

THE AMINOBORONATION REACTION

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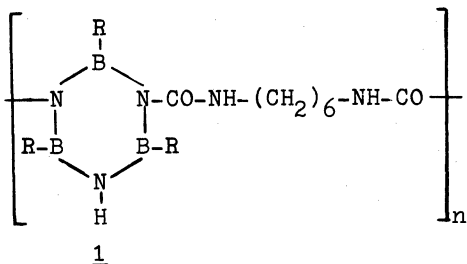
Abstract - Aminoboronation processes are surveyed and the preparative possibilities of such reactions are outlined. Several specific examples involving aminoboronation reactions with (2-pyridylamino)-diorganylboranes are presented in order to illustrate some recent developments.

INTRODUCTION

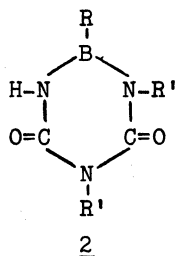
The aminoboronation reaction involves the 1,2-addition of an amino and a borane moiety of a $>B-N<$ species across a multiple bond. This process is an example of the general insertion reactions involving organometallic species (Ref. 1), the most renowned of which is the hydroboration:



However, in contrast to the extensively investigated hydroboration, relatively few aminoboronation reactions have been described and the full potential of the latter process is yet unknown. As a matter of fact, the reaction likely to be the first recorded example of an aminoboronation was not even recognized as such. In 1961 Korshak and coworkers (2) reported the reaction of B-substituted borazines with hexamethylene diisocyanate to yield copolymers containing borazine rings in the main chain, 1.



Boone and Willcockson (3) suggested this interpretation of the experimental data to be erroneous and it was noted that the cited reaction proceeds with cleavage of the borazine ring. The reaction of borazines, $(-BR-NH-)_3$, with isocyanates, $R'NCO$, was described to yield the heterocycle 2,



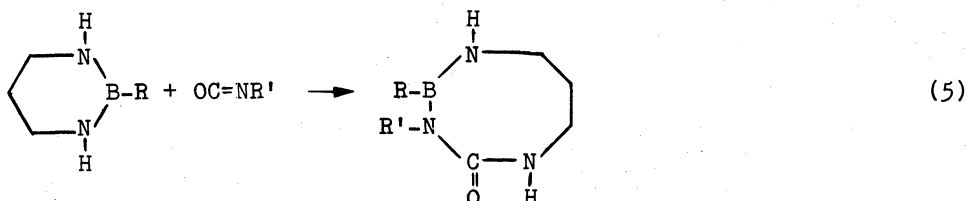
which is apparently formed in an aminoboronation/condensation reaction sequence.

SURVEY OF AMINOBORONATION REACTIONS

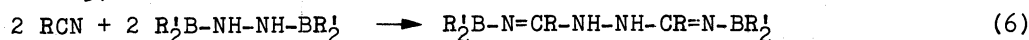
The first systematic studies on the interaction of $>N-B<$ groupings with multiple bonds described the interaction of various aminoboranes with isocyanates and isothiocyanates (Ref. 4 to 7). Although no clear reaction pattern emerged and several contradictions remained, the observed principal aminoboronation processes are readily illustrated by the following equations:



Subsequent studies provided examples of ring expansions via aminoboronation (Ref. 6 & 8 to 10):



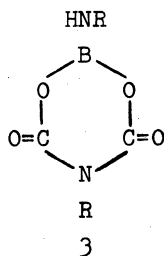
Furthermore, it was found that the CO bond of aldehydes and ketones can be aminoborated in similar fashion (Ref. 9, 11 & 12), although the great affinity between boron and oxygen may prevent the isolation of the initial aminoboronation product (Ref. 13). Also, aminoboronation of the carbon-nitrogen triple bond of nitriles with hydrazinoboranes has been described (Ref. 13):



Back-coordination of the hydrazine nitrogen to boron in the latter product was shown to result in a stable bicyclic structure involving four-coordinate boron.

AMINOBORONATION OF SMALL MOLECULES

The first aminoboronation of a small unsaturated molecule involves the reaction of carbon dioxide with tris(*t*-butylamino)borane (Ref. 4). The initial product of this reaction appears to be $RHN-B(O-CO-NHR)_2$ ($R = t$ -butyl), which immediately eliminates *t*-butylamine in an intramolecular condensation process to yield the heterocyclic species \mathfrak{J} .



A detailed investigation of the interaction of carbon dioxide with a wide variety of aminoboranes illustrated the ready aminoboronation of the former (Ref. 14). As a rule, the resultant carbamoyloxyboranes, $>B-O-CO-N<$, are formed at room temperature and can be isolated. Amines catalyze the reaction and the overall reactivity is primarily governed by the basicity of the aminoborane. Weakly basic species require relatively high reaction temperatures which tend to initiate condensation processes and thus prevent the isolation of the primary aminoboronation product. In addition, it was found that steric factors play a role in governing the reactivity of the aminoborane. It was also noted that carbon disulfide reacts much slower than carbon dioxide; this observation is readily interpreted by the various bond energy data ($B-S < B-N < B-O$). Additional aminoboronation reactions involving small molecules containing multiple bonds, e.g., CO_2 , COS and CS_2 have been

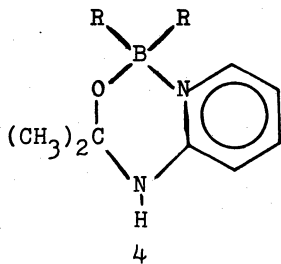
described elsewhere (Ref. 15 & 16); usually, the expected products are readily obtained. With sulfur dioxide, however, the initial aminoboronation product cannot be isolated (Ref. 17) but the overall reaction seems to offer some interesting preparative aspects, e.g.,



AMINOBORONATIONS WITH (2-PYRIDYLAMINO)DIORGANYLBORANES

(2-Pyridylamino)diphenylborane is a rather unique aminoborane species. In contrast to the chemically closely related (phenylamino)diphenylborane, the cited (pyridylamino)borane is quite insensitive to atmospheric constituents at room temperature (Ref. 11). Based on this observation a coordinated structure has been suggested for the species; a dimeric formulation obtained by coordination of the pyridyl nitrogen to the boron of a second moiety appears to account for the observed stability as well as the chemical reactions of the compound (Ref. 12). In principle, however, (2-pyridylamino)-diphenylborane reacts as an ordinary aminoborane; aldehydes, ketones, isocyanates and isothiocyanates are readily aminoboronated via a 1,2-addition of the 2-pyridylamino and the diphenylboryl moiety across the CO or CN multiple bond, respectively. Nitriles, sulfur dioxide, carbon dioxide and carbon disulfide react in analogous fashion although only one of the multiple bonds of the latter three reagents is aminoboronated.

In all cases the resultant species are stable to moisture and oxygen at ambient conditions. Boron-11 nuclear magnetic resonance data suggest the presence of four-coordinate boron in the products and, for example, 4 is suggested as the structure of the aminoboronation product of acetone.



An analogous structure is formulated for the product of the aminoboronation of the carbon-carbon triple bond of $\text{C}_6\text{H}_5\text{OC}\equiv\text{CH}$ with (2-pyridylamino)dipropylborane (Ref. 18). Indeed, the formation of a coordinated cyclic structure seems to be the major driving force for the aminoboronation reactions utilizing (2-pyridylamino)diorganylboraness - (amino)dipropylborane does not aminoboronate the cited alkyne under analogous conditions - and the aminoboronation of a carbon-carbon multiple bond constitutes a significant breakthrough in the utilization of the aminoboronation reaction.

CONCLUSION

The interaction of a >N-B< unit with a multiple bond proceeds via 1,2-addition of the amino and borane moiety across the multiple bond. This reaction can be used for chain elongation but, in some instances, subsequent intramolecular condensation occurs and can lead to the formation of heterocyclic species. Alternatively, a heterocycle containing an annular B-N bond may undergo ring expansion via insertion of a multiple bond between boron and nitrogen. The primary driving force of the aminoboronation reaction appears to be the basicity of the employed B-N derivative though steric factors can definitely promote or retard the progress of the reaction. Moreover, the possible formation of a coordinated heterocyclic system involving four-coordinate boron seems to greatly enhance the reactivity of a B-N bond toward a multiple bond and also provides for substantial chemical stability of the products.

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