was less than the experimental error in measuring the resonance frequency, it appears likely that the error introduced by the above procedure will not affect the significance of the results.

Acknowledgment.—The authors wish to thank Dr. Mansour Abedini for permitting them to use experimental data obtained by him for some of the compounds listed in Table I. They also wish to thank Mr. John Sowa for measuring the spectra of the compounds studied and for much useful advice. They are particularly indebted to Dr. E. A. V. Ebsworth, University of Cambridge, for many helpful criticisms and comments during the time this study was being carried out.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
DUKE UNIVERSITY, DURHAM, NORTH CAROLINA

Boron–Nitrogen Compounds. XVI.[1,2] Some New Boron–Nitrogen Heterocycles

BY KURT NIEDENZU, PETER FRITZ, AND JOHN W. DAWSON

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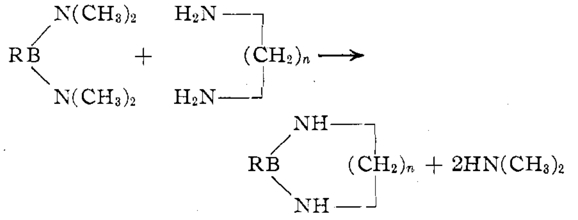
Several new 1,3,2-diazaboracycloalkanes have been prepared by a transamination reaction. In an analogous procedure, the first representative of the 1,8,10,9-triazaboradecalin system was obtained. Spectroscopic data of the newly synthesized materials were evaluated.

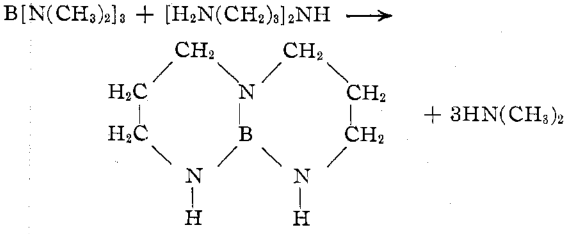
The utilization of heterocyclic boron-nitrogen-carbon compounds for cancer treatment is presently being studied.[3] However, one class of such compounds, the 1,3,2-diazaboracycloalkanes, has not yet been investigated for its physiological effects; indeed, the preparation of these compounds has received only causal attention. Of ring systems of this type only those that possess five or six annular atoms have been described. Among the five-membered rings, five derivatives have been reported[4–8] and only one six-membered ring is known.[4] In view of the recent preparation of a 1,2-azaboracycloalkane and its successful dehydrogenation,[9] an application of similar techniques on the 1,3,2-diazaboracycloalkane system should afford interesting results.

The present study reports on the synthesis of several new 1,3,2-diazaboracyclohexanes and the heretofore unknown 1,3,2-diazaboracycloheptanes. These compounds (I) are readily produced through a transamination reaction between bis(dimethylamino)boranes and aliphatic α,ω-diamines in inert solvents such as hexane or benzene (eq. 1). In addition, the transamination of tris(dimethylamino)borane with 3,3′-diaminodipropylamine was also studied. In dilute solutions, 1,8,10,-9-triazaboradecalin (II) was obtained in good yield. It is the first example of this hitherto unknown boron-nitrogen-carbon ring system.



(1)

I



(2)

II

Experimental[10]

2-Ethyl-1,3,2-diazaboracyclohexane (Typical Experiment).—A quantity, 14.8 g. (0.2 mole), of 1,3-diaminopropane was added to a solution of 25.6 g. (0.2 mole) of bis(dimethylamino)ethylborane in 150 ml. of dry hexane in an inert atmosphere. Dimethylamine evolved slowly at room temperature. On refluxing the reaction mixture, additional dimethylamine was evolved; the reaction was complete within approximately 2 hr. The solvent was stripped off and the residue distilled under reduced pressure to yield 16.1 g. (72%) of 2-ethyl-1,3,2-diazaboracyclohexane, b.p. 44–45° (13 mm.). The analytical data are compiled in Table I.

In an analogous procedure, the compounds listed in Table I were prepared by the reaction of 0.2 mole of various B-substituted bis(dimethylamino)boranes with 1,3-diaminopropane and 1,4-diaminobutane.

1,8,10,9-Triazaboradecalin (II).—A solution of 26.2 g. (0.2 mole) of 3,3′-diaminodipropylamine in 50 ml. of dry benzene was

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[9] D. G. White, *J. Am. Chem. Soc.*, **85**, 3634 (1963).

[10] Infrared spectra of the materials were recorded on a Perkin-Elmer Model 21 double-beam spectrophotometer using sodium chloride optics; ^1H nuclear magnetic resonance data were obtained with a Varian A-60 high resolution n.m.r. spectrometer, using tetramethylsilane as an external standard while ^{11}B data were obtained with a Varian V-4300-B n.m.r. spectrometer, operated at 19.3 Mc., using the diethyl etherate of BF_3 as external standard. Melting points were taken on a Mel-Temp block. Analyses were furnished by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

Table I

1,3,2-Diazaboracycloalkanes (I)

No.	*n*	R	B.p., °C. (*mm.*)	Yield, %	Analyses, %								N.m.r. data B^{11} chem. shift, p.p.m.
					Boron		Nitrogen		Carbon		Hydrogen		
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
1[a]	3	H	97–99	54[d]	12.9	12.5	33.35	33.1	42.85	44.4	10.9	11.3	$\begin{Bmatrix} -28.7 \\ -21.8 \end{Bmatrix}$
2[b]	3	CH_3	36–38 (20)[e]	65									−29.9
3[c]	3	$CH{=}CH_2$	41 (7)	47	9.8	9.6	25.4	25.1	54.6	54.5	10.0	10.3	−27.0
4[b]	3	C_2H_5	44–45 (13)	72	9.65	9.3	25.0	25.2	53.65	53.6	11.7	11.95	−30.1
5[b]	3	C_6H_5	94–95 (1)[f]	85	6.8	6.8	17.5	17.3	67.5	67.7	8.2	8.5	−27.1
6[b]	4	CH_3	39–42 (6)	59	9.6	9.3	25.0	25.1	53.6	53.8	11.7	12.0	−29.9
7[b]	4	*n*-C_4H_9	64 (1)	83	7.0	6.9	18.2	18.4	62.4	62.3	12.4	12.4	−30.7
8[b]	4	C_6H_5	102–104 (1)[g]	76	6.2	6.4	16.1	16.2	68.9	69.1	8.7	8.9	−28.5

[a] Ether used as solvent in preparation. [b] Hexane used as solvent. [c] Benzene used as solvent. [d] Molecular weight determinations in cyclohexane solution indicate substantial dimerization. [e] Lit.[4] 132° (extrapolated). [f] M.p. 50–52°. [g] M.p. 27–29°.

added to a solution of 28.6 g. (0.2 mole) of tris(dimethylamino) borane in 4 l. of dry benzene. The mixture was refluxed for 6 hr. and the solvent stripped off. Distillation of the residue under vacuum yielded 20.7 g. (75%) of 1,8,10,9-triazaboradecalin, b.p. 62° (1 mm.), m.p. 38–41°. *Anal.* Calcd. for $BN_3C_6H_{14}$: C, 51.8; H, 10.15; B, 7.8; N, 30.2; mol. wt. 139.0. Found: C, 52.1; H, 10.2; B, 7.5; N, 30.0; mol. wt. (cryoscopically in benzene), 142.

Discussion

The great potential of the transamination reaction in preparative boron–nitrogen chemistry is again demonstrated by the preparation of a variety of 1,3,2-diazaboracycloalkanes (I) and the 1,8,10,9-triazaboradecalin (II). The newly synthesized materials are thermally quite stable. However, they hydrolyze very readily. Molecular weight determinations by the cryoscopic method in benzene in about 0.05–0.1 *M* concentrations indicate the existence of a monomeric species only; no appreciable signs of association have been observed. This observation is consistent with the infrared spectra of the materials. The 1,3,2-diazaboracycloalkanes exhibit a N–H stretching frequency in the 3500–3450 cm.$^{-1}$ region, which is normally related to unassociated N–H bonds.

Other features of the newly synthesized heterocycles include a very strong B–H absorption in the infrared spectrum of compound 1 (Table I), recorded at 2510 cm.$^{-1}$. This value compares favorably with the B–H absorption of borazine, $(\text{-BHNH-})_3$, which is observed at 2530 cm.$^{-1}$.[11] The acyclic bis(dimethylamino)-borane, $HB[N(CH_3)_2]_2$, however, has a B–H absorption near 2450 cm.$^{-1}$.

The N–H stretching mode of compound 1 (Table I) is recorded at 3500 cm.$^{-1}$, that of borazine at 3490 cm.$^{-1}$; however, the N–H stretch of bis(alkylamino)-boranes is normally found near or below 3450 cm.$^{-1}$.[12] The strongest infrared absorption of all the newly synthesized materials has been assigned to a B–N stretching vibration at 1495 ± 10 cm.$^{-1}$, which again is in closer agreement with the corresponding vibration of simply substituted borazines (ν_{BN} near 1450 cm.$^{-1}$) than that of acyclic bisaminoboranes (ν_{BN} near 1390 cm.$^{-1}$). The same general situation holds true if one considers the ^{11}B chemical shift values of these same three types of compounds. Although information on the ^{11}B nuclear magnetic resonance data derived from boron–nitrogen compunds is rather limited, present data indicate a range for the ^{11}B chemical shift in borazines of about −32 to −27 p.p.m. (relative to trifluoroborane etherate), in close agreement with the values obtained for the 1,3,2-diazoboracycloalkanes (Table I). In contrast, the ^{11}B chemical shifts of some acyclic bis(alkylamino)boranes have been reported to range around −39 to −34 p.p.m.[13] In addition, the coupling constant J_{BH} = 132 c.p.s. of compound 1 (Table I) compares favorably with those of borazine (J_{BH} = 138 c.p.s.) and N-trimethylborazine (J_{BH} = 136 c.p.s.).

All the data cited above seem to indicate that the bonding of boron and nitrogen in the 1,3,2-diazaboracycloalkane system is more like that encountered in the borazines than is the case with acyclic bisaminoboranes. This observation is substantiated by an examination of molecular models which clearly show a preference for a planar arrangement of the N–B–N grouping in the boron–nitrogen–carbon heterocycles. The planarity of the N–B–N entities in borazine is well-established[14]; in acyclic bisaminoboranes, however, steric effects are responsible for a slight distortion of the N–B–N plane.[15]

It is worth noting that ^{11}B nuclear magnetic resonance data demonstrate the existence of an enhanced shielding of boron in compound 3 (Table I) over and above that of compounds 2 and 4. This situation might be interpreted to imply extensive coupling of the B-attached vinyl group with the boron moiety, a condition which is not apparent from infrared spectroscopic data.[1,8] Proton magnetic resonance studies of the cyclohexane and decalin analogs showed a distinct pattern for the ring protons. A sextet, centered at about τ 7 p.p.m., can be considered as a combination of two triplets of 1:2:1 intensity, $J_{HH} \approx 5$ c.p.s. On the basis of the n.m.r. integrals, this multiplet structure is assigned to the methylene protons of the N-attached CH_2 groups.

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[11] H. Watanabe, T. Totani, T. Nakagawa, and M. Kubo, *Spectrochim. Acta*, **16**, 1076 (1960).

[12] J. E. Burch, W. Gerrard, M. Goldstein, E. F. Mooney, and H. A. Willis, *ibid.*, **18**, 1403 (1962).

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[14] S. H. Bauer, *J. Am. Chem. Soc.*, **60**, 524 (1938).

[15] P. Fritz, Ph.D. Thesis, University of München, Germany, 1963. See also: H. J. Becher, *Z. anorg. allgem. Chem.*, **287**, 285 (1956); H. J. Becher, W. Sowodny, H. Nöth, and W. Meister, *ibid.*, **314**, 226 (1962).

Protons attached to the remaining ring carbon atom show a quintuplet pattern near τ 8.25 p.p.m.

The infrared spectrum of the decalin analog II exhibited a N–H stretch at 3400 cm.$^{-1}$. Very strong absorption in the 1500–1300 cm.$^{-1}$ region of the infrared spectra of boron–nitrogen compounds is normally associated with the B–N stretching vibration of a covalent boron–nitrogen bond in which the free electrons of the nitrogen can participate.[16] In the spectrum of the 1,8,10,9-triazaboradecalin, three bands of unusually strong intensity were recorded at 1510, 1434, and 1320 cm.$^{-1}$. Final assignment of these modes awaits isotopic studies. The ^{11}B chemical shift of compound II was found as a singlet at −22 p.p.m. with a band width at half-maximum peak height of about 100 c.p.s.

[16] H. Beyer, J. B. Hynes, H. Jenne, and K. Niedenzu, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p. 266.

CONTRIBUTION FROM THE RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY, SCHENECTADY, NEW YORK

A Partial Study of the Ternary System Disodium Monotungstate–Tungstic Oxide–Water at 25°. The Formation of Disodium Ditungstate Pentahydrate[1]

BY EDWARD L. SIMONS

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Solubility data were obtained in the ternary system disodium monotungstate–tungstic oxide–water at 25° for mixtures in which the mole ratio of WO_3 to Na_2WO_4 was less than 7:5. The equilibrium solid phases were disodium monotungstate dihydrate, decasodium dodecatungstate 28-hydrate (sodium paratungstate), and the previously unreported disodium ditungstate pentahydrate, which is incongruently soluble. The metastable equilibriums that precede the formation of the ditungstate are described, and data are presented to show that a monohydrate is formed as a stable intermediate during the thermal dehydration of the pentahydrate. Washing and drying experiments, microscopic examination, powder X-ray diffraction patterns, chemical analysis, and thermogravimetric measurements were used to characterize both the penta- and monohydrates of disodium ditungstate.

Among the more than a dozen anhydrous and hydrated sodium isopolytungstates that have been reported in the literature since the middle of the 19th century,[2,3] only the four listed in Table I have been recognized in critical reviews[4,5] as discrete compounds.

TABLE I

COMPOSITIONS OF KNOWN SODIUM ISOPOLYTUNGSTATES[a]

Anhydrous[b]	Hydrated[c]
$Na_2WO_4 \cdot WO_3$ (Disodium ditungstate)	. . .
. . .	$5Na_2WO_4 \cdot 7WO_3 \cdot 28H_2O$ (Sodium paratungstate)
$Na_2WO_4 \cdot 3WO_3$ (Disodium tetratungstate)	$Na_2WO_4 \cdot 3WO_3 \cdot 10H_2O$ (Sodium metatungstate)

[a] Formulas are written to show the mole ratio of the components of the binary or ternary system and are not meant to inply any structural information. [b] F. Hoermann, *Z. anorg. allgem. Chem.*, **177**, 145 (1928); P. Caillet, *Compt. rend.*, **256**, 1986 (1963). [c] V. I. Spitsyn, *Zh. Obsch. Khim.*, **8**, 869 (1938); A. Lottermoser, W. Riedel, and O. Bretschneider, *Z. Elektrochem.*, **36**, 183 (1930); M. L. Freedman, *J. Am. Chem. Soc.*, **81**, 3834 (1959); K. Saddington and R. W. Cahn, *J. Chem. Soc.*, 3256 (1950); G. Schott and C. Harzdorf, *Z. anorg. allgem. Chem.*, **288**, 15 (1956); R. H. Vallance, *J. Chem. Soc.*, 1421 (1931).

Although sodium metatungstate can formally be considered as a hydrate of $Na_2WO_4 \cdot 3WO_3$, sodium paratungstate has no analog in the anhydrous binary system,[6] and complete removal of its water leads to disproportionation into a mixture of $Na_2WO_4 \cdot WO_3$ and $Na_2WO_4 \cdot WO_3$.[7,8] In 1876 Lefort[9,10] reported the crystallization of $Na_2WO_4 \cdot WO_3 \cdot 6H_2O$ from a solution of the monotungstate acidified with acetic acid, but subsequent workers have been unable either to duplicate Lefort's results[2–4,8,11] or to prepare a hydrated disodium ditungstate by other methods.[12,13]

This paper presents evidence for the formation of disodium ditungstate pentahydrate ($Na_2WO_4 \cdot WO_3 \cdot 5H_2O$) as a stable but incongruently soluble solid phase in the ternary system Na_2WO_4–WO_3–H_2O at 25° and for the formation of a monohydrate as a stable intermediate during the thermal dehydration of the pentahydrate. The phase relationships in this ternary system and the slow rate of formation of the pentahydrated ditungstate may explain the failure of previous investigators to crystallize this phase from aqueous solution.

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[1] Presented before the Inorganic Division at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

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[10] J. Lefort, *Compt. rend.*, **82**, 1182 (1876).

[11] W. Gibbs, *Am. Chem. J.*, **1**, 217 (1879).

[12] A. Lottermoser, W. Riedel, and O. Bretschneider, *Z. Elektrochem.*, **36**, 183 (1930).

[13] M. L. Freedman, *J. Am. Chem. Soc.*, **81**, 3834 (1959).