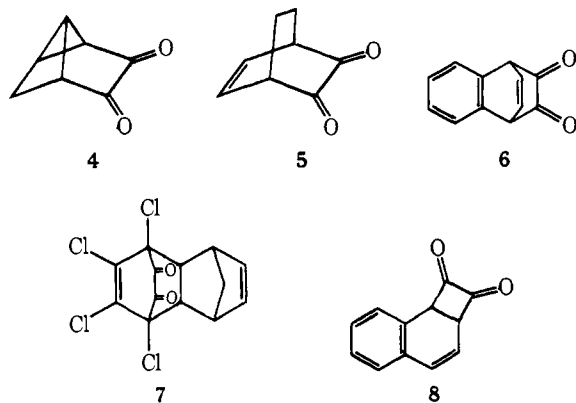Figure 1. Irradiation of $8 \times 10^{-3}$ M 1 in benzene at 404 nm.

is also apparent in Figure 1 where an isosbestic point is observed[7] at 492 nm for the initial 25–35% of the reaction. An analogous rearrangement has been observed[8] in some attempts to prepare the radical anion of 1 from compounds having the bicyclo[2.2.1] skeleton; the ESR spectrum of the radical anion of 2 was observed.

The initial quantum yield at 404 or 436 nm for disappearance of 1 or formation of 2 was $0.21 \pm 0.02$. This value was observed in the presence of air or in carefully degassed solutions in benzene or toluene; rearrangement also occurred cleanly in methylene chloride and deuteriochloroform solutions and in the solid state. No quenching by anthracene was observed even at concentrations as high as $10^{-2}$ M. Further indications that the reactive excited state of 1 might be its singlet state were provided by observations that the reaction was sensitized by anthracene, that 1 quenched the fluorescence of anthracene in benzene solution at 25 °C with a rate constant[9] of $1 \times 10^{10}$ $M^{-1}$ $s^{-1}$, and that 1 quenched all the emission of biacetyl. However, comparable quantum yields for disappearance of 1 were obtained when m-methoxyacetophenone, benzil, or acetone (50% in benzene) were used as sensitizers. These compounds also sensitized the further reaction 2 → cyclopentadiene but no products of the oxadi-π-methane type,[10] such as 4, could be detected.

The results above indicate that the photorearrangement 1 → 2 proceeds via a short-lived excited state(s) but do not permit a decision as to whether the singlet state, the triplet state, or both are reactive. We were unable to detect either fluorescence or phosphorescence from 1. It is also not possible to distinguish between concerted and stepwise mechanisms[11] at this stage.

Rearrangements to cyclobutanediones were also observed with bicyclo[2.2.2]octene-2,3-dione[12] (5), benzobicy-



clo[2.2.2]octadiene-2,3-dione (6), and the tetrachlorodione 7. Thus all of these unsaturated diones, even 6 which could bisdecarbonylate to naphthalene, yield products of 1,3-migration upon direct irradiation as is observed with β,γ-unsaturated monoketones[10] but differ from the monoketones in their reaction with triplet sensitizers. An acyclic unsaturated dione underwent intramolecular Paterno–Buchi reaction upon irradiation.[13]

The cyclobutanediones obtained in this work were stable thermally[14] with the exception of the dione 8 derived from 6 which gave naphthalene with a half-life of about 16 h at room temperature in the dark. Upon irradiation they lost carbon monoxide and were converted to the dienes (or naphthalene) previously reported.[1] Conversion of 2 to cyclopentadiene was effected by irradiation at 546 or 436 nm or by the full spectrum (through Pyrex) of a high pressure mercury vapor lamp. The reverse process, 2 → 1, was not observed in any of these experiments.

## References and Notes

(1) (a) D. Bryce-Smith and A. Gilbert, Chem. Commun., 1702 (1968); (b) J. Strating, B. Zwanenburg, A. Wagenaar, and A. C. Udding, Tetrahedron Lett., 125 (1969); (c) H. Hart, D. L. Dean, D. N. Buchanan, J. Am. Chem. Soc., 95, 6294 (1973); (d) E. E. Nunn, W. S. Wilson, and R. N. Warrener, Tetrahedron Lett., 175 (1972); (e) H.-D. Scharf and W. Kusters, Chem. Ber., 105, 564 (1972); (f) W. Friedrichsen, E. Buldt, M. Betz, and R. Schmidt, Tetrahedron Lett., 2469 (1974); (g) E. Vogel, J. Ippen, and V. Buch, Angew. Chem., Int. Ed. Engl., 14, 566 (1975); (h) H.-D. Scharf, ibid., 13, 520 (1974).
(2) (a) R. C. Haddon, Tetrahedron Lett., 3897 (1972); (b) J. Fleischhauer, M. Beckers, and H.-D. Scharf, ibid., 4275 (1973); (c) N. H. F. Beebe and J. R. Sabin, Chem. Phys. Lett., 24, 389 (1974); (d) R. C. Haddon, D. Poppinger, and L. Radom, J. Am. Chem. Soc., 97, 1645 (1975).
(3) H. Staudinger and E. Anthes, Ber., 46, 1426 (1913).
(4) Inter alia A. DeGroot, D. Oudman, and H. Wynberg, Tetrahedron Lett., 1529 (1969); H. Wynberg, S. Reiffers, and J. Strating, Recl. Trav. Chim. Pays-Bas, 89, 982 (1969); J. M. Conia and J. M. Denis, Tetrahedron Lett., 2845 (1971); H. G. Heine, Chem. Ber., 104, 2869 (1971).
(5) Satisfactory analytical and spectroscopic data were obtained for new compounds.
(6) Cf. J. M. Conia and M. J. Robson, Angew Chem., Int. Ed. Engl., 14, 473 (1975), and references contained therein.
(7) A second isosbestic point, not shown in the figure, was observed at 374 nm.
(8) G. A. Russell, K. D. Schmitt, and J. Mattox, J. Am. Chem. Soc., 97, 1882 (1975).
(9) This value was obtained from Stern–Vollmer treatment of the extent of fluorescence quenching as a function of concentration of 1.
(10) For a review see W. G. Dauben, G. Lodder, and J. Ipaktschi, Top. Curr. Chem., 54, 73 (1975).
(11) Since triplet energies of 1 and 2 probably do not differ greatly, a mechanism involving the triplet state of 1 need not necessarily occur in stepwise fashion.
(12) Experiment performed by Mr. A. Blank.
(13) R. Bishop and N. K. Hamer, J. Chem. Soc. C, 1197 (1970).
(14) 2 survived gas chromatographic analysis at 100 °C without measurable decomposition.

Mordecai B. Rubin,* Moshe Weiner

Department of Chemistry
Technion, Israel Institute of Technology
Haifa, Israel

Hans-Dieter Scharf

Institut für Organische Chemie, Technische Hochschule
Aachen, Germany

## Ion Cyclotron Resonance Investigation of the Decarbonylation of Aldehydes by $(\eta^5\text{-}C_5H_5)Ni^+$

Sir:

Ion cyclotron resonance spectroscopy (ICR) is proving to be a valuable tool for investigating the reactions,[1–6] thermochemical properties,[4–6] and photochemistry[7] of metal ions in the gas phase.[8] The most significant results to date have involved the determination of metal–ligand bond dissociation
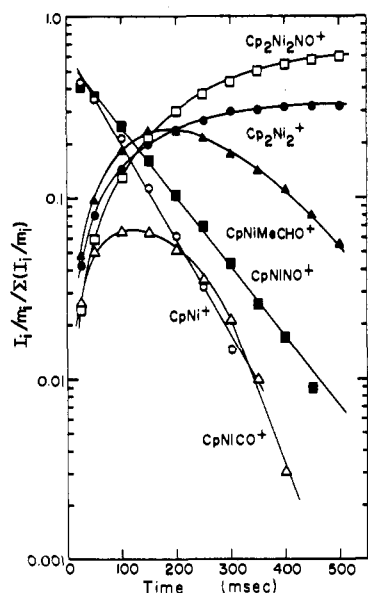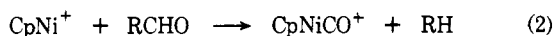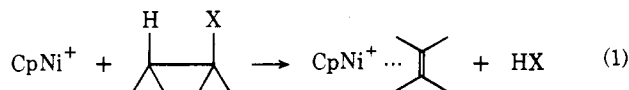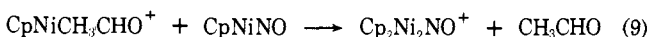
**Figure 1.** Temporal variation of relative ion abundance in a 1.2:1 mixture of CpNiNO and $CH_3CHO$ (total pressure $5 \times 10^{-7}$ Torr) following a 20-eV, 10-ms electron beam pulse.

energies of 30 n-donor bases interacting with the cyclopentadienyl nickel cation $(\eta^5\text{-}C_5H_5)Ni^+$.[6] During the course of these studies we observed many reactions of this species with the n-donor bases examined, including, for example, dehydrogenation (reaction 1, X = H), dehydrohalogenation (reaction 1, X = F, Cl), and decarbonylation (reaction 2).[9] Although the

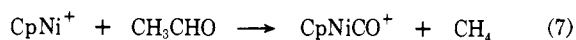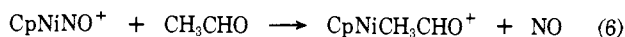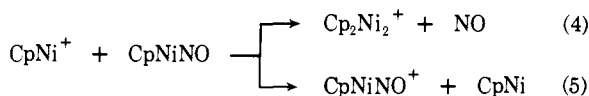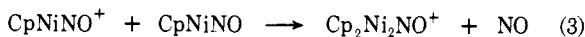$$CpNi^+ + \overset{H \quad X}{\underset{}{\bigwedge\!\!\!\!\bigwedge}} \longrightarrow CpNi^+ \cdots \overset{}{\underset{}{\bigvee}} + HX \quad (1)$$

$$CpNi^+ + RCHO \longrightarrow CpNiCO^+ + RH \quad (2)$$

general process 1 is not unexpected for a reactant ion which can behave as a Lewis acid,[3-5,10] the decarbonylation reaction 2 may be uniquely characteristic of transition metal cations due to their variable oxidation states. While decarbonylation of aldehydes has been extensively studied in solution[11,12] and on solid surfaces,[13] we feel that the observation that this reaction occurs at low pressures in the gas phase in a single bimolecular encounter is particularly significant.

When a 1.2:1 mixture of CpNiNO and acetaldehyde is examined using trapped ion ICR techniques[14] with an ionizing electron energy of 20 eV, the sequence of reactions 3–9 is initiated by $CpNiNO^+$ and $CpNi^+$ and accounts for the temporal

$$CpNiNO^+ + CpNiNO \longrightarrow Cp_2Ni_2NO^+ + NO \quad (3)$$

$$CpNi^+ + CpNiNO \left\{ \begin{array}{l} \longrightarrow Cp_2Ni_2^+ + NO \quad (4) \\ \longrightarrow CpNiNO^+ + CpNi \quad (5) \end{array} \right.$$

$$CpNiNO^+ + CH_3CHO \longrightarrow CpNiCH_3CHO^+ + NO \quad (6)$$

$$CpNi^+ + CH_3CHO \longrightarrow CpNiCO^+ + CH_4 \quad (7)$$

$$CpNiCO^+ + CH_3CHO \longrightarrow CpNiCH_3CHO^+ + CO \quad (8)$$

$$CpNiCH_3CHO^+ + CpNiNO \longrightarrow Cp_2Ni_2NO^+ + CH_3CHO \quad (9)$$
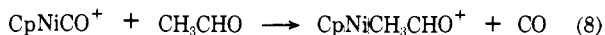
tiated by $CpNiNO^+$ and $CpNi^+$ and accounts for the temporal variation of ion abundance illustrated in Figure 1.[15] The addition of $CH_3CHO$ modifies the series of reactions observed in CpNiNO alone by the inclusion of reactions 6–9. The product of the decarbonylation reaction 7 further participates in the sequential ligand displacement reactions 8 and 9. Since it is consumed in process 8, $CpNiCO^+$ only reaches a maxi-
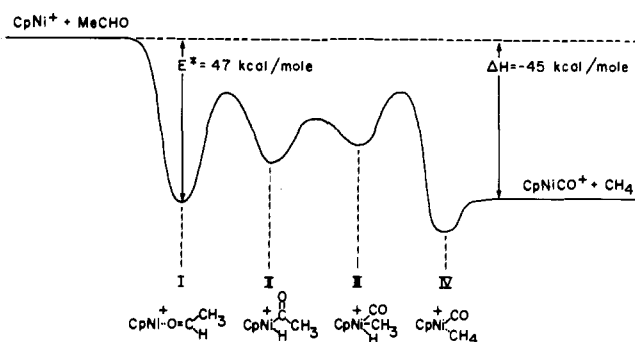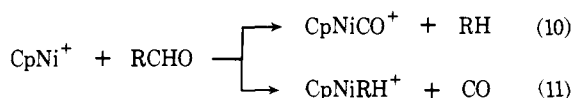
mum abundance of 7% in Figure 1. However, ion ejection techniques[16] indicate that the rate of reaction 7 is $k = (8.0 \pm 1.6) \times 10^{-10}$ $cm^3$ molecule$^{-1}$ s$^{-1}$ which is the same magnitude as the expected gas kinetic limit for ion-neutral encounters.[17]

Further observations with a variety of alkyl, alkenyl, and aryl aldehydes reveal two reaction channels, eq 10 and 11, for

$$CpNi^+ + RCHO \left\{ \begin{array}{l} \longrightarrow CpNiCO^+ + RH \quad (10) \\ \longrightarrow CpNiRH^+ + CO \quad (11) \end{array} \right.$$

decarbonylation. Reaction 10 is observed for RCHO = MeCHO, EtCHO, $i$-PrCHO, and $t$-BuCHO. $CpNiRH^+$ is observed with RCHO = 3-methylacrolein and benzaldehyde. For RCHO = acrolein, isobaric product ions result, making channels 10 and 11 indistinguishable. Decarbonylation reactions are not observed for $H_2CO$, $CF_3CHO$, $CH_3COCl$, $CH_3COBr$, $Me_2CO$, and MeOAc.

From the above observations it appears that decarbonylation reactions effected by $CpNi^+$ (1) are specific for aldehydes, (2) require that $RCO^+$ be relatively stable,[18] and (3) involve a final reaction intermediate from which competitive elimination of RH or CO can occur. The weaker of the two bonds $CpNi(RH)^+$-CO and $CpNi(CO)^+$-RH will be preferentially broken in the dissociation of this species. Reaction 11 is thus expected with $D(RH\text{-}CpNi^+) \geqslant D(CO\text{-}CpNi^+) \cong 40$ kcal/mol.[19]

An energy profile diagram and proposed intermediates for the decarbonylation of acetaldehyde is shown in Figure 2. Choice of reaction intermediates is based in part on studies of the mechanism of this process in solution.[11] The initial interaction of $CpNi^+$ with $CH_3CHO$ produces the chemically activated species I with an internal energy of 47 kcal/mol.[6] This is sufficient to allow for oxidative insertion of the metal into the C–H bond yielding II. While formation of $CH_4$ may result from a four center process starting with II, it is more likely that this is preceded by migration of $CH_3$ onto the metal, giving rise to intermediate III. The intermediate species IV results from the expected weak interaction of $CH_4$ with $CpNiCO^+$. The stabilities of the intermediates II and III and the height of the barriers connecting these species to I and IV remain unknown.[20]

The decarbonylation of aldehydes represents only one process where gas phase studies can provide insights into the energetics and mechanisms of reactions involving transition metal ions. Quantitative studies of metal-ligand interactions,[4-6] including determination of metal–hydrogen and metal–carbon bond dissociation energies,[5] will contribute in an important way to these efforts. Further studies are in progress.[9]



**Figure 2.** Proposed energy profile diagram and reaction intermediates for the decarbonylation of acetaldehyde by $CpNi^+$. The stabilities of the intermediates II and III are uncertain, as are the barriers connecting these species with the other proposed intermediates.

Grant No. E(04-3)767-8. The instrumentation used for these studies was funded by the National Science Foundation under Grant No. NSF-GP-18383.

### References and Notes

(1) M. S. Foster and J. L. Beauchamp, *J. Am. Chem. Soc.*, **93**, 4924 (1971); *ibid.*, **97**, 4808, 4814 (1975); J. L. Beauchamp, *J. Chem. Phys.*, **64**, 718, 929 (1976); R. R. Corderman and J. L. Beauchamp, *Inorg. Chem.*, **15**, 665 (1976).

(2) R. C. Dunbar, J. F. Ennever, and J. P. Fackler, Jr., *Inorg. Chem.*, **12**, 2734 (1973); R. D. Bach, J. Gauglhofer, and L. Kevan, *J. Am. Chem. Soc.*, **94**, 6860 (1972); R. D. Bach, J. Patane, and L. Kevan, *J. Org. Chem.*, **40**, 257 (1975).

(3) R. D. Wieting, R. H. Staley, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 924 (1975); A. D. Williamson and J. L. Beauchamp, *ibid.*, **97**, 5714 (1975).

(4) R. H. Staley and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 5920 (1975).

(5) J. Allison and D. P. Ridge, *J. Organomet. Chem.*, **99**, C11 (1975).

(6) R. R. Corderman and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 3998 (1976).

(7) R. C. Dunbar and B. B. Hutchinson, *J. Am. Chem. Soc.*, **96**, 3816 (1974); J. H. Richardson, L. M. Stephenson, and J. I. Brauman, *ibid.*, **96**, 3671 (1974); B. S. Freiser, R. H. Staley, and J. L. Beauchamp, *Chem. Phys. Lett.* **39**, 49 (1976).

(8) For a review see J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).

(9) R. R. Corderman and J. L. Beauchamp, unpublished results.

(10) J. Müller and W. Goll, *Chem. Ber.*, **106**, 1129 (1973); **107**, 2084 (1974).

(11) J. Halpern in "Organotransition Chemistry", Y. Ishii and M. Tsutsui, Ed., Plenum Press, New York, N.Y., 1975, p 109.

(12) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis", Academic Press, New York, N.Y., 1967, p 239; J. Tsuji and K. Ohno, *Tetrahedron Lett.*, 3969 (1965).

(13) J. McCarty, J. Falconer, and R. J. Madix, *J. Catal.*, **30**, 235 (1973); J. T. Yates, Jr., T. E. Madey, and M. J. Dresser, *ibid.*, **30**, 260 (1973).

(14) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **43**, 509 (1972).

(15) The abundance of ions from both $CH_3CHO$ alone (A. S. Blair and A. G. Harrison, *Can. J. Chem.*, **51**, 703 (1973)), and $CpNiNOH^+$ are not included in the normalization of data given Figure 1.

(16) J. L. Beauchamp and J. Y. Park, *J. Phys. Chem.*, **80**, 575 (1976); R. J. Blint, T. B. McMahon, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 1269 (1974); R. H. Staley and J. L. Beauchamp, *J. Chem. Phys.*, **62**, 1998 (1975).

(17) The Langevin, or collision rate constant,[22,23] is calculated to be $8.8 \times 10^{-10}$ $cm^3$ molecule$^{-1}$ s$^{-1}$.

(18) A measure of $RCO^+$ stability is given by the hydride affinity, or $D[RCO^+–H^-]$, of these cations. Using available thermochemical data, we compute $D[CH_3CO^+–H^-] = 233$ kcal/mol and $D[CH_3CH_2CO^+–H^-] = 225$ kcal/mol, while $D[HCO^+–H^-] = 255$ kcal/mol, for example.

(19) $D[CO–CpNi^+]$ is calculated from the proton affinity of CO, $D[CO–H^+] = 143$ kcal/mol (A. E. Roche, M. M. Sutton, D. K. Bohme, and N. I. Schiff, *J. Chem. Phys.*, **55**, 5480 (1971)) and the data given in ref 6. An additional 5 kcal/mol was added to account for $\pi$-bonding interactions.

(20) The 18-electron intermediate III may be more stable than II, a 16-electron complex, thus providing a driving force for the decarbonylation step II → III (Figure 2).

(21) Camille and Henry Dreyfus Teacher–Scholar, 1971–1976.

(22) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

(23) The value of $\alpha$ used was $4.9 \times 19^{-24}$ cm$^3$ from J. Applequist, J. R. Carl, and K.-K. Fung, *J. Am. Chem. Soc.*, **94**, 2952 (1972).

**Reed R. Corderman, J. L. Beauchamp*[21]**

*Contribution No. 5335, Arthur Amos Noyes Laboratory of Chemical Physics*
*California Institute of Technology*
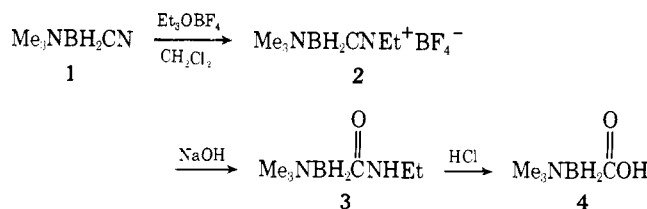*Pasadena, California 91125*
*Received May 21, 1976*

# Boron Analogues of Amino Acids. Synthesis and Biological Activity of Boron Analogues of Betaine

*Sir:*

As a class of compounds, the $\alpha$-amino acids are of unquestioned importance, being the principal constituents of protein and living matter. The postulation of a series of isoelectronic and isostructural boron analogues of the amino acids would give rise to questions about their chemical stability and the possibility of biological activity. Providing important information on this subject, we wish to report on the synthesis and structure of $Me_3NBH_2CO_2H$ (**4**) the (protonated) boron analogue of the dipolar amino acid betaine, $Me_3N^+CH_2CO_2^-$, and its *N*-ethylamide derivative (**3**). Further, we wish to issue

a preliminary report on the antitumor and hypolipidemic activity of these compounds in mice.

**3** and **4** may be obtained by the general scheme shown below.

$$Me_3NBH_2CN \xrightarrow[CH_2Cl_2]{Et_3OBF_4} Me_3NBH_2CNEt^+BF_4^-$$
$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$

$$\xrightarrow{NaOH} Me_3NBH_2\overset{\displaystyle O}{\overset{\|}{C}}NHEt \xrightarrow{HCl} Me_3NBH_2\overset{\displaystyle O}{\overset{\|}{C}}OH$$
$$\mathbf{3} \qquad\qquad\qquad\qquad \mathbf{4}$$

Although **1** may be prepared by a variety of methods,[1] we have found it to be conveniently prepared by the reaction of $NaBH_3CN^2$ with $Me_3N\cdot HCl$ (suspension) in THF.[3] The *N*-ethylnitrilium salt (**2**) was prepared by refluxing (under dry $N_2$) a solution of **1** in $CH_2Cl_2$ with 2 equiv of triethyloxonium tetrafluoroborate for 24 h. **2** was not isolated but a 1.0 N NaOH solution added slowly with vigorous stirring until basic. The organic layer was separated and the aqueous layer extracted three times with $CH_2Cl_2$. The combined $CH_2Cl_2$ solutions were dried over $CaCl_2$, concentrated (rotary evaporator), and vacuum distilled at 80 °C and $10^{-3}$ Torr to give **3**, a clear viscous liquid, in 60% yield: $^1$H NMR $(CDCl_3)$ $\delta$ 1.07 (t, $J = 8$ Hz $CH_2CH_3$), 2.75 (s, $CH_3N$), 3.57 (m, $CH_2CH_3$), 5.43 (broad s, NH); $^{13}$C NMR $(CDCl_3)$ $\delta^4$ 15.3 $CH_3CH_2$, 31.5 $CH_2CH_3$, 51.8 $CH_3N$, 182.8 CO; $^{11}$B $(CDCl_3)$, 50 °C, $\delta^{5a}$ 7.4 (1:2:1 t, $J = 90$ Hz); ir (neat in cm$^{-1}$) 3289 $\nu_{NH}$, 2915 $\nu_{CH}$, 2330 $\nu_{BH}$, 1590 amide I, 1480 amide II; mass spectral $m/e$, 144 (M$^+$, $C_6H_{17}{}^{11}BN_2O$). Anal. $(C_6H_{17}BN_2O)$ C, H, B, N.[5b]

To obtain **4**, 0.3 N HCl was added to **3** and refluxed for a period of 8 h. The solution was evaporated to dryness under reduced pressure and the residue washed with $CCl_4$ and extracted with $CHCl_3$. After evaporation of $CHCl_3$, the residue was fractionally crystallized from $H_2O$ to give a white crystalline solid (dried under vacuum, 1 h), mp (under vacuum) 147 °C with dec. Typical overall yields of **4** from **1** of 25% have been obtained.[6] $^1$H NMR $(D_2O)$ $\delta$ 2.72 (s $CH_3N$) 4.65 (s HDO); ir (KBr in cm$^{-1}$) 3130 $\nu_{OH}$ broad and superimposed with $\nu_{CH}$ in 2950–3310 region, 2380 $\nu_{BH}$, 1645 $\nu_{CO}$; mass spectral $m/e$, 118 (M$^+$, $C_4H_{12}{}^{11}BNO_2$). Anal. $(C_4H_{12}BNO_2)$ C, H, B, N.[5b]

A ca. 0.15 M solution[7] of **4** in distilled $H_2O$ (in an evacuated flask) was stable towards $H_2$ evolution for a period of 1 month. After standing for 1 week (in an evacuated flask) a ca. 0.15 M solution of **4** in 1 N HCl gave a 25.7% theoretical yield of $H_2$ and 52.8% after 3 weeks.[8] No changes in the ir spectra of **4** were noted after exposure to the atmosphere for a period of 2 months.[9]

Attempts to prepare **4** directly by acid or base hydrolysis of **1** were unsuccessful giving either boric acid or borate salts. This result is consistent with the kinetic study by Kelly[1c] on the hydrolysis of **1** to yield $B(OH)_4{}^-$. Structures **3** and **4** may also be viewed as trimethylamine derivatives of boranocarbamate, $H_3BC(O)NHR^-$, and boranocarbonate, $H_3BCO_2{}^{2-}$, ions as synthesized by Parry and co-workers.[10]

The molecular geometry of **4** was established by single-crystal x-ray analysis. Orthorhombic crystals of **4**, grown by slow evaporation of an aqueous solution, belong to the space group *Pna2*$_1$, with: $a = 12.59$ (1), $b = 5.95$ (1), $c = 19.54$ (1) Å, $U = 1464$ Å$^3$, $d_m$ (flotation in heptane-$CCl_4$) = 1.05 g cm$^{-3}$, $Z = 8$, $d_c = 1.061$ g cm$^{-3}$. Weissenberg photographs of the reciprocal lattice levels recorded from several crystals rotating about the *a* axis consistently showed that diffuse streaking was present along festoons with constant *k* when *h* was odd; the origin of this observation is under further investigation. For the x-ray analysis the intensities of 1288 reflections with $\theta < 65°$ were recorded at 25 °C on an Enraf-Nonius