methaneboronate (1) in 50 mL of THF at -78 °C. The solution was allowed to reach room temperature overnight and then treated with concentrated aqueous ammonium chloride and ether. Distillation of the ether extracts yielded **4a** and **5a**: 79%; bp 120 °C (0.6 torr) (lit.[3b] for **4a** 100 °C (0.1 torr)).

(+)-Pinanediol 1-Phenylpentane-1-boronate (6a and 7a). The reported procedure[3] was followed: 85% yield, bp 145-150 °C (0.7 torr) (lit.[3] 125-128 °C (0.1 torr)).

1-Phenylpentanol (8). Oxidation of 1.74 mmol of **4a** and **5a** with 1.5 mL of 30% hydrogen peroxide and 5 mL of 3 M aqueous sodium hydroxide in 10 mL of THF at 0 °C yielded 85% 1-phenylpentanol: $[\alpha]^{21}_{589}$ +8.33° (*c* 3.3, benzene) (lit.[6] 31.3° (*c* 3.3, benzene)).

(+)-Pinanediol 1-Phenylpentane-1-boronate (6b and 7b). Treatment of (+)-pinanediol dichloromethaneboronate (1) with phenyllithium in THF at -78 °C, warming to 0 °C for 1 h, cooling again to -78 °C, and treating with an equivalent amount of *n*-butyllithium, and the usual workup yielded 80% of **6a** and **7b**. Hydrogen peroxide oxidation of this batch according to the procedure in the preceding paragraph yielded 1-phenyl-1-pentanol: $[\alpha]^{21}_{589}$ -10.5° (*c* 2.7, benzene).

(+)-Pinanediol 1-Chloro-3-methylbutane-1-boronate (4c and 5c). Isobutylmagnesium chloride was added to an equivalent amount of (+)-pinanediol dichloromethaneboronate (1) in THF at -78 °C and allowed to warm to 25 °C overnight. The magnesium chloride that separated was filtered, and the product **4c** and **5c**[8] was chromatographed on silica with ether/petroleum ether: yield 79%.

(+)-Pinanediol 1-Acetamido-3-methylbutane-1-boronate (9c and 10c). The mixture of **4c** and **5c** from the preceding paragraph was treated with lithiohexamethyldisilazane followed by acetic acid and acetic anhydride under the conditions described previously[4] to yield a mixture of **9c** and **10c**, which was chromatographed: mp 68-70 °C; $[\alpha]^{17}_{546}$ +31.0° (*c* 13, $CHCl_3$). The 200 MHz NMR spectrum was similar to that of purer **9c**: $[\alpha]^{23}_{546}$ -34.2° (*c* 8, $CHCl_3$), prepared from (+)-pinanediol isobutaneboronate,[8] though with some extra peaks in multiplets, with the major difference being that the NH peaks at δ 9.36 (**9c**) and 8.94 (**10c**) appeared in the ratio 34:66. Anal. Calcd for $C_{17}H_{30}BNO_3$: C, 66.46; H, 9.84; B, 3.52; N, 4.56. Found: C, 66.55; H, 10.01; B, 3.59; N, 4.38.

(+)-Pinanediol 1-Acetamidoethane-1-boronate (9d and 10d). Methylmagnesium bromide was added to 1 and the same general procedure described for preparation of **4c** and **5c** was used to prepare **4d** and **5d**, which was then converted in the usual manner[4,8] to **9d** and **10d**, ratio 22/78 from the respective NMR NH peaks at δ 9.39 and 9.24. Anal. Calcd for $C_{14}H_{24}BNO_3$: C, 63.42; H, 9.12; N, 5.28. Found: C, 64.02; H, 9.30; N, 4.83.

Zinc Chloride Catalysis. A. (+)-Pinanediol 1-Acetamido-3-methylbutane-1-boronate (9c and 10c). The same procedure described in a preceding paragraph was used to prepare **4c** and **5c**, except that 0.5 equiv of anhydrous zinc chloride was added after mixing the Grignard reagent and 1 at -78 °C.[5] The **4c** and **5c** was converted by the usual procedure to **9c** and **10c**, ratio 92/8 from the NH peaks: $[\alpha]^{27}_{546}$ -36.9° (*c* 13, $CHCl_3$); recrystallized from dichloromethane/hexane, mp 143-145 °C: $[\alpha]^{27}_{546}$ -36.9° ($CHCl_3$). Anal. ($C_{17}H_{30}BNO_3$) C, H, B, N.

B. (+)-Pinanediol 1-Acetamidoethane-1-boronate (9d and 10d). By similar procedures to the foregoing, a mixture of **9d** and **10d** was prepared, ratio 51/49 from the NH peaks at δ 9.86 and 9.71: $[\alpha]^{24}_{546}$ +11.9° (*c* 5, $CHCl_3$), mp 139-141 °C.

Acknowledgment. We thank the National Science Foundation for support, Grant No. CHE-8025229, and the Boeing Corp. for a gift in support of the departmental Nicolet 200-MHz NMR instrument.

Registry No. 1, 87249-60-3; **4a**, 85167-13-1; **4c**, 85167-14-2; **4d**, 85167-12-0; **5a**, 87247-48-1; **5c**, 87304-47-0; **5d**, 87247-50-5; **6a**, 87190-31-6; **7a**, 87247-53-8; **8r**, 19641-53-3; **8s**, 33652-83-4; **9c**, 87304-49-2; **9d**, 87249-62-5; **10c**, 87249-61-4; **10d**, 87304-48-1; $Cl_2CHB(OH)_2$, 62260-98-4; *n*-BuLi, 109-72-8; PhLi, 591-51-5; $LiN(SiMe_3)_2$, 4039-32-1; (+)-pinanediol, 22422-34-0; isobutyl chloride, 513-36-0; methyl bromide, 74-83-9.

Stereochemistry of Titanium-Assisted Additions of Organoaluminum Compounds to Hydroxybicyclo[2.2.1]hept-2-enes[1]

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In the presence of a titanium(IV) compound, dimethylaluminum chloride and diethylaluminum chloride add to *syn*-bicyclo[2.2.1]hept-2-en-7-ol to produce 2-*exo*-methyl- and 2-*exo*-ethyl-*syn*-bicyclo[2.2.1]heptan-7-ol and to *endo*-bicyclo[2.2.1]hept-5-en-2-ol to produce 5-*endo*-methyl- and 5-*endo*-ethyl-*endo*-bicyclo-[2.2.1]heptan-2-ol. These results indicate a preference in such titanium-assisted additions of alkylaluminum compounds to alkenols for attachment of the alkyl group to the side of the double bond nearer the hydroxyl group.

Thompson and co-workers have reported a variety of titanium-assisted additions of organoaluminum compounds to the multiple bonds of alkenols and alkynols.[2-8] In some instances, the reactions were carried out by treating the alcohol with Cp_2TiCl_2, $Ti(acac)_2Cl_2$, or $TiCl_4$ to form an alkoxychlorotitanium(IV) compound (1) which then was allowed to react with an organoaluminum compound. In other reactions, an excess of the organoaluminum com-

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[1] Much of this work is taken from: Moses, L. M. M.S. Dissertation, The Pennsylvani State University, University Park, PA, 1981.

[2] Harris, T. V.; Coleman, R. A.; Dickson, R. B.; Thompson, D. W. *J. Organomet. Chem.* **1974**, *69*, C27.

[3] Coleman, R. A.; O'Doherty, C. M.; Tweedy, H. E.; Harris, T. V.; Thompson, D. W. *J. Organomet. Chem.* **1976**, *107*, C15.

[4] Tweedy, H. E.; Hahn, P. E.; Smedley, L. C.; Youngblood, A. V.; Coleman, R. A.; Thompson, D. W. *J. Mol. Catal.* **1977**, *3*, 239.

[5] Tweedy, H. E.; Coleman, R. A.; Thompson, D. W. *J. Organomet. Chem.* **1977**, *129*, 69.

[6] Smedley, L. C.; Tweedy, H. E.; Coleman, R. A.; Thompson, D. W. *J. Org. Chem.* **1977**, *42*, 4147.

[7] Youngblood, A.V.; Nichols, S. A.; Coleman, R. A.; Thompson, D. W. *J. Organomet. Chem.* **1978**, *146*, 221.

[8] Brown, D. C.; Nichols, S. A.; Gilpin, A. B.; Thompson, D. W. *J. Org. Chem.* **1979**, *44*, 3457. Schiavelli, M. D.; Plunkett, J. J.; Thompson, D. W. *J. Org. Chem.* **1981**, *46*, 807.

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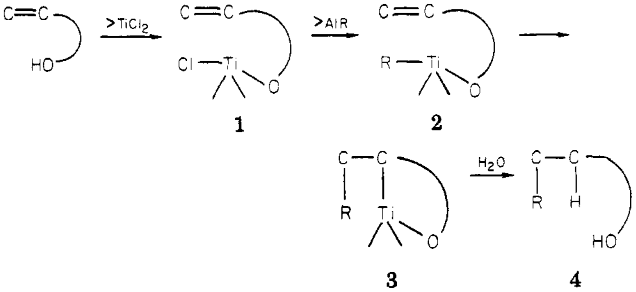


1 2 3 4

pound was first added to the alcohol, followed by addition of the resulting solution to a catalytic or stoichiometric amount of Cp_2TiCl_2 or $TiCl_4$.

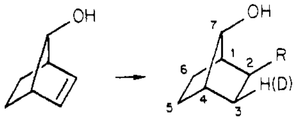
Since additions of organoaluminum compounds to isolated carbon–carbon multiple bonds of alkenes or alkynes are not ordinarily as facile,[9] the titanium plays a role in assisting the additions. It was suggested that the additions might result from reactions of species of structure **2**, formed from **1** by replacement of a chlorine by an alkyl group from the organoaluminum compound.

Stereochemical studies could provide information important in helping to define the mechanism of these additions. In this manuscript, we report the results of a study to determine whether the organic group R becomes attached to the face of the double bond near to or remote from the hydroxyl function.

Results and Discussion

We hoped in this study to effect addition under the same conditions to **5** and **9**, a pair of hydroxy-substituted bicyclo[2.2.1]hept-2-enes in which the hydroxyl group is close to but on opposite sides of the double bond. If attachment of R (from the organoaluminum compound) to a carbon of the double bond involves assistance in some manner by a metalated hydroxyl group and if that assistance is associated with a particular stereochemical relationship, then R should become attached at an exo position of one alcohol but an endo position of the other.

With use of procedures essentially identical with ones already described for reactions of acyclic alcohols,[5] a reaction of **5** (ROH) with $Ti(acac)_2Cl_2$ and pyridine was used to produce $ROTi(acac)_2Cl$. A dichloromethane solution of this species was then added to a hexane–dichloromethane solution[10] of dimethylaluminum chloride at 0 °C and maintained at that temperature for 4 h. After the reaction was hydrolyzed, GC analysis[11] showed the presence of a 95% yield of one product.

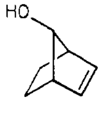


5 **6**, R = Me
7, R = Et

The ^1H NMR spectrum of the product is identical with that assigned convincingly to **6** by Gerteisen and Kleinfelter.[12] The same stereochemical assignment can be reached on the basis of the ^{13}C NMR spectrum. If it is assumed that a 2-endo-methyl would cause the same shift at C-6 in bicyclo[2.2.1]heptan-7-ol as in bicyclo[2.2.1]heptane,[13] then C-6 in the endo-methyl isomer of **6** should absorb at 18.4 ppm (downfield from Me_4Si).[14] However, the highest field absorptions of the addition compound are at 22.4 (probably due to the methyl carbon) and 25.6 ppm. Also consistent with the addition product having the syn-hydroxy-exo-methyl configuration is the similarity of its ^{13}C NMR spectrum to that of the corresponding 2-exo-propyl compound, whose configuration has been established by chemical methods.[15]

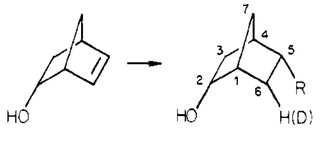
GC analysis[11] showed only a single product (64% yield) from a similar reaction of **5** with diethylaluminum chloride. By analogy with the reaction with dimethylaluminum chloride, this product can be assumed to be **7**. The stereochemical assignment is confirmed by the close resemblance of its ^{13}C NMR spectrum to that of **6** and the absence (except for the absorption of the methyl carbon at 12.8 ppm) of any absorption at higher field than 25.6 ppm. Mass spectral analysis of **7** obtained from a similar reaction that was quenched with D_2O showed it to contain approximately 0.5 excess D, and repetition of the experiment gave a similar value. Addition of increments of europium tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) [$Eu(fod)_3$] made visible a ^1H NMR absorption corresponding to 0.5 H in the deuterated sample. By extrapolation, this absorption was at about δ 1.5 in the absence of the lanthanide shift reagent. It is reasonable to assign this absorption to the C-3 exo-H. Its position is right and, as expected, shifts dramatically on addition of the shift reagent. Except for the shift of the absorption of the C-7 H (taken as 1.00), the shift of this absorption (0.64) is the greatest; the shifts of the C-1 and C-4 H absorptions, for example, are 0.56 and 0.57, respectively.

GC analysis[11] of a similar reaction of the epimeric alcohol **8** and diethylaluminum chloride showed the absence of any addition product and the presence of most (>85%) of the **8**.



8

A similar reaction of **9** and dimethylaluminum chloride also gave a single addition product, but in only 6% yield,[11] and a substantial amount of **9** was recovered. The identity of this compound is established convincingly because its ^{13}C NMR spectrum is virtually identical with that reported[16] for **10** (no absorption more than 0.2 ppm from a reported value) but quite different from those reported for the seven other methylbicyclo[2.2.1]heptanols that have



9 **10**, R = Me
11, R = Et

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[9] Mole, T.; Jeffery, E. A. "Organoaluminum Compounds"; Elsevier: Amsterdam, 1972.

[10] Since commercial hexane solutions were used as the source of the organoaluminum compounds, some hexane was present in the reactions reported in this paper in addition to the dichloromethane used as the solvent in the previously reported investigations.[2-8]

[11] See the Experimental Section for a description of the procedures and assumptions used in determining yields by GC analysis.

[12] Gerteisen, T. J.; Kleinfelter, D. C. *J. Org. Chem.* **1971**, *36*, 3255.

[13] Stothers, J. B.; Tan, C. T.; Teo, K. C. *Can. J. Chem.* **1973**, *51*, 2893.

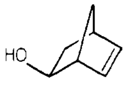
[14] The absorption due to all of the methylene carbons in bicyclo[2.2.1]heptan-7-ol is at about 25.9 ppm (estimated from the information in: Schneider, H.-J.; Bremser, W. *Tetrahedron Lett.* **1970**, 5197).

[15] Richey, H. G., Jr.; Wilkins, C. W., Jr.; Bension, R. M. *J. Org. Chem.* **1980**, *45*, 5042.

[16] Stothers, J. B.; Tan, C. T.; Teo, K. C. *Can. J. Chem.* **1976**, *54*, 1211.

methyl exo or endo at C-6 or C-5 and hydroxyl exo or endo at C-2.

A similar reaction of **9** and diethylaluminum chloride also gave a single addition product, but the yield was again low (~9%). By analogy to the reaction with dimethylaluminum chloride, this compound must certainly be **11**. Spectral observations confirm this assignment. The chemical shift and the splitting pattern of the NMR absorption of the H at C-2 are characteristic of an *endo*-bicyclo[2.2.1]heptan-2-ol.[17] Of the four possible attachments of the ethyl group (exo or endo at C-5 or C-6), the ^{13}C NMR spectrum is consistent only with the 5-endo attachment.[18] Although the sample of **9** used in most of this work contained some of the epimeric alcohol **12**, the product did not form from **12**. GC analysis of a small-scale reaction of a pure sample of **12** showed the presence only of reactant.



12

Several reactions were tried in which **9** (ROH) was added to an excess of diethylaluminum chloride to form ROAl(Et)Cl, and then the resulting solution added to an equivalent amount of Cp_2TiCl_2. These procedures (see Experimental Section), modeled after some used with acyclic alkenols and alkynols,[4,6,8] did not give **11** in yields greater than 10%.

Addition of increments of $Eu(fod)_3$ made visible a ^{1}H NMR absorption of **11** that corresponded to only 0.15 H when the **11** was obtained from a reaction quenched with D_2O. This absorption, at about δ 1.5 in the absence of the lanthanide shift reagent, is most reasonably assigned to the C-6 endo-H. Its position is reasonable, and, except for the shift of the C-7 H absorption (taken as 1.00), this absorption (0.74) shifts the most on addition of the shift reagent. The next largest shifts were 0.70, probably due to the C-3 *endo*-H, and 0.53, due to the C-1 H.

Since no additions of dimethylaluminum chloride to **5** and **9** were noted in control reactions in which the titanium compounds were omitted, we conclude that the additions were assisted in some manner by the presence of a titanium species. We also assume that a metalated hydroxyl group was involved in the mechanism, presumably by a linking of the oxygen to titanium either directly or through other atoms. Involvement of a metalated hydroxyl group is suggested by the failure of **8** and **12** to form addition products and particularly by the different stereochemistries of attachment of an alkyl group in additions to **5** and to **9**. The exo attachment in an addition to **5** might result from an inherent preference for this attachment in additions to bicyclo[2.2.1]hept-2-enes. In fact, exo attachment of the organic group has been noted in additions of triethylaluminum and triisobutylaluminum to bicyclo[2.2.1]hept-2-ene and to dicyclopentadiene[19] and in additions of triphenylaluminum to bicyclo[2.2.1]hepta-2,5-diene,[20,21] 5-*exo*-phenylbicyclo[2.2.1]hept-2-ene,[20] and some benzobicyclo[2.2.1]hepta-2,5-dienes.[22] However, that preference cannot be the explanation for the endo attachments in the additions to **9**. In fact, in the absence of a hydroxyl-assisted pathway, an adverse steric effect of the endo-hydroxyl group of **9** would probably accentuate any preference for exo attachment.

We observed no product of addition of dimethylaluminum chloride in the presence of $Ti(acac)_2Cl_2$ to bicyclo[2.2.1]hept-2-ene, the hydrocarbon parent of **5** and **9**. Only a small amount of the bicycloheptene was recovered, presumably because of competing reactions that lead to products having much higher molecular weights. Species resulting from mixing organoaluminum compounds with titanium compounds are known to function as olefin metathesis catalysts[23,24] and as Zeigler catalysts.[25,26] Both ring-opening polymerization (a special case of the olefin metathesis reaction) and vinyl polymerization are reported to result from treating bicyclo[2.2.1]hept-2-ene with such catalysts.[27] Indeed, ring-opened polymer as well as considerable amounts of dimers and oligomers have also resulted from treating bicyclo[2.2.1]hept-2-ene with ethylaluminum dichloride in the absence of a transition metal.[28,29] Competition by such reactions obviously is less significant in the reactions with hydroxy-substituted bicycloheptenes used in this work.

We conclude that in titanium-assisted additions, there is a preference for attachment of the organic group to the face of the double bond nearer the hydroxyl group. In the reaction with **5**, such addition leads to exo attachment of alkyl, and an excellent yield of addition product is obtained. In the reactions with **9**, endo attachment is required, and the yields are poor. Of course, endo attach-

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(17) For example, see Musher, J. I. *Mol. Phys.* **1963**, *6*, 93.

(18) The ^{13}C NMR spectra of the four 5- or 6-ethyl-*endo*-bicyclo[2.2.1]heptan-2-ols can be predicted from the known spectra[16] of the four corresponding methyl-substituted bicyclo[2.2.1]heptan-2-ols by adding the amounts for the effects of new α, β, and γ carbons when methyl is replaced by ethyl. The same conclusions are reached for any reasonable set of values, though below we specifically assume 9.1, 9.4, and −2.5 ppm for the effects of α, β, and γ carbons (Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1964**, *86*, 2984). Some of the obvious discrepancies between the observed spectra and predictions for other isomers are noted below. (1) For an endo-ethyl group at C-6, the absorption of C-2 is predicted to be at 76.4 ppm, but 73.2 ppm is observed. (2) For an exo-ethyl group at C-6, the absorption of C-1 is predicted to be at 46.7 ppm, but with the exception of the absorption of C-2, the lowest field absorption is at 43.1 ppm. (3) For an exo-ethyl group at C-5, the highest field absorptions (except for the absorption of the methyl carbon) are predicted to be at 27.7 (C-6) and 31.5 (methylene carbon of ethyl group) ppm; however, absorptions are observed at 24.4 and 26.2 ppm. By contrast, when absorptions are arranged in order of chemical shift, no absorption of the addition product is more than 1.6 ppm from the corresponding absorption predicted for **9**, and the average deviation is less than 0.6 ppm.

(19) Schimpf, R.; Heimbach, P. *Chem. Ber.* **1970**, *103*, 2122. The configurations were assigned on the basis of the ^{1}H NMR spectra, but the criteria employed were not specified.

(20) Eisch, J. J.; Liu, S. J. Y. *J. Organomet. Chem.* **1970**, *21*, 285.

(21) Eisch, J. H.; Burlinson, N. E.; Boleslawski, M. *J. Organomet. Chem.* **1976**, *111*, 137.

(22) Eisch, J. J.; Burlinson, N. E. *J. Am. Chem. Soc.* **1976**, *98*, 753.

(23) See examples in: Haines, R. J.; Leigh, G. J. *Chem. Soc. Rev.* **1975**, *4*, 155.

(24) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074. Klabunde, U.; Tebbe, F. N.; Parshall, G. W.; Harlow, R. L. *J. Mol. Catal.* **1980**, *8*, 37. Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876.

(25) Ref 9, Chapter 15.2. Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.

(26) For the relation between metathesis and Zeigler reactions, see: Rooney, J. J.; Stewart, A. *Catalysis (London)* **1977**, *1*, 277.

(27) Truett, W. L.; Johnson, D. R.; Robinson, I. M.; Montague, B. A. *J. Am. Chem. Soc.* **1960**, *82*, 2337. Sartori, G.; Ciampelli, F.; Cameli, N. *Chim. Ind. (Milan)* **1963**, *45*, 1478. Tsujino, T.; Saegusa, T.; Furukawa, J. *Makromol. Chem.* **1965**, *85*, 71.

(28) Ivin, K. J.; Rooney, J. J.; Stewart, C. D. *J. Chem. Soc., Chem. Commun.* **1978**, 603.

(29) Products resulting formally from addition followed by dehydrometalation were not observed in the reactions reported in this paper. However, such products have been observed in reactions in the presence of Cp_2TiCl_2 of alkylaluminium compounds with other alkenes[30,31] and sometimes with alkynes.[32]

(30) Barber, J. J.; Willis, C.; Whitesides, G. M. *J. Org. Chem.* **1979**, *44*, 3603.

(31) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

(32) Van Horn, D. E.; Valente, L. F.; Idacavage, M. J.; Negishi, E.-I. *J. Organomet. Chem.* **1978**, *156*, C20. Eisch, J. J; Manfre, R. J.; Komar, D. A. *Ibid.* **1978**, *159*, C13. Snider, B. B.; Karras, M. *Ibid.* **1979**, *179*, C37.

ments to bicyclo[2.2.1]hept-2-enes generally are much slower than exo attachments. Because of the inherent difficulty in an endo attachment, addition may compete only poorly with other processes that also consume the organometallic compounds. The products obtained from D_2O quenching, C-3 exo-D in **7** and C-6 endo-D in **11**, are consistent with carbometalation occurring in a syn fashion, the metal also being on the face of the double bond near the hydroxyl group. We cannot rule out the possibility, however, that the observed stereochemistry results from epimerization of the carbon–metal bond after addition occurred.

The conclusion that the alkyl group adds from the side of the double bond nearer the hydroxyl group is consistent with the proposal that the reaction proceeds through a species such as **2**. Actually, the active species must be more complicated, including aluminum as well as titanium.[33,34]

Experimental Section

^1H NMR spectra were taken with Me_4Si as an internal standard. Absorptions are reported with the following notations: s, singlet; d, doublet; t, triplet; m, a more complex multiplet; c, complex overlapping absorptions; b, broad. For determination of the effects on chemical shifts of added europium tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) [Eu(fod)$_3$], small portions of a CCl_4 solution of Eu(fod)$_3$ were added to a CCl_4 solution of the compound in an NMR tube, and a spectrum (200 or 360 MHz) was recorded after each addition. Proton-decoupled ^{13}C NMR spectra were obtained with $CDCl_3$ as an internal lock; absorptions are reported relative to Me_4Si. High- and low-resolution mass spectra were obtained by using a Kratos MS9/50 mass spectrometer. Melting points were taken in capillary tubes and are uncorrected.

Analytical and preparative GC separations were performed with the following columns: A, 5% SE-30 on Gas-Chrom P (60–80 mesh), 0.25 in. × 9 ft (aluminum tubing); B, 3% SP-2100 on Supelcoport (100–120 mesh), 0.25 in. × 6 ft (glass tubing); C, 15% SE-30 on Gas-Chrom P (60–80 mesh), 0.25 in. × 6 ft (aluminum tubing); D, 20% Carbowax 20M on Gas-Chrom P (60–80 mesh), 0.25 in. × 12 ft (aluminum tubing). Columns A, C, and D were used with a thermal conductivity instrument using helium as the carrier gas; peak areas were determined by cutting out and weighing the peak tracings. Column B was used with a flame ionization instrument; peak areas were determined by using an electronic integrator. When amounts of components of a crude reaction mixture were determined by GC analysis, a weighed amount of a normal alkane was sometimes added as a standard, and the amount of a component was determined from the area of its GC peak relative to the peak due to the internal standard. In reactions in which most of the reactant was recovered, the yield of an addition product was sometimes estimated by assuming that the recovered reactant plus the addition product totaled 100%. It was always assumed that the response of the detector to different compounds was proportional to their molecular weights. Components present in 1% yield should have been detected by the GC analyses. Small samples were collected for spectral analysis by using glass U-shaped tubes cooled in liquid nitrogen and inserted into the exit port of the chromatograph.

Materials. *syn*-Bicyclo[2.2.1]hept-2-en-7-ol (**5**) was prepared from the monoepoxide of bicyclo[2.2.1]hepta-2,5-diene as previously reported[12] and purified by sublimation; mp 77–80 °C (lit.[12] mp 79–80 °C). *anti*-Bicyclo[2.2.1]hept-2-en-7-ol (**8**) was prepared from 7-*tert*-butoxybicyclo[2.2.1]hepta-2,5-diene as previously reported.[35] *endo*-Bicyclo[2.2.1]hept-5-en-2-ol (**9**) was obtained (Aldrich Chemical Co.) as a semisolid containing some of the exo isomer. Treating the mixture with a small amount of pentane and filtering the resulting mixture freed the bicycloheptenols from less soluble materials. Evaporation of the pentane left a white solid, mp 98–101 °C (lit.[36] mp 108–109 °C), shown by the ratios of the ^1H NMR absorptions[37] of the C-2 H's to be approximately 71% **9** and 29% **12**. A sample of **12** (retention time of 1.23 relative to that of **9**) was obtained by collection from column D (130 °C). Bicyclo[2.2.1]hept-2-ene was a commercial sample (Aldrich Chemical Co.). Commercial (Ventron Corp.) hexane solutions of dimethylaluminum chloride and diethylaluminum chloride were used. Their concentrations were estimated from the ratios in the ^1H NMR spectra of absorptions due to CH_3Al or CH_2Al to those due to hexane. Cp_2TiCl_2 and Ti(acac)$_2$Cl$_2$ were commercial samples (Ventron Corp.). Benzene was distilled from calcium hydride and dichloromethane from phosphorus pentoxide. Pyridine was dried over potassium hydroxide and diethyl ether over sodium.

Reaction of *syn*-Bicyclo[2.2.1]hept-2-en-7-ol (5) with Me_2AlCl and Ti(acac)$_2$Cl$_2$. A solution of **5** (2.00 g, 18.2 mmol) and pyridine (2.0 mL, 26 mmol) in benzene (3.6 mL) was added dropwise to a slurry of Ti(acac)$_2$Cl$_2$ (7.92 g, 25.0 mmol) in benzene (15 mL) that was maintained in a bath at 0 °C. The resulting deep red solution was stirred for 3 h at 0 °C and then for 2 h at ambient temperature, during whicch time it turned to a yellow-red suspension. While it was continually maintained under an argon atmosphere, the solution was freed from the precipitate by filtering it through a plug of glass wool. The precipitate (pyridine hydrochloride) was washed repeatedly with small portions of benzene until it was colorless. The solvent was removed from the filtrate at reduced pressure, and dichloromethane (35 mL) was added to the oil that remained to make a solution (aproximately 0.7 M) of ROTi(acac)$_2$Cl. This solution was added dropwise over 1 h to a stirred solution of Me_2AlCl (13.0 mL, ~1.45 M, ~19 mmol) in dichloromethane (25 mL) that was maintained in a bath at 0 °C. After the resulting red solution was stirred for an additional 4 h at 0 °C, methanol (8 mL) was added dropwise, followed by water (15 mL). A sodium hydroxide solution (6 M, 75 mL) was added, and the blue mixture was stirred under oxygen until the blue color had disappeared (about 2 h). The suspension was filtered over a bed of Celite and the solid washed with water and with diethyl ether. The filtrate was saturated with sodium chloride, the layers were separated, and the aqueous layer was extracted with five 50-mL portions of diethyl ether. The combined organic layers were dried ($MgSO_4$) and then concentrated to a volume suitable for GC analysis by removing most of the solvent by distillation through a Vigreux column. GC analysis (column A, 120 °C) showed only one peak (retention time 2.2 relative to that of nonane, the internal standard) with a retention time greater than that due to nonane. No peak due to **5** (retention time 0.9 relative to nonane) was seen. The compound affording the observed peak was **6**: 95% yield; ^1H NMR (60 MHz, CCl_4) δ 0.83–1.80 (c, 12), 1.95 (b s, 1, H at C-4), 3.89 (s, 1 CHOH); ^{13}C NMR ($CDCl_3$) δ 22.4, 25.6, 27.8, 36.4, 37.0, 41.5, 46.4, 80.7.

Reaction of *syn*-Bicyclo[2.2.1]hept-2-en-7-ol (5) with Et_2AlCl and Ti(acac)$_2$Cl. The procedure was identical with that for the reaction of **5** with Me_2AlCl. GC analysis (column B) showed only one peak with a retention time greater than that of nonane. No peak due to **5** was observed. The compound responsible for the observed peak was **7**: 64% yield; ^1H NMR (360 MHz, CCl_4) δ 0.77 (t, 3, J = 7.4 Hz, CH_3), 0.97 (m, 2), 1.25 (m, 1), 1.30–1.53 (c, 6), 1.64 (b s, 1, C-1 H), 1.82 (b s, 1, C-4 H), 1.87 (s, 1, OH), 3.71 (s, 1, C-7 H); ^{13}C NMR ($CDCl_3$) δ 12.8, 25.6, 27.7, 29.5, 35.0, 40.8, 44.3, 44.4, 80.3; high-resolution mass spectrum, m/z 140.1193 (M^+, calcd $C_9H_{16}O$ 140.1201).

Two other reactions were similar to that above except that one-fourth the amounts of reagents were used, quenching was with D_2O (3 mL) rather than methanol, and after addition of D_2O the reaction was allowed to stir for 12 h before addition of the sodium hydroxide solution. Low-resolution mass spectra (using M^+)

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(33) The role of aluminum compounds in stabilizing organotitanium species is shown particularly dramatically in the titanium methylene compounds first prepared by Tebbe and his co-workers: references 24 and 31. Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *Ibid.* **1980**, *102*, 3270. Tebbe, F.; Harlow, R. L. *Ibid.* **1980**, *102*, 6149. Hartner, F. W., Jr.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 4979.

(34) In the presence of a catalytic amount of Cp_2TiCl_2, ethylmagnesium bromide reacts with alkenols to give products that result from hydrometalation rather than carbometalation: Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1978**, *160*, C8.

(35) Story, P. R. *J. Org. Chem.* **1961**, *26*, 287.

(36) Alder, K.; Rickert, H. F. *Justus Liebigs Ann. Chem.* **1940**, *543*, 1.

(37) Wong, E. W. C.; Lee, C. C. *Can. J. Chem.* **1964**, *42*, 1245.

indicated that **7** contained ~0.5 excess D.

Reaction of *anti*-Bicyclo[2.2.1]hept-2-en-7-ol (8) with Et_2AlCl and $Ti(acac)_2Cl_2$. The procedure was similar to that used for the reaction of **5** and Me_2AlCl. GC analysis (column B, 80 °C) showed only a peak (retention time 1.3 relative to that of nonane, the internal standard) for **7** (>85%).

Reaction of *endo*-Bicyclo[2.2.1]hept-5-en-2-ol (9) with Me_2AlCl and $Ti(acac)_2Cl_2$. The procedure was the same as that with **5** described above. GC analysis (column A, 115 °C) showed a peak with a retention time identical with that of **9** and only one additional peak (retention time 1.9 relative to **9**) with a retention greater than 0.5 relative to **9**. The material responsible for the first peak was shown by its ^1H NMR spectrum to be **9** and its yield to be 47% (dodecane internal standard, retention time 4.8 relative to **9**). The new peak was shown to be due to **10**: 6% yield; ^1H NMR (60 MHz, CCl_4) δ 1.01 (d, 3, J = 6 Hz, CH_3), ~1.20–2.25 (c, 9), 2.49 (s, 1, OH), 4.10 (m, 1, C*H*OH); ^{13}C NMR ($CDCl_3$) δ 16.2, 27.5, 31.3, 34.2, 39.4, 42.6, 43.6, 73.2.

In one instance, before $ROTi(acac)_2Cl$ was dissolved in dichloromethane, a ^1H NMR spectrum (60 MHz, $CDCl_3$) was obtained to be certain that this compound had formed. Absorptions characteristic of the acac group were noted: δ 2.04 (s, CH_3) and 5.70 (s, =CH). The absorptions due to the bicycloheptyl system, though complicated, were clearly different from those of **9**. Another portion of the oil was dissolved in methylene chloride and then hydrolyzed and worked up as above. The ^1H NMR spectrum of the material that was isolated showed it to be **9** (still containing some of the exo isomer).

Reaction of *endo*-Bicyclo[2.2.1]hept-5-en-2-ol (9) with Et_2AlCl and $Ti(acac)_2Cl_2$. The procedure was the same as that in the reaction of **5** and Me_2AlCl described above. GC analysis (column A, 125 °C) showed a substantial peak due to **9** and one additional peak (retention time 3.2 relative to **9**). The new peak was shown to be due to **11**:[38] 9% yield; ^1H NMR (360 MHz, CCl_4) δ 0.78 (t, 3, J = 7.4 Hz, CH_3), 1.01–1.63 (c, 10), 1.91 (m, 1, C-4 H), 1.98 (m, 1, C-1 H), 3.95 (m, 1, C-2 H); ^{13}C NMR ($CDCl_3$) δ 13.1, 24.4, 26.2, 31.6, 39.0, 40.4, 42.1, 43.1, 73.2.

Another reaction was similar to that above except that one-fourth the amounts of reagents were used, quenching was with D_2O (3 mL) rather than methanol, and after addition of D_2O the reaction was allowed to stir for 12 h before addition of the sodium hydroxide solution.

Reactions of *endo*-Bicyclo[2.2.1]hept-5-en-2-ol (9) with Et_2AlCl and Cp_2TiCl_2. A solution of **9** (2.20 g, 20.0 mmol) in dichloromethane (25 mL) was added dropwise over 15 min to a stirred solution prepared by adding a hexane solution of Et_2AlCl (51 mL, ~2.4 M, ~120 mmol) to dichloromethane (42 mL) that was maintained in an ice bath. The resulting solution was stirred for about 2 h and then transferred to an addition funnel attached to another reaction flask and added dropwise over 1 h to a solution containing Cp_2TiCl_2 (0.553 g, 2.22 mmol) in dichloromethane 50 mL) maintained at the temperature specified below for each reaction. After the specified reaction time, methanol (8 mL) was added dropwise followed by a 5% sulfuric acid solution (50 mL) that had been saturated with sodium chloride The resulting mixture was stirred under air for 1 h, filtered, and extracted with five 50-mL portions of diethyl ether. The combined ether extracts were dried ($MgSO_4$), and then the solution was concentrated at reduced pressure to a volume suitable for GC analysis and filtered from some solid (presumably mainly Cp_2TiCl_2) that formed during this reduction in volume.

GC analysis (125 °C) showed the presence of a peak due to **9** and of two new peaks (retention times 2.1 and 3.1 relative to that of **9**). The first of the new peaks was shown by its retention time compared to that of an authentic sample to be due to dicyclopentadiene. The material responsible for the second peak had a ^1H NMR spectrum essentially identical with that assigned to **11**. A reaction for 6 h at 0 °C gave 11% of **11**, at 0 °C for 48 h gave 9%, and at ambient temperature for 24 h gave 6%. A reaction at −78 °C for 13 h gave no detectable amount of **11**. A reaction at 0 °C for 4 h in which 1.5 times as much $CpTiCl_2$ was used gave 10% of **11**.

Reaction of *exo*-Bicyclo[2.2.1]hept-5-en-2-ol (12) with Et_2AlCl and $Ti(acac)_2Cl_2$. Except that smaller amounts of reagents were used, the procedure was identical with that used for the reaction of **5** and Me_2AlCl. GC analysis (column B, 70 °C) showed only a peak (retention time 0.57 relative to that of decane) for **12**.

Reaction of Bicyclo[2.2.1]hept-2-ene with Me_2AlCl and $Ti(acac)_2Cl_2$. A solution was prepared by adding bicyclo[2.2.1]hept-2-ene (1.00 g, 10.6 mmol) in dichloromethane (2 mL) to $Ti(acac)_2Cl_2$ (3.96 g, 12.5 mmol) in dichloromethane (8 mL) and benzene (2 mL). This red solution was added dropwise over 15 min to a stirred solution prepared from a hexane solution of Me_2AlCl (7.0 mL, ~1.5 M, ~10.5 mmol) and dichloromethane (12.5 mL) and maintained in a bath at 0 °C. The solution was stirred for 4 h at 0 °C, and then methanol (4 mL) was added dropwise, followed by water (8 mL). An aqueous sodium hydroxide solution (6 M, 38 mL) was added, and the resulting mixture was stirred under air until the blue color had disappeared (about 1 h). The suspension was filtered over a bed of Celite and the solid washed with water and with diethyl ether. The layers of the filtrate were separated, and the aqueous layer was extracted with five 50-mL portions of diethyl ether. The combined organic layers were dried ($MgSO_4$), and then the solution was concentrated by removing most of the solvents by distillation through a Vigreux column. GC analysis (70 °C) showed only one small peak (retention time 0.49 relative to nonane, the internal standard) after a peak (retention time 0.24) due to bicyclo[2.2.1]hept-2-ene. The ^1H and ^{13}C NMR spectra of the material responsible for this peak indicated that it was probably not a methylbicyclo[2.2.1]heptane or a methylbicyclo[2.2.1]hept-2-ene. Analysis (nonane internal standard) showed that the weight of the material responsible for the new peak was only 2% of that of the bicyclo[2.2.1]hept-2-ene used for the reaction and that only 9% of the bicyclo[2.2.1]hept-2-ene remained.

Reactions of *syn*-Bicyclo[2.2.1]hept-2-en-7-ol (5), of *endo*-Bicyclo[2.2.1]hept-5-en-2-ol (9), and of Bicyclo[2.2.1]hept-2-ene with Me_2AlCl. A solution of **5** (1.00 g, 9.1 mmol) in dichloromethane (41 mL) was added dropwise over 1 h to a stirred solution prepared from a hexane solution of Me_2AlCl (5.5 mL, ~1.65 M, ~9.1 mmol) and dichloromethane (12 mL) maintained in a bath at 0 °C. The solution was stirred at 0 °C for an additional 4 h, and then methanol (4 mL) was added dropwise, followed by water (8 mL). Then aqueous sodium hydroxide solution (6 M, 38 mL) was added, and the mixture was stirred for a few minutes, the layers were separated, and the aqueous layer was extracted with five 50-mL portions of diethyl ether. The combined organic layers were dried ($MgSO_4$), and then most of the solvents were removed by distillation through a Vigreux column. GC analysis of the remaining solution, in the same maner as in the corresponding reaction in which $Ti(acac)_2Cl_2$ had been used, showed the presence of 69% of **5** but no **6**.

GC analysis of the material obtained from a similar reaction of **9** showed the presence of a 49% yield of **9** but no **10**. The material obtained from a similar reaction of bicyclo[2.2.1]hept-2-ene contained 68% of the bicycloheptene and exhibited no significant peak having a greater retention time.

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Registry No. **5**, 13118-70-2; **6**, 31337-69-6; **7**, 87116-67-4; **8**, 694-70-2; **9**, 694-97-3; **10**, 60322-66-9; **11**, 53340-05-9; $Ti(acac)_2Cl_2$, 17099-86-4; Cp_2TiCl_2, 1271-19-8; Et_2AlCl, 96-10-6; Me_2AlCl, 1184-58-3; bicyclo[2.2.1]hept-2-ene, 498-66-8.

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