Journal of Organometallic Chemistry, 241 (1983) C37—C40
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

EXCEPTIONALLY RAPID THERMAL ISOMERIZATION OF *B*-(3-HEXYL)-BIS(BICYCLO[2.2.2]OCTYL)BORANE. A CONVENIENT AND HIGHLY EFFICIENT SYNTHETIC ROUTE FOR THE CONVERSION OF INTERNAL ACYCLIC OLEFINS INTO TERMINAL OLEFINS AND THEIR DERIVATIVES

HERBERT C. BROWN* and UDAY S. RACHERLA
Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907 (U.S.A.)

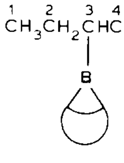
(Received October 1st, 1982)

Summary

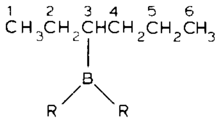
The thermal isomerizations of *B*-(3-hexyl)bis(bicyclo[2.2.2]octyl)borane and *B*-(3-hexyl)bis(bicyclo[2.2.1]heptyl)borane were compared with that of *B*-(3-hexyl)bis(2,5-dimethylcyclohexyl)borane at 150°C in diglyme. *B*-(3-Hexyl)bis(bicyclo[2.2.2]octyl)borane isomerizes approximately 3 times faster than *B*-(3-hexyl)bis(2,5-dimethylcyclohexyl)borane and nearly 60 times more rapidly than *B*-(3-hexyl)bis(bicyclo[2.2.1]heptyl)borane and also yields a 100% equilibrium boron distribution on C(1) in just 15 minutes, both characteristics making the thermal isomerization of organoboranes a more attractive synthetic route for the conversion of internal acyclic olefins into terminal olefins and their derivatives.

We previously reported [1] that at 150°C *B*-(3-hexyl)bis(2,5-dimethylcyclohexyl)borane (I) isomerizes approximately 100 times more rapidly than 3-hexyldicyclohexylborane (II), 500 times more rapidly than tris(3-hexyl)borane (III) and about 4,000 times faster than *B*-3-hexyl-9-BBN (IV). We rationalized our results in terms of increasing steric crowding in the organoboranes undergoing the isomerization and subsequently demonstrated the importance of steric factors by a careful examination of the thermal isomerization of various 3-hexyldicycloalkylboranes [2].

Encouraged by these findings, we decided to explore the possibility of increasing the rates by incorporating bulky bicycloalkyl moieties into the trialkylborane, moieties that are structurally similar and possibly sterically more demanding than

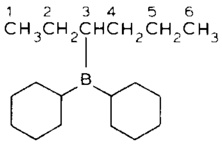


(IV)

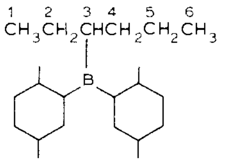


(R = 3-hexyl)

(III)

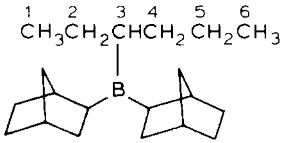


(II)

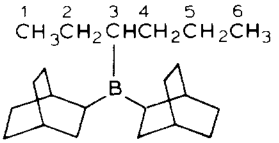


(I)

the moieties in the trialkylborane (I). The two choices we made for this study were: *B*-(3-hexyl)bis(bicyclo[2.2.1]heptyl)borane (V) and *B*-(3-hexyl)bis(bicyclo[2.2.2]octyl)borane (VI).



(V)



(VI)

Accordingly, we hydroborated *cis*-3-hexene with bis(bicyclo[2.2.1]heptyl)borane and bis(bicyclo[2.2.2]octyl)borane and obtained the organoboranes V and VI respectively. We then examined the thermal isomerization of these two organoboranes under our standard conditions, 150°C in diglyme.

It is indeed a pleasure to report that *B*-(3-hexyl)bis(bicyclo[2.2.2]octyl)borane (VI) isomerizes even faster than *B*-(3-hexyl)bis(2,5-dimethylcyclohexyl)borane (I), approximately three times faster than this derivative in the initial phase of the reaction and nearly 60 times faster than *B*-(3-hexyl)bis(bicyclo[2.2.1]heptyl)borane (V, Fig. 1). Apparently, the more rigid nature of the bicyclo[2.2.1]heptyl structure decreases its steric requirements and decreases the rate of isomerization. Earlier we observed that 3-hexyldicyclopentylborane undergoes isomerization at a rate considerably slower than the corresponding 3-hexyldicyclohexylborane, presumably for the same reason [2].

We further found that both *B*-(3-hexyl)bis(bicyclo[2.2.2]octyl)borane (VI) and *B*-(3-hexyl)bis(bicyclo[2.2.1]heptyl)borane (V) yield an essentially quantitative boron distribution on C(1) at the completion of isomerization. However, organoborane VI takes a significantly shorter time for completion of the isomerization than does organoborane V (Table 1).

B-(3-Hexyl)bis(bicyclo[2.2.2]octyl)borane (VI) was prepared by hydroborating *cis*-3-hexene with bis(bicyclo[2.2.2]octyl)borane. This in turn was obtained cleanly by hydroborating bicyclo[2.2.2]octene with $BH_3 \cdot SMe_2$ in THF at 25°C in 5 h. The reaction here stops cleanly at the dialkylborane stage. On the other hand, *B*-(3-hexyl)bis(bicyclo[2.2.1]heptyl)borane (V) was prepared by reduction of bis(bicyclo[2.2.1]heptyl)bromoborane using $LiAlH_4$ in the presence of *cis*-3-hexene [3]. Hydroboration of bicyclo[2.2.1]heptene with $H_3B \cdot SMe_2$ proceeds past the R_2BH stage to R_3B, further evidence for the greater steric requirements of the more flexible bicyclo[2.2.2]octyl system.

The following procedure is representative for thermal isomerization. Into an oven-dried, 50-ml, round-bottom flask flushed with N_2 and fitted with a reflux condenser and connecting tube, 3.64 g of *B*-(3-hexyl)bis(bicyclo[2.2.2]octyl)-

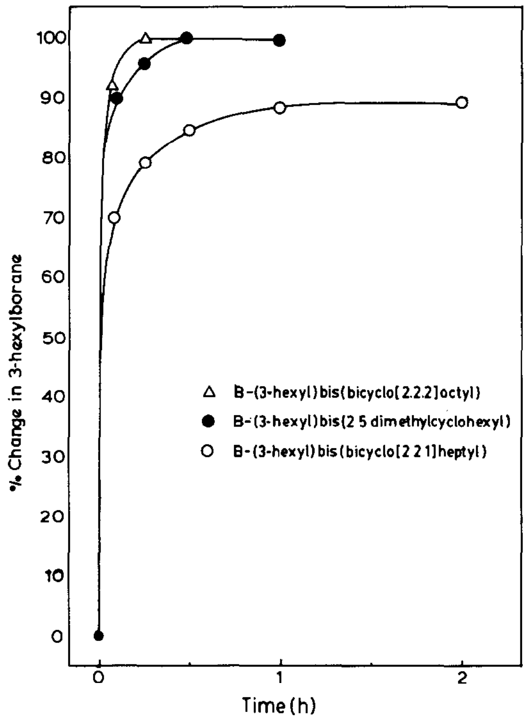
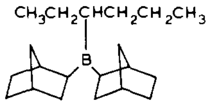
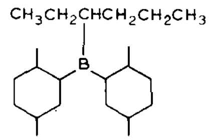
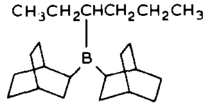


Fig. 1. A comparison of the rates of thermal isomerization.

TABLE 1

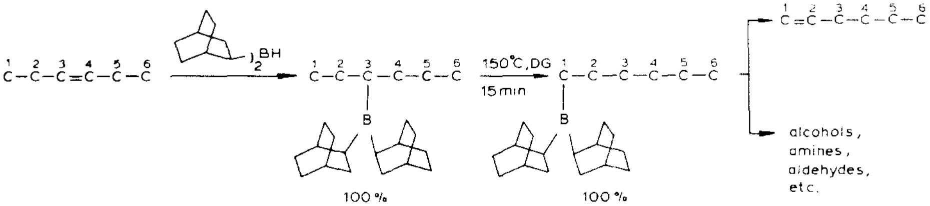
THERMAL ISOMERIZATION[a] OF ORGANOBORANES

Organoborane	$t_{1/2}$ [b] (s)	Time to reach equilibrium (h)	% Composition of hexanols at equilibrium		
			1-ol	2-ol	3-ol
 (V)	60	24	100	0	0
 (I)	3	0.5	100	0	0
 (VI)	1	0.25	100	0	0

[a] All thermal isomerizations were done at 150 ± 2°C in diglyme. [b] $t_{1/2}$ was determined graphically from kinetic data obtained in each case; it indicates the time required for the disappearance of 50% of the starting 3-hexylborane.

borane (10 mmol) was taken and to that 10 ml of dry diglyme was added. The resulting mixture was heated in an oil bath at 150 ± 2°C whose temperature was constantly maintained using a Thermowatch. Then 1-ml aliquots were withdrawn at regular intervals of time and oxidized using 2 ml of 3 *M* NaOH and 2 ml of 30% H_2O_2 by a standard procedure [4]. The alcohols were then extracted into ether, dried over 3 Å molecular sieves and analyzed by GC; The standard conditions used for GC analysis were: 10% Carbowax 1540 on Chromosorb W (1/8" × 12') and isothermal analysis at 70°C (Varian 1200 FID GC). A nitrogen atmosphere was maintained until the completion of oxidation.

The present study therefore brings out a very rapid and highly efficient synthetic route for the conversion of internal acyclic olefins into terminal olefins and their derivatives (Scheme 1).



SCHEME 1

We have thus far systematically examined the thermal isomerizations of 3-hexyldialkylboranes, employing a wide variety of dialkylboranes and clearly demonstrated the influence of steric factors on the rate and equilibrium of isomerization. Out of this study a gradual pattern has emerged in the migratory aptitude of these dialkylboranes, with bis(bicyclo[2.2.2]octyl)borane being the most powerful. We hope to examine the thermal isomerization of this new dialkylborane on a number of representative olefinic structures in the future in order to precisely understand the generality of its synthetic usefulness.

Acknowledgement

We gratefully acknowledge support from the National Science Foundation, Grant CHE 79-18881, and the Exxon Research and Engineering Company, which made this investigation possible.

References

1 H.C. Brown, U.S. Racherla and H. Taniguchi, J. Org. Chem., 46 (1981) 4313.
2 H.C. Brown and U.S. Racherla, Organometallics, 1 (1982) 765.
3 H.C. Brown and S.U. Kulkarni, J. Organometal. Chem., 218 (1981) 309.
4 H.C. Brown, Organic Synthesis via Boranes, Wiley-Interscience, New York, 1975.