On the Morpholine Borane Reduction of Acetone

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Abstract: The reaction of morpholine borane with acetone in aqueous solution at pH 5 and 25° results in the formation of 2-propanol and the evolution of hydrogen. The total molar quantity of these products equals three times the molar quantity of amine borane consumed. The number of hydridic hydrogens, per BH_3 unit, used for reduction of the carbonyl varies from unity in dilute acetone solution to about 2.7 in concentrated acetone. This product distribution is attributed to competition between ketone and water for hydride-containing intermediates, possibly hydroxyboranes, formed after the rate-determining step. In anhydrous acetone, only two-thirds of the available hydride is used for reduction of the ketone suggesting that, in the absence of water, diisopropoxyborane may be a reaction product.

It previously had been reported that, in aqueous solution, the morpholine borane reduction of acetone to 2-propanol proceeds with evolution of hydrogen, indicating hydrolysis of soluble hydride, even under conditions where hydrolysis of the amine borane itself is negligible.[1] This contrasts to the reaction of various ketones with sodium borohydride where all four hydridic hydrogens are used to reduce the carbonyl function[2,3] and has prompted us to investigate the stoichiometry of the former reaction by studying product distribution as a function of reactant concentration.

Experimental Section

Materials. Spectroquality reagent acetone, obtained from Matheson Coleman and Bell, was used without further purification for the product distribution studies and stored over potassium carbonate or calcium hydride prior to use in vacuum-line reactions. Morpholine borane was prepared, as previously described,[4] in greater than 95% purity based on its hydridic hydrogen content. Further purification resulted from recrystallization from water. *Anal.* Calcd for $O(CH_2)_4NHBH_3$: H (hydridic), 3.00; B, 10.72; N, 13.87. Found: H (hydridic), 2.97; B, 10.71; N, 13.97. Analytical grade 2-propanol (Baker) was used without further treatment. Morpholine (Fisher) was distilled *in vacuo* and stored over calcium hydride prior to use. Diborane was prepared according to the method of Finholt and coworkers.[5] Diisopropoxyborane was prepared by a method similar to that of Brown, Schlesinger, and Burg.[6] The infrared spectrum of this compound exhibited frequencies consistent with assignments of Lehman, Weiss, and Shapiro.[7] Analysis was based on hydrogen evolved on hydrolysis. *Anal.* Calcd for $C_6H_{15}O_2B$ (129.8): H (hydridic), 0.77. Found: H (hydridic), 0.79; mol wt (vapor density), 138, 134.

Product Distribution Studies. A 100-ml, round-bottom flask was equipped with a 125-ml pressure-equalizing dropping funnel which was connected, by means of a ground-glass adapter and Tygon tubing, to a water-filled gas buret. Morpholine borane, in the form of an aqueous solution of known concentration or as the solid reagent, was contained in the flask. Acetone (anhydrous or as an aqueous solution) was admitted to the dropping funnel. The apparatus was made leak-tight and submerged in a constant-temperature water bath (Precision Scientific Co.) which was maintained at 25 ± 0.02°. The reaction was begun by adding acetone to the amine borane. Most reactions were allowed to proceed until greater than 99% of the morpholine borane had been consumed (1–2 days) as determined by an iodometric analysis[8] of the final solutions (Table I). In order to ensure that, during analysis, no amine borane would be consumed by the acid-catalyzed reduction of acetone,[1] the analysis, which is normally carried out in strong acid solution, was performed in buffered solutions (pH 3) where the consumption of iodine by soluble hydride is still very rapid compared with the rate of reduction of acetone.

Evolved hydrogen was determined manometrically. Reaction mixtures were analyzed for 2-propanol using a Wilkins 600D Aerograph with flame ionization detector in conjunction with a Sargent Model SR recorder, by comparing the appropriate chromatographic peak area with those obtained with standard 2-propanol–aqueous acetone solutions. Potassium acid phthalate was used to buffer the solutions at pH 5 when the acetone concentration was less than 12 *M*.

In a study of the reactivity of morpholine borane with 2-propanol, a 0.0505-g (0.50 mmole) sample of morpholine borane was added to 50 ml of an aqueous (0.03 *M*) solution of 2-propanol buffered at pH 5. After 24 hr at 25°, less than 0.13% of the morpholine borane had reacted as determined by an iodate analysis.

Vacuum-Line Experiments. A conventional high-vacuum apparatus[9] was employed. In a typical experiment, 0.54 g (5.36 mmoles) of morpholine borane was treated with 9.1 g (0.16 mole) of acetone, and the solution was stirred 4 days at 23–26°. A total of 3.7 mmoles of hydrogen was collected in a Toepler pump. The infrared spectrum of the solution showed strong absorption at 1327, 1371, 1395, and 1430 cm^{-1}.

In a separate experiment, 0.70 mmole of diisopropoxyborane was condensed *in vacuo* onto 2.1 mmoles of morpholine in 5.4 ml of acetone, and the solution was allowed to stand 4 days at 25°. A total of 0.15 mmole of hydrogen was collected. Evaporation of volatile material gave a hygroscopic white solid whose infrared spectrum showed strong absorption between 1300 and 1400 cm^{-1} and a strong band at 2410 cm^{-1}. In a similar experiment, 0.25 mmole of hydrogen was evolved from the reaction of 0.58 mmole of diisopropoxyborane with 19.3 mmoles of morpholine in 3 ml of acetone. Volatile material was removed leaving a white solid residue. Treatment of the residue with water resulted in the evolution of an additional 0.13 mmole of hydrogen. No gas was evolved on treating the volatile condensate with water.

Results and Conclusions

The total molar quantity of 2-propanol plus hydrogen produced from the reaction of morpholine borane with acetone at 25° equals the molar quantity of hydride (three times the molar quantity of BH_3) consumed. The average number of hydridic hydrogen atoms per BH_3 unit used to reduce the carbonyl (measured by 2-propanol formation) is dependent on the concentration of acetone (Table I) and varies from unity in dilute

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[8] D. A. Lyttle, E. H. Jensen, and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952)

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Table I. Product Distribution in the Morpholine Borane Reduction of Acetone at 25°

$[CH_3COCH_3]_0$,[a] M	CH_3COCH_3 Initial[c]	CH_3COCH_3 Final[c]	$O(CH_2)_4NHBH_3$ reacted[c,d]	H_2 produced[c]	$(CH_3)_2$-CHOH produced[c]	$CH_3)_2CHOH$ produced/$O(CH_2)_4NHBH_3$ reacted, mole ratio
0.119	2.7	1.5	1.03[e]	1.91	1.18	1.14
0.593	13.6	12.3	1.13	1.80	1.35	1.20
0.771	17.7	16.0	1.14	1.77	1.73	1.52
1.091	27.3	25.2	1.13	1.29	2.07	1.83
1.637	40.9	38.2	1.13	1.08	2.44	2.16
2.274	54.6	52.0	1.13	0.87	2.53	2.24
3.147	81.9	79.3	1.11	0.75	2.58	2.32
6.063	54.6	51.5	1.21	0.70	3.03	2.50
10.91	54.6	51.4	1.18	0.61	3.16	2.68
12.27	122.7	119.4	1.22	0.68	3.36	2.75
13.64[b]	68.2	66.0	1.20	0.96	2.26	1.88
13.64[b]	40.9	38.7	1.15	0.96	2.21	1.92
13.64[b]	68.2	65.8	1.22[f]	1.01	2.42	1.98
13.64[b]	40.9	38.6	1.22	1.41	2.30	1.88

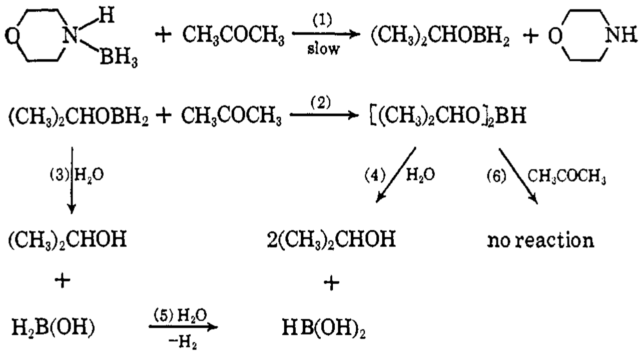
[a] Initial concentration of acetone in aqueous solution. [b] Dry acetone used as solvent. [c] Moles × 10^3. [d] Represents consumption of >99% of the morpholine borane introduced into reaction mixture. [e] 91% consumption of initial morpholine borane. [f] 98.7% consumption.

aqueous solution to about 2.7 in 12 M acetone. Previous studies of the rate of reaction in water have shown the loss of morpholine borane to be first order in both amine borane and ketone and to be catalyzed by hydrogen ion. In the absence of added water, the reaction proceeds at a rate some 20-fold slower than that in aqueous solution ($k_2 = 1 \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$ in 0.1 M acetone; $k_2 = 4 \times 10^{-6}\ M^{-1}\ \text{sec}^{-1}$ in dry acetone), and only two-thirds of the available hydride is used for reduction of the carbonyl group.

The reaction of diborane with acetone has been shown to result predominantly in the formation of diisopropoxyborane, $[(CH_3)_2CHO]_2BH$.[6] The use of only two-thirds of the hydride in morpholine borane for reduction of acetone in the absence of added water suggests that diisopropoxyborane also may be formed in this system. Further reduction by hydride may be prevented by steric hindrance to attack, by diisopropoxyborane, of another molecule of ketone. Diisopropoxyborane is quite hygroscopic, however, and absorption of water from the moist atmosphere, *e.g.*, from the gas buret, followed by hydrolysis would account for the observed product distribution of 2 moles of alcohol and 1 mole of hydrogen per mole of amine borane consumed.

The fact that more than two-thirds of the available hydride is used to reduce the carbonyl when the reaction is carried out in wet concentrated acetone suggests the formation of hydride-containing intermediates in which such steric restrictions have been removed. Such intermediates could be hydroxyboranes, *e.g.*, H_2BOH and/or $HB(OH)_2$, possibly hydrated, and formed by hydrolysis of borates arising from addition of the B–H linkage across the carbonyl. Reactions represented by steps 1–6 in Scheme I appear reasonable.

Scheme I



Subsequent reactions in which water and ketone compete for hydroxyborane and dihydroxyborane would account for the formation of hydrogen and additional amounts of 2-propanol, although the product distributions suggest that if dihydroxyborane is formed *via* step 4, its rate of reaction with acetone is negligible compared to that with water. It should be noted, also, that the reaction of morpholine borane with 2-propanol is extremely slow relative to the reduction of acetone and, therefore, does not contribute to the consumption of morpholine borane in this study.

This mechanism demands that the borate linkage hydrolyze faster than the borane linkage in the intermediate isopropoxy boron hydride(s). This seems quite reasonable. Hydrolysis of numerous alkyl borates has been shown to be rapid;[10–14] *e.g.*, Steinberg and Hunter[10] have estimated a first-order rate constant greater than $6.9 \times 10^7\ \text{sec}^{-1}$ for hydrolysis of triisopropyl borate in 60% aqueous dioxane at 21°. In view of the mechanism proposed by Scattergood and coworkers[14] for borate hydrolysis, and in consideration of the relative steric hindrance to attack of these borates by solvent, the hydrolysis of mono- or diisopropoxyborane would be expected to be even more rapid. It seems reasonable that step 2 in the above mechanism may be negligible in the presence of water. As yet, however, we have no independent evidence for the relative rates of borate and borane hydrolysis in these compounds. It is interesting that Jolly and Schmitt[15,16] have proposed H_2OBH_2OH as an intermediate and $H_2OBH(OH)_2$ as a product in the reaction of diborane with aqueous ethanol at reduced temperatures. The same intermediates may be involved in both systems.

The reaction of morpholine borane with dry acetone *in vacuo* results in a mixture whose infrared spectrum (in acetone) shows absorption in the boron–oxygen stretch-

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ing region[7,17] and is similar to the spectrum of diisopropoxyborane, but attempts to isolate this compound from this reaction mixture by conventional high-vacuum techniques, to date, have been unsuccessful. This may be due to the subsequent reaction of the alkoxyborane with morpholine, a by-product of the ketone reduction. Numerous reactions of amines with borate esters have been reported,[18-22] and we have found that diisopropoxyborane does, in fact, react with morpholine in acetone solution to produce a hygroscopic white solid and slowly evolve hydrogen. This product is being investigated further.

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Bis(trifluoromethyl)dithiophosphinic Acid and Related Derivatives[1]

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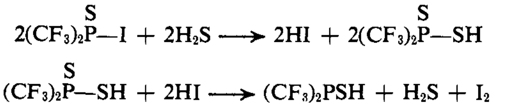
Abstract: The readily volatile new dithiophosphinic acid $(CF_3)_2PS_2H$ (mp 14°; bp estd 105°; monomeric, unlike the analogous oxygen compound) has been made by the H_2S cleavage of the nonvolatile $[(CF_3)_2PS]_2S$ (presumed), obtained by heating $[(CF_3)_2P]_2S$ with sulfur. Another process, in which $(CF_3)_2P(S)I$ is attacked by H_2S, depends upon a novel reduction process, liberating iodine. The spontaneous loss of iodine from $(CF_3)_2P(S)I$ was pushed forward by mercury, giving a 66% yield of $[(CF_3)_2P]_2S$; probably the reaction involves an anti-Arbuzov type of rearrangement. Other new derivatives of the dithiophosphinic acid include the chloride, the methyl ester, and two amides. Also reported are the thiophosphonic dichloride $CF_3P(S)Cl_2$ and the corresponding bis(dimethylamide). All of these have been fully characterized in regard to melting point, volatility, and infrared spectra, with P=S stretching and bending frequencies demonstrating a theoretically interesting trend of bond order.

The $(CF_3)_2P$ phosphines and phosphinic acid derivatives differ enough from the analogous R_2P compounds (R = ordinary alkyl or aryl) to suggest that the chemistry of the compounds of type $(CF_3)_2P(S)X$ (X = SH, SR, Cl, I, or an amido group) may not be fully predictable. Accordingly, we have made and studied such thiophosphinic compounds, as well as two examples of the thiophosphonic type $CF_3P(S)X_2$.

The new dithiophosphinic acid $(CF_3)_2PS_2H$ was obtained by two methods: addition of sulfur to $[(CF_3)_2P]_2S$[2,3] at 150° to form a nonvolatile liquid assumed to be $[(CF_3)_2PS]_2S$, which is cleaved by hydrogen sulfide at 100°; or by photochemical formation of the iodide $(CF_3)_2P(S)I$ from $[(CF_3)_2P]_2S$ and I_2, followed by an interesting reaction with H_2S, whereby half of the phosphinic material is reduced to the phosphinous state.

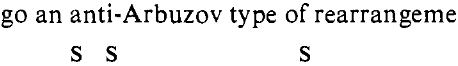


$$2(CF_3)_2\overset{S}{P}{-}I + 2H_2S \longrightarrow 2HI + 2(CF_3)_2\overset{S}{P}{-}SH$$

$$(CF_3)_2\overset{S}{P}{-}SH + 2HI \longrightarrow (CF_3)_2PSH + H_2S + I_2$$

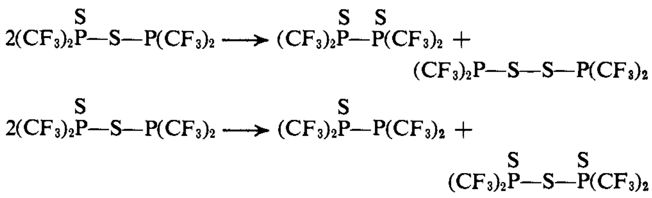
Apparently the reduction is the driving force for this result, for the analogous reaction of $(CF_3)_2P(S)Cl$ does not occur.

Although obtainable almost quantitatively as a colorless liquid, the iodide $(CF_3)_2P(S)I$ easily loses iodine, with interesting chemical results. Using mercury to remove the iodine, one might expect to obtain the diphosphine disulfide, but this would have good reason to undergo an anti-Arbuzov type of rearrangement[4]



$$(CF_3)_2\overset{S}{P}{-}\overset{S}{P}(CF_3)_2 \longrightarrow (CF_3)_2\overset{S}{P}{-}S{-}P(CF_3)_2$$

after which the resulting P-S-P compound would be expected to exchange groups in at least two ways.



$$2(CF_3)_2\overset{S}{P}{-}S{-}P(CF_3)_2 \longrightarrow (CF_3)_2\overset{S}{P}{-}\overset{S}{P}(CF_3)_2 + (CF_3)_2P{-}S{-}S{-}P(CF_3)_2$$

$$2(CF_3)_2\overset{S}{P}{-}S{-}P(CF_3)_2 \longrightarrow (CF_3)_2\overset{S}{P}{-}P(CF_3)_2 + (CF_3)_2\overset{S}{P}{-}S{-}\overset{S}{P}(CF_3)_2$$

Then the anti-Arbuzov rearrangement of the diphosphine monosulfide would produce $(CF_3)_2PSP(CF_3)_2$, which would come also from the action of mercury upon the P-S-S-P compound, and the diphosphine disulfide would go through the whole process again. If the two group exchanges should occur in equal

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(1) Supported by Grants GP-199, GP-3812, and GP-6751X from the National Science Foundation, which assisted also toward providing the instruments required for some parts of this research.

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