

from fifteen to forty-five minutes. The ester was then distilled directly from the flask through a fractionating column.

The solid residue, after organic matter had been removed, was shown by analysis to contain one mole of ammonia. When treated with concentrated sulfuric acid and heated, the residue gave a large amount of boron fluoride gas. It is possible to recover practically all of the boron fluoride by the treatment with sulfuric acid.

### Summary

It has been shown that the addition compound formed between acetamide and boron fluoride reacts rapidly with alcohols and with phenol to form acetates and monoammino boron fluoride.

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## Notes

### Note on the Oxidation Products of Benzophenone Oxime<sup>1</sup>

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The work presented in this paper was begun a number of years ago, but unfortunately it had to be interrupted before it was completed. Recently, v. Auwers and Wunderling<sup>2</sup> have published a paper under the above title, and it therefore seems advisable for us to present a summary of our own work in this field, even though it is still incomplete.

**Oxidation with Ferricyanide.**<sup>3</sup>—Twenty grams of benzophenone oxime was dissolved in 200 cc. of ethyl alcohol by adding a small amount of 1:1 aqueous sodium hydroxide. This solution was then added to one liter of ice cold alkaline ferricyanide (40 g. of ferricyanide, 40 g. total of sodium hydroxide). The temperature was kept at 0° and the mixture stirred for two hours. The floating blue mass was removed and boiled with 500 cc. of ethyl alcohol, filtered from the fine white precipitate, and the alcohol evaporated. The residue was stirred repeatedly with separate portions of petroleum ether, and was again boiled with ethyl alcohol and filtered. Several such alternations of solvents gave three products: (I) a compound soluble in alcohol and in petroleum ether; when "seeded" with benzophenone it gave crystals melting at 47°. When mixed with benzophenone the melting point was unchanged; yield, 11 g. (II) a compound soluble in alcohol and insoluble in petroleum ether. Recrystallized from hot alcohol, this gave 2 g. of yellow needles, m. p. 156–157°.

*Anal.* Calcd. for  $C_{26}H_{20}ON_2$ : C, 82.98; H, 5.32; N, 7.45; mol. wt., 348. Found: C, 82.98; H, 6.1; N, 7.51; mol. wt. by freezing point in benzene, 357.

(1) Part of the work presented in this paper is taken from a thesis by Walter S. Dyer presented to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Master of Science, September, 1925.—L. I. SMITH.

(2) v. Auwers and Wunderling, *Ber.*, **66**, 538 (1933).

(3) Holleman, *Rec. trav. chim.*, **13**, 429 (1894).

(III) a compound insoluble in alcohol. This was boiled with fresh portions of alcohol until the constant m. p.  $193^{\circ}$  with decomposition was reached; yield, 4 g., white powder.

*Anal.* Calcd. for  $(C_{13}H_{10}NO)_4$ : C, 79.53; H, 5.14; N, 7.1; mol. wt., 728. Found: C, 79.63; H, 5.08; N, 7.06; mol. wt. by freezing point in benzophenone, 722.

That the product (II) retains the benzophenone nucleus seems certain since (1) with boiling 3 *N* hydrochloric acid an 87% yield of benzophenone results; (2) with boiling concentrated hydrochloric acid almost 100% conversion to benzophenone occurs; (3) attempts at reduction yield benzophenone.

That the product (III) retains the benzophenone nucleus seems certain since, (1) upon reduction, benzophenone and benzophenone oxime are produced; (2) with phosphorus pentachloride in dry ether benzophenone and benzanilide are formed; (3) with glacial acetic acid benzophenone is obtained; (4) with boiling acetone the compound slowly decomposes to benzophenone and benzophenone oxime; (5) after standing for a year small amounts of benzophenone can be extracted with alcohol.

**Oxidation with Iodine in a Dry Medium.** *Preparation.*—The sodium salt of the oxime was prepared by adding a solution of 0.5 g. of sodium in 10 cc. of absolute alcohol to 4.3 g. of benzophenone oxime dissolved in 25 cc. of dry ether. The mixture was placed in a vacuum until only a sirupy mass remained. 100 cc. of dry ether was added and the mass stirred for several minutes until a white precipitate appeared. The container and contents were placed in a desiccator for several hours and then filtered rapidly. The white solid was washed with dry ether and dried in a vacuum.

(1) Iodine and the dry sodium salt of benzophenone oxime were placed in separate containers in a vacuum. The iodine vaporized and the sodium compound became dark brown and wax-like. This brown waxy material was moistened with water and a bright greenish-blue color appeared which soon changed to yellow. The products were benzophenone, a red tar-like mass, and a 65% yield of sodium iodide.

(2) 4.5 grams of the dry sodium salt was placed in 100 cc. of dry benzene. To this was slowly added, with shaking, 2.6 g. of iodine in 100 cc. of dry benzene. Rapid decolorization took place until about one-half the iodine had been added. The mixture was put on the shaker for twelve hours and then filtered. The filtrate was distilled under reduced pressure. The residue from the distillation yielded 2 g. of benzophenone and 1.25 g. of a tarry mass which contained iodine, as well as sodium iodide, sodium salt of the oxime, and oxime. Similar results were obtained by boiling under reflux for one-half hour instead of shaking, or by using pyridine as the solvent.

**Oxidation with Silver Oxide.** (1) *In Benzene.*—Five grams of benzophenone oxime was dissolved in 100 cc. of dry benzene. To this was added 5.8 g. of freshly precipitated and dried silver oxide, together with a little anhydrous sodium sulfate, and the mixture was boiled under reflux for two hours. By this time a silver mirror had formed on the flask, and the solution was deep yellow. The mixture was filtered and the benzene distilled. The residue from the distillation was stirred with petroleum ether until it solidified. The solution contained 1.3 g. of benzophenone. The residue was boiled with alcohol and gave 0.1 g. of compound (III). The alcohol solution contained a mixture which could not be separated.

(2) *In Ether.*—Twenty-five grams of benzophenone oxime was dissolved in 200 cc. of dry ether and to this was added 42 g. of silver oxide. The mixture was boiled under reflux for eighteen hours, filtered, and the ether evaporated. The residue from the evaporation when subjected to alternate alcohol and petroleum ether treatments gave a yield of 17 g. of benzophenone and 3 g. of compound (I).

**Summary.**—Benzophenone oxime has been oxidized in aqueous and non-aqueous media. The definite products are benzophenone, a yellow

compound  $C_{26}H_{20}ON_2$ , melting at  $156-7^\circ$ , and a white compound  $(C_{13}H_{10}NO)_4$ , melting at  $193^\circ$  with decomposition.

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## An Improved Method of Preparing Diethylgermanium Derivatives

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In a previous paper<sup>1</sup> a method of preparing diethylgermanium derivatives, involving bromination of triethylgermanium fluoride, was described. A much simpler and more economical method of preparing these compounds is as follows.

Ethylgermanium triiodide and an excess of 40-60 lead-bismuth alloy are heated together, in the absence of air, to  $150^\circ$  for one or two days, shaking occasionally to subdivide the molten metal into droplets. When reaction appears complete the product is extracted with dry ether or ligroin, preferably in the absence of air. After distilling off the solvent the viscous yellow residue<sup>2</sup> is dissolved in ethyl iodide and the solution, in an air-free sealed tube, heated at  $125^\circ$  for two or three days. The excess ethyl iodide is now distilled off and the impure diethylgermanium diiodide is purified by fractional distillation *in vacuo*. If the oxide is desired, the impure diiodide may be hydrolyzed with aqueous sodium hydroxide, boiled for a few minutes, cooled, and the diethylgermanium oxide filtered off.

The characteristics of these new substances are as follows: diethylgermanium dichloride  $((C_2H_5)_2GeCl_2)$ ; colorless liquid with pungent odor; b. p.  $175^\circ$  (758 mm.); m. p.  $-39$  to  $-37^\circ$ ; Ge, calcd.: 36.01%; found: 36.03, 35.76%; Cl, calcd.: 35.18%; found: 35.26, 35.17%. Diethylgermanium diiodide  $((C_2H_5)_2GeI_2)$ ; colorless liquid; b. p.  $252^\circ$  (759 mm.); m. p.  $-2$  to  $-1^\circ$ ; Ge, calcd.: 18.88%; found: 18.90, 18.85%; I, calcd.: 66.02%; found: 66.45, 66.27%.

When the former method of preparation is used considerable difficulty is encountered in separating the diethylgermanium derivatives from the triethylgermanium compounds usually present, whereas in the present method the probable impurities are monoethylgermanium derivatives which, being water-soluble, are easily removed. Where a supply of germanous sulfide is available the simplicity of the present method is particularly marked in that only four steps are involved all of which may be carried out in good yields while some eight steps were involved in the former method.

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(1) Flood, *This Journal*, **54**, 1667 (1932).

(2) Analyses of this residue indicated it to be impure  $(C_2H_5GeI)_2$ . Calcd.: I, 55.6%. Found: I, 58.5%. This interesting compound will be studied later.