featureless, absorption in this region. In accord with the observed addition of nucleophiles at the *meso* position, each *meso* carbon atom of the porphyrin dication has a calculated excess positive charge of 0.32 electron.

The isoporphyrin described here represents direct evidence of nucleophilic attack upon the porphyrin nucleus. Formation of the isocyclic ring of chlorophyll (reported by Cox, *et al.*[9]) may also proceed through an isoporphyrin intermediate. These authors showed that a magnesium porphyrin substituted with a β-keto ester side chain was oxidized, by iodine in methanolic sodium carbonate, to a porphyrin containing an isocyclic ring. This ring formation was envisaged as a coupling between a porphyrin cation radical and an enolate radical. However, in view of the low oxidation potential[10] ($E_{1/2}$ = 0.77 V *vs.* sce) at which magnesium porphyrin dications may be formed, we suggest that formation of the isocyclic ring involves attack of the β-keto ester *enolate anion* onto the *porphyrin dication.*[11] The resulting isoporphyrin can in this case lose a proton to form a neutral *meso*-substituted porphyrin.

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(9) M. T. Cox, T. T. Howarth, A. M. Jackson, and G. M. Kenner, *J. Amer. Chem. Soc.*, 91, 1232 (1969).

(10) A. Stanienda and G. Biebl, *Z. Physik. Chem.* (Frankfurt), 52, 254 (1967).

(11) Aside from direct oxidation of magnesium porphyrins to the dication state, disproportionation of the π cation radical also affords a small yield of the dication, *viz.* 2Mg(porphyrin)$^+$ $\rightleftarrows$ Mg(porphyrin) + Mg(porphyrin)$^{2+}$.

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On the Exchange of Trimethylamine with Trimethylamine–Borane in Benzene. A Caveat Concerning the Interpretation of Nuclear Magnetic Resonance Data

Sir:

A recent publication in this journal[1] presented conclusive nmr evidence concerning the rapid exchange at room temperature of trimethyamine–trimethylborane and of trimethylphosphine–trimethylborane with the corresponding free Lewis base. The same paper also stated that trimethylamine–borane exchanged with trimethylamine in benzene solution, whereas mixtures of the same components in glyme (1,2-dimethoxyethane) showed no evidence of exchange even at 80°. The conclusions concerning exchange were based on the temperature dependence of the chemical shift of trimethylamine–borane when mixed with trimethylamine in benzene, and on the lack of such a temperature dependence in glyme. These results were surprising, since they seemed to require a specific and strong participation of the solvent in the assumed exchange process, and since they were at odds with the observation that tertiary amine–boranes only slowly equilibrate with other amines in benzene solution and at room temperature.[2] It was, therefore, decided to examine more closely the nmr behavior of trimethylamine–borane and of trimethylamine in benzene over wide concentration and temperature ranges.

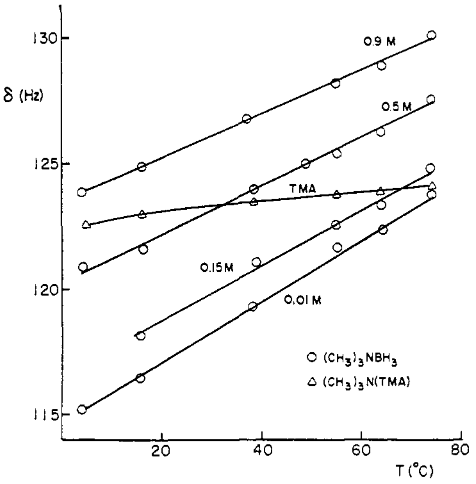

Figure 1. Temperature and concentration dependence of the chemical shifts of trimethylamine–borane and of trimethylamine. (The chemical shift of trimethylamine is independent of concentration and nearly independent of temperature.)

All spectra were run at 60 MHz on a Varian A-60A spectrometer, on solutions prepared from sublimed trimethylamine–borane and solvents dried over molecular sieve 3A. Side bands generated from internal tetramethylsilane and placed in close proximity to the peaks of interest were used to minimize errors in the determination of chemical shifts. Chemical shift data are referred to internal tetramethylsilane and correspond to the methyl protons in free or coordinated trimethylamine; they are quoted in hertz downfield from the reference, with a probable error no larger than ±0.2 Hz. Temperatures were calibrated by the chemical shift differences in methanol or ethylene glycol.

The following facts were established. The chemical shift of trimethylamine in benzene is independent of concentration in the range 0.01–0.9 *M*, only slightly dependent on temperature in the range 4–74°, and independent of admixed trimethylamine–borane. The chemical shift of trimethylamine–borane in benzene, on the other hand, depends on all of the above variables. First, there is a downfield shift with increasing concentration. Second, at fixed concentration, there is a downfield shift with increasing temperature. The temperature coefficient of the shift is larger at the lower concentrations and the combined effect of concentration changes in the range 0.01–0.9 *M* and temperature changes from 4 to 74° can produce chemical shift differences as large as 15 Hz. The results are given in Figure 1. Finally, mixtures of trimethylamine–borane and trimethylamine gave chemical shifts for the borane adduct which were *always downfield* relative to the shift

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(1) A. H. Cowley and J. L. Mills, *J. Amer. Chem. Soc.*, 91, 2911 (1969).

(2) G. E. Ryschkewitsch, unpublished results.

for the borane adduct by itself. The magnitude of the downfield shift increased with the trimethylamine concentration, and again depended on the concentration of trimethylamine–borane and on the temperature (Tables I and II).

Table I. Chemical Shift Differences[a] between Trimethylamine (TMA) and Trimethyamine–Borane (TMAB) in Benzene Solution

Temp, °C	δ(TMA) − δ(TMAB), Hz[b] Separate components	Mixture	δ(TMA) − δ(TMAB), Hz[c] Separate components	Mixture
4	1.6	+1.0	8.4	6.9
16	1.3	>0	6.4	6.2
38	−0.5	−1.7	4.1	4.0
55	−1.8	−2.6	2.4	2.2
64	−2.5	−3.9	1.6	1.5
74	−3.5	−4.8	0.4	

[a] Measured in Hz at 60 MHz. [b] [TMAB] = 0.5 *M*, [TMA] = 0.2 *M*. [c] [TMAB] = [TMA] = 0.01 *M*.

Table II. Effect of $(CH_3)_3N$ on the Chemical Shift[a] of $(CH_3)_3NBH_3$ in Benzene Solution

[TMAB],[b] *M*	[TMA],[c] *M*	δ(TMA) − δ(TMAB), Hz 38°	74°
0.9	0	−3.3	−6.1
0.9	0.09	−3.9	−6.2
0.9	0.6	−4.9	−7.1

[a] Measured in Hz at 60 MHz. [b] TMAB = $(CH_3)_3NBH_3$. [c] TMA = $(CH_3)_3N$.

Two observations now can be made concerning the data represented by Figure 1. First, in the absence of an interaction between the two components, the chemical shifts defined by the temperatures and concentrations falling below the trimethylamine curve should behave qualitatively as if exchange were taking place, *i.e.*, the two peaks move closer together as the temperature is raised. Mixtures in fact duplicate this behavior. Reference to Table I shows that an increase in concentration of the components in the mixture also decreases the difference in the chemical shifts, as would be expected as the result of exchange. Second, in the absence of exchange the two peaks should move farther apart for conditions represented by the region above the trimethylamine curve, *i.e.*, at high enough concentrations of amine–borane or at higher temperatures. This is indeed confirmed by the data in Table I, which are representative of a larger number of experiments with mixtures. These data and the ones in Table II show an increase in the peak separation with increasing temperature and are not compatible with the hypothesis that exchange between free and bound amine is taking place on the nmr time scale, whether by a dissociative or by a bimolecular displacement mechanism. Thus, the role of benzene in influencing the nmr behavior does not consist in assisting the exchange kinetics, as previously proposed,[1] but must be related to special and differentiating solvation effects on the separate components of the system.

A clue to the role of benzene is found when the chemical shifts of trimethylamine and of trimethylamine–borane are compared in benzene and in diethyl ether, using tetramethylsilane in either solvent as a common reference. Transfer of trimethylamine from ether to benzene produces an upfield shift of only 3.0 Hz, whereas 0.5 *M* trimethylamine–borane shifts by 30.5 Hz.[3] Apparently benzene solvates trimethylamine–borane in a conformationally much more specific way than it does the free amine, so that the magnetic anisotropy is more fully felt. The larger temperature coefficient of the chemical shift for the borane adduct is then explainable in terms of a reduction of the anisotropy associated with the solvent sphere through averaging over more conformers as the temperature increases. Since trimethylamine–borane is associated to a considerable degree in benzene,[4] high concentration, where association is greatest, should reduce specific solvation and thus would lead to downfield shifts, as is observed. Introduction of magnetically isotropic constituents into the solution which also could associate preferentially with the amine–borane likewise should give downfield shifts. This is indeed observed when trimethylamine is added. An additional confirmation of this notion is found in the fact that diethyl ether, added in small concentrations to trimethylamine–borane in benzene, produces downfield shifts of similar magnitude.

This kind of behavior is rarely predictable. Care must, therefore, be exercised in the interpretation of chemical shifts and their temperature dependence for mixtures. Rapid self-association equilibria and specific solvation effects may very well combine to simulate data expected for rapidly equilibrating solutes.

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[3] Tetramethylsilane shifts by 12 Hz upfield going from ether to benzene.

[4] H. Nöth and H. Beyer, *Chem. Ber.*, **93**, 923 (1969).

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1-Cyano Substituent Effects on 2-Apo- and 2-Apoisobornyl Solvolysis

Sir:

Much work has been devoted to the solvolysis study of the bicyclo[2.2.1]hept-2-yl system.[1] One major problem yet unresolved is whether the considerably large *exo*:*endo* rate ratio is due to σ participation in the transition state of *exo* derivatives or to other factors.[2]

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[2] (a) P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts,