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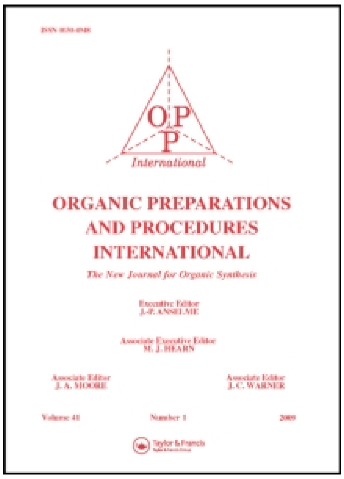

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TRIMETHYLBOROXINE

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TRIMETHYLBOROXINE

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The boronic anhydrides were first systematically prepared and studied by Snyder, Kuck and Johnson in 1938.[1] The boronic esters were prepared from alkyl or aryl borates and a Grignard reagent, and hydrolyzed to produce the boronic acid. Subsequent dehydration and cyclization produced the boronic anhydrides or trisubstituted boroxines. This method was extended to trimethyl boroxine by Burg[2] and further developed by McCusker.[3] Low yields of impure material were reported in the former method while in the latter, yields up to 33 per cent were obtained. Goubeau and Keller[4] have described a method involving the reaction between boric oxide and trimethylborane at 300° in a sealed bomb which produces $B_3O_3(CH_3)_3$ in 96%. However, McCusker[5] described an improved synthesis involving the reaction of the trialkylborane with B_2O_3 produced from the decomposition of trimethoxyboroxine. Both these routes require the use of trimethylborane, which is difficult to handle and is not readily available.[6] Moreover, the yields reported by Goubeau and Keller are difficult to reproduce. More recently, Rathke and Brown[7] have reported the preparation of trimethylboroxine (in tetrahydrofuran) by the reaction of carbon monoxide with a solution of diborane in THF in the presence of small amounts of sodium borohydride.

We required significant amounts of $B_3O_3(CH_3)_3$ for subsequent studies

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and were not satisfied with the methods available, nor were we able to obtain it commercially. We report a method which is, although not altogether new, certainly the best combination of past experience which produces $B_3O_3(CH_3)_3$ in quantitative yield and can be conveniently carried out on a relatively large scale. The method involves the preparation of a tetrahydrofuran-trimethylboroxine solution using essentially the technique of Brown, followed by the precipitation of the methylboronic acid and its subsequent dehydration and cyclization.

$$3H_3B.THF \quad + \quad 3CO \longrightarrow B_3O_3(CH_3)_3 \quad + \quad THF$$

$$B_3O_3(CH_3)_3 \quad + \quad 3H_2O \longrightarrow 3CH_3B(OH)_2$$

$$3CH_3B(OH)_2 \quad \xrightarrow[200^{\circ}]{CaSO_4} \quad B_3O_3(CH_3)_3 \quad + \quad 3H_2O$$

The advantage of this procedure over those reported in the past for the preparation of trimethylboroxine is that it results in a pure product. The hydrolysis of the trimethylboroxine to give methylboronic acid which is easily purified by sublimation is the key to the success of this method. When the methylboronic acid is dehydrated and cyclized the water remains behind in the drying tube and only pure product is obtained. We, therefore, report a method of purifying trimethylboroxine rather than a method for its preparation.

PROCEDURE

A two necked, round bottomed 250 ml, flask containing a stirring bar and a catalytic amount of $NaBH_4$ is attached to a vacuum line and filled with an atmosphere of dry carbon monoxide (Matheson Research Grade). The vacuum line, which is shown in the figure, has a mercury manometer A, a dead volume B and stopcocks for gas transfer. Two access points C and D are available; C is connected to the two necked flask and D to a lecture bottle of CO. The second neck of the flask is equipped with a serum cap

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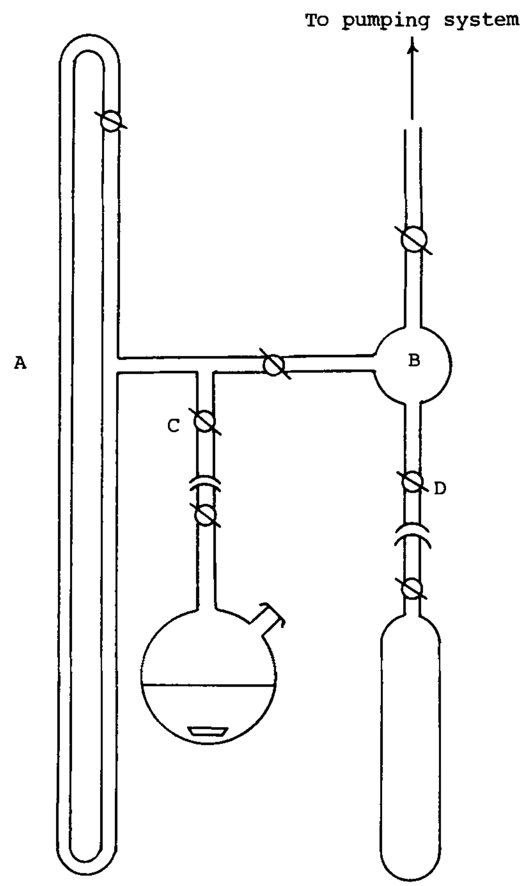

Apparatus for the preparation of
Trimethylboroxine

whereby 100 ml of 1M BH_3.THF (Alpha Inorganics) is introduced using a syringe. Absorption of CO by the solution is initiated by stirring, the rate of absorption being dependent on stirrer speed. The rate of absorption is monitored by observing the decrease in CO pressure.[8] Appropriate pressure - volume calibrations for the vacuum line are necessary. The CO in the system is periodically replenished from the lecture bottle. After the theoretical amount of CO, or very close to it, has been absorbed an excess of water is syringed into the flask, slowly at first because reaction with any unreacted borane liberates H_2. The solution is then cooled to -196° and the flask evacuated. The pressure may have to be reduced before cooling if significant amounts of H_2 are evolved. The solution is then warmed to room temperature and the THF distilled off leaving a white residue of methylboronic acid $CH_3B(OH)_2$ and minor amounts of H_3BO_3. The $CH_3B(OH)_2$ is sublimed into a clean flask and the residue in the original flask is discarded. A calcium sulfate drying tube with a flask attached to it is connected to the vacuum line and the $CH_3B(OH)_2$ is sublimed through the tube. Usually, repeated sublimations through the drying agent are required to dehydrate all the acid. After an hour or so, the drying agent must be regenerated. This requires heating the $CaSO_4$ with a heat gun and collecting the vapors in the flask containing the $CH_3B(OH)_2$. After vapors are no longer evolved under gentle heating, the flask containing $B_3O_3(CH_3)_3$ is closed off and the $CaSO_4$ is heated to 200° "in vacuo" to drive off the water. Quantitative yields of $B_3O_3(CH_3)_3$ can be obtained if sufficient time is allowed for absorption of all the CO.

Although the usual methods of identification are useful, eg bp 78°, vp 8mm at 23°, instrumental techniques are applicable here. The infrared spectrum in the gas phase[9] gives bands below 1400 cm^{-1} at 1384, 1226, 919, 892, 783, 570 and 459 cm^{-1}. The nmr spectrum taken neat showed a single

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methyl proton resonance with a chemical shift of 0.395 with respect to TMS. The mass spectrum is very characteristic and its details can be found in the literature.[10] However, mass spectral evidence for boroxines is inconclusive, as the boronic acids and a whole series of cyclic boronates give the boronic acid anhydride when introduced into the ion source of a mass spectrometer.

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