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Preliminary communication

REACTIONS OF BICYCLIC ORGANOBORANES WITH SILVER NITRATE

I. MEHROTRA and D. DEVAPRABHAKARA*

Department of Organic Chemistry, Indian Institute of Science, Bangalore-560012 (India) and Department of Chemistry, Indian Institute of Technology, Kanpur-208016 (India)

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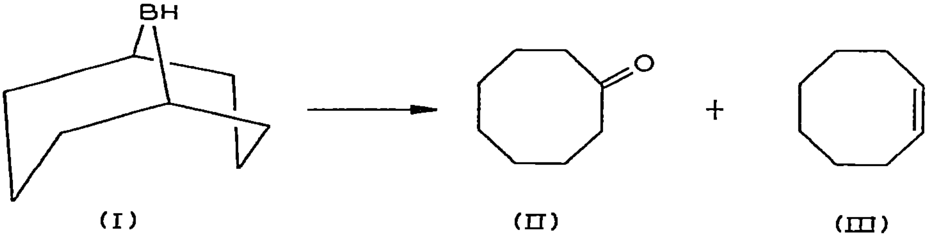
Summary

Bicyclic organoboranes (9-borabicyclo[3.3.1]nonane, 10-borabicyclo[4.3.1]-decane and 11-borabicyclo[5.3.1]undecane) react with alkaline silver nitrate solution to give a mixture of monocyclic ketone and *cis*-monocyclic olefin.

The reaction of trialkylboranes with solutions of silver nitrate and potassium hydroxide is known to bring about intermolecular coupling of two similar or dissimilar alkyl groups [1]. Consequently, the combined hydroboration-coupling procedure is a highly convenient route to the synthesis of a wide variety of carbon structures [2]. It therefore appeared of interest to examine the behaviour of bicyclic organoboranes in this coupling reaction.

9-Borabicyclo[3.3.1]nonane (I, 9-BBN) prepared from *cis,cis*-1,5-cyclooctadiene [3] in THF on treatment with aqueous $AgNO_3$ (1/1 molar ratio) and potassium hydroxide at ca. 10° gave a mixture of 85% cyclooctanone (II) and 15% *cis*-cyclooctene (III) in 65% overall yield (Scheme 1). By contrast, the reaction of I and $AgNO_3$ (1/3) yielded III as the major product (90%). The use of a catalytic amount of $AgNO_3$ led to a severe cut in the yield of the products**.

Scheme 1



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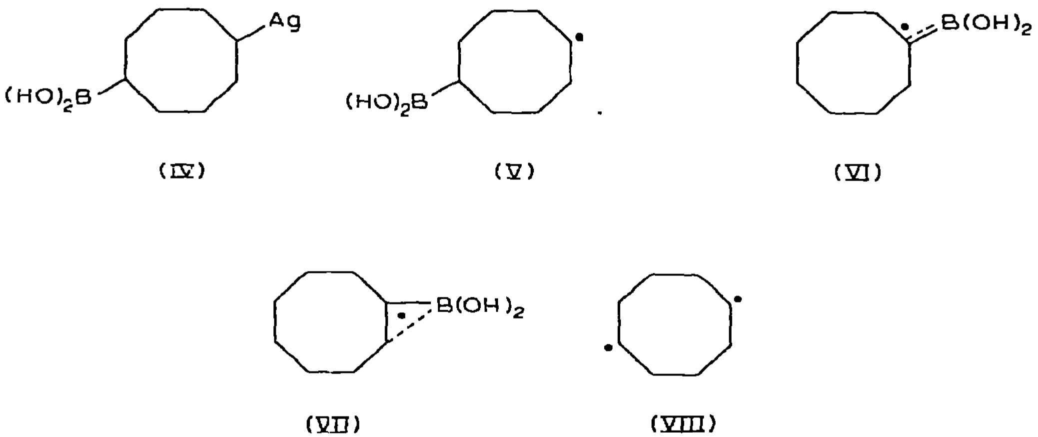
[*] Inquiries may be directed to this author at the Indian Institute of Science.

[**] The identity of the products was established unambiguously using authentic samples.

Even 10-borabicyclo[4.3.1]decane and 11-borabicyclo[5.3.1]undecane [4] gave similar results.

The plausible intermediates for the formation of II and III from I are shown in Scheme 2. First, the reaction of I with silver hydroxide can lead to the organosilver compound IV, the C—Ag bond in which may undergo homolytic cleavage to give the free-radical species V, which in turn can give rise to the radical VI by a 1,5-hydrogen shift or to VII by a 1,4-hydrogen shift. The odd electron in VI or VII can be delocalized with the electrophilic boron. The relative proportions of VI and VII may be dictated by the favourable transition state involved in the formation of the radical concerned from V or/and their thermodynamic stabilities. Interconversion of VI and VII is also possible by a 1,2-hydrogen shift. In principle, the radical species VI and VII could proceed via several routes to yield II and III respectively. We propose the diradical intermediate VIII when 9-BBN (I) is treated with excess of $AgNO_3$ as III can arise from VIII.

Scheme 2



The mechanism of this interesting transformation is being further studied.

Acknowledgements

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