The Reaction of Dimethylamidotrihydroborate(1−) with Diborane. A New Synthesis of μ-Dimethylaminodiborane

Sir:

The recent study of the basicity of sodium dimethylamidotrihydroborate(1−), $Na(CH_3)_2NBH_3$, by Gilje and Ronan[1] prompts us to report our findings on the chemistry of this material. We have compared $(CH_3)_2NBH_3^-$ and its isoelectronic counterpart trimethylamine in their behavior toward diborane. It is well known that trimethylamine reacts with diborane to produce trimethylamine–borane,[2] a symmetrical cleavage product;[3] unlike trimethylamine, $Na(CH_3)_2NBH_3$ reacts with diborane in diglyme (diethylene glycol dimethyl ether) to generate the unsymmetrical cleavage products μ-dimethylaminodiborane and sodium tetrahydroborate in good yield.

$$(CH_3)_2NBH_3^- + B_2H_6 \rightarrow \mu\text{-}(CH_3)_2NB_2H_5 + BH_4^-$$

The $Na(CH_3)_2NBH_3$ was prepared by the reaction of dimethylamine–borane with sodium hydride in monoglyme (ethylene glycol dimethyl ether) and isolated by precipitation with dioxane to form $Na(CH_3)_2NBH_3 \cdot 0.5C_4H_8O_2$.[4] In a typical experiment a 500-ml reaction vessel was charged in a dry nitrogen atmosphere with 1.328 g (10.60 mmoles) of $Na(CH_3)_2NBH_3 \cdot 0.5C_4H_8O_2$ and 8 ml of dry diglyme, transferred to the vacuum line, and evacuated. The vessel was cooled to −196° and a 17.50-mmole sample of diborane was condensed in. The bulb was sealed, removed from the vacuum line, and warmed to room temperature with intermittent swirling of the solution. After 20 min, the vessel was opened to the vacuum line, and all volatile materials were distilled through a trap maintained at −45° into a trap at −196°. Complete separation of the more volatile products from diglyme required repeated fractionation through the −45° trap, and for this reason the amount of solvent employed should be kept to a minimum. The μ-dimethylaminodiborane was separated from the liberated dioxane by fractionation through a −78° trap and from the excess diborane by distillation into a −112° trap. The μ-dimethylaminodiborane was identified by comparison of its gas-phase infrared spectrum with that reported in the literature[5] and by its characteristic vapor pressure of 101 mm at 0°.[6] The presence of sodium tetrahydroborate was confirmed by an ^{11}B nmr spectrum[7] of a monoglyme solution of the solid material remaining in the reaction vessel. Recovered in this experiment were 8.72 mmoles of diborane, implying a loss of 8.78 mmoles, and 6.65 mmoles of μ-dimethylaminodiborane, a yield of 63% based upon $Na(CH_3)_2NBH_3 \cdot 0.5C_4H_8O_2$.

Yields of pure μ-dimethylaminodiborane as high as 80% can be attained when more diglyme is used, but this is offset by the tedious separation of the product from the solvent. Yields are generally higher if at least a 50% excess of diborane is employed. For preparative purposes the actual isolation of $Na(CH_3)_2NBH_3$ is unnecessary, and a diglyme solution of this material, separated from excess sodium hydride, may be directly treated with diborane to give satisfactory yields of μ-dimethylaminodiborane.

We have also compared the ^{11}B nmr spectra of $(CH_3)_2NBH_3^-$ and dimethylamine–borane to determine the effect of removing the NH proton on the chemical shift and coupling constant. The spectrum of $Na(CH_3)_2NBH_3 \cdot 0.5C_4H_8O_2$ in monoglyme consists of a quartet with $J = 84$ Hz and δ +14.7 ppm relative to $(C_2H_5)_2OBF_3$ (internal capillary). The spectrum of dimethylamine–borane in monoglyme obtained under identical conditions shows a quartet with $J = 95$ Hz and δ +13.5 ppm. Although the chemical shift of dimethylamine–borane determined in this work is not in exact agreement with the published value of +14.2 ppm,[8] there is no doubt concerning the coupling constants and the relative upfield shift of the $(CH_3)_2NBH_3^-$ quartet compared to dimethylamine–borane. The removal of the NH proton from dimethylamine–borane causes a redistribution of electronic charge resulting in a slight increase in shielding at the boron nucleus and the CH protons, which is reflected in a similar upfield shift of 1.3 ppm[1] for the methyl resonance in the proton spectrum. It is interesting to note that the decrease in ^{11}B–H coupling upon removal of the NH proton from dimethylamine–borane is paralleled by a similar decrease in ^{13}C–H coupling when the NH proton is removed from the trimethylammonium ion. The ^{13}C–H coupling constants for trimethylammonium ion and trimethylamine are 144[9] and 131 Hz,[10] respectively.

Acknowledgment. This work was supported by the National Science Foundation.

(1) J. W. Gilje and R. J. Ronan, *Inorg. Chem.*, **7**, 1248 (1968).
(2) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 780 (1937).
(3) R. W. Parry and L. J. Edwards, *ibid.*, **81**, 3554 (1959).
(4) V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *ibid.*, **83**, 2471 (1961).
(5) D. E. Mann, *J. Chem. Phys.*, **22**, 70 (1954).
(6) A. B. Burg and C. L. Randolph, Jr., *J. Am. Chem. Soc.*, **71**, 3451 (1949).
(7) The ^{11}B nmr spectra discussed in this paper were obtained with a Varian HA-100 spectrometer operating at 32.1 MHz.
(8) D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **86**, 1505 (1964).
(9) Determined from ^{13}C satellites in the proton spectrum of trimethylammonium chloride in D_2O.
(10) E. A. V. Ebsworth and N. Sheppard, *J. Inorg. Nucl. Chem.*, **9**, 95 (1959).

Philip C. Keller
Department of Chemistry, University of Arizona
Tucson, Arizona 85721
Received July 31, 1968

The Supposed Reduction of Nitrogenpentaammineruthenium(II) Salts by Sodium Borohydride

Sir:

We have reported[1,2] that nitrogenpentaammineruthenium(II) salts, $[Ru^{II}(NH_3)_5N_2]X_2$, are reduced by sodium borohydride, yielding up to one molecule of ammonia per molecule of nitrogen in the complex. Recent experiments by Shilov and coworkers[3] and by Chatt and coworkers[4] using N^{15}-labeled nitrogen have indicated that no reduction takes place. Further experi-

(1) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).
(2) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967).
(3) Yu. G. Borodko, A. K. Shilova, and A. E. Shilov, private communication.
(4) J. Chatt, R. L. Richards, J. E. Fergussen, and J. L. Love, private communication.

ments in these laboratories show that the latter conclusion is correct and that the nitrogen molecule in nitrogenpentaammineruthenium(II) salts cannot be reduced with borohydride.

Distillation of an aqueous alkaline (NaOH) mixture of $[Ru^{II}(NH_3)_5N_2]Cl_2$ or $[Ru^{II}(NH_3)_5N_2]I_2$ and $NaBH_4$ into either nickel ammonium sulfate solution[5] or hydrochloric acid yields more base when $NaBH_4$ is present than when it is absent. The amount of excess base varies with the amount of NaOH in the starting material and with the salt (chloride or iodide) used. The excess base (over that required for five molecules of ammonia per complex ion) is not reproducible, but up to 16% excess has been obtained. However, experiments using hexaammineruthenium(II) ($[Ru^{II}(NH_3)_6]Cl_2$ or $[Ru^{II}(NH_3)_6]I_2$[6]) gave exactly similar results, and ammonium chloride yields a slight excess (approximately 3%) on treatment with borohydride.

The source of the excess base is unknown. Blank experiments on $NaBH_4$ and NaOH solutions were negative. $[Ru^{II}(NH_3)_5N_2]Cl_2$ was prepared by the reaction between aquopentaammineruthenium(III), $[Ru^{III}(NH_3)_5H_2O]^{3+}$, and sodium azide, NaN_3 (method 3 of ref 2), and was recrystallized three times from water. The iodide salt was prepared metathetically from this material. Tests for hydrazine with *p*-dimethylaminobenzaldehyde[7] on both the nitrogenpentaammineruthenium(II) starting material and on the distillate from the reactions were also negative. However, it is clear from the results using hexaammineruthenium(II) that the source of the excess base is not the nitrogen molecule.

Acknowledgment. We wish to thank Dr. L. R. Melby of E. I. du Pont de Nemours, Wilmington, Del., for advice and assistance with this work, and the National Research Council of Canada for financial support.

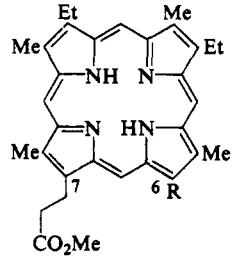
(5) R. Belcher and A. J. Nutten, "Quantitative Inorganic Analysis," Butterworth & Co., Ltd., London, 1960, p 160.
(6) F. M. Lever and A. R. Powell, Special Publication No. 13, The Chemical Society, London, 1959, p 135.
(7) M. Pesez and A. Petit, *Bull. Soc. Chim. France*, [5] **14**, 122 (1947).

A. D. Allen, F. Bottomley
Lash Miller Chemical Laboratories
University of Toronto, Toronto 5, Ontario, Canada
Received December 4, 1968

Formation of the Isocyclic Ring in Chlorophyll

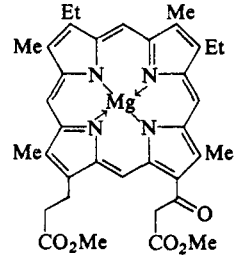
Sir:

Magnesium protoporphyrin IX is a biogenetic precursor of chlorophyll,[1] and much is known about the intervening steps.[2] However, the mode of formation of the isocyclic ring has hitherto remained obscure. Fischer[3] drew attention to the formal possibility that the propionate side chain at position 6 could be transformed to a β-keto acid derivative before cyclization, and speculations about cyclization of such derivatives have been advanced.[4] We now report the first *in vitro* cyclization of a porphyrin β-keto ester to a phaeoporphyrin derivative, and we believe that this is analogous to the *in vivo* process.

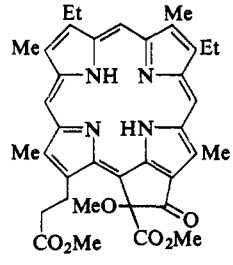


Ia, R = CO_2Me
b, R = CO_2H
c, R = $COCH(CO_2Me)CO_2Bu$-*t*
d, R = $COCH_2CO_2Me$

Rhodoporphyrin XV dimethyl ester (Ia), synthesized by the b-oxobilane route,[5] was saponified and then partially reesterified (methanolic sulfuric acid, 16 hr at 18°) to the monoester Ib.[6] The acid chloride derived from Ib was condensed with *t*-butyl methyl sodiomalonate, suspended in tetrahydrofuran. The resultant Ic was not purified, but treated directly with trifluoroacetic acid (20 min at 18°), yielding the crystalline β-keto ester Id, which was partially enolized in $CDCl_3$ (nmr spectrum); visible spectrum in chloroform, λ_{max} 410, 509, 544, 573, and 630 nm (log ε_{max} 5.35, 4.08, 4.20, 4.03, and 3.32, respectively), in 0.1 *M* sodium methoxide, λ_{max} 396, 497, 533, 568, and 620 nm (log ε_{max} 5.24, 4.11, 3.98, 3.80, and 3.58, respectively). The mass spectrum of Id did not show a molecular ion but included ions derived by fragmentation of the keto ester side chain,[7] *i.e.*, *m/e* 550 ($M-C_2H_2O_2$) and 508 ($M-C_4H_4O_3$).



II



III

Attempted cyclizations of Id under acidic or basic catalysis were all unsuccessful, as was base-catalyzed cyclization of its magnesium complex II. However, II underwent rapid oxidative cyclization on treatment with iodine in 98% methanol containing sodium carbonate at 20°. After removal of the magnesium, 10-methoxyphaeoporphyrin a_5 dimethyl ester (III)[8] was isolated in 7% yield. Formation of the isocyclic ring may be envisaged

(1) Direct proof for this has been obtained in these laboratories by Carr and Cox using specifically tritiated material [synthesized by the method of R. P. Carr, P. J. Crook, A. H. Jackson, and G. W. Kenner, *Chem. Commun.*, 1025 (1967)] in the isolated chloroplast system developed by J. M. Charlton, K. J. Treharne, and T. W. Goodwin, *Biochem. J.*, **105**, 205 (1967).
(2) L. Bogorad in "The Chlorophylls," L. P. Vernon and G. R. Seely, Ed., Academic Press, New York, N.Y., Chapter 15.
(3) H. Fischer and A. Stern, "Die Chemie des Pyrrols," Vol. II (ii), Akademische Verlag, Leipzig, 1940.
(4) A. C. Jain and G. W. Kenner, *J. Chem. Soc.*, 185 (1959); R. B. Woodward, *Ind. Chim. Belge*, 1293 (1962).
(5) A. H. Jackson, G. W. Kenner, G. McGillivray, and G. S. Sach, *J. Am. Chem. Soc.*, **87**, 676 (1965); A. H. Jackson, G. W. Kenner, G. McGillivray, and K. M. Smith, *J. Chem. Soc., C*, 294 (1968); T. T. Howarth, Ph.D. Thesis, Liverpool, 1967.
(6) Location of the free carboxylic acid group in conjugation with the macrocycle was shown by change of visible absorption spectrum from "rhodo type" in chloroform to "etio type" in methanolic sodium methoxide, and the assignment was confirmed by nmr and by the mass spectrum of the 6-ethyl-7-methyl ester prepared *via* the acid chloride of Ib.
(7) Other porphyrin β-keto esters behaved in an analogous manner on electron impact (A.E.I. MS9 spectrometer, 50 μA, 70 eV, direct inlet at 240°).