800 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.60; N, 6.11. Found: C, 73.43; H, 6.50; N, 5.91.

Isopropyl *N*-[1-(1-naphthyl)ethyl]carbamate (14): mp 92–94 °C (hexane); ^1H NMR ($CDCl_3$) δ 1.20 (d, 6 H), 1.60 (d, 3 H), 4.90 (septet, 1 H), 4.8–5.1 (broad d, 1 H), 5.60 (quintet, 1 H), 7.2–8.2 (m, 7 H); IR ($CHCl_3$) 3680, 3620, 3440, 3020, 2980, 1710, 1500, 1240, 1110, 1060, and 810 cm^{-1}. Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.54; H, 7.29; N, 5.57.

2-(1,3-Dichloropropyl) *N*-[1-(1-naphthyl)ethyl]carbamate (15): mp 104.5–105.5 °C (hexane–CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.63 (d, 3 H), 3.68 (broad d, 4 H), 5.10 (quintet, 1 H), 5.2 (broad d, 1 H), 5.60 (quintet, 1 H), 7.3–8.2 (m, 7 H); IR ($CHCl_3$) 3690, 3620, 3440, 3030, 2980, 1725, 1505, 1240, 1200, 1065, and 810 cm^{-1}. Anal. Calcd for $C_{16}H_{17}NO_2Cl_2$: C, 58.91; H, 5.25; N, 4.29; Cl, 21.74. Found: C, 58.98; H, 5.24; N, 4.12; Cl, 21.83.

Methyl *N*-methylcarbamate (16): clear, colorless liquid; bp 76–78 °C (45 torr); ^1H NMR ($CDCl_3$) δ 2.75 (d, 3 H), 3.70 (s, 3 H), 5.0–5.4 (broad s, 1 H); IR (film) 3350, 2940, 1725, 1540, 1340, 1260, 1000, 900, and 775 cm^{-1}.

Methyl *N*-*tert*-butylcarbamate (17): clear, colorless liquid; bp 57–58 °C (15 torr); ^1H NMR ($CDCl_3$) δ 1.32 (s, 9 H), 3.58 (s, 3 H), 4.5–4.9 (broad s, 1 H); IR (film) 3350, 2950, 1715, 1530, 1350, 1260, 1215, 1180, 1100, 930, 775, and 715 cm^{-1}.

Ethyl *N*-*tert*-butylcarbamate (18): clear, colorless liquid; bp 66–67 °C (15 torr); ^1H NMR ($CDCl_3$) δ 1.20 (t, 3 H), 1.35 (s, 9 H), 4.05 (quartet, 2 H), 4.5–4.8 (broad s, 1 H); IR (film) 3350, 2950, 1715, 1525, 1450, 1380, 1260, 1210, 1080, 925, 870, and 775 cm^{-1}.

***tert*-Butyl *N*-*tert*-Butylcarbamate (19).** To a solution of di-*tert*-butyl dicarbonate (7.21 g, 33 mmol) in 25 mL of CH_2Cl_2 was added slowly a solution of 2.20 g (30 mmol) of *tert*-butylamine and 3.10 g (31 mmol) of triethylamine in 15 mL of CH_2Cl_2. The reaction was stirred for 1 h, extracted with 3 N HCl (2 × 25 mL) and H_2O (1 × 25 mL), and dried ($MgSO_4$). Evaporation of the solvent gives 4.62 g of **19** (89%): bp 72–73 °C (15 torr); clear, colorless liquid which solidifies in receiving vessel; mp 37–39 °C; ^1H NMR ($CDCl_3$) δ 1.30 (s, 9 H), 1.45 (s, 9 H), 4.3–4.6 (broad s, 1 H).

Dynamic Nuclear Magnetic Resonance Studies. Proton spectra were obtained on Varian Associates EM-390 (90 MHz) or HR-220 (220 MHz) spectrometers. Carbon spectra were obtained on a Jeol JNM-FX60 spectrometer operating in the FT mode, using 8 K data points and a frequency width of 2500 Hz (167 ppm), corresponding to a data point resolution of 0.61 Hz (0.04 ppm). Temperature calibration was done using Varian's standard methanol sample. Samples were prepared in the appropriate solvent at about 0.5 M concentration. Experimental line shapes were matched to the Block-McConnell theoretical line shapes calculated with an IBM 360/75 computer.

Conclusion

Since the ^1H NMR and the chromatographic behavior of diastereomeric type 1 carbamates are strongly influenced by their conformational behavior, demonstration that a pair of diastereomers behaves very similarly in conformational terms is reassuring. All such diastereomers herein studied predominantly populate the *Z* conformation to an extent of ca. 82 ± 5%, a value but slightly perturbed by solvent polarity. In view of these findings, our earlier correlations of NMR spectral differences and chromatographic behavior are still reliable. However, the present study has shown that NMR measurements made in the stopped exchange region have greater informational content and lead to even more facile assignments of stereochemistry.

Acknowledgment. We wish to thank the National Science Foundation and the National Institute of Health for funding this work.

Registry No. 2b, 71927-70-3; **3b**, 65337-09-9; **4a**, 71871-94-8; **4b**, 71871-95-9; **5b**, 65337-07-7; **6a**, 71871-96-0; **6b**, 71871-96-0; **7b**, 65414-55-3; **8a**, 71885-03-5; **8b**, 71885-04-6; **9a**, 71871-97-1; **9b**, 71885-37-5; **10a**, 71871-98-2; **10b**, 71885-05-7; **11a**, 71927-76-9; **11b**, 71885-06-8; **12a**, 71871-99-3; **12b**, 71872-00-9; **13**, 71872-01-0; **14**, 71872-02-1; **15**, 71885-38-6; **16**, 6642-30-4; **17**, 27701-01-5; **18**, 1611-50-3; **19**, 71872-03-2; di-*tert*-butyl dicarbonate, 24424-99-5; *tert*-butylamine, 75-64-9.

Selectivity of Olefin Formation from Platinacyclobutanes

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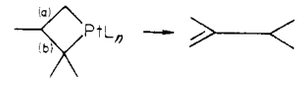
Platinacyclobutanes were shown to prefer olefin formation along the least-substituted edge of the platinacyclobutane when the olefin formed via a β-hydrogen abstraction from a ring carbon. In addition, the formation of olefins was sensitive to α substituents, which led to a preference for cis over trans olefins.

We recently reported[1] upon labeling experiments with dichlorobis(pyridine)(1,1,2-trimethylpropane-1,3-diyl)-platinum(IV) (1), which indicated the *mode* of olefin formation from this platinacyclobutane occurred via a β-hydrogen abstraction–reductive elimination process rather than by an α-hydrogen abstraction–reductive elimination process. In the same study, we also established that a β-hydrogen could be abstracted from a methyl substituent as well as from a ring carbon. While hydrogen abstraction from a substituent can lead to only one olefin, hydrogen abstraction from a ring carbon can often lead to two different olefins. In this study we report upon the *selectivity* in forming olefins from platinacyclobutanes.

The platinacycle 1 produced 2,3-dimethyl-1-butene as the only olefin although one could, theoretically, also form 2,3-dimethyl-2-butene from 1. We thought it was interesting that the olefin formed upon what would be the least-substituted edge (a) of the platinacycle. This gave a thermodynamically less stable olefin than if the olefin formation had occurred along the more-substituted edge (b). Hydrogen abstraction from a substituent methyl was shown to occur in conjunction with hydrogen abstraction from a ring carbon. This process, however, could lead only



1

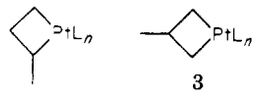
(1) Johnson, T. H.; Cheng, S.-S. *J. Am. Chem. Soc.* **1979**, *101*, 5277.

0022-3263/79/1944-4896$01.00/0

to the observed product. We were interested in determining if olefin formation along the least-substituted edge was a general reaction for platinacyclobutanes.

Results

Methylcyclopropane was reported[2] to react with Zeise's dimer[3] to give a mixture of **2** and **3**.[4] However, the decomposition of this mixture gave only 1-butene. The isomer **2** could give 1-butene by either β-hydrogen abstraction–reductive elimination reactions from the methyl substituent or from the ring carbon along the least-substituted edge. Olefin formation directed along the substituted edge should give 2-butene. The isomer **3** could



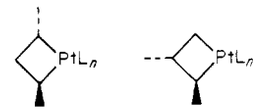
2 **3**

give only isobutylene by this process. These results are explained[2] by hypothesizing a fast equilibrium between **2** and **3** where **2**, being sterically hindered, formed a platinum–(1-butene) complex which in turn would liberate 1-butene. The rearrangement of a 1-phenyl substituted platinacyclobutane to a 2-phenyl substituted platinacyclobutane has been the subject of several recent papers.[5] Therefore, the proposed equilibrium between **2** and **3** seemed quite reasonable.

We took a somewhat different approach. Rather than allowing platinacyclobutanes to decompose to olefins in solution as has been done in the past, we decomposed THF solutions of the platinacyclobutanes directly in a VPC injection port at 130 °C. This technique has been used previously for examining olefin products from the decomposition of titaniacyclopentanes[6] and was found to give a different distribution of olefins from that which was obtained by solution mediated decompositions. By using this technique we examined the olefin products of platinacyclobutanes prepared from methylcyclopropane, *trans*-1,2-dimethylcyclopropane, and 1,1-dimethylcyclopropane. The analysis of the isomeric butenes and pentenes is easily accomplished by the use of a silver nitrate–ethylene glycol column[7,8] (see Experimental Section for additional details).

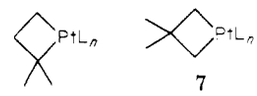
The preparation of **2** and **3** by literature methods[2] and subsequent decomposition at 130 °C led to 1-butene (81%) and *cis*-2-butene (19%).[9] We did not observe any *trans*-2-butene or isobutylene.[10] Interestingly, we observed *cis*-2-butene, which can be accounted for by hydrogen abstraction from a ring carbon with olefin formation along a substituted edge of the platinacyclobutane **2**.

One can obtain two different platinacyclobutanes, **4** and **5**, from Zeise's dimer and *trans*-1,2-dimethylcyclopropane. The two isomers can arise from two different platinum insertion pathways or from a rearrangement of **4** to **5**. Decomposition of the platinacycles obtained from this reaction gave 1-pentene (43%), *cis*-2-pentene (30%), 2-methyl-1-butene (17%), and 3-methyl-1-butene (10%). The olefins 1-pentene and 2-pentene could come only from **4** whereas 2-methyl-1-butene and 3-methyl-1-butene could come only from **5**. Thus, the presence of **4** and **5** can be confirmed by the olefin products themselves.



4 **5**

From Zeise's dimer and 1,1-dimethylcyclopropane, one can obtain the platinacycles **6** and **7**. The isomer **6** could give, theoretically, 2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene whereas **7**, not having any β-hydrogens, would not be expected to give olefins formed by this pathway upon decomposition. We obtained only two of the possible three olefins: 2-methyl-1-butene (51%) and 3-methyl-1-butene (49%).



6 **7**

In addition, we reacted *cis*-1,2-dimethylcyclopropane with Zeise's dimer. It has been reported that *cis*-1,2-dialkylcyclopropanes do not undergo formation of platinacyclobutanes.[11,12] Indeed, we were unsuccessful in obtaining a platinacyclobutane from this cyclopropane. However, an interesting set of olefins was obtained directly as products. These were 1-pentene (23%), *cis*-2-pentene (20%), 2-methyl-1-butene (15%), 3-methyl-1-butene (6%), and 2-methyl-2-butene (36%). We still did not observe any *trans*-2-pentene.

Discussion

The olefins formed from the platinacycles **2** and **3** are similar to the solution result except that some *cis*-2-butene was also obtained. This isomer can arise by olefin formation along the substituted edge of the platinacyclobutane **2**. Conversely, 1-butene can arise by two modes: olefin formation along the least-substituted edge of the platinacycle or hydrogen abstraction from a methyl substitutent. The formation of 2-butene is a departure from forming olefins exclusively along the unsubstituted edge of the platinacycle as was found for **1**. It is also interesting that only the cis isomer was found.

(2) Al-Essa, R. J.; Puddephatt, R. J.; Tripper, C. F. H.; Thompson, P. J. *J. Organomet. Chem.* **1978**, *157*, C40.

(3) Zeise's dimer is di-μ-chloro-dichloro(η^2-ethene)diplatinum(II).

(4) The presence of **2** and **3** was determined by NMR.[2]

(5) Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *Chem. Commun.* **1976**, 626. Al-Essa, R. J.; Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Am. Chem. Soc.* **1979**, *101*, 364. Al-Essa, R. J.; Puddephatt, R. J. *Inorg. Chim. Acta.* **1979**, *34*, L187. Johnson, T. H. *J. Org. Chem.*, **1979**, *44*, 1356. Casey, C. P.; Scheck, D. M.; Shusterman, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 4233.

(6) McDermatt, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529.

(7) Bednas, M. E.; Russel, D. S. *Can. J. Chem.*, **1958**, *36*, 1272.

(8) All of the possible isomeric butenes and pentenes are well separated and thus easily identified by this column. Structural confirmation was carried out by isolation and spectroscopic comparison to authentic samples.

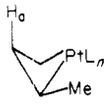
(9) The percentages represent percent of olefin product. In all of the platinacyclobutanes decomposed in this study, we also obtain the parent cyclopropane in addition to the olefins. For example, from **2** and **3** we obtained methylcyclopropane in addition to 1-butene and *cis*-2-butene. Methylcyclopropane could form by a formal reductive elimination step and does not require the two-step β-hydrogen abstraction–reductive elimination process being discussed here for olefin formation. Hence, the formation of cyclopropanes does not bear upon the present study of selectivity in olefin formation.

(10) A control experiment was used in all of the platinacyclobutane decompositions to confirm that olefins (isomeric butenes or pentenes) are not isomerized under the reaction conditions. In addition, the presumed platinum–olefin complexes were prepared from Zeise's dimer and the appropriate olefin. These complexes were injected into the VPC at 130 °C and found to give only the same olefin as was used to prepare the complex.

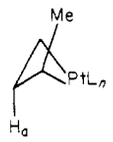
(11) McQuillin, F. J.; Powell, K. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2123.

(12) The lack of observable platinacycle formation from *cis*-1,2-dialkylcyclopopanes has been erroneously interpretted, by some, as the lack of reactivity for the cis isomer vs. the trans isomer. This is false. The cis isomers do react but do not form isolable platinacycles. This difference was noted by the original reporters of this type of reaction (ref 11, p 2125).

Platinacyclobutanes are puckered[13] and thus one can draw two possible conformations, **2a** and **2b**, for **2**. The olefins 1-butene and 2-butene could be formally derived from either of these conformations. However, one should obtain only *trans*-2-butene from **2a** and only *cis*-2-butene from **2b**. The results clearly demonstrated an overwhelming preference for *cis*-2-butene. This seems to suggest that if olefin formation along a substituted edge does occur, then it will occur along that edge where the α substituent and H_a are on the opposite face of the platinacycle. In **2**, this would correspond to the formation of *cis*-2-butene from **2b**. This observation further suggests that the α substituent somehow impedes olefin formation along the substituted edge of the platinacycle if both it and H_a reside on the same face of the platinacyclobutane. The source of this inhibition may well be steric, but without an X-ray analysis of **2**, it is not possible to make that assessment at this time.



2a



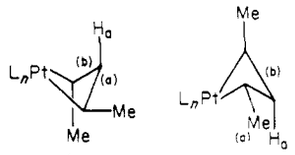
2b

The platinacycle **4** can give 1-pentene and 2-pentene, and these products account for 73% of the olefins formed. The other two olefins, 2-methyl-1-butene and 3-methyl-1-butene, account for the other 27% and can arise only from **5**. In addition, each of these four olefins can come only by one mode of olefin formation as well as from only one platinacycle. Therefore, 1-pentene comes from **4** via hydrogen abstraction from a methyl group, *cis*-2-pentene comes from **4** via hydrogen abstraction from a ring carbon, 2-methyl-1-butene comes from **5** via hydrogen abstraction from a ring carbon along the least-substituted edge of the platinacyclobutane, and 3-methyl-1-butene comes from **5** via hydrogen abstraction from a methyl substituent. The selectivity for olefin formation along the least-substituted edge is evidenced by the formation of 2-methyl-1-butene and the total absence of 2-methyl-2-butene which would arise from the same hydrogen abstraction but along the substituted edge.

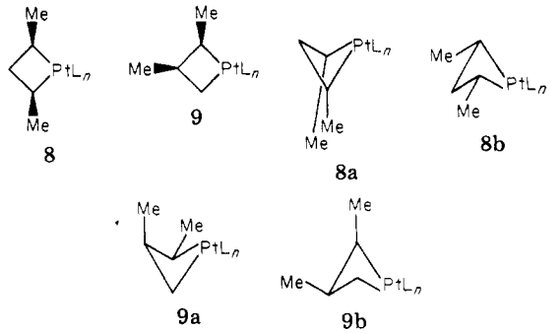
This type of selectivity is observed again for the olefin products derived from **6**. Hydrogen abstraction from a methyl substituent gives 2-methyl-1-butene whereas hydrogen abstraction from a ring carbon would give 3-methyl-1-butene (the observed product) if the olefin formed along the unsubstituted edge or 2-methyl-2-butene (not observed) if the olefin formed along the substituted edge of the platinacyclobutane.

The preference for *cis*-2-pentene in the decomposition of **4** is consistent with the observations made for **2**. Two conformations, **4a** and **4b**, can be drawn for **4**, but here they are enantiomeric. Both edges (a) and (b) are substituted. Olefin formation along edge (a) leads to *trans*-2-pentene whereas olefin formation along edge (b) would give *cis*-2-pentene. Olefin formation along edge (b) has the α substituent and H_a on opposite faces of the platinacyclobutane, and thus, the formation of *cis*-2-pentene is consistent with the observations made with **2**.

The olefins obtained from *cis*-1,2-dimethylcyclopropane may occur through the intermediacy of a platinacyclobutane, although one is not observed in this instance. If this occurred, then one would expect the formation of platinacyclobutanes **8** and **9**, and these would be expected to be quite unstable. Thus, decomposition to form olefins is quite understandable. The structures **8** would possess severe 1,3-diaxial interaction in **8a**. While the structure **8b** would relieve this interaction, it still would not be expected to be as stable as platinacycles formed from *trans*-1,2-dimethylcyclopropane. In **8a**, the axial proton at C-2 is not encumbered by either of the methyl groups whereas this proton in **4** is always encumbered by one of the methyl groups. Thus, the isomer **8** could readily form olefins to relieve this strain or rearrange to **9**. In **8b**, the axial proton at C-2 is encumbered by both methyl groups. This would make formation of 2-pentene difficult, but the formation of 1-pentene is still quite viable. In the case of **4** and **5**, we saw 73% of the olefins arising out of the 1,3-dimethyl-substituted platinacycle **4** whereas here only 43% of the olefins arose from the 1,3-dimethyl-substituted platinacycle **8**. This could possibly indicate that the rearrangement of **8** to **9** is more facile than olefin formation from **8**, although it is still competitive with this process.



4a 4b



Conclusions

A few observations upon the selectivity of olefin formation from platinacyclobutanes seem apparent from this study. First, olefin formation which results from β-hydrogen abstraction from a ring carbon seems to overwhelmingly prefer to give the least-substituted olefin by forming the olefin along the least-substituted edge of the platinacyclobutane. It should be noted, however, that this is not an exclusive type of selectivity, as one sometimes observes the more-substituted olefin as well (e.g., in the case of **2**). The preference is such that the least-substituted olefin always dominated over the more-substituted olefin in this study. Second, if cis and trans isomers are possible, then the cis isomer seems to be highly favored over the trans isomer. The origination of these preferences may be due to interaction between the β-hydrogen and ring substituents. However, in the absence of X-ray data, it is difficult to assess the viability of this proposition. Additionally, it is noteworthy that the olefins obtained as major products are often the least-substituted olefins. Therefore, an alternate explanation for this selectivity may involve the greater stability of the presumed platinum–olefin complex for less-substituted olefins over more-substituted olefins.

Experimental Section

The platinacyclobutanes were prepared by literature methods.[2,5,11] The platinacycles were dissolved in THF and then injected into a Varian 940 gas chromatograph with an injection

(13) For examples of X-ray structures of platinacyclobutanes see: Gillard, R. D.; Keeton, M.; Mason, R.; Pilbrow, M. F.; Russell, D. R. *J. Organomet. Chem.* **1971**, 33, 247. McGinnity, J. A. *Ibid.*, **1973**, *59*, 429.

port temperature of 130 °C. The analysis was carried out using a 19 ft × $^1/_8$ in. $AgNO_3$–ethylene glycol on 80/100 Chromosorb P column prepared by a modification of the method of Bednas and Russel.[7] The modifications include (a) a 19 ft instead of an 11 ft column, (b) smaller mesh size for the support, and (c) column packing under 80 psi of nitrogen. The column was operated at 40 °C under a flow of 25 mL/min of N_2 and gave clean separation of all of the isomers.[14] Confirmation of the isomers was done by comparison with authentic samples.[8]

(14) In our hands, the column had a useful lifetime of about 2 weeks under constant use before the quality of separation began to deteriorate.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. A generous loan of platinum salts by the Matthey-Bishop Company is also gratefully acknowledged.

Registry No. Methylcyclopropane, 594-11-6; 1-butene, 106-98-9; *cis*-2-butene, 590-18-1; *trans*-1,2-dimethylcyclopropane, 2402-06-4; 1-pentene, 109-67-1; *cis*-2-pentene, 627-20-3; 2-methyl-1-butene, 563-46-2; 3-methyl-1-butene, 563-45-1; 1,1-dimethylcyclopropane, 1630-94-0; *cis*-1,2-dimethylcyclopropane, 930-18-7; Zeise's dimer, 12073-36-8.

Competitive Exo Hydroboration of *syn*-7-Arylnorbornenes[1]

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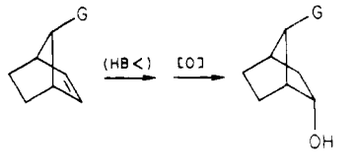
Received May 18, 1979

Hydroboration–oxidation of a series of *syn*-7-arylnorbornenes (**2**-Ar) produces an unexpectedly large percentage of exo alcohol (**3x**-Ar, 42–60%, depending upon the aryl group). Substituent effects [*p*-OCH_3, *p*-CH_3, *p*-Cl, *o*-CH_3, 2,4,6-$(CH_3)_3$] are minor. Other addition reactions on *syn*-7-phenylnorbornene itself (**2**-Ph) proceed essentially as expected for a sterically hindered norbornene (oxymercuration, diimide addition, thiophenol addition). The results may be rationalized, when contrasted to those reported for apobornene (7,7-dimethylnorbornene), in terms of a smaller steric size for phenyl relative to methyl, or preferably in terms of π complexation of borane by the aryl group. The latter rationalization appears to be more consonant with the unique behavior of hydroboration compared with the other additions studied.

Considerable documentation supports the contention that addition reactions onto norbornenes are affected both in rate and orientation by the presence of bridge (syn-7) substituents.[2] Groups studied include CH_3,[3] Br,[4] NR_3^+–BH_3^-,[5] and *t*-C_4H_9,[6] and the reactions studied vary from small ring transition state processes (e.g., epoxidation, carbene addition, Ag^+ complexation) to larger ring cases (e.g., 1,3-dipolar cycloaddition, diimide addition) and even noncyclic transition state processes (e.g., CF_3COOH addition, PhSH addition).[2] One of the conclusions reached from these studies was that bulky groups at the syn-7 position force those addends using small ring transition states to add endo to norbornenes or perhaps not to add at all. Larger transition state cycles or stepwise processes were less affected.[7]

Among the processes that added evidence for the mechanistic conclusion above was hydroboration, a process proceeding via a small ring transition state.[8] As shown in eq 1, increased bulk at syn-7 led to more endo hydroboration, as measured by oxidation of the intermediate organoborane(s).



(1)

G = H	0.5% (ref 9)
G = CH_3[3]	~78% (ref 9)
G = *t*-C_4H_9[10]	~100% (ref 6)

During another investigation,[11] a result was obtained

(1) Taken from the M.S. Thesis of V.P.N., 1978.

(2) (a) H. C. Brown, J. H. Kawakami, and K.-T. Liu, *J. Am. Chem. Soc.*, **95**, 2209 (1973); (b) F. Freeman, *Chem. Rev.*, **75**, 439 (1975).

(3) Brown and co-workers[2a] have studied the 7,7-dimethyl grouping extensively, emphasizing the presence of the syn-7 methyl. We know of no study using *syn*-7-methylnorbornene itself. Throughout this paper no distinction is made between the 7,7-dimethyl group's *actual* effect and the *syn*-7 methyl's *putative* effect.

(4) Additions to *anti*-7-bromobenzonorbornadiene (contains a *syn*-7-bromonorbornene moiety) were studied by R. Caple and C. S. Ilenda, *J. Am. Chem. Soc.*, **92**, 3817 (1970).

(5) P. S. Anderson, *Tetrahedron Lett.*, 1141 (1976).

(6) W. C. Baird, Jr., and J. H. Surridge, *J. Org. Chem.*, **37**, 1182 (1972).

(7) For an excellent review of this and other such criteria relating addition processes and their attendant activated complexes, see ref 2b.

(8) Uniform agreement on the transition state for hydroboration is not at hand. A four-membered ring state, using concerted bond formation and cleavage, appears to be favored, although in its usual depiction it would be forbidden by orbital symmetry considerations. Another concerted mode is, however, allowed. Moreover, a π complex preceding this state may occur. For a discussion, see D. J. Pasto, B. Lepeska, and T.-C. Cheng, *J. Am. Chem. Soc.*, **94**, 6083 (1972), and A. Streitwieser, Jr., L. Verbit, and R. Bittman, *J. Org. Chem.*, **32**, 1530 (1967). Steric effects are clearly observable in hydroboration, but electronic effects are less defined. Correlation with σ^+ (ρ = –0.7) has been claimed in the hydroboration of styrenes by H. C. Brown and R. L. Sharp, *J. Am. Chem. Soc.*, **88**, 5851 (1966), while no correlation with any single Hammett-type parameter has been found for essentially the same process by J. Klein, E. Dunkelblum, and M. A. Wolff, *J. Organomet. Chem.*, **7**, 377 (1967).

(9) H. C. Brown and J. H. Kawakami, *J. Am. Chem., Soc.*, **92**, 1990 (1970).

(10) 9-BBN was used here (20 h, 25 °C). Starting material was recovered (25%) and the yield based on consumed olefin was 54%. The reaction with borane appears to be unreported.

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