given and cited by du Vigneaud and Stevens.

This note was suggested as a historical record by Chemical Corps Technical Command, Army Chemical Center, Md.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TEXAS
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[1] du Vigneaud and Stevens, THIS JOURNAL, **69**, 1808 (1947).

The Preparation of *p*-Dimethylaminobenzoic Anhydride

BY WILLIAM S. FONES

In connection with other work under way in this Laboratory it was necessary to prepare *p*-dimethylaminobenzoic anhydride. By heating *p*-dimethylaminobenzoic acid in acetic anhydride V. Meyer and Askenasy[1] isolated a substance (m. p. 109°) that analyzed correctly for an addition complex consisting of one molecule of *p*-dimethylaminobenzoic anhydride and one of acetic anhydride. This work was repeated by Van Der Haar,[2] who reported the complex (m. p. 109°) lost acetic anhydride when heated above its melting point to yield a substance sintering at less than 200° and melting at 218°. He assumed the latter material to be the free anhydride.

This assumption is shown to be in error by the present work. The anhydride was prepared by the action of phosphorus pentoxide on *p*-dimethylaminobenzoic acid in boiling xylene (method A) or by adding phosphorus oxychloride to a solution of *p*-dimethylaminobenzoic acid and triethylamine in chloroform (method B). The product from either reaction upon recrystallization from benzene had a m. p. of 157–159° (cor.); a mixed melting point determination showed no depression. By method A the anhydride was obtained in a yield of 30% based on acid used with a 36% recovery of unreacted acid whereas a 50% yield was obtained by method B but no starting material was recovered.

The pure compound gave the expected analysis and was further characterized by conversion to the known methyl *p*-dimethylaminobenzoate,[3] and *p*-dimethylaminobenzamide[4] through the action of methanol and ammonia, respectively.

Experimental

***p*-Dimethylaminobenzoic Anhydride (Method A)**.—To a stirred suspension of 9.1 g. of *p*-dimethylaminobenzoic acid in 450 ml. of refluxing *m*-xylene there was added 8 g. of phosphoric anhydride. Stirring and refluxing were continued for seven hours with an additional 8-g. portion of phosphoric anhydride being added at the end of the first,

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[1] V. Meyer and P. Askenasy, *Ber.*, **26**, 1365 (1893).

[2] A. W. Van Der Haar, *Rec. trav. chim.*, **47**, 324 (1928).

[3] John Johnston, *Proc. Roy. Soc.* (*London*), **A78**, 82 (1906).

[4] German Patent 77,329 (1892); *Frdl.*, **4**, 173 (1899).

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]

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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.

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[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
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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

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[1] Present address: Caracas, Venezuela.

[2] Hofmann, *Ber.*, **5**, 247 (1872).

[3] Van Alphen, *Rec. trav. chim.*, **54**, 937 (1935).