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Preliminary communication

CHROMIC ACID OXIDATION OF BICYCLIC ORGANOBORANES

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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) on oxidation with an excess of aqueous chromic acid give monocyclic ketones. A mechanism is proposed to account for the formation of this unexpected product.

Oxidation of organoboranes with aqueous chromic acid is known to give ketones in good yield [1], and the reaction has been used in the synthesis of a variety of ketones [1-5] from alkenes or dienes. However, Lansburg and Nienhouse [6] observed the formation of a rearranged product, nortricyclanone during the direct chromic acid oxidation of organoborane from norbornadiene, and we thought it would be interesting to examine the behaviour of bicyclic organoboranes during chromic acid oxidation.

The bicyclic organoboranes, 9-borabicyclo[3.3.1]nonane, 10-borabicyclo-[4.3.1]decane and 11-borabicyclo[5.3.1]undecane, were prepared from *cis,cis*-1,5-cyclooctadiene, *cis,cis*-1,5-cyclononadiene and *cis,cis*-1,6-cyclodecadiene, respectively, via cyclic hydroboration—isomerization [7, 8], and oxidized with excess aqueous 8 *N* chromic acid (1/4 molar ratio) in diethyl ether according to the procedure of Brown and Garg [1]. The results are summarized in Table 1, and show that bicyclic organoboranes behave differently from acyclic organoboranes. The results can be explained by assuming protonolysis of one of the carbon—boron bonds prior to complete oxidation of both the carbon—boron bonds. The possible pathway for the formation of cyclooctanone (VI) from 9-borabicyclo-[3.3.0]nonane (I) is represented in Scheme 1. Reaction of I with aqueous chromic acid initially gives II. The organoborane II could then undergo protonolysis of the carbon—boron bond either through an intramolecular six-membered cyclic transition state or by an intermolecular process. (The driving

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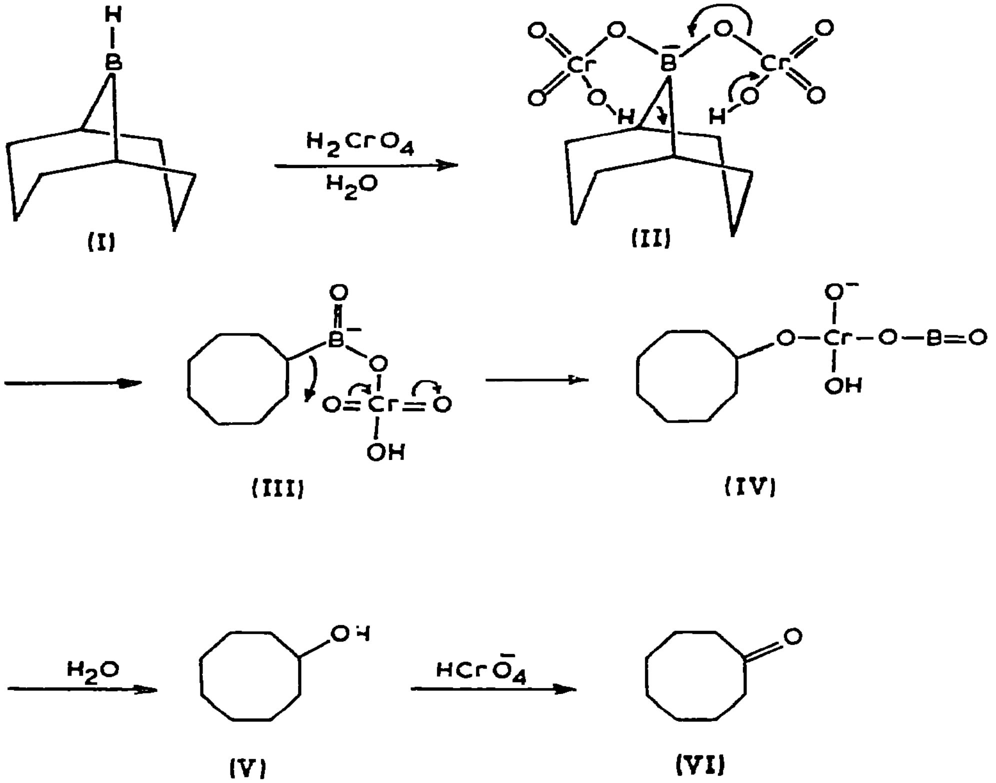
TABLE 1

OXIDATION OF BICYCLIC ORGANOBORANES WITH CHROMIC ACID

Organoborane	Product[a]	Yield (%)
9-Borabicyclo[3.3.0]nonane	Cyclooctanone	60
10-Borabicyclo[4.3.0]decane	Cyclononanone	65
11-Borabicyclo[5.3.0]undecane	Cyclodecanone	62

[a] All the ketones were identified by comparison of IR and GLC retention times with those of authentic samples.



SCHEME 1. Possible mechanistic pathway for the oxidation of 9-borabicyclo[3.3.0]nonane (I) to cyclooctanone (VI).

force for such a reaction could be the greater strength of boron—oxygen bonds as compared to boron—carbon bonds) Such a protonolysis of II would give III, which could undergo normal chromic acid oxidation via IV and cyclooctanol (V) to cyclooctanone (VI).

Work is in progress with other monocyclic, bicyclic and tricyclic organoboranes, and also to check the validity of the proposed mechanism.

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References

1 H.C. Brown and C.P. Garg, J. Amer. Chem. Soc., 83 (1961) 2951.
2 J.F. Bagli, P.F. Morana and R. Gaudry, J. Org. Chem., 27 (1962) 2938.
3 R.K. Hill and A.G. Edwards, Tetrahedron, 21 (1965) 1501.
4 L.G. Wideman, J. Org. Chem., 33 (1968) 4541.
5 W.R. Moore and W.R. Moser, J. Org. Chem., 35 (1970) 908.
6 P.T. Lansbury and E.J. Nienhouse, Chem. Commun., (1966) 273.
7 E.F. Knights and H.C. Brown, J. Amer. Chem. Soc., 90 (1968) 5280.
8 I. Mehrotra and D. Devaprabhakara, Tetrahedron Lett., (1970) 4493.