maximum reducing power was determined in critical cases, such as represented by curve 3, Fig. 1, and was found to be within 3% of the value calculated for the conversion of all the sucrose into invert sugar.

The sucrose was a finely ground dry sample of Domino cane sugar, adant cut loaf, over 99.9 wt. % sucrose containing less than 0.018 wt. % invert sugar.[3] The water was triply distilled and was free of all impurities. The other materials were of analytical reagent or C.P. quality.[2]

The results are presented in Fig. 1. In the case of curve 3 autocatalysis increased the rate of the reaction sixfold (6b) by the time 90% of the sucrose had been hydrolyzed, and this was accompanied by a decrease in the *p*H of the reacting mixture. The increase in the acidity corresponded quantitatively to the increase in the rate. The *p*H values were measured with a glass electrode after the solutions had been cooled to 25°.

The extent of the autocatalysis was found to increase when there was an increase in (1) the per cent. sucrose hydrolyzed (curve 3), (2) the initial concentration of sucrose (*cf.* curves 1 and 2), (3) the temperature at which the hydrolysis was carried out (*cf.* curves 2 and 5B) and when there was (4) a decrease in the initial concentration of the acid (*cf.* curves 3 and 4B).

(3) L. J. Heidt and F. W. Southam, THIS JOURNAL, **72**, 580 (1950).

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## Boron–Nitrogen Systems. II. Diethylaminoboron Dichloride[1]

BY ROBERT C. OSTHOFF[2] AND CHARLES A. BROWN

RECEIVED JANUARY 5, 1952

The first paper of this series[3] was devoted to a discussion of the physical and chemical properties of dimethylaminoboron dichloride, in both its monomeric and dimeric forms. In this paper the properties of diethylaminoboron dichloride, $(CH_3CH_2)_2NBCl_2$, will be discussed.

Wiberg[4] has reported the preparation of diethylaminoboron dichloride by the action of boron trichloride upon diethylamine, but no yield data or experimental details were presented. Wiberg also found that diethylaminoboron dichloride formed no dimer, even after standing for one year at room temperature. This lack of dimer formation is in sharp contrast to the behavior of dimethylaminoboron dichloride which readily forms a rather stable dimer.[3] It was stated by Wiberg that diethylaminoboron dichloride reacts with hydrohalogen acids and with tertiary amines, but the properties of the resulting compounds have not been published.

### Experimental

**Preparation of $(CH_3CH_2)_2NBCl_2$.**—Diethylaminoboron dichloride was obtained by fractionation of the reaction mixture which resulted from the action of excess boron trichloride (Matheson) upon diethylamine (Eastman Kodak Co. "White Label") used as supplied by the manufacturer without further purification, since none of the contaminants would give rise to products which would decrease the purity of the diethylaminoboron dichloride. The reactants were brought together at −196° *in vacuo*. By warming the reaction mixture slowly to room temperature (over about a 4-hour period) it was possible to fractionate the volatile products by passing them through traps at −20, −80 and −196°. Diethylaminoboron dichloride was collected in the trap which was held at −20° and further purified by bulb to bulb vacuum distillation. Based on the amount of diethylamine that was employed, the yield of product was 40%; the calculation of the yield was made by assuming that the preparative reaction may be formulated as

$$BCl_3 + 2HN(CH_2CH_3)_2 \longrightarrow (CH_3CH_2)_2NBCl_2 + (CH_3CH_2)_2NH{\cdot}HCl$$

A mole ratio of amine to boron trichloride of about 1.5 was used in the preparation of diethylaminoboron dichloride in order that none of the higher substitution products of boron trichloride (*i.e.*, bisdiethylaminoboron chloride and trisdiethylaminoboron) would be formed.

**Characterization of Diethylaminoboron Dichloride.**—In Table I are summarized the physical properties of diethylaminoboron dichloride which have been reported previously by Wiberg,[4] as well as the corresponding values which were observed by the authors.

The authors determined the melting point visually; the boiling point, the heat of vaporization, and the Trouton constant were evaluated by the authors from a study of the vapor pressure of the pure compound as will be described below. The experimental methods employed by Wiberg for the evaluation of these constants are not given in the literature.

TABLE I

PHYSICAL PROPERTIES OF DIETHYLAMINOBORON DICHLORIDE

| Property | Reported by Wiberg[4] | Observed |
|---|---|---|
| M.p., °C. | −25.5 | −23.0 |
| B.p., °C. | 150 | 148 |
| Heat of vaporization, cal./mole | 9560 | 9480 |
| Trouton constant, cal./deg. | 22.6 | 22.5 |

Measurements of vapor density at 22° by the authors gave an observed molecular weight of 151 (calcd. for $(CH_3CH_2)_2NBCl_2$, 153.9). It had been reported earlier by Wiberg[4] that this compound remained monomeric after standing at room temperature for one year. This was observed to be the case, since the authors found no evidence of dimer formation in samples which were stored for 18 months at room temperature in the absence of air and moisture. When sealed tubes of diethylaminoboron dichloride were heated to 190° in attempts to form a dimer, we observed only carbonization of the ethyl groups.

**Liquid Density.**—A dilatometric pycnometer was employed to evaluate the density of liquid diethylaminoboron dichloride in the temperature range of 5 to 95°. By application of the method of least squares to the observed data, the linear equation relating the density to the Centigrade temperature was found to be

$$d = 1.0796 - 0.001161\, t \text{ (g./ml.)}$$

Some of the observed and calculated values of the density are summarized in Table II. These values of the density were estimated to be accurate to about 0.05%.

**Vapor Pressure.**—By employment of isoteniscopes of the type described by Smith and Menzies,[5] the vapor pressure of diethylaminoboron dichloride was studied between 24 and 140°. In order to ensure the removal of adsorbed water from the isoteniscopes, the apparatus was repeatedly flamed in high vacuum. Above 80° each of the observed pressures was corrected by the subtraction of the vapor pressure of mercury at that temperature.

By application of the method of selected points to the vapor pressure data of two independent runs, the constants of the Antoine[6] equation were evaluated. Thus the vapor

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[1] Taken from Ph.D. thesis of Robert C. Osthoff, Harvard University, 1951.

[2] Procter and Gamble Fellow in Chemistry, Harvard University, 1951. Present address: Research Laboratory, General Electric Co., Schenectady, N. Y.

[3] C. A. Brown and R. C. Osthoff, THIS JOURNAL, **74**, 2340 (1952).

[4] E. Wiberg, "Fiat Review of German Science," Vol. 23, Part I, pp. 217, *et seq.*

[5] A. Smith and A. W. C. Menzies, THIS JOURNAL, **32**, 1412 (1910).

[6] G. W. Thomson, *Chem. Revs.*, **38**, 1 (1946).

TABLE II

CALCULATED AND OBSERVED VALUES OF THE DENSITY OF DIETHYLAMINOBORON DICHLORIDE AT VARIOUS TEMPERATURES

| $t$, °C. | $d$, obsd. | $d$, calcd. |
|---|---|---|
| 5.0 | 1.0744 | 1.0738 |
| 10.0 | 1.0680 | 1.0680 |
| 41.0 | 1.0313 | 1.0320 |
| 50.0 | 1.0211 | 1.0215 |
| 60.00 | 1.0100 | 1.010 |
| 70.0 | 0.9979 | 0.9983 |
| 80.0 | .9857 | .9863 |
| 90.0 | .9746 | .9741 |

pressure of liquid diethylaminoboron dichloride may be calculated at a given temperature by means of the equation

$$\log_{10} P_{\text{mm}} = 7.1825 - \frac{1618}{t + 230}$$

In Table III some of the observed and calculated values of the vapor tensions at various temperatures are presented.

TABLE III

CALCULATED AND OBSERVED VALUES OF THE VAPOR PRESSURES OF DIETHYLAMINOBORON DICHLORIDE

| $t$, °C. | $P_{\text{mm}}$, obsd. | $P_{\text{mm}}$, calcd. |
|---|---|---|
| 24.0 | 6.5 | 6.5 |
| 30.0 | 9.9 | 9.2 |
| 40.0 | 14.9 | 15.5 |
| 50.0 | 25.7 | 25.4 |
| 60.0 | 40.7 | 40.1 |
| 70.0 | 61.7 | 61.6 |
| 80.0 | 92.8 | 91.9 |
| 90.0 | 135.8 | 133.7 |
| 110.0 | 269.5 | 265.3 |
| 125.0 | 420.0 | 421.5 |

From the vapor pressure equation, the heat of vaporization was found to be 9480 g. cal. per mole, and the normal boiling point was found to be 148° by extrapolation. By combination of these values in the usual fashion, the Trouton constant was found to be 22.5 e.u.

**Surface Tension.**—By employment of the twin capillary method of Mills and Robinson,[7] the surface tension of diethylaminoboron dichloride was evaluated at various temperatures *in vacuo* (suitable precautions to prevent hydrolysis due to traces of moisture in the vacuum apparatus were observed).

The equation which relates the surface tension to the centigrade temperature is

$$\gamma(\text{vapor}) = 28.81 - 0.0984\,t \text{ (dynes per cm.)}.$$

Some calculated and observed values of the surface tension are given in Table IV.

TABLE IV

CALCULATED AND OBSERVED VALUES OF THE SURFACE TENSIONS OF DIMETHYLAMINOBORON DICHLORIDE

| $t$, °C. | $\gamma$, obsd. | $\gamma$, calcd. |
|---|---|---|
| 10.0 | 27.82 | 27.83 |
| 15.0 | 27.18 | 27.00 |
| 22.5 | 26.53 | 26.58 |
| 25.0 | 26.35 | 26.33 |
| 30.0 | 25.87 | 25.86 |
| 35.0 | 25.30 | 25.37 |
| 40.0 | 24.99 | 25.07 |
| 45.0 | 24.42 | 24.38 |
| 50.0 | 23.69 | 23.89 |
| 55.0 | 23.40 | 23.41 |
| 60.0 | 23.06 | 22.91 |

By application of the Eötvös equation to the surface tension data in the usual manner,[8] it was found that the surface energy may be expressed by means of the equation

$$\gamma(Mv)^{2/3} = 2.1(379 - t - 6) \text{ (ergs)}$$

where $\gamma$ = the surface tension in dynes per cm., $M$ = the molecular weight, $v$ = the specific volume, and $t$ = the centigrade temperatures.

Thus the Eötvös constant was found to be 2.1; this indicates that liquid diethylaminoboron dichloride is not appreciably associated. From this treatment it was possible to estimate the critical temperature as 279°.

From the surface tension data and the density data, the mean value of the parachor of diethylaminoboron dichloride in the temperature range of 10 to 60° was found to be 331.7 parachor units. In the first paper of this series[3] it was shown that a suitable value for the atomic parachor of boron in this type of compound is 20.3. By use of this value in conjunction with the atomic parachor values of Sugden,[9] the calculated value of the molar parachor of diethylaminoboron dichloride was found to be 331.9.

**Reaction with Hydrogen Chloride.**—Anhydrous hydrogen chloride ($2.280 \times 10^{-3}$ mole) was introduced into a vacuum chain by means of a compensating gas buret. Diethylaminoboron dichloride was then added in small amounts and the pressure of the system was determined at constant volume and constant temperature following each of the additions.[10] In this manner the graph of Fig. 1 was constructed in which the mole ratio $(CH_3CH_2)_2NBCl_2/HCl$ is plotted against the pressure. The nature of the curve of Fig. 1 is clearly indicative of the formation of the one-to-one addition compound of empirical formula, $(CH_3CH_2)_2NBCl_2\cdot HCl$.

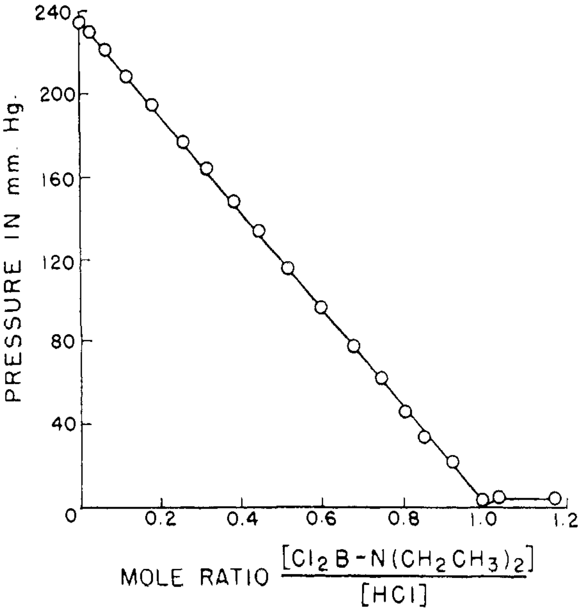

Fig. 1.—Pressure *vs.* mole ratio $[(CH_3CH_2)_2NBCl_2/HCl]$ for the reaction of diethylaminoboron dichloride with hydrogen chloride at 24.0°.

*Anal.* Calcd. for $(CH_3CH_2)_2NBCl_2\cdot HCl$: C, 25.28; H, 5.78; N, 7.37; Cl, 55.93. Found: C, 25.20; H, 6.07; N, 7.18, Cl, 55.21.

$(CH_3CH_2)_2NBCl_2\cdot HCl$ is somewhat soluble in anhydrous ethyl ether and may be purified by recrystallization from this solvent. The compound gives an instant precipitate of silver chloride when silver nitrate is added to its aqueous solution.

**Reaction with Trimethylamine.**—By the method described above, the the reaction of diethylaminoboron di-

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[7] H. Mills and P. L. Robinson, *J. Chem. Soc.*, 1823 (1927).

[8] S. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., Chapter VII, D. Van Nostrand Co., Inc., New York, N. Y., 1946.

[9] S. Sugden, *J. Chem. Soc.*, **127**, 1540 (1925).

[10] R. C. Osthoff, C. A. Brown and F. H. Clarke, THIS JOURNAL, **73**, 4045 (1951).

chloride with trimethylamine was studied. Eastman Kodak Company White Label trimethylamine (vapor pressure at 0°, 676 mm.; calcd., 681 mm.[11]) was employed in the reaction. The course of this reaction, which was studied by means of a graph similar to that of Fig. 1, indicated that a one-to-one addition compound was formed. However, in the vicinity of a mole ratio of one, the straight line was rounded off and the pressure dropped only to about 20 mm. Inasmuch as this pressure is greater than the vapor pressure of diethylaminoboron dichloride, dissociation of the addition compound is indicated. The melting point of the trimethylamine adduct was observed to be about 20° with decomposition.

When the solid adduct was treated with water at about 10°, rapid hydrolysis took place, as indicated by the formation of an instant precipitate of silver chloride when the solution was treated with silver nitrate. Because of the low stability of the addition compound, it was impossible to obtain an elementary analysis for this substance.

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(11) A. Simon and J. Huter, *Z. Elektrochem.*, **41**, 28 (1935).

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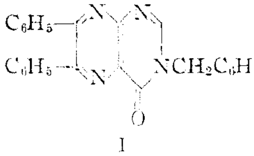
## Pteridines. IX. Hydrolytic Ring Cleavage of 3-Benzyl-6,7-diphenyl-4(3*H*)-pteridinone

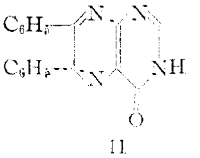
BY E. C. TAYLOR, JR.

RECEIVED NOVEMBER 23, 1951

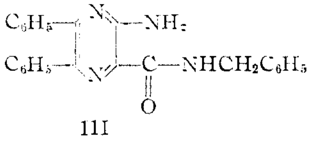
A project at present under investigation in this Laboratory is the conversion of N-substituted amides of 3-aminopyrazinoic acids into 3-substituted 4(3*H*)-pteridinones. One compound of the latter type, 3-benzyl-6,7-diphenyl-4(3*H*)-pteridinone (I), has already been reported.[1] In an attempt to prepare I by an alternate route, 6,7-diphenyl-4(3*H*)-pteridinone (II) was treated with benzyl chloride and potassium hydroxide in methanol solution. Upon treatment of the reaction solution with dilute alkali, a yellow crystalline solid separated which proved to be 3-amino-N-benzyl-5,6-diphenylpyrazinamide (III) rather than the expected pteridinone (I). In order to test the hypothesis that this product arose by hydrolytic cleavage of I formed initially, an authentic sample of 3-benzyl-6,7-diphenyl-4(3*H*)-pteridinone (I) was treated with potassium hydroxide and 90% methanol. III was formed smoothly in 87.5% yield. If the reaction of 6,7-diphenyl-4(3*H*)-pteridinone (II) with benzyl chloride and potassium hydroxide in stock methanol was worked up after a shorter reaction period and the final addition of aqueous alkali was avoided, it was possible to isolate unreacted II, a small amount of I and some III from the reaction mixture. No III was formed under the same conditions when freshly prepared, absolute methanol was used as a solvent rather than stock methanol; under these conditions only a poor yield of pure I could be isolated from the reaction mixture. Attempts to synthesize I from 6,7-diphenyl-4(3*H*)-pteridinone (II) and benzyl chloride in the absence of alkali were unsuccessful, as were attempts to effect ring cleavage of II with dilute alkali alone.



I



II



III

The stability of II toward ring cleavage in dilute alkali is undoubtedly due to ready distribution of the negative charge of the anion over the pteridine ring system. Such a stabilization is impossible with I, as it cannot form a simple anion, and hydrolytic attack at $C_2$ followed by ring cleavage occurs with ease. A more general study of the hydrolytic cleavage of 3-substituted 4(3*H*)-pteridinones is under investigation.

These experiments support the generalization recently made by Albert, *et al.*,[2] that substituents on the pteridine nucleus are best introduced before ring closure.

### Experimental[3]

**6,7-Diphenyl-4(3*H*)-pteridinone (II).**—A suspension of 15.0 g. (0.059 mole) of 5,6-diamino-4-hydroxy-2-mercaptopyrimidine sulfate[4] in 300 ml. of boiling water was treated with 20% sodium carbonate solution until all the suspended solid had dissolved. The *p*H was adjusted to 10 by the addition of dilute hydrochloric acid and 80 g. of wet Raney nickel added in small portions. After the violent evolution of gas had ceased, the mixture was heated under reflux for four hours. The reaction mixture was then allowed to cool, the nickel removed by filtration, and 12.4 g. (0.059 mole) of benzil dissolved in a mixture of 100 ml. of ethyl methyl ketone and 350 ml. of ethanol added to the filtrate. The resulting mixture was heated under reflux for eight hours. Acidification of the hot yellow solution and cooling caused the separation of colorless platelets which were collected by filtration and recrystallized from aqueous dimethylformamide; yield 13.2 g. (75%); m.p. (dec.) 297–298°.

*Anal.* Calcd. for $C_{18}H_{12}N_4O$: C, 72.0; H, 4.0; N, 18.7. Found: C, 72.0; H, 4.1; N, 18.6.

**3-Amino-N-benzyl-5,6-diphenylpyrazinamide (III).** Method A.—A mixture of 0.50 g. (0.00167 mole) of 6,7-diphenyl-4(3*H*)-pteridinone, 30 ml. of methanol, 0.2 ml. (0.00174 mole) of benzyl chloride and 0.16 g. (0.00286 mole) of potassium hydroxide was heated under reflux for two hours. Addition of 15 ml. of 2 *N* sodium hydroxide and warming caused the immediate separation of yellow needles. The reaction mixture was allowed to cool to room temperature, the crystals collected by filtration and recrystallized from ethanol; yield 0.483 g. (76%); m.p. 188.5–189°.

Method B.—To a solution of 75 mg. of 3-benzyl-6,7-diphenyl-4(3*H*)-pteridinone in 30 ml. of methanol was added 5 ml. of water *containing 0.1 g. of potassium hydroxide and* the solution heated under reflux for 10 minutes. The reaction mixture rapidly turned yellow with the simultaneous separation of yellow needles. Addition of 5 ml. of water and cooling gave 64 mg. (87.5%) of III in the form of long, yellow needles; m.p. 188.5–189°.

Mixed melting points of the products obtained by Methods A and B with an authentic sample of 3-amino-N-benzyl-5,6-diphenylpyrazinamide[1] showed no depression; infrared spectra of all three samples were identical.

**3-Benzyl-6,7-diphenyl-4(3*H*)-pteridinone (I).**—A mixture of 1.0 g. (0.00333 mole) of 6,7-diphenyl-4(3*H*)-pteridinone, 0.186 g. (0.00332 mole) of potassium hydroxide, 3.8 ml. (0.00332 mole) of benzyl chloride and 30 ml. of stock meth-

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(1) E. C. Taylor, Jr., THIS JOURNAL, **74**, 1651 (1952). It was prepared from 3-amino-N-benzyl-5,6-diphenylpyrazinamide (III) and formic acid in the presence of acetic anhydride.

(2) A. Albert, D. J. Brown and G. Cheeseman, *J. Chem. Soc.*, 474 (1951).

(3) All melting points are corrected.

(4) W. Traube, *Ann.*, **331**, 73 (1904).