In conclusion, cmr spectroscopy provides a simple way to observe conformations of acyclic pentadienyl anions and can be used in conjunction with coupling data from pmr spectroscopy to assign their structures. The principal conformations of pentadienyllithiums are W with substantial amounts of sickle present in certain cases.

**Acknowledgments.** We thank R. Thrift and S. Silber for technical help with the spectra, R. B. Bates for communicating to us his revised pentadienyllithium chemical shifts, the Phillips Petroleum Co. for a fellowship (M. N.), and the National Science Foundation for partial funding of the Fourier transform cmr system. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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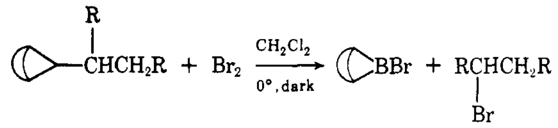
## Competitive Bromination of *B*-Isopropyl-9-borabicyclo[3.3.1]nonane. The Remarkable Selectivity and Enhanced Reactivity of the $\alpha$ Hydrogen in *B*-*sec*-Alkyl-9-borabicyclo[3.3.1]nonanes

*Sir:*

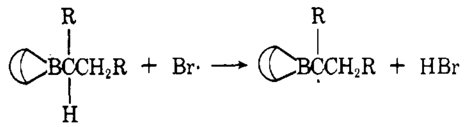
Competitive bromination of *B*-isopropyl-9-borabicyclo[3.3.1]nonane (*B*-*i*-Pr-9-BBN) reveals that the $\alpha$ hydrogen of the isopropyl group is 5.5 times as reactive as the highly activated tertiary hydrogen of cumene. Consequently, the boron moiety activates the $\alpha$ position to an even greater extent than the phenyl group. The $\alpha$-hydrogen atoms at the bridgehead are not substituted competitively. This feature makes it possible to synthesize and isolate the $\alpha$-bromoalkyl derivatives and to utilize them in synthesis. Thus treatment of 2-bromo-2-propyl-9-BBN with water results in a carbon–boron migration with the formation of a new bicyclic boron derivative. Alternatively, the $\alpha$-bromo compound is readily converted by treatment with methyllithium at −78° into *B*-*t*-Bu-9-BBN.

Recently, *B*-*sec*-alkyl-9-borabicyclo[3.3.1]nonanes have been shown to undergo a dark reaction with bromine to afford the corresponding secondary alkyl bromides (eq 1).[1] Although the reaction provides a highly convenient procedure for the anti-Markovnikov hydrobromination of internal olefins, the mechanistic implications are of special interest.

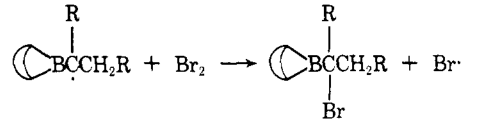


$$\mathrm{B{-}CH(R)CH_2R + Br_2 \xrightarrow[0^\circ,\ dark]{CH_2Cl_2} BBr + RCH(Br)CH_2R} \quad (1)$$

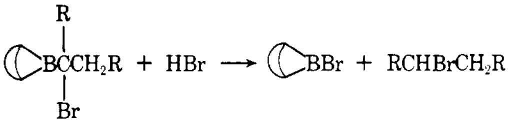
It was proposed that the reaction does not involve direct rupture of the carbon–boron bond by the bromine molecule but proceeds instead through a highly selective free radical substitution of the $\alpha$ position of the *sec*-alkyl group (eq 2, 3). Protonolysis of the intermediate by the hydrogen bromide affords the final product (eq 4).



$$\mathrm{BC(H)(R)CH_2R + Br\cdot \longrightarrow B\dot{C}(R)CH_2R + HBr} \quad (2)$$



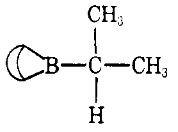
$$\mathrm{B\dot{C}(R)CH_2R + Br_2 \longrightarrow BC(Br)(R)CH_2R + Br\cdot} \quad (3)$$



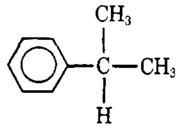
$$\mathrm{BC(Br)(R)CH_2R + HBr \longrightarrow BBr + RCHBrCH_2R} \quad (4)$$

Yields in the neighborhood of 90% were realized. This suggests that the $\alpha$ position of the alkyl group must be exceptionally activated to achieve such a selective substitution at this position.[2] This conclusion has now been tested by examining the competitive bromination of *B*-*i*-Pr-9-BBN and cumene. Treatment of an equimolar solution of 9-BBN (**1**), cumene (**2**), and cyclohexane in methylene chloride with bromine at 0° revealed that the relative reactivity of **1**/**2** is 5.5, as shown by glpc analysis for residual **1** and **2**. No substitution of the cyclohexane occurs.

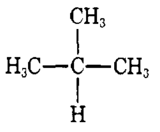
If we utilize the literature value of 120 for the relative reactivities of cumene and isobutane[3] (**3**), this results in a relative reactivity of the tertiary hydrogen in *B*-*i*-Pr-9-BBN to isobutane of 660. Clearly, the activation toward attack by bromine atoms of the tertiary position provided by the 9-BBN moiety in **1** exceeds that provided by the phenyl group in **2**.



**1**
660



**2**
120



**3**
1.00

Rel react

This remarkable activation can be attributed to stabilization of the free radical produced in the hydrogen abstraction step (eq 2) by the interaction of the odd electron with the vacant p orbital of the boron atom. Attack on the other two $\alpha$ positions (bridgehead) of the 9-BBN moiety is apparently much less facile because in these positions the odd electron would necessarily occupy an orbital which is orthogonal to the vacant p orbital on boron.

By carrying out the bromination of **1** in methylene chloride with continuous removal of hydrogen bromide under the vacuum afforded by a water aspirator,[4] it was possible to avoid the protonolysis (eq 4) and achieve

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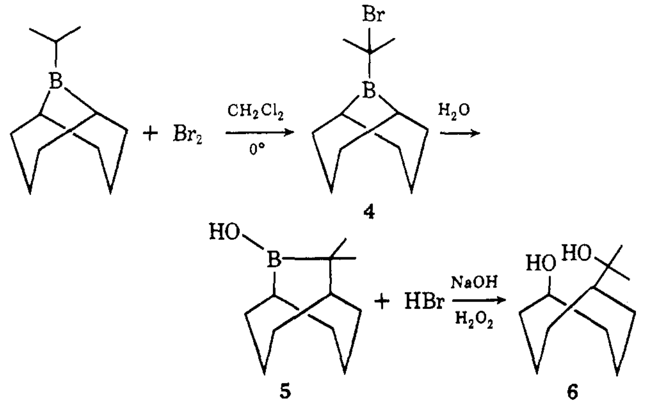
(1) C. F. Lane and H. C. Brown, *J. Organometal. Chem.*, **26**, C51 (1971).

(2) Qualitative evidence, in part conflicting, that the $\alpha$ position in boron derivatives may be activated toward attack by bromine atoms has been reported by several investigators: D. J. Pasto, J. Chow, and S. K. Arora, *Tetrahedron*, **25**, 1557 (1969); J. Grotewold, E. A. Lissi, and J. J. Scaiano, *J. Organometal. Chem.*, **19**, 431 (1969); C. F. Lane and H. C. Brown, *J. Amer. Chem. Soc.*, **92**, 7212 (1970). It was also noted that a boron substituent serves to stabilize an organic radical in free radical additions to vinylborinates: D. S. Matteson, *ibid.*, **82**, 4228 (1960).

(3) G. A. Russell and D. DeBoer, *J. Amer. Chem. Soc.*, **85**, 3136 (1963).

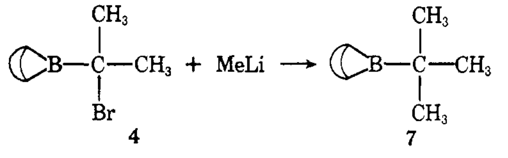
(4) H. C. Brown and Y. Yamamoto, *J. Amer. Chem. Soc.*, **93**, 2796 (1971).

the isolation of 2-bromo-2-propyl-9-borabicyclo[3.3.1]-nonane (**4**) by removal of the solvent. This product decomposed on attempted distillation, even at very low pressures. However, the crude product could be utilized in various syntheses. Thus, treatment with water results in the migration of one of the bicyclooctyl bonds from boron to carbon to produce an interesting new bicycloorganoborane derivative (**5**), 9,9-dimethyl-10-hydroxy-10-borabicyclo[3.3.2]decane. The structure of **5** was confirmed by oxidation with hydrogen peroxide[5] to the diol, *cis*-5-(2-hydroxy-2-propyl)cyclooctanol[6] (**6**), mp 102.5–103°.



Alternatively, this synthesis can be achieved in essentially one operation by carrying out the bromination of **4** in the presence of water.[7]

Treatment of **4** with methyllithium in pentane at −78° results in an essentially quantitative formation (eq 5) of *B*-*t*-Bu-9-BBN (**7**). This product (**7**) was



$$\mathrm{B{-}\overset{CH_3}{\underset{Br}{C}}{-}CH_3 + MeLi \longrightarrow B{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3} \qquad (5)$$

**4** **7**

identified by oxidation of *tert*-butyl alcohol and by glpc comparison with an authentic sample made from *B*-MeO-9-BBN and *tert*-butyllithium.[8] Clearly, these developments open the possibility for the synthesis of *B*-alkyl-9-BBN derivatives, such as **7**, not directly available by hydroboration.

(5) The oxidation was difficult and required forcing conditions, according to the procedure described in H. C. Brown, Y. Yamamoto, and C. F. Lane, *Synthesis*, 304 (1972).

(6) Physical data were all consistent with the assigned structure of the diol **6**.

(7) C. F. Lane and H. C. Brown, *J. Amer. Chem. Soc.*, **93**, 1025 (1971).

(8) We are indebted to G. W. Kramer for the authentic sample. The results of a detailed study of the reaction of *B*-MeO-9-BBN with organolithium reagents by G. W. Kramer will be published shortly.

(9) Graduate research assistant on Grant No. GP-27742X from the National Science Foundation.

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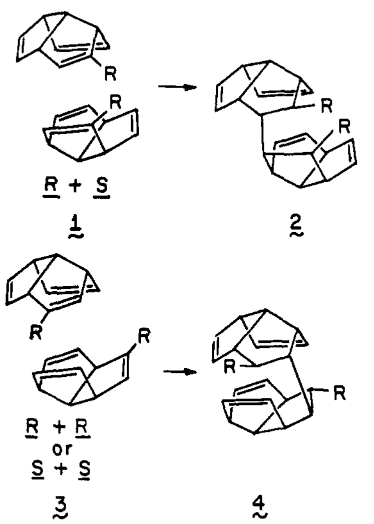
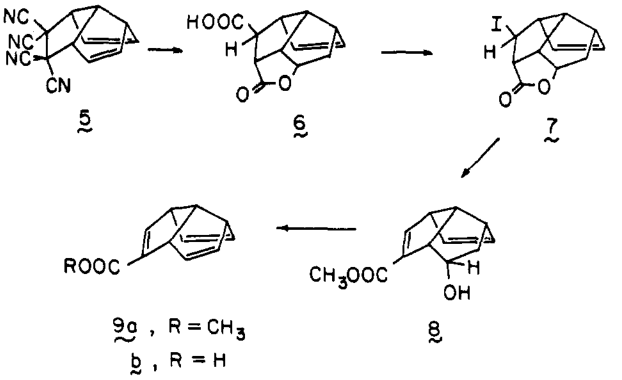
## An Efficient Synthesis of (−)-Triquinacene-2-carboxylic Acid

*Sir:*

There is special interest in 2-substituted triquinacenes because of the possibility that appendage of an appropriate R group at $C_2$ could facilitate and direct endo,-endo coupling of the monomeric units in a manner which has not been realized with the parent hydrocarbon.[1] In this connection, there is seen to exist an intriguing relationship between the dissymmetry of such derivatized triquinacenes and the structural features of the corresponding "dimers." For the hypothetical reactions **1** → **2** and **3** → **4** where the coupling products



are drawn in their sterically encumbered conformations to facilitate visual analysis, it is evident that only when bonding between trienes of like configuration operates will a molecular array directly relatable to dodecahedrane result.[2] Because enantiomerically pure 2-substituted triquinacenes would be unable to produce **2**, the availability of such tricyclo[5.2.1.$0^{4,10}$]deca-2,5,8-trienes might permit efficient construction of the possible dodecahedrane precursor **4**. We report here the development of a convenient synthetic approach[3] to (−)-triquinacene-2-carboxylic acid (**9b**), a primary focal point for elaboration of this concept.



The tetranitrile **5**, readily available in 94% yield from cyclooctatetraeneiron tricarbonyl,[4] was hydrolyzed

(1) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *J. Amer. Chem. Soc.*, **86**, 3162 (1964).

(2) Specifically, we note that 1,4-disubstituted dodecahedranes are of $C_2$ symmetry, requiring therefore precursor halves of the same configuration.

(3) Dr. Tadamichi Fukunaga, Central Research Department, E. I. du Pont de Nemours and Co. has kindly informed us that Professor R. B. Woodward and he have been aware of this interesting stereochemical aspect of optically active triquinacene derivatives and have also prepared optically active **9b** by suitable structural modification of triquinacene itself.

(4) (a) L. A. Paquette, S. V. Ley, M. J. Broadhurst, D. Truesdell, J. Fayos, and J. Clardy, *Tetrahedron Lett.*, 2943 (1973); (b) D. J. Ehntholt and R. C. Kerber, *J. Organometal. Chem.*, **38**, 139 (1972).