25. A New Synthesis of 2,3,1-Diazaborines

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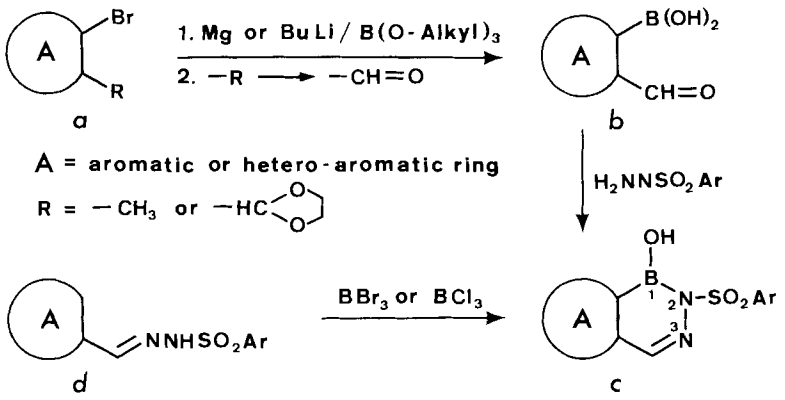
Summary

A new method for the preparation of 2,3,1-diazaborines is described. It is suggested that the observed formation of the C,B-bond by electrophilic attack with a boron halide is facilitated and *o*-directed by the sulfonyl hydrazone group of the educts.

The chemistry of the aromatic 2,3,1-diazaborine system has been investigated by several research groups [1–5] and a variety of benzo-, furo- or thieno-fused diazaborines have been described. Our interest in this class of compounds originates from the antibacterial properties which have been reported for 2-arylsulfonyl derivatives [6–7] of the general structure *c*. The present communication discloses a new synthesis, which offers in our view some advantages over the established procedures for the preparation of these compounds. According to numerous examples described in the literature diazaborines of type *c* are prepared from an *o*-substituted aromatic or hetero-aromatic bromide *a via* metalation and introduction of the boronic acid function with a trialkyl borate, followed by cyclisation *(b→c)* with an arylsulfonyl hydrazine. We have now found that arylsulfonyl hydrazones *d* can be cyclized with boron halides directly to 2,3,1-diazaborines *c*.

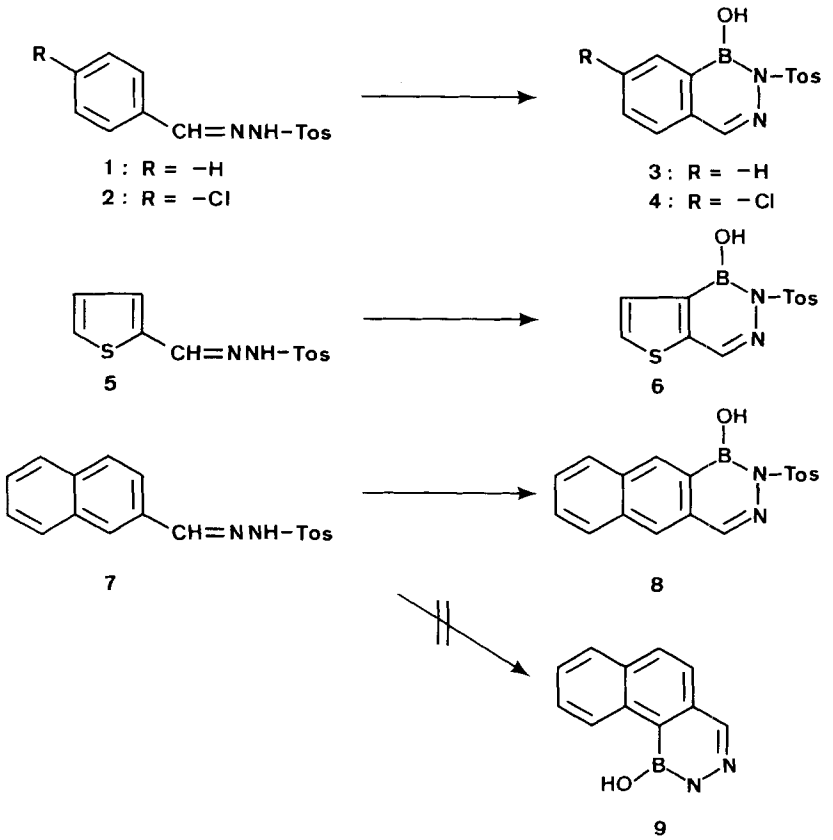


In a typical experiment, a suspension of 2.2 g (8.0 mmol) of benzaldehyde *p*-toluenesulfonyl-hydrazone (**1**) in 50 ml of CCl_4 was stirred at 60°, and 4.6 ml (48.0 mmol) of BBr_3 was added in small portions over a period of 4 h. After 26 h the reaction mixture was cooled to 5°; 10 ml of methanol and subsequently 3 ml of water were then added cautiously. Evaporation at reduced pressure gave a crystalline residue which was recrystallized from ethanol/water. The diazaborine obtained was identical (m.p., IR, UV, ^{1}H-NMR., TLC.) with a sample of **3** prepared independently from 2-formylphenyl boronic acid [4]. With BCl_3 (sealed tube) instead of BBr_3 the diazaborine **3** was obtained in low yield only *(Table 1)*.

Table 1. *Diazaborine formation with BBr_3 or BCl_3* (sealed tube) *in CCl_4*

Compound	M.p. (°)	Reagent (mol-equiv. in parentheses)	Reaction time and temperature	Yield[a]) %
3	156–158	BBr_3 (6)	26 h/60°	56
3	156–158	BCl_3 (12)	30 h/60°–80°	10
4	169–171	BBr_3 (3)	24 h/50°	21
6	171–176	BBr_3 (3)	24 h/50°	66
8	196– 98	BBr_3 (2)	20 h/50°	55

[a]) The yields refer to isolated, pure material and have not been optimized systematically.



The same procedure was also successfully applied in the preparation of the chloro-substituted diazaborine **4**[1]) from the *N*-tosylhydrazone **2** and in the conversion of **5** to the thieno-fused compound **6**. Starting from the hydrazone **7**, only one of the two possible naphthalene-fused products **8** or **9** was obtained[1]). The ^{1}H-NMR. spectrum of this compound (100 MHz, DMSO-d_6) shows two characteristic singlets at δ 8.24 (1 H) and 8.27 (1 H). These signals are compatible with structure **8**, but not with the alternative structure **9**.

These examples illustrate that a variety of fused 2,3,1-diazaborines can be prepared from the corresponding sulfonyl-hydrazones in one step. Owing to the ready accessibility of the starting materials and the preparative simplicity, this procedure might represent an attractive alternative to the established methods.

The fact that the observed cyclization occurs at relatively mild conditions suggests that the electrophilic attack of the boron trihalide is facilitated and *o*-directed by the sulfonyl hydrazone group of the reactant *d*. The formation of the C,B-bond in the above examples may therefore be influenced by similar effects of *o*-substituents as more generally established in organo metallic chemistry.

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REFERENCES

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[1]) Compounds **4** and **8** have not been reported in the literature so far; their structures have been established by spectroscopy (IR., UV., ^{1}H-NMR.) and elemental analysis.