(27) For a complete account, see J. T. Groves and M. Van Der Puy, *J. Am. Chem. Soc.*, **97**, 7118 (1975).
(28) It is important to note that no evidence for 1,2-hydride shifts (loss of deuterium) were observed when cyclohexanol deuterated at C-2 or C-4 was hydroxylated with $Fe(II)H_2O_2$ in contrast to the stereospecific hydride shift that has been reported to accompany cyclohexyl tosylate solvolysis. (a) J. B. Lambert, G. J. Putz, and C. E. Mixan, *J. Am. Chem. Soc.*, **94**, 5132 (1972); (b) J. E. Nordlander and T. J. McCrary, Jr., *ibid.*, **94**, 5133 (1972).
(29) K. Alder, F. H. Flock, and H. Wirtz, *Chem. Ber.*, **91**, 609 (1958).

Hydroboration. 43. Effect of Structure on the Reactivity of Representative Olefins toward Hydroboration by 9-Borabicyclo[3.3.1]nonane

Herbert C. Brown,* Ronald Liotta,[1a] and Charles G. Scouten[1b]

Contribution from the Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907. *Received December 24, 1975*

Abstract: The relative reactivities of 37 selected olefins toward hydroboration by 9-borabicyclo[3.3.1]nonane (9-BBN) in tetrahydrofuran solution were determined by two competitive techniques. The data for these reactions are presented to make clear the effect of each structural feature on the relative rate. Wherever comparable data are available, a comparison is made between 9-BBN and a second dialkylborane, disiamylborane, and the similarities and differences in the selectivities of the two reagents are pointed out. Both reagents have large steric requirements, reacting preferentially with the least hindered double bond. On the other hand, 9-BBN is far more sensitive to electronic influences, attributed to the greater electrophilic character of the bridging >BH moiety in the strained 9-BBN structure.

The utility of the 9-BBN group as a blocking group in syntheses via organoboranes[2] and its highly selective hydroborating ability[3] have been reported. 9-BBN exhibits remarkable regio- and stereoselectivity giving the highest degree of selectivity yet achieved.[3] For example, 1-hexene reacts to give 99.9% of the 1 isomer (regioselectivity) and norbornene reacts to yield 99.5% of the exo isomer (stereoselectivity). 9-BBN shows a remarkable preference for forming a carbon–boron bond to the least hindered terminal of a double bond, 4-methyl-2-pentene reacting to give 99.8% of the 2 isomer.[3] In view of these unique characteristics, it appeared appropriate to explore the effect of olefin structure on the rate of hydroboration with 9-BBN. Accordingly, we undertook a relative rate study of olefin hydroboration utilizing 9-BBN in THF solution at room temperature.

Results

Competitive Hydroboration of Olefins with 9-BBN in THF. The previous study[3] established the time required to achieve essentially complete hydroboration for olefins of different structural types. To obtain more precise reactivity data, selected pairs of olefins were treated with 9-BBN and the relative reactivities determined competitively. Two different experimental procedures were utilized. Both involved the mixing of two olefins in equimolar amounts (0.5 M in THF) in a reaction flask and the subsequent addition of only 1 equiv of 9-BBN (0.5 M in THF). An inert hydrocarbon (internal standard) was also added. In procedure A the mixture was analyzed by GLC for residual olefin after the hydroboration was complete. A stripper column[4] (¼ × 6 in. – 20% THEED column) was used to retain the intermediate organoborane and not allow it to pass into the second column (⅛ in. × 6 ft – 10% adiponitrile). The ratio of unreacted olefin to internal standard could now be easily determined. In procedure B the intermediate organoborane was oxidized with alkaline hydrogen peroxide to give 1,5-cyclooctanediol and the two alcohols corresponding to the organoboranes produced from the starting olefins. The alcohol to internal standard ratio was determined by GLC (⅛ in. × 12 ft – 10% SE-30) for each product. In both procedures the concentration of unreacted olefin can be determined following completion of the hydroboration. With these values in hand along with the initial concentration of each olefin, the relative rate is obtained by use of the Ingold and Shaw[5] expression: relative rate = $k_x/k_y = (\ln x_0 - \ln x)/(\ln y_0 - \ln y)$, where x_0 and y_0 are the initial concentrations and x and y are the residual concentrations of the two olefins being compared. Many olefin pairs were run using both procedures A and B and the results proved consistent.[6] Unless otherwise stated, the reactions lead cleanly to a quantitative conversion of product and all relative rates reported are at 25.00 ± 0.03 °C (procedure A) or ambient room temperature (procedure B).

The relative reactivities data for 9-BBN are summarized in Table I.

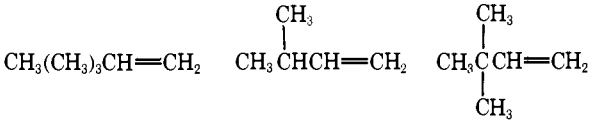
Discussion

9-BBN proved to be a highly selective reagent, with major similarities and difference from the selectivity exhibited by disiamylborane.[7,8] (On the other hand, diborane itself is a relatively insensitive reagent, exhibiting only minor effects of structure upon rate.[8]) Accordingly, it is of interest to compare the selective properties of 9-BBN with those of disiamylborane where such data are available, for examination of the similarities and differences.

Terminal Olefins, $RCH{=}CH_2$. The data for straight-chain 1-alkenes indicate that the rate of hydroboration is nearly independent of chain length. Thus, 1-hexene, 1-octene, 1-decene, and 1-dodecene all show similar reactivity with either 9-BBN or disiamylborane, as indicated by the relative rates.

	$CH_3(CH_2)_3CH{=}CH_2$	$CH_3(CH_2)_5CH{=}CH_2$
9-BBN	1.00	1.10
Sia_2BH	1.00	1.08

Branching in the R group decreases the rate of hydroboration significantly. Thus in going from 1-hexene to 3-methyl-1-butene, the rate with 9-BBN decreases by a factor of two and 3,3-dimethyl-1-butene reacts four times slower than the straight-chain olefin. A more dramatic decrease in rate is realized with disiamylborane.



9-BBN	1.00	0.50	0.23
Sia_2BH	1.00	0.57	0.047

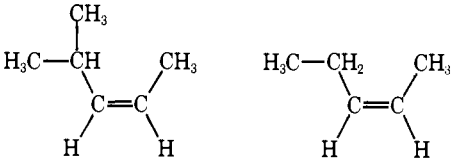
These results suggest that disiamylborane is somewhat more sensitive to the steric requirements of the alkene than is 9-BBN.

Branching at a position more remote from the double bond, such as at position 4, has little or no effect upon the rate.

Internal Olefins. The rate of 9-BBN hydroboration of *cis*-2-pentene is 100 times slower than that of 1-hexene. That is, internal olefins are considerably more sluggish in their reactivity than terminal olefins.

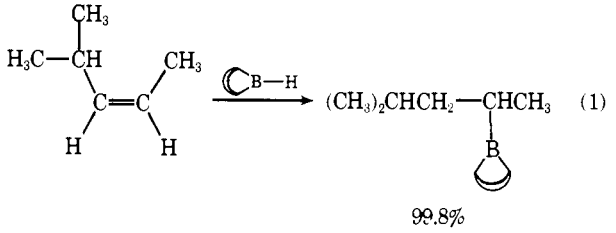
	$CH_3(CH_2)_3CH=CH_2$	$CH_3CH_2CH=CHCH_3$
9-BBN	100	1.00
Sia_2BH	50	1.00

If only one side of the internal olefin is branched, then the rate of 9-BBN hydroboration is only moderately reduced.



9-BBN	0.61	1.00

Apparently, this behavior follows from the fact that the 9-BBN reacts almost exclusively at the less-hindered side of the asymmetrically substituted double bond (eq 1). The steric

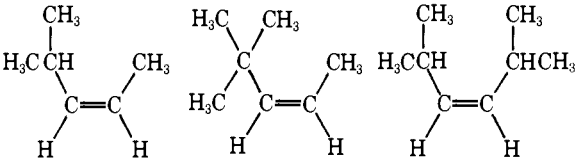


(1)

99.8%

environment at C2 of both olefins is essentially identical for the 9-BBN moiety.

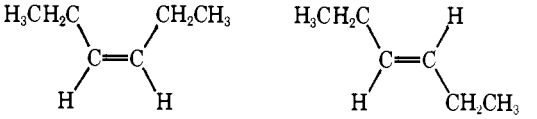
If the alkyl groups on both sides of the double bond are branched, the rate of 9-BBN hydroboration drops sharply. In a molecule such as 2,5-dimethyl-3-hexene there is no means available to the 9-BBN moiety to avoid the strain at the crowded alkyl groups.



9-BBN	160	100	1.00
Sia_2BH	6.25	1.00	1.25

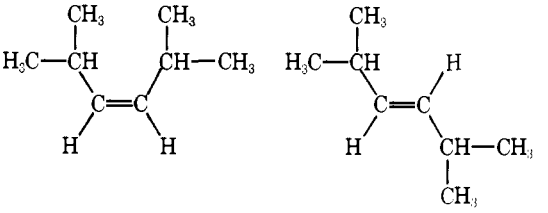
The rates of reaction of disiamylborane with these hindered internal olefins are all very slow and reveal much smaller effects of structure. It is possible that disiamylborane, with its larger steric requirements, finds it less possible to minimize the strain in the unsymmetrical derivatives in the manner achieved by 9-BBN.

Cis and Trans Isomers. It has long been established that cis alkenes undergo hydroboration with disiamylborane at a rate considerably faster than that of the corresponding trans alkenes. It is therefore fascinating to discover that the reverse is true for 9-BBN.



9-BBN	1.00	2.16
Sia_2BH	10.0	1.00

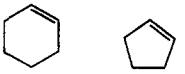
The phenomenon appears to be general and holds even for isomers containing highly branched alkyl groups.



9-BBN	1.00	2.9
Sia_2BH	2.5	1.00

Originally the greater reactivity of cis alkenes toward disiamylborane was attributed to the more strained double bond in the cis isomer.[8] The precise reason for the reversal in reactivity observed with 9-BBN is not clear. Nevertheless, this reversal in reactivity can be most useful in synthetic applications of hydroboration. It makes it possible to hydroborate preferentially either the cis or trans isomer merely by the proper selection of the hydroborating agent.

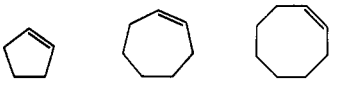
Cyclic Olefins. Cyclohexene is remarkably sluggish in the hydroboration reaction, both toward disiamylborane and 9-BBN. On the other hand, cyclopentene is quite reactive. Thus we have a major difference in the reactivities of these two structurally quite similar olefins.



9-BBN	1.00	107
Sia_2BH	1.00	140

The double bond in the cyclopentene molecule is considerably more strained than the double bond in cyclohexene.[9] Presumably this strain is responsible for the higher reactivity of cyclopentene toward both reagents.

Both cycloheptene and cyclooctene have highly strained double bonds.[9,10] Both exhibit reactivities considerably higher than that of cyclohexene with both reagents. However, whereas disiamylborane distinguishes considerably between the three strained olefins, 9-BBN does not.



9-BBN	1.00	1.10	0.96
Sia_2BH	1.00	18.6	68.6

Again, the precise basis for this difference in the reactivity pattern for the two hydroborating agents is not evident.

Finally, a bicycloalkene, norbornene, containing a highly strained double bond, exhibits an enhanced reactivity toward 9-BBN.

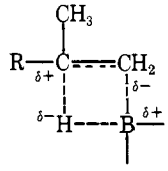
9-BBN	1.00	20

Effect of α-Methyl Substituents. Surprisingly, an α-methyl substituent increases the rate toward 9-BBN over that of the parent 1-alkene, in spite of the larger steric requirements. That is, the more sterically hindered double bond in 2-methyl-1-pentene reacts preferentially with 9-BBN over the less-hindered double bond in 1-hexene. The opposite is true for disi-

	$CH_3(CH_2)_3CH=CH_2$	$CH_3(CH_2)_2\underset{\displaystyle CH_3}{\underset{\vert}{C}}=CH_2$
9-BBH	1.00	1.94
Sia_2BH	1.00	0.049

amylborane. Here we find a factor of 20 favoring the less-substituted double bond.

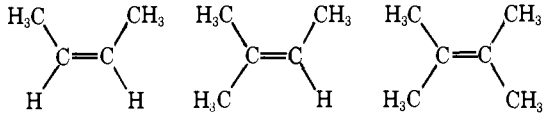
It is true that the inductive effect of the α-methyl substituent must increase the electron availability in the double bond of 2-methyl-1-pentene, thereby favoring the hydroboration reaction. To the extent that the transition state involves the development of an electron deficiency at C2 (partial carbonium ion character) with partial hydridic character at the >B–H moiety (**1**), the presence of the α-methyl should be favorable.



1

In the case of 9-BBN the relative openness of the boron atom must allow these electronic influences to operate. The much greater steric congestions in disiamylborane must swamp these small electronic contributions so that the steric factor predominates.

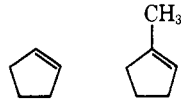
Addition of an α-methyl group to 2-butene has little effect on the rate with 9-BBN. On the other hand, the rate with disiamylborane is very slow.



9-BBN	1.00	0.90	0.0064

In 2-methyl-2-butene the steric environment at the atom adding the 9-BBN moiety must be very similar to that it experiences in *cis*-2-butene. The argument is the same as that used earlier to account for the close similarity in the reactivities toward 9-BBN of *cis*-2-pentene and *cis*-4-methyl-2-pentene.

An α-methyl substituent in cyclopentene results not in an increase, but in a small decrease in rate. Evidently in trisubstituted systems such as 2-methyl-2-butene and 1-methylcyclopentene, the steric factor must overcome the small electronic interactions that enhance the rate of 2-methyl-1-pentene (see above).

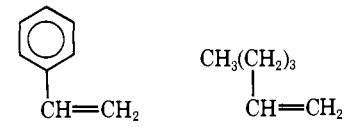


9-BBN	1.00	0.21

In 2,3-dimethyl-2-butene, the 9-BBN moiety can no longer adjust the situation so as to minimize the steric interactions. The rate drops sharply (see above). Disiamyborane fails to react with this hindered olefin at any measurable rate.

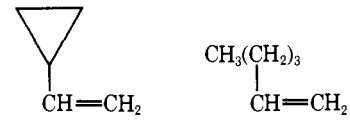
Effect of α-Conjugating Substituents. Both aromatic groups and cyclopropyl groups can conjugate strongly with an electron-deficient center.[11] It was of interest to explore their influence on the rate of hydroboration of double bonds containing them as substituents.

Styrene, the simplest olefin with a phenyl substituent on the double bond, is much less reactive than simple 1-alkenes. Thus, it reacts with 9-BBN at a rate 40 times slower than 1-hexene.



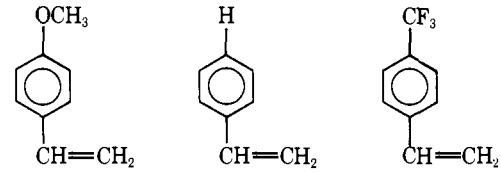
9-BBN	1.00	40
Sia_2BH	1.00	36

On the other hand, a cyclopropyl group increases the reactivity of the double bond.



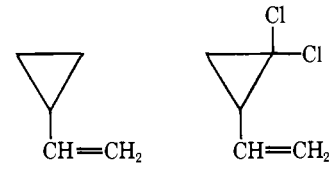
9-BBN	2.3	1.0

The introduction of electron-supplying substituents into the aromatic ring facilitates the reaction with 9-BBN, and vice versa for electron-withdrawing substituents.



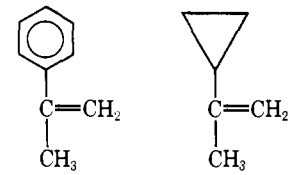
9-BBN	14.0	1.00	0.2
Sia_2BH	1.4	1.00	0.9

Although we do not have data for electron-supplying substituents, the introduction of electron-withdrawing substituents into the cyclopropane ring has the predicted effect of decreasing the rate.



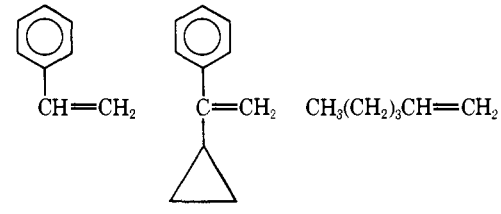
9-BBN	1.00	0.044

An α-methyl substituent enhances the rate of both styrene (1.00) and vinylcyclopropane (1.00).



9-BBN	5.62	2.8
Sia_2BH	1.21	

Finally, we note that a cyclopropyl group largely overcomes the deactivating effect of a phenyl group.



9-BBN	0.025	0.28	1.00

Summary and Conclusions

The relative reactivities of the olefins studied are arranged in decreasing order of reactivity relative to 1-hexene as 1.00 and are summarized in Table I.

Table I. Relative Reactivities of Representative Olefins Toward 9-BBN in THF at 25 °C (1-Hexene = 1.00)

2-Cyclopropylpropene[b]	6.37	Styrene[a,b]	0.025
Vinylcyclopropane[b]	2.3	1-Methylcyclopentene[a]	0.015
2-Methyl-1-pentene[a,b]	1.94	*trans*-3-Hexene[b]	0.012
Norbornene[a,b]	1.45	*cis*-2-Pentene[a]	0.010
1-Dodecene[b]	1.12	*cis*-2-Butene[b]	9.5×10^{-3}
1-Octene[a,b]	1.10	2-Methyl-2-butene[a]	8.6×10^{-3}
1-Decene[a]	1.08	*trans*-4-Methyl-2-pentene[b]	7.6×10^{-3}
1-Hexene	1.00	*cis*-4-Methyl-2-pentene[a]	6.1×10^{-3}
3-Methyl-1-butene[a]	0.50	*cis*-3-Hexene[a,b]	5.6×10^{-3}
p-Methoxystyrene[b]	0.349	*p*-Trifluoromethylstyrene[b]	5.2×10^{-3}
α-Cyclopropylstyrene[b]	0.28	*cis*-4,4-Dimethyl-2-pentene[a]	3.8×10^{-3}
3,3-Dimethyl-1-butene[a]	0.236	Cyclohexene[a]	6.7×10^{-4}
2-*p*-Tolylpropene[b]	0.21	*trans*-Propenylbenzene[a]	6.3×10^{-4}
α-Methylstyrene[b]	0.14	*cis*-Propenylbenzene[a]	2.5×10^{-4}
2,2-Dichlorocyclopropylethene[b]	0.10	*trans*-2,5-Dimethyl-3-hexene[a]	1.1×10^{-4}
Cycloheptene[a]	0.076	1-Methylcyclohexene[a]	1.1×10^{-4}
Cyclopentene[a,b]	0.072	4-*tert*-Butylcyclohexene[b]	7.7×10^{-5}
Cyclooctene[a]	0.069	2,3-Dimethyl-2-butene[a]	6.1×10^{-5}
		cis-2,5-Dimethyl-3-hexene[a]	3.8×10^{-5}

[a] Experimental procedure A. [b] Experimental procedure B.

The organic chemist now has available for synthetic applications a new dialkylborane, 9-BBN, which has a predictable regio- and stereochemistry and is both convenient to use and readily available. This reagent, together with disiamylborane, provides the organic chemist with powerful procedures for achieving selective hydroboration.

Disiamylborane is a relatively gentle hydroborating reagent with large steric requirements. In many instances it proves relatively insensitive to the electronic situation with its reaction controlled primarily by the steric factor. Thus it reacts preferentially with 1-hexene in the presence of 2-methyl-1-pentene.

On the other hand, 9-BBN is much less sensitive to the steric factor. It reacts quite readily with a hindered olefin such as 2,3-dimethyl-2-butene, one which is inert toward disiamylborane. Because of its lower sensitivity to steric forces, it can be influenced by electronic factors that disiamylborane ignores. Thus 9-BBN reacts preferentially with 2-methyl-1-pentene in the presence of 1-hexene.

Even where steric forces are not a factor, 9-BBN is far more sensitive to the electron availability in the double bond than is disiamylborane. Thus, the difference in reactivity between *p*-trifluoromethylstyrene and *p*-methoxystyrene is 1.5 for disiamylborane and 67 for 9-BBN.

The versatility made possible by the application of these two different dialkylboranes is indicated by the results with cis-trans isomeric pairs. Disiamylborane reacts preferentially with the cis isomer, 9-BBN with the trans.

It should be recognized that the reactivities of double bonds will vary greatly with the structure of the molecule. Consequently, absolute predictions for new structures will necessarily be uncertain. Nevertheless, the availability of the reactivity data for the representative olefins in Table I should greatly ease the task of the chemist in selecting the proper reagent for a particular selective hydroboration.

Experimental Section

The organoboranes were always handled under an atmosphere of prepurified nitrogen (Airco) with careful exclusion of both oxygen and water. All glassware, syringes, and needles were oven dried at 130 °C before use. The glassware was assembled while hot and cooled under a flow of nitrogen. When the assembled apparatus was cool and had been thoroughly flushed with nitrogen, the injection port of the reaction flask was capped with a rubber serum stopple. A small positive pressure of nitrogen was maintained thereafter, using a mercury bubbler as a pressure relief valve. Syringes were assembled and fitted with needles while hot, then cooled as assembled units; H NMR, ir, and mass spectra were obtained with a Varian T-60, a Perkin-Elmer 700, and a Hitachi RMU-6A, respectively. GLC analyses of alcohols and olefins were carried out using a Varian Model 1200 F.I.D. or a Hewlett-Packard 5750 chromatograph equipped with the indicated columns.

Materials. The preparation of 9-BBN[3,12] and disiamylborane[8] solutions in THF was carried out as previously described. Styrene (J. T. Baker) (bp 36 °C (19 mm), n^{20} D 1.5474) was distilled immediately before use. THF was distilled from $LiAlH_4$ and maintained under nitrogen. 2,2-Dimethylcyclopropylethene[13] was prepared according to a published procedure. Vinylcyclopropane, 2-cyclopropylpropene, α-cyclopropylstyrene and 2-*p*-tolylpropene were synthesized following general procedure for closely related molecules.[14] All compounds have ir and ^{1}H NMR which are consistent with structure. *p*-Methoxystyrene, *p*-trifluoromethylstyrene, α-methylstyrene, and norbornene were purchased from Aldrich. The styrene derivatives were stored at 0 °C in a cold room and distilled from $LiAlH_4$ (except for *p*-trifluoromethylstyrene) immediately before use. 1-Dodecene, 2-methyl-1-pentene, *cis*-3-hexene, *trans*-2,5-dimethyl-3-hexene, *cis*-2,5-dimethyl-3-hexene, and 1-methylcyclohexene were purchased from Chemical Samples. Cyclooctene was purchased from Columbia Carbon Co. All other olefins and hydrocarbons (internal standards) were purchased from Phillips. All commercial olefins were used after checking indices of refraction and GLC (⅛ in. × 12 ft 10% SE-30 on Chromosorb W column).

Experimental Procedure A. A dry 100-ml flask with an injection inlet was equipped with a magnetic stirring bar and a connecting tube leading to a low-pressure nitrogen source. The flask was thoroughly flushed with nitrogen before the injection inlet was capped with a rubber serum stopple. A slight positive pressure of nitrogen was maintained thereafter. The flask was immersed in a water bath at 25.00 ± 0.03 °C and charged via syringe with 5 mmol (2.5 ml) each of two olefins and 0.5 ml of octane (internal standard). Several minute (0.1 ml) samples were removed and analyzed by GLC (¼ × 6 in. 20% THEED column in series with a ⅛ in. × 12 ft 10% SE-30 on 100–120 mesh Varaport 30 maintained at 70–80 °C) for the initial olefin/octane ratio.

To the stirred olefin mixture was then added (via syringe) 10 ml of the 0.5 M 9-BBN/THF solution. Sufficient time was allowed to ensure complete reaction, then samples were removed and analyzed by GLC for the final olefin/octane ratios.

Experimental Procedure B. A dry 200-ml round-bottom flask with a septum inlet (which was sealed with a rubber serum stopple), a magnetic stirring bar, and a reflux condenser fitted with an adapter which was connected to a mercury bubbler was purged with prepurified nitrogen (Airco) for 5–10 min. Two dry-nitrogen flushed syringes equipped with spring-loaded stainless steel stopcocks were used to weigh out 15 mmol each of two olefins. These olefins were injected directly into the 200-ml flask. *n*-Nonane (1.00 ml) was added as an internal standard. A stock solution of 9-BBN (0.50 M THF) supplied 15.0 mmol (30.0 ml) of hydride. The 30.0 ml of 9-BBN/THF was added (via syringe) slowly (2–4 min) with stirring. A slight amount of heat is noticed if addition is too fast. After sufficient time for

complete reaction, the mixture was oxidized. NaOH solution (3 M, 6 ml, large excess) was injected into the flask followed by H_2O_2 (30% solution, 6 ml, excess), which was added dropwise over 15–25 min. (More rigorous conditions, 1 h at 50 °C, were utilized for the more hindered derivatives, such as *B*-thexyl-9-BBN.)

The mixture was stirred for an additional 1.0–1.5 h, then the water layer was saturated with K_2CO_3 (anhyd) and the THF layer was separated and dried ($MgSO_4$, anhyd). The water layer was extracted with two 15-ml portions of diethyl ether, which were dried ($MgSO_4$, anhyd) and combined with the first extract. GLC analysis was carried out on a Varian 1200 Aerograph (⅛ in. × 12 ft 10% SE-30 on 100–120 mesh Varaport 30) and/or Hewlett-Packard 5750 (¼ in. × 6 ft 10% SE-30 on Chromosorb W). The alcohol/internal standard ratios were determined.

References and Notes

(1) (a) Graduate research assistant on Grant GM 10937 of the National Institutes of Health; (b) Graduate research assistant on Grant GP-6942X of the National Science Foundation.
(2) E. F. Knights and H. C. Brown, *J. Am. Chem. Soc.*, **90**, 5250 (1968).
(3) H. C. Brown, E. F. Knights, and C. G. Scouten, *J. Am. Chem. Soc.*, **96**, 7765 (1974).
(4) Blank runs were performed using known olefin/octane ratios to ensure the reliability of the procedure.
(5) C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2818 (1927).
(6) Table I shows six relative rate values were obtained by both procedures. The actual experiment numbers were identical to within ±2%.
(7) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 3222 (1960).
(8) H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **83**, 3417 (1961).
(9) R. B. Turner and W. R. Meador, *J. Am. Chem. Soc.*, **79**, 4133 (1957).
(10) The values reported for the rate constants for the reaction of disiamylborane with cycloheptene and cyclooctene, Table III of H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **85**, 2063 (1963), should be corrected as follows:

	Rel reactivity	k_2, 10^{-4} l. mol^{-1} s^{-1}
Cycloheptene	7	72
Cyclooctene	26	266

In this same table *cis*- and *trans*-2,4-dimethyl-2-pentene should read *cis*- and *trans*-2,5-dimethyl-3-hexene.

(11) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 2397 (1973).
(12) 9-BBN is available from the Aldrich Chemical Co., Milwaukee, Wisc.
(13) R. C. Woodward and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 2542 (1959).
(14) The ketone was converted to the tertiary alcohol using the procedure of J. D. Buhler, *J. Org. Chem.*, **38**, 904 (1973). The tertiary alcohol was then dehydrated to the desired olefin by using a catalytic amount of iodine and distilled through a 20-cm Widmer column.

Solvolysis of 1-Substituted-2-adamantyl Sulfonates. Bridging or No Bridging?

D. Fărcaşiu[1]

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540.

Received October 17, 1974

Abstract: The solvolysis rates (50% ethanol) of 2-adamantyl tresylate (**1a**-OTres, Tres = $CF_3CH_2SO_2$–) and deactivated substrates 1-carbomethoxy (**1g**-OTres) and 1-cyano-2-adamantyl tresylate (**1h**-OTres) are correlated with σ^* constants by a straight line of slope $\rho^* = -4.09$ ($r = 0.9986$) at 25 °C. A small amount (6%) of rearranged product is obtained from **1g**, while **1h** gives 38% rearranged product (for which the 8-cyano-4-*exo*-protoadamantanol structure is established). The extent of rearrangement for **1h** is one-third larger than that for 1-methyl-2-adamantyl substrate (**1b**), which solvolyzes 14–40 times faster than **1a.** It has been concluded previously that ionization of **1b** is anchimerically assisted. On this basis, a rate-product correlation requires that ionization of **1h** be even more so. However, considering all effects upon rate, anchimeric assistance in **1b** must be at best marginal, the possible extent of stabilization by bridging being less than 1 kcal/mol. An equally satisfactory model can be based on the assumption that σ bridging is absent in the solvolysis of these substrates, but ionization is limiting (k_c) and rearrangement takes place subsequently. Other findings which can be used as arguments for a σ-bridged intermediate in the solvolysis of **1b** are examined critically. It is concluded that the existing data do not permit a definite decision to be made for one of the two models (marginal acceleration by σ bridging or no σ bridging).

The 2-adamantyl system (**1a**) is exceptional among *sec*-alkyl substrates, since it solvolyzes by a limiting[2] (k_c) mechanism, with little or no solvent (k_s) or anchimeric (k_Δ) participation.[3,4] A 1-methyl group (as in **1b**) increases the rate of solvolysis by a factor of 14–38 over **1a** and leads to significant amounts (28%) of the rearranged product 4-methyl-4-*exo*-protoadamantanol (**2a**-OH) and some olefin.[5] The same reaction products (with minor variations in distribution) are formed from the protoadamantyl precursors, **2a**-ODNB and **2b**-OTs.[5] The rate enhancement and extent of rearrangement are even more important for the higher 1-alkyl derivatives (**1c–f**-OTs).[5b] This fact, together with other mechanistic criteria (vide infra), led to the conclusion that solvolyses of **1b–f** involve the σ-bridged ions **3a** as intermediates.[5] We undertook to test this conclusion and to evaluate quantitatively the acceleration by bridging in **1b** by an established procedure,[6] namely by studying the solvolysis rates of 2-adamantyl sulfonates with representative deactivating groups in the 1 position (**1g,h**), thereby establishing the magnitude of acceleration in **1a** through the deviation from a Hammett-Taft plot.[6]

The required alcohols,[7] 1-carbomethoxy- (**1g**-OH) and 1-cyano-2-adamantanol (**1h**-OH) were obtained from protoadamantanone[8] (**2c**) via the epoxide **2d,** which in acidic medium gave the diol **1i.** Chromic acid oxidation of **1i** gave 1-carboxy-2-adamantanone (**1,** R = COOH; R′, X = O),[9] from which **1g** and **1h** were obtained by standard procedures (see Experimental Section). The tresylates of **1a,b,g,h** (X = $CF_3CH_2SO_2O$, OTres) were prepared[8b,10] and solvolyzed. The rates are given in Table I.[11] The rates for **1a**-OTres, **1g**-OTres, and **1h**-OTres were plotted[13] against the σ^* values,[14] giving a straight line (line A in Figure 1) with the slope $\rho^* = -4.09$ (correlation coefficient $r = 0.9986$) at 25 °C. As foreseen, the rate for the 1-methyl-2-adamantyl tresylate (**1b**-OTres) exhibits an upward deviation.

The solvolysis products (in 60% acetone[5]) were analyzed by GLC–mass spectrometry. Besides the expected alcohol (**1g**-OH and **1h**-OH, respectively) an isomeric alcohol was found in a small amount (6%) for **1g,** but in an important amount (38%) for **1h.** The mass spectra of these indicated the protoadamantanol structure **2e** and **2f,** respectively. Also, the