$$(CH_3)_3SiCH_2NH_2HCI \xrightarrow{NaNO_2} \left[(CH_3)_3Si-CH_2 - N \cong N \right]^+$$

$$(CH_3)_3SiCH_2^+ \qquad (CH_3)_3SiOH + CH_2N_2$$

$$II \qquad \downarrow H^+$$

$$(CH_3)_3SiOSi(CH_3)_3$$

$$III$$

The striking contrast between this reaction and the reaction of neopentylamine³ may be attributed to the ease of nucleophilic attack through the *d*-orbitals of the silicon.

To a solution of 25.0 g. (0.18 mole) of aminomethyltrimethylsilane hydrochloride4 and 37.0 g. (0.53 mole) of sodium nitrite in 200 ml. of water, 100 ml. of 6N hydrochloric acid was added dropwise with cooling. After the addition had been completed (2 hr.), the mixture was heated at reflux for an hour. The mixture was extracted with ether, the ethereal extracts washed with base to remove any nitrous acid also extracted and then concentrated by distillation. Fractional distillation yielded 7.8 g. (56%) of hexamethyldisiloxane (III), b.p. 98-100°, n_D^{21} 1.3765 [lit., b.p. 99-100°, n_D^{20} 1.3772]. The infrared spectra of this material and of an authentic sample of hexamethyldisiloxane were identical, Gas phase analysis (5' Silicone column, T = 100°) of the concentrated ethereal extracts prior to distillation indicated the absence of hydroxymethyltrimethylsilane,6 sym-tetramethyldiethyldisiloxane,7 and chloromethyltrimethylsilane.8 Each of these compounds was prepared independently and could be easily distinguished from hexamethyldisiloxane in gas chromatographic analysis. Aminomethyltrimethylsilane hydrochloride and sodium nitrite, in the absence of acid, do not react.

Evidence for the release of diazomethane is indirect. An attempt to remove it from the reaction mixture by co-distillation with ether was unsuccessful. However, distillation of the acidic aqueous reaction mixture yielded methanol (gas phase chromatography identification using a 10' Carbowax column at $T=102^{\circ}$). Also, in one run, when 3.5-dinitrobenzoic acid was added to the reaction mixture, a 43% yield of methyl 3.5-dinitrobenzoate was isolated, m.p. $107-108^{\circ}$ [lit., 9 m.p. 107°].

The scope of this reaction and its possible use as an alternate route for the synthesis of diazoalkanes are now under investigation.

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Received February 15, 1961

A New Approach to Polycyclic Bases. I. The 1-Azabicyclo [3.2.0] heptane System¹

Sir:

We wish to report a novel procedure for the preparation of polycyclic bases from acyclic starting materials which does not require the isolation of intermediates. The method involves the treatment of ditertiary glycols with ω -chloronitriles in concentrated sulfuric acid followed by the reduction of the resulting C=N link with sodium borohydride and then the addition of alkali to induce intramolecular alkylation. As a result of this technique, we were able to obtain 2,2-dimethyl-4-isopropylidene-1-azabicyclo[3.2.0]heptane (I) a derivative of a hitherto unreported bicyclic system.

The formation of I illustrates a further example of a new and general route to N-heterocycles which have, to date, led to 1-pyrrolines, 5,6-dihydropyridines, 2 dihydro-1,3-oxazines, 3 dihydro-1,3-thiazines, 2-thiazolines, 4 and bis(N-heterocycyl)alkanes. 5

The 1-azabicyclo [3.2.0]heptane(I) was prepared in 60% over-all yield based on the dimethylhexanediol. The intermediate 2-chloroethyl-1-pyrroline (Ia) was formed when 3-chloropropionitrile was treated with 2,5-dimethyl-2,5-hexanediol in cold concentrated sulfuric acid. This compound was

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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. $107-108^{\circ}$ (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. $166-167^{\circ}$. 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.

Acknowledgment. The authors wish to express their gratitude to the Louisiana Division of the American Cancer Society for a Summer Research Fellowship (to W.Y.L.).

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Received January 30, 1961

Preparation and Storage of Diphenylborinic Acid and Its Anhydride¹

Sir:

We have noted with interest Neu's continuing advocacy² 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.³ 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,⁴ 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 etherinsoluble 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; 5 calcd. for C₂₄H₂₀B₂O: 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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Received January 31, 1961

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