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Steric Effects in the Synthesis of Ortho and Para Isomers of Unsymmetrically Substituted Borazines

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The investigation of the effects of substituents and reagents on the reactivity and properties of unsymmetrically substituted borazines presents some unique challenges to the synthetic chemist. There are a variety of data which are consistent with the hypothesis that the π electrons of borazines are delocalized, at least partially. A substitutent on boron can interact with the π system by means of a resonance effect to alter the electron density at the other positions around the ring. Correlations of NMR data[1-3] provided the initial evidence for π-electron delocalization. Further comparisons of NMR data for similarly substituted borazines and amine–boranes supported the hypotheses of delocalization and resonance effects instead of simple field effects.[4]

Chemical reactivity studies have demonstrated that a substitutent on one boron has a definite influence on the reactions of the groups bound to the other boron atoms. For example $H_3B_3N_3H_3$ reacts readily with silver salts[2,3] such as AgCN to form $H_2(CN)B_3N_3H_3$ in very high yields. In contrast, $H_2(CN)B_3N_3H_3$ is totally unreactive toward silver salts under similar conditions. The compound $Cl_3B_3N_3H_3$ reacts with a stoichiometric quantity of $N(CH_3)_2H$ to form $Cl_2[N(CH_3)_2]B_3N_3H_3$ in essentially quantitative yields.[5] The dimethylamino group, an electron-donating substituent, apparently alters the chemical properties of the borazine ring to make a chlorine bound to boron in $Cl_2[N(CH_3)_2]B_3N_3H_3$ much less reactive than one in $Cl_3B_3N_3H_3$. It is certainly clear that a substituent on one boron influences the reactivity at another boron position, positions meta to each other.

Table I

Isomer Distribution for $H_2XB_3N_3H_2CH_3$

Isomer	Statistical	Reagent $HgCl_2$[6]	$SnCl_4$	BCl_3	BBr_3
% ortho	67	34	42	56	52
% para	33	66	58	44	48

Isomer Distribution for $HX_2B_3N_3H_2CH_3$

Isomer	Reagent $HgCl_2$	$SnCl_4$	BCl_3	BBr_3
% ortho,ortho	45	54	53	54
% ortho,para	55	46	47	46

There is much less research on the effects of substituents on the ring nitrogen atoms on the reactivity at the boron atoms, the relative ortho and para positions. The reaction of $H_3B_3N_3H_2CH_3$ with $HgCl_2$ yields a mixture of isomers[6] of $H_2ClB_3N_3H_2CH_3$, 70% para and 30% ortho. It was suggested that this isomer distribution must be due to some type of directive influence operative during the course of the reaction.[6] If the reaction had been random, there should have been a 67% yield of the ortho isomer and 33% of the para isomer. For comparison the chlorination of toluene[7] using $FeCl_3$ leads to the formation of 87% *p*-chlorotoluene. The directive influences in this reaction are based on electronic and steric effects of all reactants. There is some relevant chemistry which demonstrates that a steric effect[8,9] in the borazine reagent is an important factor determining reactivity. The reaction of 1,3-dimethyl-5-cyclohexylborazine[9] with either methyl or ethyl Grignard reagents leads to the formation of 80% para and 20% ortho isomers. The compound 1,3-diethyl-5-cyclohexylborazine[9] was attacked less selectively by the methyl or ethyl Grignard reagents as 60% para and 40% ortho isomers were formed.

It is clear that substituents on nitrogen have a significant steric effect on the course of substitution reactions. Substituents on boron apparently have important electronic effects which alter the reactivity at the corresponding meta positions. In this paper we report results which demonstrate the significance of a steric effect of the reagent which reacts with the borazine. We have studied the halogenation of 1-methylborazine using BCl_3, BBr_3, $SnCl_4$, and $HgCl_2$. Our data clearly indicate that the nature of the halogenating reagent has an important influence on the isomer distribution from the substitution reaction.

The compound $H_3B_3N_3H_2CH_3$ was reacted with a variety of halogenating reagents such as $HgCl_2$, $SnCl_4$, BCl_3, and BBr_3. The chlorinated products $H_2ClB_3N_3H_2CH_3$ and $HCl_2B_3N_3H_2CH_3$ were isolated by vacuum distillation and then converted to the corresponding dimethylamino derivative for isomer identification.[6] Previous research[6] has shown that the ortho and para isomers of $H_2ClB_3N_3H_2CH_3$ cannot be quantitatively separated or identified. However, the relative amounts of isomers[6] in a given sample can be determined from the relative intensities of the ^1H NMR lines of the isomers of $H_2[(CH_3)_2N]B_3N_3H_2CH_3$. The reaction for the preparation of the dimethylamino derivative uses extremely mild conditions and there is no isomerization during reaction.[6] In all cases, the entire yield of $H_2ClB_3N_3H_2CH_3$ and $HCl_2B_3N_3H_2CH_3$ from a given reaction was converted to $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ and $H[(CH_3)_2N]_2B_3N_3H_2CH_3$ to ensure against loss of a given isomer. Table I gives the relative yields of isomers. The percentages are the averages from three separate preparative reactions. Percentages of a given isomer using a specific halogenating reagent did not vary by more than ±3%.

The isomer distributions of $H_2XB_3N_3H_2CH_3$ (X = Cl, Br) clearly demonstrate that steric effects in the halogenating agent play a major role in determining the site of substitution. As

Table II. ^{1}H NMR Chemical Shift Data[a]

$H_2XB_3N_3H_2CH_3$	Ortho isomer			Para isomer	
	p-NH[b]	*o*-NH[b]	*o*-CH_3[b]	*o*-NH[b]	*p*-CH_3[b]
F	5.05	4.50	2.85	4.50	2.99
Cl	5.17	5.17	3.00	5.17	3.00
Br	5.44	5.44	3.05	5.44	3.08
$N(CH_3)_2$	4.78	4.16	3.00	4.16	2.93

[a] Chemical shifts (δ) are given in ppm downfield from Me_4Si. [b] Positions in a given isomer are relative to the boron substituent.

the coordination number about the central atom of the chlorinating agent increases, the percentage of para isomer formed increases. The reagent BCl_3 which has a coordination number of 3 yields more ortho than para isomer, whereas $SnCl_4$ with tetrahedral symmetry gives a slight excess of the para isomer. The reagent $HgCl_2$ which gives a large predominance of the para isomer must be reacting as a higher coordinated species rather than the simple linear triatomic molecule. A simple linear $HgCl_2$ species would have been expected to give more ortho then para isomer. The most reasonable explanation is that $HgCl_2$ is reacting as the solid in which the coordination number about mercury is six, a distorted octahedron.[10] This conclusion is consistent with the experimental conditions, *n*-pentane as reaction solvent. Since none of the reactions produce the statistical distribution expected from random attack on $H_3B_3N_3H_2CH_3$, the *N*-methyl group exerts some type of directive effect. The most probable directive effect is a steric effect but an electronic effect cannot be discounted.

It is of interest to compare the relative amounts of different isomers from the BCl_3 and BBr_3 reactions. The yield of the para isomer is larger for BBr_3, as expected. However, the difference is almost within the experimental error. Thus, these results would suggest that the coordination number about the central atom is more important than the size of the halogen atom. However, other data demonstrate that the nature of the particular halogen atom can have a very significant effect on reactivity. For example, $HgBr_2$ does not react with $H_3B_3N_3H_3$ under the identical conditions used for $HgCl_2$ reactions.[4] All of our data are consistent with the hypothesis that these reagents react with the borazine by a polar mechanism.[4,11] Steric effects are very important in determining the specific site of reaction. However, we do not have sufficient data to ascertain the influence of electronic effects due to substituents on nitrogen.

The ^{1}H NMR spectra of the compounds $H_2FB_3N_3H_2CH_3$, $H_2ClB_3N_3H_2CH_3$, $H_2BrB_3N_3H_2CH_3$, and $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ are interesting to compare (Table II). The most important feature of these spectra is that the ortho and para isomers can be distinguished by the ring N–CH_3 resonances in each case, except for the chloro derivative. It should be realized that the only pure isomers which have been isolated and whose spectra have been recorded are the para isomers[6] of $H_2ClB_3N_3H_2CH_3$ and $H_2[N(CH_3)_2]B_3N_3H_2CH_3$. Only mixtures of isomers of $H_2FB_3N_3H_2CH_3$ and $H_2BrB_3N_3H_2CH_3$ have been studied. The chemical shift data for both ortho and para isomers are also consistent with an additivity effect per substituent as previously observed for B-disubstituted borazine derivatives.[3] These data would suggest that both N and B substitutents interact with the π system by means of a resonance effect to alter chemical shifts of protons around the ring. However, the limitations on the nature of the possible nitrogen substituents preclude a definitive conclusion. Other factors might also influence ^{1}H NMR chemical shifts in partially delocalized systems such as borazines.

Experimental Section

Materials. All compounds described in this investigation were manipulated in a vacuum system or a purified nitrogen atmosphere. Solvents were dried and purified by conventional means. The preparation[6,12] of $H_3B_3N_3H_2CH_3$ and its reaction[6] with $HgCl_2$ in C_5H_{12} as well as product isolation[6] and isomer identification[6] using $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ have been previously described. The reactions of $H_3B_3N_3H_2CH_3$ with BCl_3, $SnCl_4$, and BBr_3 were run neat at 25 °C. The reaction times for best results were 5 h (BCl_3), 2 h ($SnCl_4$), and 1 h (BBr_3). In the case of the BBr_3 reaction, the products have not been previously described. The compound $H_2BrB_3N_3H_2CH_3$, which was obtained from both −46 and −78 °C traps in a fractionation train using −23, −46, −78, and −196 °C trap temperatures, was a liquid at room temperature with a vapor pressure of 4.0 mm at 24 °C. The solid product, $HBr_2B_3N_3H_2CH_3$, was isolated with the −23 °C trap and had a vapor pressure of 0.8 mm at 24 °C.

Compound $H_2FB_3N_3H_2CH_3$ was prepared from $H_2[(CH_3)_2N]B_3N_3H_2CH_3$ by the analogous reaction and techniques used for $H_2FB_3N_3H_3$.[1] The product $H_2FB_3N_3H_2CH_3$ was isolated in a −78 °C trap by very careful repeated fractionations and had a vapor pressure of 47 mm at 24 °C. The product was identified by mass spectral analysis and ^{1}H NMR data. Since BCl_3 and BBr_3 reacted with $H_3B_3N_3H_2CH_3$, the analogous reaction using BF_3 was attempted. There was no observed reaction after the mixture was allowed to stand at room temperature for 12 h. Both the BF_3 and $H_3B_3N_3H_2CH_3$ were recovered unchanged.

Nuclear Magnetic Resonance Spectra. The ^{1}H NMR spectra were recorded at 100 MHz by means of a Jeolco Model MH-100 spectrometer. In all cases the solvent was $Si(CH_3)_4$ for the 10% solutions.

Registry No. $H_2FB_3N_3H_2CH_3$ (ortho isomer), 63325-10-0; $H_2FB_3N_3H_2CH_3$ (para isomer), 63325-11-1; $H_2ClB_3N_3H_2CH_3$ (ortho isomer), 37053-90-0; $H_2ClB_3N_3H_2CH_3$ (para isomer), 36953-63-6; $H_2BrB_3N_3H_2CH_3$ (ortho isomer), 52920-79-3; $H_2BrB_3N_3H_2CH_3$ (para isomer), 52920-81-7; $H_2N(CH_3)_2B_3N_3H_2CH_3$ (ortho isomer), 37013-94-8; $H_2N(CH_3)_2B_3N_3H_2CH_3$ (para isomer), 37133-10-1; $HCl_2B_3N_3H_2CH_3$ (ortho,ortho isomer), 63325-12-2; $HCl_2B_3N_3H_2CH_3$ (ortho,para isomer), 63325-13-3; $HBr_2B_3N_3H_2CH_3$ (ortho,ortho isomer), 63325-14-4; $HBr_2B_3N_3H_2CH_3$ (ortho,para isomer), 63325-15-5; $HgCl_2$, 7487-94-7; $SnCl_4$, 7646-78-8; BCl_3, 10294-34-5; BBr_3, 10294-33-4.

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Influence of Internal Hydrogen Bonding on the Kinetics of Complex Formation with Nickel(II). 2. Alizarin Yellow G

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When internally hydrogen-bonded acids act as ligands in the formation of labile metal ion complexes, the reaction takes place with rate constants which are considerably below those typical for the cation in question.[1-4] These acids are also known to lose their proton to bases at rates far below the usual, diffusion controlled value.[5]

In continuation of our program of investigating the correlation between these effects we have now studied the reaction between Ni(II) and alizarin yellow G (4-(*m*-nitrophenylazo)salicylate; its monoprotonated form will be abbreviated HL^-). This enables us to draw comparisons between Ni(II)