

not isolated, but rather it was treated directly with an aqueous solution of sodium borohydride in weakly acidic medium (pH 3-4) and then with sodium hydroxide to effect intramolecular ring closure. Steam distillation of the alkaline mixture followed by ether extraction of the distillate and then concentration of this solution yielded I, b.p. 107-108° (40 mm.),  $n_D^{30} = 1.4645$ . *Anal.* Calcd. for  $C_{11}H_{19}N$ : C, 80.00; H, 11.51, N, 8.48. Found: C, 79.94; H, 11.39; N, 8.39. *Picrate*, m.p. 166-167°. *Methiodide*, m.p. 148°.

The 1-azabicyclo[3.2.0]heptane derivative was identified by: (a) examination of its infrared spectrum which exhibited no N—H and C=N bands, (b) the absence of active hydrogen as determined by the Zerewitinoff method, (c) the isolation and identification of acetone upon oxidative cleavage with potassium permanganate, and (d) characterization of its picrate and methyl iodide salts. The free base exhibited unusual thermal stability by distilling cleanly at atmospheric pressure (b.p., 198°) and showed no signs of decomposition after exposure to direct light for several weeks. The preparation of the parent ring system by the described method has so far proved unsuccessful and an attempt to obtain this compound by an alternative method is currently in progress.

Pyrrolizidines, octahydropyrrocolines, and other polycyclic systems have also been prepared by this method, the details of which will be reported in a subsequent communication.

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## Preparation and Storage of Diphenylborinic Acid and Its Anhydride<sup>1</sup>

Sir:

We have noted with interest Neu's continuing advocacy<sup>2</sup> of the use of sodium tetraphenylborate,  $NaB(C_6H_5)_4$ , as a source material for preparing diphenylborinic acid and its anhydride. Of particular interest are the high yields claimed for his method. However, contacts with colleagues active in this field lead us to the impression that the  $NaB(C_6H_5)_4$

route leaves much to be desired in terms of economy and reliability.

For several years, our procedure in obtaining the acid and its anhydride conveniently and in a pure state has embodied the approach suggested by Snyder *et al.*<sup>3</sup> of preparing first an amino alcohol ester of the acid. Specifically, the ethanolamine ester of diphenylborinic acid is prepared in a high state of purity and in acceptable yield by the procedure of Letsinger and Remes,<sup>4</sup> a method readily adapted to production on a relatively large scale as a routine procedure. The pure product has been stored on the shelf up to three years without deterioration. It thus serves admirably as a stable form in which the acid may be kept.

When the acid is required, the necessary amount of the aminol ester is dissolved in a minimum amount of methanol, hydrolyzed by addition of 1M hydrochloric acid with agitation, and the gummy, water-insoluble diphenylborinic acid (solubility about 0.45 g. per l.) is extracted with ether. The ethereal solution may be dried over sodium sulfate or magnesium sulfate, but it should not be allowed to stand, since the acid begins to undergo degradation in aqueous or ethereal solutions within about one hour. (Such degradation may be inhibited by the addition of a small amount of strong mineral acid, however.) The ethereal solvent may be removed under aspirator vacuum and replaced by a different solvent when that is desired for synthetic purposes.

To obtain the pure diphenylborinic anhydride, the hydrolyzed acid is extracted with petroleum ether (b.p. 30-60°) the extract shaken twice with 1M hydrochloric acid and then repeatedly with distilled water until neutral, dried over magnesium sulfate, decolorized with Darco or Norit, and evaporated under high vacuum in absence of any heat. Fresh petroleum ether is added to the resultant viscous liquid, and the vacuum evaporation is continued until the petroleum ether-insoluble anhydride precipitates. The solid is washed on the filter with anhydrous petroleum ether, dried, and stored under vacuum. It melts at 118°, in excellent agreement with the value found by Neu;<sup>5</sup> calcd. for  $C_{24}H_{20}B_2O$ : 83.41 C, 5.83 H; found 83.12 C, 6.16 H. Since the anhydride is relatively sensitive to the atmosphere, it must be kept in the vacuum, and its preparation for large scale storage is undesirable.

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