

A Modified Preparation of Triacetyl Borate

One of the recommended, standard procedures for obtaining anhydrous glacial acetic acid is to distill the acid from triacetyl borate.^{1,2} The procedure for making the reagent is given in a short passage of an undergraduate organic laboratory text,² based on the original German article.³ In the August 20, 1973 issue of *Chemical and Engineering News*, there was a letter from L. M. Lerner describing an explosion which occurred when following this procedure and warning others of the potential hazards of the prep.⁴

We were aware of this letter, so when we needed to prepare this reagent, we used the standard² procedure with adequate safety precautions. The temperature of the reaction was slowly brought up to 45° over a 2-hr period, and when no visible change had occurred, the temperature was raised slightly. At some point soon thereafter, a very vigorous reaction occurred, expelling the contents of the flask out the condenser and depositing them on large areas of the hood.

Since there is no possibility of an oxidation-reduction in this reaction, it seemed likely that the reaction was simply autocatalytic, in the sense that by-product acetic acid would both catalyze the reaction of boric acid with acetic anhydride, and also increase the solubility of boric acid in the reaction medium. With increasing conversion, and hence increasing temperature, these factors would lead to a dramatic autocatalytic rate increase in the exothermic acylation process. There are thus two obvious ways of moderating the reaction: add acetic acid at the beginning, and dilute the reaction mixture with solvent. By so doing, it is our opinion that the resulting procedure is both safer and more convenient than the original.

We have had frequent use for triacetyl borate and have used the following procedure several times, although we have not attempted to optimize conditions. In no case has a mishap occurred, though adequate precautions are nonetheless taken. Besides affording the reagent in reproducible yield, the product contains less residual acetic acid and is easily dried. The experimental details follow.

To a 1000-ml three-neck flask fitted with condenser, thermometer and mechanical stirrer were added 50 g boric acid, 2.5 ml acetic acid, and 230 ml benzene. The mixture was stirred for 2 hr (an arbitrary period), after which 250 g acetic anhydride was added. Over the next hour, the temperature was raised to 45°C and during the following two hours to 60°C. The mixture was left stirring overnight at this temperature.

The solution turned from cloudy white to clear during this time. The flask was then allowed to cool to room temperature, whereupon the product crystallized. The white solid was collected by suction filtration through a Buchner funnel, the operation being conducted under an inverted funnel fitted to a dry nitrogen source. After rinsing with benzene, the product was dried in a vacuum desiccator until no more solvent or acetic acid condensed in the receiving trap; yield, 73.6 g (49%); duplicate run, 76.4 g (51%). No attempt was made to isolate residual product from the mother liquor, in which the triacetate is appreciably soluble.

¹ Popov, A. I., "The Chemistry of Nonaqueous Solvents," Vol. 3, (Editor: Lagowski, J. J.,) Academic Press, New York, 1970, p. 243.

² Fieser, L. F., "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Company, Boston, 1955, p. 281.

³ Pictet, A., and Geleznoff, A., *Chem. Ber.*, **36**, 2219 (1903).

⁴ Lerner, L. M., *Chem. Eng. News*, **51** (34), 42 (1973).

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