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UNUSUAL CHANGES IN MECHANISM AND REACTION COURSE IN THE REACTION OF BROMINE WITH B-ALKYL-9-BORABICYCLO[3.3.1]NONANES

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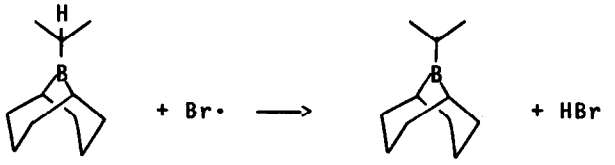
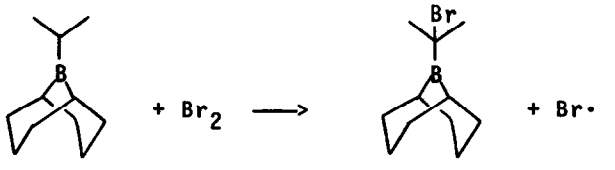
In the presence of ordinary laboratory light, *B*-isopropyl-9-BBN, **1**, and related derivatives containing a tertiary hydrogen in the α-position readily undergo a substitution reaction with bromine to give the α-bromo derivatives, **2**. The substitution evidently involves a free radical chain reaction (eq 1-2).[1,2]



(1)

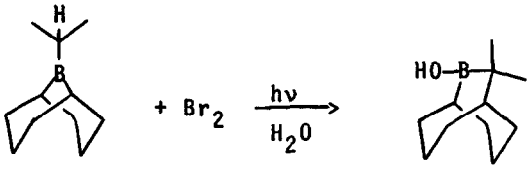
1



(2)

2

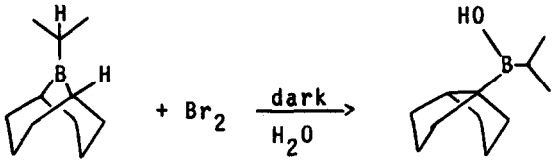
Either treating **2** with water or carrying out the bromination of **1** in the presence of water in ordinary light produces **3** (eq 3).[1]



(3)

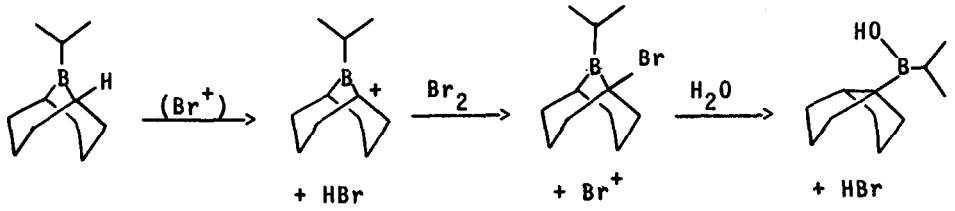
3

In the dark, another reaction course is followed (eq 4).



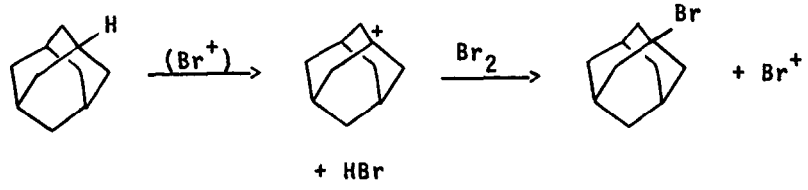
(4)

This new reaction course evidently involves an ionic attack by bromine at the bridgehead hydrogen (eq 5).



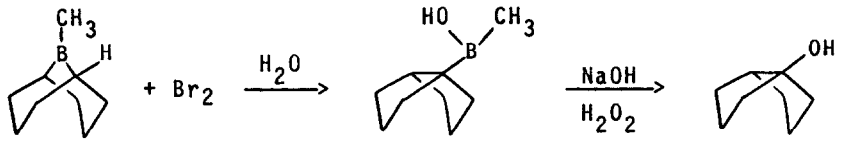
(5)

A similar mechanism has been observed in the bromination of adamantane and bicyclo-[3.3.1]nonane (eq 6).[3]



(6)

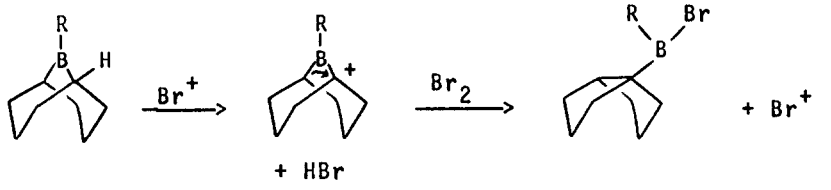
Treatment of *B*-methyl- and *B*-ethyl-9-BBN with bromine in the presence of light or dark also results in attack at the bridgehead hydrogen. The reaction is complex unless water is present to circumvent cleavage of the boron-carbon bonds by the liberated hydrogen bromide. Oxidation provides 88-94% yields of *cis*-bicyclo[3.3.0]octan-1-ol (eq 7).[5]



(7)

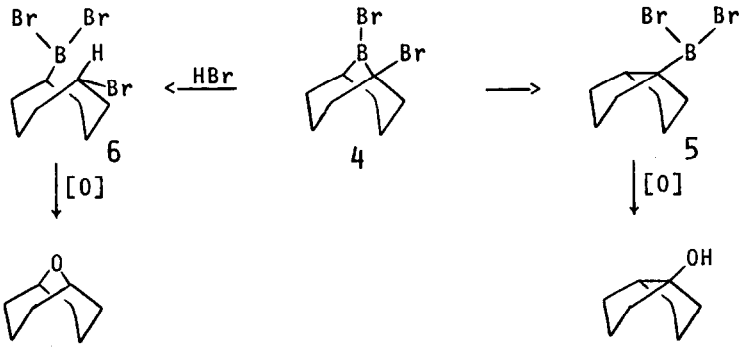
Presumably, free radical attack of primary or secondary α-hydrogens by bromine atoms is so slow that the ionic pathway involving the bridgehead hydrogen is the preferred course.

Despite a number of attempts, we were unable to isolate and identify the bridgehead α-bromoborane in these reactions. It is possible that this derivative is not formed because of an exceptionally facile rearrangement of the intermediate carbonium ion (eq 8).



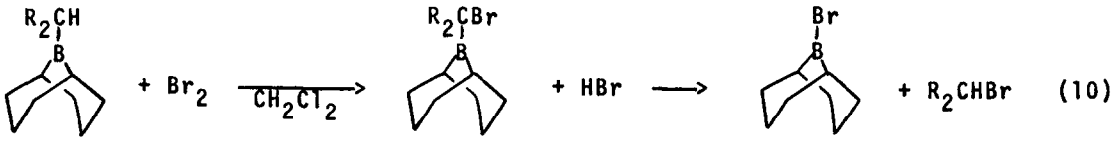
(8)

In the case of the bromination of *B*-bromo-9-BBN with removal of hydrogen bromide, we were able to obtain evidence for the formation of such an intermediate bridgehead α-bromoborane 4. ^{1}H NMR analysis of 4 shows resonances at δ 1.40-2.0 (m, ∿9H) and δ 2.18 (t, ∿4H). On standing at room temperature for 24 hours, 4 rearranges to 5 (^{1}H NMR, broad envelope at δ 2.21), readily oxidized to *cis*-bicyclo[3.3.0]octan-1-ol. Alternatively, if 4 is allowed to react with the hydrogen bromide, cleavage of the boron-carbon bond occurs, producing 6 (^{1}H NMR: δ 1.60, m, ∿1H; δ 1.82, m, ∿8H; δ 2.23, m, 4H; δ 4.28, quin, 1H), readily oxidized to 9-oxabicyclo[3.3.1]nonane (eq 9).[4]



(9)

These observations emphasize the remarkable chemistry of this bicycloorganoborane. Treatment of derivatives having *B*-alkyl moieties containing tertiary α-hydrogens with bromine in methylene chloride in the dark yields the corresponding alkyl bromide. The mechanism is postulated to involve formation of the α-bromoborane (eq 1 and 2) followed by protonolysis of the intermediate by hydrogen bromide (eq 10).



(10)

By performing the reaction under vacuum, the hydrogen bromide can be removed and the α-bromoborane derivatives 2 can be isolated (eq 1-2).

By carrying the reaction out in the presence of water and light, the hydrogen bromide cleavage is circumvented and the intermediate is rearranged (eq 3).

A totally different rearrangement occurs if the reaction is carried out in the dark in the presence of water, or if an alkyl group not competitively susceptible to free radical substitution, such as methyl, is used (eq 4 and 7).

Thus, it is possible to direct the reaction of the *B*-alkyl-9-borabicyclo-[3.3.1]nonanes along several highly interesting pathways by modest changes in reaction conditions. These results illustrate the remarkable versatility of the chemistry of organoboranes and especially that of the 9-BBN bicyclic structure.

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4. 9-Oxabicyclo[3.3.1]nonane is similarly formed in the bromination of *B*-methoxy-9-BBN. H. C. Brown and Y. Yamamoto, *J. Org. Chem.*, 39, 861 (1974).