

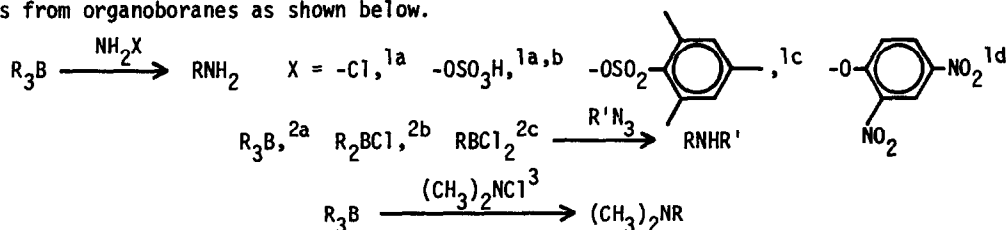
NITROGEN STITCHING: THE FACILE CONVERSION OF PERHYDROBORAPHENALENE TO
13-AZABICYCLO[7.3.1]TRIDECAN-5-OL AND PERHYDROAZAPHENALENE

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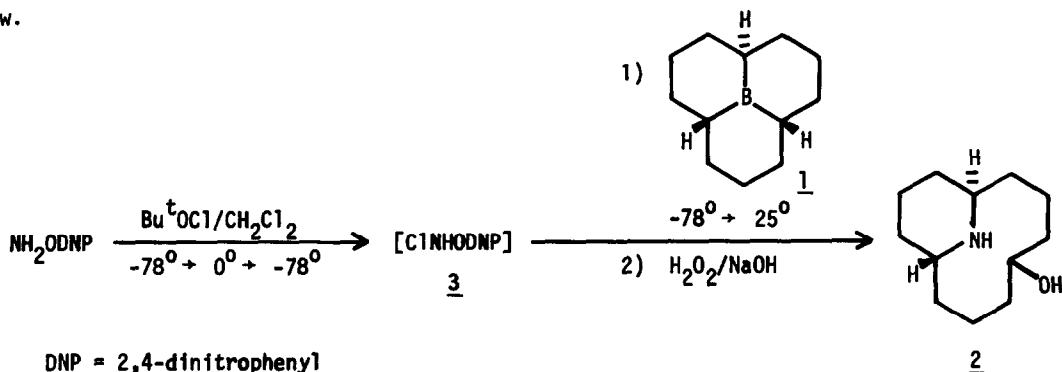
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A number of methods exist for the preparation of primary,¹ secondary,² and tertiary³ amines from organoboranes as shown below.



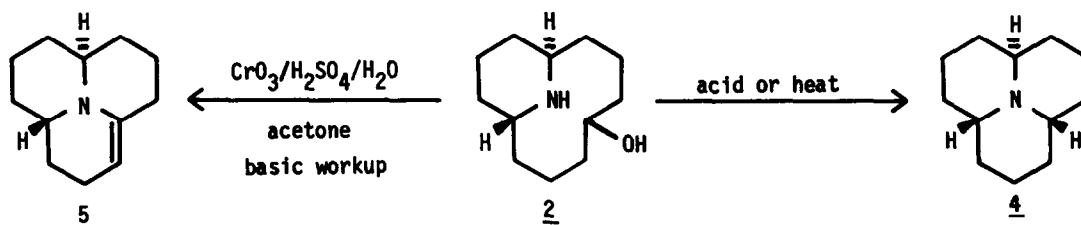
Common to all these methods is the transfer of only one alkyl group from the organoborane to the same nitrogen atom, a direct consequence of the use of reagents carrying only one leaving group on nitrogen. This letter reports the first example of a reaction in which two alkyl groups are transferred from an organoborane to the same nitrogen atom, the conversion of the perhydroboraphenalene 1⁴ to the aminoalcohol trans-13-azabicyclo[7.3.1]tridecan-5-ol (2). This "nitrogen stitching" reaction was accomplished through the use of the presumed (*vide infra*) reagent N-chloro-0-2,4-dinitrophenylhydroxylamine (3), which carries two leaving groups on the nitrogen atom. The *in situ* preparation and reaction of 3 with the organoborane 1 are described below.



One equivalent of *t*-butyl hypochlorite was added to a stirred suspension of 0-2,4-dinitrophenylhydroxylamine⁵ in dichloromethane under nitrogen and cooled in a dry ice/isopropanol bath. The cold bath was removed and the reaction mixture was allowed to warm slowly until a homogeneous, light yellow solution was obtained (usually between -5 and 0°C). The mixture was then immediately returned to the cold bath;⁶ since no crystallization of NH₂ODNP occurred on cooling, reaction to form C1NHODNP was presumed to have taken place. After 10 min one equivalent of perhydroboraphenalene 1 was added all at once; an immediate exothermic reaction occurred and the mixture became dark red in color. After 10 min the cold bath was removed and the reaction

mixture allowed to warm to 25°C. The solvent was evaporated *in vacuo* and the deep red residue was oxidized with excess aqueous basic hydrogen peroxide in ether for 15 min with ice/water cooling. Aqueous sodium bisulfite was added to destroy excess peroxide. The water layer was acidified, extracted with ether, basified, and extracted with 3:1 ether/hexane. The extract was dried over potassium carbonate and the solvent removed *in vacuo*. The resulting crude red oil was purified by passage through a short silica gel column with ether to afford the aminoalcohol 2⁷ as a light yellow oil in 50% yield (purity *ca.* 97% by VPC). The *trans* stereochemistry of 2 was demonstrated by conversion to the known⁸ *trans*-enamine 5. The conversion of 1 to 2 was highly stereoselective; very little, if any, of the *cis* piperidine ring isomer of 2 was formed.

Aminoalcohol 2 was found to undergo a remarkably facile cyclization to form the tertiary amine 4, which had been prepared previously by another route.⁸ This reaction frustrated attempts



at further purification of 2. Although the aminoalcohol could be obtained in chromatographically pure form by the Sharpless calcium chloride purification procedure,⁹ vacuum distillation to remove the last traces of solvent resulted in partial conversion (*ca.* 5%) to 4. In fact, heating the crude aminoalcohol at 180°C for 15 min gave a 66% yield of 4 (94% pure by VPC) from 1. Also, attempts to form and recrystallize (refluxing ethanol) the picrate of 2 resulted in formation of the picrate¹⁰ of 4 in high yield.¹¹

Investigation of the reaction of reagent 3 with other organoboranes is underway.

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References and Footnotes:

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- If the reagents are mixed at 25°C, gas evolution (N_2 ?, HCl) usually occurs within 5-15 min and the yield of aminoalcohol 2 is low and variable (G. Maniloff, unpublished).
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- Mp 200-202°C; combustion analysis was within 0.2%.
- Cf.* A. J. Sisti and D. L. Lohner, *J. Org. Chem.*, **32**, 2026 (1967).