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Preliminary communication

NOVEL HETEROCYCLIC ORGANOBORANES

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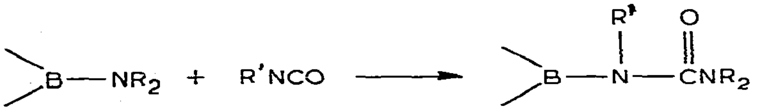
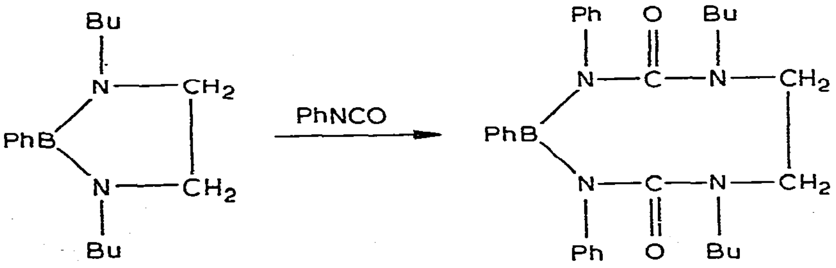
Summary

Novel heterocyclic organoboranes are obtained from the interaction of an organic isocyanate and heterocyclic aminoboranes.

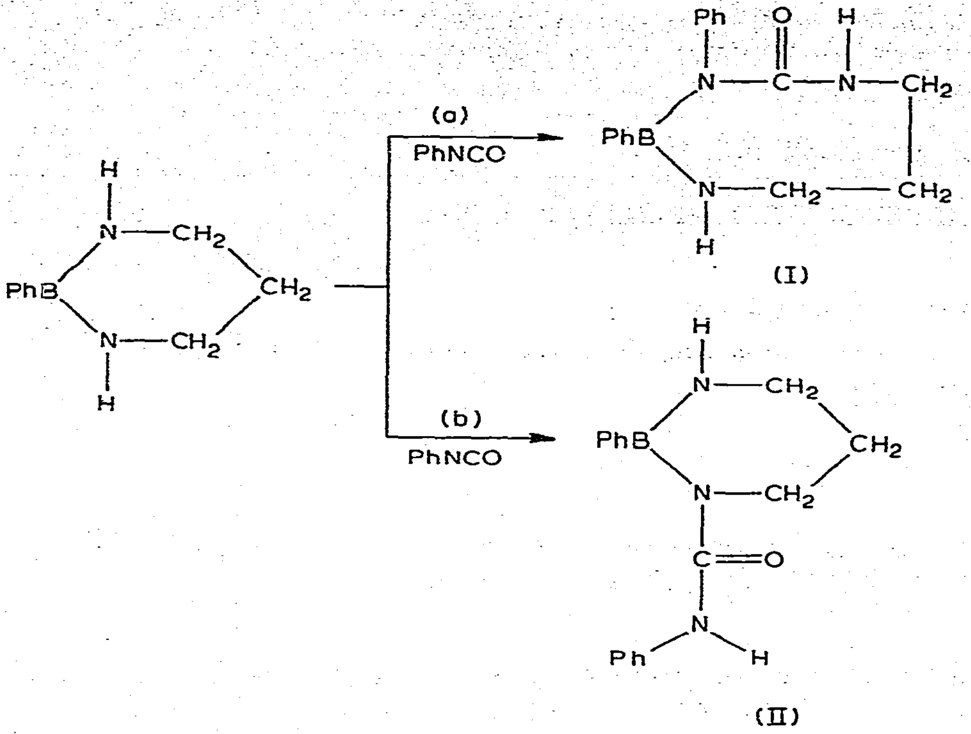
The reaction between an organic isocyanate and an aminoborane, resulting in the formation of a ureidoborane, is well established [1].



Some years ago we extended this reaction to systems in which the B—N bond was part of a heterocyclic ring [1]. This resulted in a novel synthetic route to large ring heterocyclic organoboranes.



Recently there have been two reports concerning the reaction of phenyl isocyanate and 2-phenyl-1,3,2-diazaboracyclohexane [2, 3]. However, in systems of this type there are two possible reactions namely (a) insertion into the B—N bond leading to ring expansion and (b) reaction with the hydrogen atom of the NH group.



In the absence of X-ray crystallographic data it is difficult to distinguish between the two possible products of reaction because the analytical data is the same and hydrolysis or alcoholysis of I or II yields identical products.

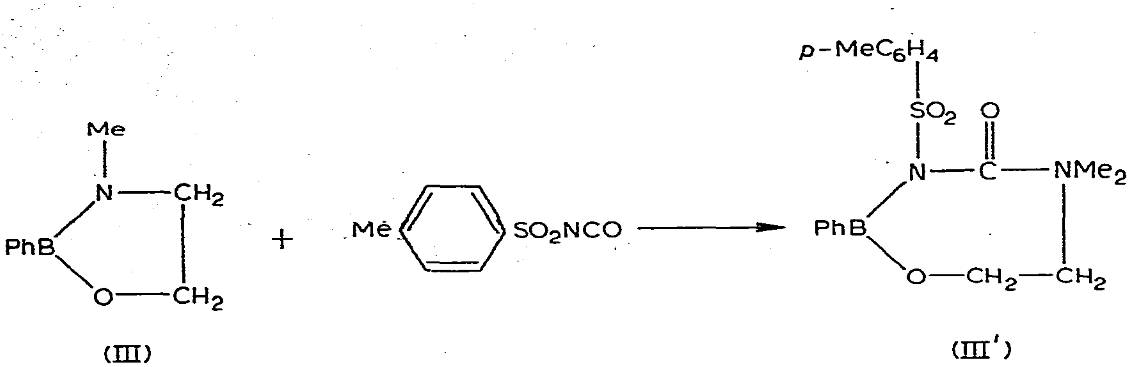
In order to eliminate reaction (b) and also to demonstrate that the reaction of an organic isocyanate with a heterocyclic aminoborane results in ring expansion we have studied the reactions between an organic isocyanate and heterocycles III, IV and V. In each case the analytical results and infrared spectra are consistent with compounds formed by ring expansion.

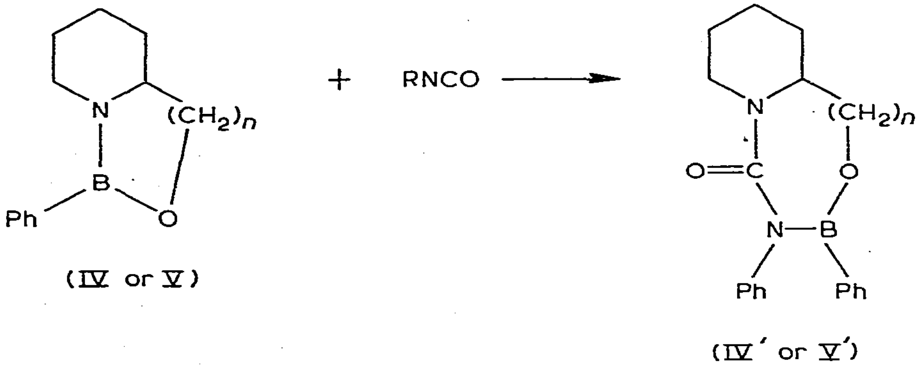
We are currently investigating the applicability of the insertion reaction to the synthesis of large-ring heterocyclic organoboranes.

Experimental

Interaction of p-toluenesulphonyl isocyanate and 2-phenyl-3-methyloxazaborolan. 2-Phenyl-3-methyloxazaborolan (1.61 g, 0.01 mol) was dissolved in toluene (30 cm^3) and *p*-toluenesulphonyl isocyanate (1.97 g, 0.01 mol) was added, the reaction being exothermic. The mixture was refluxed for 12 h and on removal of the solvent the residue, after purification, afforded III′ (3.3 g, 92%), m.p. 80—82°C. (Found: C, 55.66; H, 6.38; N, 7.41. $C_{17}H_{19}N_2O_4SB$ calcd.: C, 56.98; H, 5.31; N, 7.82%).

Interaction of phenyl isocyanate and IV. Phenyl isocyanate (1.19 g, 0.01 mol) and IV (2.01 g, 0.01 mol) were dissolved in toluene (30 cm^3). The mixture was refluxed for 48 h and on removal of the solvent the residue, after purification,





(IV, $n = 1$; V, $n = 2$; R = Ph or p-MeC$_6$H$_4$SO$_2$)

afforded IV′ (2.9 g, 90%) m.p. 105°C. (Found: C, 70.41; H, 7.09; N, 8.75. $C_{19}H_{21}N_2O_2B$ calcd.: C, 71.25; H, 6.56; N, 8.75%).

Interaction of p-toluenesulphonyl isocyanate and V. p-Toluenesulphonyl isocyanate (1.97 g, 0.01 mol) and V (2.15 g, 0.01 mol) were dissolved in toluene (30 cm^3), the reaction being exothermic. The mixture was refluxed for 12 h and on removal of the solvent the residue, on distillation, afforded III′ (3.8 g, 92%) b.p. 145°C/0.2 mmHg. (Found: C, 60.97; H, 6.67; N, 6.27. $C_{21}H_{25}N_2O_4SB$ calcd.: C, 61.17; H, 6.08; N, 6.80%).

References

1 R.H. Cragg, M.F. Lappert and B.P. Tilley, J. Chem. Soc., (1964) 2108.
2 U.W. Gerwarth and K.D. Muller, J. Organometal. Chem., 96 (1975) C33.
3 K.D. Muller and U.W. Gerwarth, J. Organometal. Chem., 110 (1976) 15.