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Alkenylborazines

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ALKENYLBORAZINES

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Abstract: A series of vinyl, allyl and styryl borazines were prepared by substitution reactions of B-trichloro-N-trimethyl and B-trihydrido-N-triphenyl borazines with Grignard reagents. The compounds prepared were characterized by a combination of infrared spectroscopy, ^1H , ^{13}C , ^{11}B NMR spectroscopy, mass spectrometry, and elemental analysis. The free radical polymerization of the monomers was investigated as was their copolymerization behavior with styrene.

INTRODUCTION

Considerable interest exists in the development of precursors to boron-nitride (BN) solid state ceramic materials. Typically, these materials are prepared by high energy means (high temperature, high pressures, pyrolysis, etc.) involving simple starting materials.¹⁻³ Recently alternate routes have attracted attention which involve the combination of the boron and nitrogen atoms as adducts or strategically prepared polymeric precursors.⁴⁻⁷ The goal to these investigations has been to prepare boron and nitrogen containing polymeric materials which are easier to handle and conversion to ceramic material can be carried out at lower energy. The concept has

been successfully applied to the preparation of silicon-carbide/silicon-nitride ceramic materials.⁸

Polymers containing a boron-nitrogen backbone are difficult to prepare due to the thermal stability of the related trimeric rings. Therefore, most BN polymer precursors involve the linking together of borazine rings and has allowed for the preparation of a number of cyclomatrix and cyclolinear polymers.^{6,7} In this paper we report a group of cyclic borazine derivatives which bear polymerizable organic pendant groups. These type of compounds do not incorporate the boron-nitrogen groups into the backbone but allow for the preparation tractable linear polymers which potentially can be fabricated before final pyrolysis.

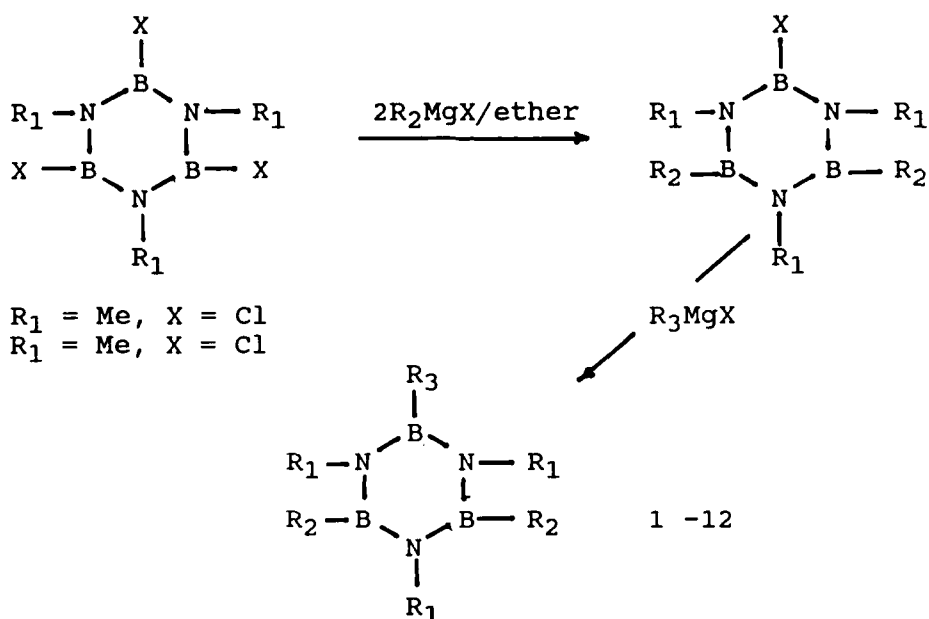
RESULTS AND DISCUSSION

Preparation of the Monomers

A series of twelve unsymmetrically substituted cyclic borazines were prepared by the reactions of the appropriate Grignard reagent with B-chloro-N-methyl^{9,10} and B-hydrido-N-phenyl^{11,12} borazines as described in Scheme 1.

It has been previously reported that reaction of Grignard reagents with the B-chloro-N-methyl borazine to prepare unsymmetrically substituted borazines proceeded with some degree of alkyl/aryl exchange.¹⁰ This was found to be true in this case and prevented the preparation of pure quantities of B-vinyl-(1), B-allyl-pentamethyl borazines (2) and the B-styryl-B-diphenyl-N-trimethyl borazine (6). The composition of these materials was estimated using capillary gas chromatography. Attempted separation of these

Scheme 1



$\text{R}_1 = \text{Me}, \text{R}_2 = \text{Me}, \text{R}_3 = \text{vinyl}(1), \text{allyl}(2), \text{styryl}(3)$
 $\text{R}_1 = \text{Me}, \text{R}_2 = \text{Ph}, \text{R}_3 = \text{vinyl}(4), \text{allyl}(5), \text{styryl}(6)$
 $\text{R}_1 = \text{Ph}, \text{R}_2 = \text{Me}, \text{R}_3 = \text{vinyl}(7), \text{allyl}(8), \text{styryl}(9)$
 $\text{R}_1 = \text{Ph}, \text{R}_2 = \text{Ph}, \text{R}_3 = \text{vinyl}(10), \text{allyl}(11), \text{styryl}(12)$

mixtures by chromatography on silica gel resulted in the decomposition of the material.

The B-styryl-B-dimethyl-N-trimethylborazine, compound 3, was found to be a solid and could be isolated in pure form by vacuum sublimation. The exchange of substituent groups also occurred in the preparations of the unsymmetrically substituted B-vinyl- (4), and B-allyl-B-diphenyl-N-trimethyl borazines (5), however the desired products were solids and could be isolated by crystallization.

The preparation of the desired monomers from the B-hydrido-N-triphenyl borazine proceeded with only a small degree of exchange. Again the substitution of

the hydrogen atoms was a stepwise process and allowed for the preparation of good yields of the desired unsymmetrically substituted borazine.

Polymers

Polymerization of the vinyl and styryl substituted borazines were attempted by free radical means using AIBN as the initiator. It was found from these studies that only the styryl substituted borazines underwent polymerization. Unsuccessful attempts at polymerization of the allyl substituted borazines were conducted using Ziegler-Natta type catalysts ($\text{TiCl}_4/\text{AlEt}_3$). Monomer degradation due to coordination with the catalyst was observed in this system.

The attempted polymerization of the vinyl substituted monomers have thus far also been unsuccessful. The B-vinyl substituted borazines were not susceptible to free radical polymerization by AIBN and nearly all of the starting material in each case was recovered. The ^{13}C and ^{11}B NMR data obtained for each compound were examined in an attempt to uncover some of the reasons for this lack of reactivity. The beta carbon chemical shifts indicate electron donation to boron but the range of shifts is not significantly different from simple vinyl boranes.¹³ The difference in ^{11}B shifts between B-methyl and B-vinyl centers is not large thereby suggesting small shifts in charge density. These data suggest that the vinyl group may not be able to stabilize a free radical thus be a poor propagating species. Other effects such as radical hydrogen atom transfer in the N-methyl borazines and steric crowding in the N-phenyl borazines undoubtedly

also play a significant role in the observed reluctance of these monomers to undergo radical addition polymerization.

The styrl substituted monomers have been found to readily undergo polymerization via free radical methods. In the case of the B-styrl-B-dimethyl-N-trimethylborazine (3), which was obtained as a pure compound, the polymer obtained was a crosslinked material. Attempted copolymerization with styrene yielded similar results. This indicated that the monomers themselves can generate free radicals and induce polymerization. The formation of free radicals of N-methyl borazines via hydrogen abstraction has been reported previously by other workers.¹¹

The B-styrl-B-dimethyl-N-triphenyl borazine (9) was also polymerized by free radical methods and in this case yielded linear homopolymer and copolymers with styrene. The molecular weights for the homopolymer and copolymers obtained by GPC measurements relative to styrene are relatively low (10,000-74,000 M_w) suggesting facile chain termination. The homopolymer and copolymers with high borazine loading (< 50 %) were found to crosslink when left at room temperature for several weeks. The process which results in crosslinking may also be responsible for chain termination.

This study shows the potential for the preparation of organic polymers bearing the borazine ring as a pendant functionality. Studies are presently underway to examine the potential use of these and related materials as polymeric precursors to ceramic materials.

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References

1. A. Meller, Gmelin Handbuch der Anorganische Chemie. Boron Compounds Second Supplement, 1, p. 304 (1983).
2. C. S. Kalyoncu, Cerma. Eng. Sci. Proc. p.1356 (1985).
3. N. J. Archer, Chem. Soc. (London) Spec. Pub. No. 30 p. 167 (1977).
4. K. J. Paciorek, R. H. Kratzer, D. H. Harris and M. E. Smythe, Polymer Prepr. (Am. Chem. Soc., Div. Polym. Chem.), 25 p. 15 (1984).
5. K. J. Paciorek, D. H. Harris and R. H. Kratzer, J. Polym. Chem. Ed., 24, p. 173 (1986).
6. C. K. Narula, R. T. Paine and R. Schaeffer, Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.), 28, p. 454 (1987).
7. C. K. Narula, R. T. Paine and R. Schaeffer, J. Amer. Chem. Soc., 109, p. 5556 (1987).
8. K. J. Wynne and R. W. Rice, Ann. Rev. Mater. Sci., 14, p. 297 (1984).
9. G. E. Ryschkewitsch, J. J. Harris and H. H. Sisler, J. Amer. Chem. Soc., 80, p. 4515 (1958).
10. L. A. Melcher, J. L. Adcock and J. J. Lagowski, Inorg. Chem., 11, p. 1247 (1972).
11. S. J. Groszos and S. F. Stafief, J. Amer. Chem. Soc., 80, p. 1357 (1958).
12. S. J. Groszos and J. H. Smalley, J. Amer. Chem. Soc., 81, p. 582 (1959).
13. L. W. Hall and J. D. Odom and P. D. Ellis, J. Amer. Chem. Soc., 97, p. 4527 (1975).