Effects of Proximate Polar Groups on the Rates of Hydrosilylation

Victoria J. Eddy and John E. Hallgren*

General Electric Corporate Research and Development Center, Schenectady, New York 12301

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Endo-, exo-, and trans-2,3-disubstituted bicyclo[2.2.1]hept-5-enes were found to react with dimethylchlorosilane in the presence of a platinum catalyst to yield the corresponding 5-silyl derivatives. The reaction of the endo anhydride proceeded in high yield, although quite slowly. The exo anhydride was found to react faster than the analogous endo epimer. Furthermore, the endo *N*-phenylimide did not react under these conditions, while the exo *N*-phenylimide epimer reacted rapidly and in high yield. A similar ordering of reactivity was observed with the *endo*-, *trans*-, and *exo*-2,3-dicarbomethoxybicyclo[2.2.1]hept-5-enes. Silicon was found exclusively on the exo face of the bicycloheptyl skeleton, remote from substituents at the 2,3-positions. Purely steric arguments are insufficient to explain the anomalous reactivity of the endo anhydride and endo *N*-phenylimide. However, the reactivity differences can be rationalized in terms of field effects exerted by the electron-deficient anhydride and imide rings.

Addition of an SiH silane to an olefin (hydrosilylation) is a versatile and industrially important method for the preparation of functional silanes.[1] However, cyclohexene or substituted cyclohexenes are unusually unreactive olefins in hydrosilylation reactions and have required forcing conditions.[2] Thus, hydrosilylation of double bonds contained within six-membered rings has been commercially unattractive. Accordingly, attempts to prepare commercial quantities of anhydride functional silanes via hydrosilylation of tetrahydrophthalic anhydride have not been successful. However, bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (Ia) had been reported[3] to react with dimethylchlorosilane in the presence of a typical platinum hydrosilylation catalyst to produce the corresponding alkylsilane in high yield. In our hands, the hydrosilylation of Ia proceeded in high yield although at a much slower rate than other 1,2-disubstituted olefins.

The anomalously slow rate of hydrosilylation of Ia prompted us to investigate the hydrosilylation of 2,3-disubstituted bicyclo[2.2.1]hept-5-enes. Herein we describe the effects of nonvicinal, proximate polar groups on the rates of hydrosilylation.

Results and Discussion

2,3-Disubstituted bicyclo[2.2.1]hept-5-enes Ia–h were found to react with dimethylchlorosilane in the presence of a platinum catalyst[4] to form the corresponding 2,3-disubstituted *exo*-5-(dimethylchlorosilyl)bicyclo[2.2.1]heptanes IIa–h (eq 1; Table I). The reactions proceeded in high yield to form products with silicon exclusively on the exo face. Epimerization of the substituents at the 2,3-positions was not observed. The rates of hydrosilylation varied widely with substitution at the remote 2,3-positions. The reaction of bicyclo[2.2.1]hept-5-ene-*exo*-2,3-dicarboxylic anhydride (Ib) with dimethylchlorosilane in the presence of a platinum catalyst was complete within 1 h at 80 °C in toluene solution to yield *exo*-5-(dimethylchlorosilyl)bicyclo[2.2.1]heptane-*exo*-2,3-dicarboxylic anhydride (IIb). Under similar conditions, the reaction of the endo epimer bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (Ia) proceeded slowly, typically requiring 2–3 days for complete conversion to *exo*-5-(dimethylchlorosilyl)bicyclo[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride (IIa).

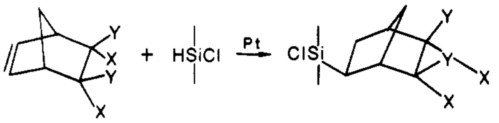

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Table I. Hydrosilylation of Substituted Bicyclo[2.2.1]hept-5-enes with Dimethylchlorosilane

	X,X	Y,Y	product	% yield	time, h
Ia	CO–O–CO	H,H	IIa[a]	95	48
Ib	H,H	CO–O–CO	IIb[a]	99	<0.5
Ic	CO–N(C_6H_5)–CO	H,H	IIc	0	48
Id	H,H	CO–N(C_6H_5)–CO	IId[a]	99	0.5
Ie	CO_2Me,-CO_2Me,	H,H	IIe[a]	99	2
If	H,CO_2Me	H,CO_2Me	IIf[a]	99[b]	0.5
Ig	H,H	CO_2Me,CO_2Me	IIg[a]	99	1
Ih	CH_2OCH_2	H,H	IIh[a]	99	<0.5
Ii	H,H	H,H	IIi[a]	99	<0.5

[a] Formula confirmed by high-resolution mass spectra. [b] Approximately a 1:1:1:1 ratio of the four diastereomers was observed.

Table II. Effect of Silane on Hydrosilylation of Bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic Anhydride

silane	% yield	time, h	silane	% yield	time, h
Et_3SiH	0	48	$MeSiHCl_2$	62[a]	48
Me_2SiHCl	95	48	$HSiCl_3$	0	48
Me_2PhSiH	95[a]	48			

[a] Composition of product confirmed by high-resolution mass spectra.

The reactivity differences between the endo and exo epimers were more pronounced with the *N*-phenylimide epimers than with the anhydride epimers. The exo imide Id reacted rapidly with dimethylchlorosilane in the presence of a platinum catalyst at 80 °C in toluene solution to form *exo*-5-(dimethylchlorosilyl)bicyclo[2.2.1]heptane-2,3-dicarboxylic *N*-phenylimide (IId) in high yield. Under similar conditions, the endo imide, Ic, did not react and could be recovered unchanged after 4 days.

Small differences in reactivity were noted between the dicarbomethoxy isomers. *endo*-, *exo*-, and *trans*-2,3-dicarbomethoxybicyclo[2.2.1]hept-5-enes (Ie–g), reacted with dimethylchlorosilane under typical reaction conditions to form the corresponding esters, IIe–g. The rate of reaction

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(1) For a recent review, see: Lukevics, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. *J. Organomet. Chem. Libr.* 1977, *5*, 1.

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(4) A commercial platinum hydrosilylation catalyst[15] was employed in this investigation. Identical results were obtained with $PtCl_4$.

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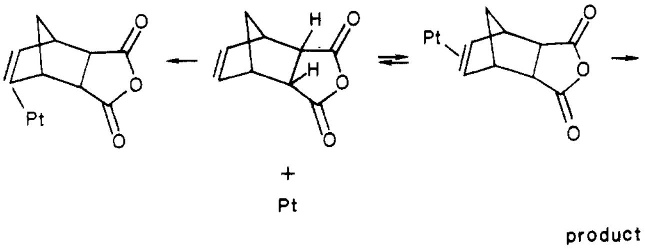
Scheme I

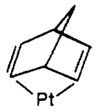


of the endo epimer Ie was noticeably slower than that of the trans or exo isomers, If and Ig, respectively.

The differences in reactivity between endo and exo epimers were unexpected. Comparisons with the rate of hydrosilylation of the parent olefin bicyclo[2.2.1]heptene (Ii) suggested that the rates of hydrosilylation of the endo anhydride and imide epimers were anomalously slow.

The unusually slow rate of hydrosilylation of the endo anhydride Ia was not limited to reactions with dimethylchlorosilane but was observed with a variety of silanes (Table II). Bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (Ia) was found to react with phenyldimethylsilane and methyldichlorosilane to form *exo*-(phenyldimethylsilyl)bicyclo[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride and *exo*-(methyldichlorosilyl)bicyclo[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride, respectively, in high yields. Phenyldimethylsilane was found to be approximately as reactive as dimethylchlorosilane, while methyldichlorosilane was considerably less reactive. Surprisingly, neither trichlorosilane nor triethylsilane reacted with Ia under the typical reaction conditions.

The reactions of the endo epimers may be slowed by poisoning of the catalyst via formation of an unreactive platinum complex. In principle, the endo epimers could function as bidentate ligands coordinating platinum on the endo face through both the olefin and the oxygen (nitrogen) atom of the anhydride (imide) ring. An intermediate with platinum chelated on the endo face, III, has been postulated previously in the hydrosilylation of bicyclo[2.2.1]heptadiene to explain formation of *endo*-2-(trimethylsilyl)bicyclo[2.2.1]hept-5-ene.[5] Although only exo addition products were observed in the hydrosilylation of 2,3-disubstituted bicyclo[2.2.1]hept-5-enes, formation of such a platinum chelate could reduce the concentration of the active catalyst, slowing the rate of hydrosilylation (Scheme I).



III

Attempts were made to prepare these and similar platinum chelates in order to test this hypothesis. However, we were unable to isolate or detect such a complex.

Scheme I can be tested indirectly by comparing the rate of hydrosilylation of the pure exo epimer with that of the exo epimer in the presence of the endo epimer. Chelation of platinum by the endo epimers should reduce the concentration of the active catalytic species, thus slowing the rates of hydrosilylation of both epimers. A mixture of the anhydrides Ia and Ib was allowed to react with a deficiency of dimethylchlorosilane under typical reaction conditions. Similarly, the imides Ic and Id were allowed to compete for a deficiency of dimethylchlorosilane. In both cases, silane was rapidly consumed, and only the exo epimers Ib and Id reacted to produce IIb and IId, respectively. Furthermore, within experimental error, the exo epimers reacted at the same rates in the presence of the endo epimers as in the absence of the endo epimers. Thus, Scheme I is precluded as the cause of the slow rates observed for hydrosilylation of Ia and Ic.

Table III. Relative Rates of Hydrosilylation of 2,3-Substituted Bicyclo[2.2.1]hept-5-enes

	X,X	Y,Y	product	rel rate
Ia	CO–O–CO	H,H	IIa	0.01
Ib	H,H	CO–O–CO	IIb	2.4
Id	H,H	CO–N(C_6H_5)–CO	IId	5.6
Ie	CO_2Me,CO_2Me	H,H	IIe	0.54
If	H,CO_2Me	H,CO_2Me	IIf	1.00
Ig	H,H	CO_2Me,CO_2Me	IIg	1.50
Ih	CH_2–O–CH_2	H,H	IIh	2.00
Ii	H,H	H,H	IIi	250

The mechanism for hydrosilylation, first proposed by Chalk and Harrod,[6] requires that silicon be delivered to the face to which platinum is coordinated. Since exclusively exo addition products were observed, platinum would be expected to coordinate to the olefin on the exo face, remote from the 2,3-substituents. Molecular models suggest that the presence of an endo anhydride or endo imide ring should not cause severe steric crowding in either the proposed intermediates or the products. Therefore, it is difficult to explain the large differences in rates of hydrosilylation between these endo and exo epimers by steric considerations alone; electronic effects must be considered.

Similar reactivity differences have been noted in the electrophilic addition of 2,4-dinitrobenzenesulfonyl chloride to *endo*- and *exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (Ia and Ib, respectively). The exo isomer was found to react ca. 56 times faster than the endo isomer.[7] This rate difference could not be attributed to steric effects, but rather was ascribed to an electronic effect generated by the proximate electron-withdrawing endo anhydride ring.

Reactivity differences between the various isomers of 2,3-dicarbomethoxybicyclo[2.2.1]hept-5-enes Ie–g have been noted previously. For example, the rate of 1,3-addition of diazomethane[8] was faster for the exo- than the endo-substituted epimer. The trans-substituted isomer reacted at an intermediate rate. The opposite order of reactivity was observed for epoxidation of Ie–g by perbenzoic acid.[9] The rates of epoxidation and of 1,3-diazomethane addition to endo epimer Ie and exo epimer If have been reported to differ by factors of 1.73–1.90. These rate differences have been attributed to a field effect[10,11] exerted by electron-withdrawing groups in the endo 2,3-positions.

Diazomethane addition, epoxidation, 2,4-dinitrobenzenesulfonyl chloride, and hydrosilylation[12] reactions of 2,3-disubstituted bicyclo[2.2.1]heptenes have been shown to occur exclusively on the exo face, and the rates of reaction are influenced by the presence of proximate polar groups. Field effects in hydrosilylation have not been noted previously, and these observations warranted further study.

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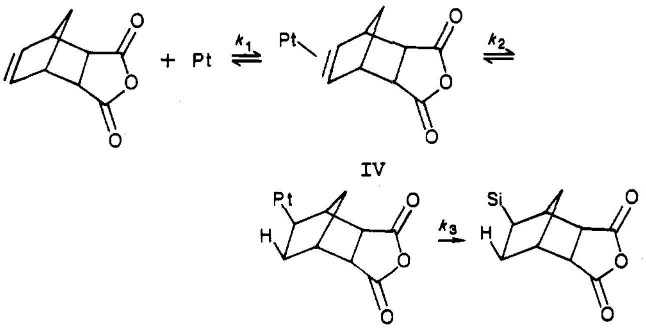
Scheme II



endo-, *exo*-, and *trans*-2,3-dicarbomethoxybicyclo[2.2.1]hept-5-enes Ie–g were found to undergo hydrosilylation with dimethylchlorosilane in high yield (vide supra). In order to compare the magnitude of the rate differences in hydrosilylation with that in 1,3-diazomethane addition, the relative rates of hydrosilylation of Ie–g were determined. Deficiencies of dimethylchlorosilane were allowed to react with binary mixtures of Ib and Ia, Id, Ie, If, Ig, or Ii. The relative rate data are summarized in Table III.

The magnitudes of the relative rates of hydrosilylation of the esters are similar to those observed previously. These results are consistent with a field effect for an electrophilic addition reaction. Thus, the through-space interaction of the olefin with the electron-deficient anhydride or imide ring is believed to be responsible for the slow rates of addition of silane to the endo anhydride and imide Ia and Ic, respectively.

Further support for a field effect was obtained from hydrosilylation of the endo ether Ih. Unlike the endo anhydride or imide, the endo ether does not contain electron-withdrawing 2,3-substituents. Hydrosilylation was rapid under the usual hydrosilylation conditions and was similar in rate to that observed for bicyclo[2.2.1]heptene (Ii) and at least 1000 times faster than the rate of addition of dimethylchlorosilane to the endo anhydride. The rate of hydrosilylation of endo 2,3-disubstituted bicyclo[2.2.1]hept-5-enes was a function of the electron-withdrawing ability of the endo 2,3-substituents.

Although it is not known which step in the hydrosilylation reaction is affected by the proximate electron-withdrawing groups, it seems plausible that the formation of the intermediate platinum–olefin complex IV may be disfavored for the olefins substituted with endo electron-withdrawing substituents relative to olefins with exo substituents or olefin substituents that are not electron withdrawing. Alternatively, the rate of transfer of the electropositive silane moiety to form product may be slowed (Scheme II).

Either decreasing the concentration of the intermediate or slowing the rate of transfer of silane could account for the observed differences in the rates of hydrosilylation of the anhydride and imide epimers.

Experimental Section

General Procedures. Dimethylchlorosilane (Silar), bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (Kodak), and bicyclo[2.2.1]heptene (Aldrich) were used as received. Bicyclo[2.2.1]hept-5-ene-*exo*-2,3-dicarboxylic anhydride,[13] *endo*-, *exo*-, and *trans*-2,3-dicarbomethoxybicyclo[2.2.1]hept-5-enes,[14] and the platinum catalyst[15] were prepared according to the literature procedures. The imides Ic and Id were prepared by reaction of aniline with the corresponding anhydrides and characterized spectroscopically.[16] GC analyses were performed with a Varian 3760 gas chromatograph equipped with 6-ft 3% OV-17 columns and a flame ionization detector. IR spectra were obtained in neat form or in chloroform solution with a Perkin-Elmer Model 598 infrared spectrometer. NMR analyses were performed with a Varian EM-390 or a Varian XL-300 operating in the FT mode. Satisfactory combustion analyses were obtained for all new compounds.

Preparation of *exo*-5-(Dimethylchlorosilyl)bicyclo[2.2.1]heptane-*endo*-2,3-dicarboxylic Anhydride (IIa). A 500-mL three-necked flask equipped with a pressure-equalizing addition funnel, spin bar, and Dean–Stark trap with reflux condenser was charged with 100 mL of toluene and 100 g (0.61 mol) of bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (Ia). The mixture was dried by azeotropic removal of water. The Dean–Stark trap was removed, the solution was cooled to 80 °C, and 0.05 g (0.26 mmol) of platinum catalyst was added. The addition funnel was charged with 64.0 g (0.67 mol, 10% excess) of dimethylchlorosilane. The silane was added dropwise to the olefin solution to maintain a gentle reflux at 80 °C. After all of the silane had been added, the mixture was maintained at temperature for 48 h. The progress of the reaction was followed by ^{1}H NMR, observing the disappearance of the olefin resonance at 6.5 ppm. After all the olefin had reacted, solvent and excess silane were removed under reduced pressure. The resulting solid was vacuum distilled, bp 165–170 °C (0.15 Torr), to obtain 150.1 g (95% yield) of a white solid, mp 105–107 °C. ^{1}H NMR ($CDCl_3$): 3.48–3.45 (2 H, m, H_2, H_3), 2.92–2.87 (2 H, m H_1, H_4), 1.92–1.60 (4 H, m, H_6, H_7), 0.91 (1 H, t, H_5, J = 9 Hz), 0.44 and 0.39 (6 H, s, methyl) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 171.8 (C_8 or C_9), 171.6 (C_9 or C_8), 52.3 (C_1), 49.1 (C_4), 41.2 (C_3), 40.8 (C_2), 39.9 (C_7), 26.7 (C_6), 26.2 (C_5), 0.10 (C_{10}, C_{11}) ppm. $^{29}Si\{^1H\}$ NMR (CD_2Cl_2): 30.4 ppm. IR ($CDCl_3$): 2940 (w), 2870 (w), 1850 (m), 1772 (s), 1250 (w), 1077 (m), 970 (w), 955 (w), 905 (m), 840 (w), 830 (w) cm^{-1}.

Preparation of *exo*-5-(Dimethylchlorosilyl)bicyclo[2.2.1]heptane-*exo*-2,3-dicarboxylic Anhydride (IIb). In a typical hydrosilylation reaction, a 50-mL three-necked round-bottom flask equipped with a spin bar, thermometer, Thermowatch temperature controller, heating mantle, and a nitrogen inlet atop a reflux condenser was charged with 5.0 g (30 mmol) of Ib and 20 mL of toluene. The olefin dissolved as the mixture was stirred and heated to 80 °C, and 2.5 mg (12.8 μmol) of platinum catalyst was added, followed by rapid addition of 3.41 g (36 mmol) of dimethylchlorosilane via a 50-mL pressure-equalizing addition funnel. GC indicated that the reaction was complete within 15 min. The product was isolated by vacuum distillation at 165 °C (0.15 Torr) to obtain 7.37 g (95%) of *exo*-5-(dimethylchlorosilyl)bicyclo[2.2.1]heptane-*exo*-2,3-dicarboxylic anhydride, mp 124–126 °C. ^{1}H NMR ($CDCl_3$): 2.97–2.88 (4 H, m, H_{1-4}), 1.76–1.59 (2 H, m, H_6, $H_{6'}$), 1.55–1.50 (1 H, m, H_7), 1.27–1.22 (1 H, m, $H_{7'}$), 0.92–0.86 (1 H, m, H_5), 0.42 and 0.39 (6 H, s, methyl) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 172.5 (C_8 or C_9), 171.9 (C_9 or C_8), 52.0 (C_1), 48.3 (C_4), 41.5 (C_7), 41.4 (C_2, C_3), 33.7 (C_6), 29.4 and 29.3 (C_5), 0.5 and 0.4 (C_{10}) ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): 30.28 ppm. IR ($CHCl_3$): 2940 (w), 1880 (w), 1860 (m), 1830 (m), 1770 (s), 1700 (s), 1370 (m), 1070 (m), 900 (s) cm^{-1}.

Preparation of *exo*-5-(Dimethylchlorosilyl)bicyclo[2.2.1]heptane-*exo*-2,3-dicarboxylic *N*-Phenylimide (IId). A 50-mL flask equipped as before was charged with 2.0 g (8.6 mmol) of bicyclo[2.2.1]hept-5-ene-*exo*-2,3-dicarboxylic *N*-phenylimide (Id) dissolved in 20 mL of toluene. The solution was heated to 80 °C, and 0.70 mg (3.6 μmol) of platinum catalyst and 0.95 g (10 mmol) of dimethylchlorosilane were added. After 15 min the reaction appeared complete by ^{1}H NMR. Product was isolated by recrystallization from a toluene–heptane mixture to obtain 1.89 g (68%) of the title compound, mp 228–229 °C. IR (neat): 2940 (m), 2880 (w), 1760 (m), 1690 (s), 1590 (w), 1365 (s), 1300 (m), 1250 (w), 1220 (w), 960 (w), 900 (w), 885 (w) cm^{-1}. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 177.7 (C_8 or C_9), 177.1 (C_9 or C_8), 129.1, 128.6, 126.2 (aromatic), 51.9 (C_1), 48.1 (C_4), 41.0 (C_2), 40.8 (C_3), 32.8 (C_7), 30.3 (C_7), 30.1 (C_5), 0.6 (C_{10}, C_{11}) ppm. ^{1}H NMR ($CDCl_3$): 7.52–7.22

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(5 H, m, aromatic), 2.91–2.84 (4 H, m, H_{1-4}), 1.78–1.28 (4 H, m, H_7, $H_{7'}$, H_6), 0.98 (1 H, t, H_5, $J = 9.2$ Hz), 0.46 and 0.43 (6 H, s, methyl) ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): 30.08 ppm.

Preparation of *endo*-2,3-Dicarbomethoxy-*exo*-5-(dimethylchlorosilyl)bicyclo[2.2.1]heptane (IIe). A 50-mL flask equipped as before was charged with 5.0 g (23.8 mmol) of Ie dissolved in 25 mL of toluene. The mixture was warmed to 80 °C, and 2.24 mg (11.5 μmol) of platinum catalyst and 2.7 g (28.5 mmol) of dimethylchlorosilane were added. After 2 h, the mixture was worked up by distillation to obtain 3.5 g (48%) of the title compound, bp 110 °C (0.2 Torr). IR (neat): 2940 (s), 2860 (m), 1730–1710 (s), 1425 (s), 1340 (s), 895 (s), 860 (s), 840 (s), 805 (s), 785 (s), 765 (s), 700 (m), 670 (m) cm^{-1}. ^1H NMR ($CDCl_3$): 3.66 (3 H, s, methoxy), 3.62 (3 H, s, methoxy), 3.2–2.8 (2 H, m, H_2, H_3), 2.64–2.57 (2 H, m, H_1, H_4), 1.74–1.60 (4 H, m, H_6, H_7), 1.45 (1 H, m, H_5), 0.46 and 0.38 (6 H, s, methyl) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 172.8 (C_8 or C_9), 172.5 (C_9 or C_8), 51.4 (methoxy), 51.0 (methoxy), 49.2 (C_1), 45.8 (C_4), 41.3 (C_2), 40.1 (C_3), 38.8 (C_7), 27.3 (C_6), 23.5 (C_5), 0.5 and 0.3 (methyl) ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): 31.7 ppm.

Preparation of *exo*-2,3-Dicarbomethoxy-*exo*-5-(dimethylchlorosilyl)bicyclo[2.2.1]heptane (IIf). A 100-mL flask equipped as before was charged with 11.0 g (52 mmol) of If dissolved in 55 mL of toluene. The mixture was warmed to 80 °C, and 5.5 mg (28.2 μmol) of platinum catalyst and 6.0 g (63.4 mmol) of dimethylchlorosilane were added. After 15 min, product was isolated by distillation to obtain 7.5 g (47% yield) of the title compound, bp 143–145 sC (0.3 Torr). IR (neat): 2940 (s), 2860 (m), 1730–1715 (s), 1425 (s), 1330 (s), 1300 (m), 1255 (s), 1230 (s), 1185 (s), 1130 (m), 1110 (w), 1030 (s), 965 (w), 925 (m), 905 (m), 840 (s), 810 (s), 780 (s), 735 (w), 680 (w), 650 (w) cm^{-1}. ^1H NMR ($CDCl_3$): 3.573 (3 H, s, methoxy), 3.566 (3 H, s, methoxy), 2.7 (2 H, m, H_2, H_3), 2.59 (2 H, s, H_1, H_4), 2.00–1.27 (4 H, m, H_6, H_7), 0.77 (1 H, t, H_5, $J = 8.5$ Hz), 0.35 and 0.34 (6 H, s, methyl) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 173.3 (C_8 or C_9), 172.8 (C_9 or C_8), 54.2 (C_1), 51.5 (methoxy), 50.0 (C_4), 40.7 (C_2), 40.1 (C_3), 35.3 (C_7), 30.7 (C_5, C_6), 0.47 (methyl) ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): 29.98 ppm.

Preparation of *trans*-2,3-Dicarbomethoxy-*exo*-5-(dimethylchlorosilyl)bicyclo[2.2.1]heptane (IIg). A 50-mL flask equipped as before was charged with 2.0 g (9.5 mmol) of Ig dissolved in 10 mL of toluene. The mixture was warmed to 80 °C, and 0.98 mg (5.0 μmol) of platinum catalyst and 1.08 g (11.4 mmol) of dimethylchlorosilane were added. After 1 h, the product was isolated by distillation at 110 °C (2.0 Torr) to obtain 1.5 g (51%) of the title compound. IR ($CDCl_3$): 2940 (s), 2860 (m), 1730–1710 (s), 1425 (s), 1365 (s), 1320 (s), 1285 (s), 1170 (s), 1130 (m), 1015 (s), 975 (w), 960 (w), 905 (m), 840 (s), 805 (s), 785 (s), 700 (m), 660 (m) cm^{-1}. ^1H NMR ($CDCl_3$): 3.63–3.60 (6 H, s, methoxy), 3.22–3.14 (2 H, m, H_1, H_4), 2.85–2.55 (2 H, m, H_2, H_3), 1.55–1.31 (4 H, m, H_6, H_7), 0.89 and 0.74 (1 H, t, H_5, $J = 9$ Hz), 0.33–0.28 (6 H, s, methyl) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 174.8 (endo C_8 or C_9), 174.2 (endo C_9 or C_8), 173.8 (exo C_8 or C_9), 173.3 (exo C_9 or C_8), 52.3 (methoxy), 51.9 (methoxy), 51.8 (methoxy), 48.7 (C_1), 47.8 (C_4), 42.3 (C_2), 42.0 (C_2), 41.0 (C_3), 40.4 (C_3), 37.5 (C_7), 37.3 (C_7), 31.1 (C_6), 30.3 (C_6), 26.7 (C_5), 25.4 (C_5), 0.6 (methyl), 0.5 (methyl), 0.3 (methyl) ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): 30.67 ppm.

Preparation of the Endo Ether Ih. A 300-mL flask equipped with a spin bar, pressure-equalizing addition funnel, reflux condenser, and nitrogen inlet was charged with 11.3 g (73.3 mmol) of *endo*-2,3-bis(hydroxymethyl)bicyclo[2.2.1]hept-5-ene[17,18] dissolved in 100 mL of dry THF. A 2.5 M solution (60.0 mL, 150.0 mmol) of butyllithium in hexane was added slowly. After the mixture was stirred for 1 h, 14.3 g (75.0 mmol) of toluenesulfonyl chloride dissolved in 100 mL of THF was added and the mixture warmed to reflux. Product was isolated by vacuum distillation at 110 °C (0.2 Torr) to obtain 1.8 g (18%) of Ih, mp 58–60 °C. IF (film): 2960 (s), 2930 (m), 2870 (m), 1745 (m), 1465 (w), 1435 (w), 1420 (w), 1380 (m), 1340 (w), 1240 (m), 1160 (s), 1110 (s), 1055 (w), 1000 (m), 910 (w), 850 (w), 730 (w) cm^{-1}. ^1H NMR ($CDCl_3$): 7.24 (2 H, s, H_5, H_6), 3.44 (4 H, m, H_8, H_9), 2.67 (2 H, m, H_2, H_3), 2.54 (2 H, m, H_1, H_4), 1.42 (2 H, m, H_7 and $H_{7'}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 135.0 (C_5, C_6), 68.1 (C_8, C_9), 49.4 (C_1, C_4), 49.4 (C_7), 46.1 (C_2, C_3) ppm.

Synthesis of the Silylated Endo Ether IIh. A 25-mL reaction vessel equipped as before was charged with 0.32 g (2.4 mmol) of Ih dissolved in 5 mL of toluene and warmed to 80 °C. To this were added 0.40 mg (2.0 μmol) of platinum catalyst and 0.27 g (2.85 mmol) of dimethylchlorosilane. The course of the reaction was monitored by GC. After 30 min, all of the olefin had been consumed to form a single product. The chlorosilane was converted to the disiloxane to simplify isolation by the addition of a trace of water. Sublimation at 200 °C (0.2 Torr) yielded 0.15 g (26%) of the title compound as a waxy solid. IR (neat): 2955 (s), 2850 (w), 1480 (w), 1450 (w), 1410 (w), 1365 (w), 1325 (w), 1305 (w), 1297 (w), 1288 (w), 1255 (s), 1207 (m), 1190 (m), 1145 (w), 1125 (w), 1090 (s), 1050 (s), 1000 (m), 975 (w), 952 (w), 930 (w), 920 (w), 907 (m), 832 (m), 800 (m), 780 (m), 737 (w), 730 (w), 705 (w), 680 (w), 663 (w) cm^{-1}. ^1H NMR ($CDCl_3$): 3.7–3.8 (2 H, dd, H_8, H_9), 3.3–3.4 (2 H, dd, $H_{8'}$, $H_{9'}$), 2.52 (2 H, br s, H_2, H_3), 2.15 (2 H, br s, H_1, H_4), 1.63 (1 H, t, H_6 endo, $J = 10.5$ Hz), 1.44 (2 H, AB pattern, H_7, $H_{7'}$), 1.23 (1 H, dt, H_6 exo, $J = 10.5$ Hz, $J = 3.5$ Hz), 0.95 (1 H, t, H_5, $J = 8.5$ Hz), 0.04 (6 H, s, methyl) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 68.9 (C_8 or C_9), 68.8 (C_9 or C_8), 47.8 (C_1), 46.0 (C_4), 41.7 (C_2), 41.5 (C_7), 40.7 (C_3), 24.7 (C_6), 22.6 (C_5), –0.6 (methyl) ppm.

Preparation of *exo*-2-(Dimethylchlorosilyl)bicyclo[2.2.1]heptane (IIi). A 300-mL reaction vessel equipped as before was charged with 20.0 g (0.206 mol) of bicyclo[2.2.1]heptene dissolved in 100 mL of toluene and the resultant mixture warmed to 80 °C. To this were added 0.01 g (51 μmol) of platinum catalyst and 24.0 g (0.25 mol) of dimethylchlorosilane. After 15 min, ^1H NMR indicated the reaction was complete. Product was isolated by distillation at 192–200 °C to obtain 32.0 g (81%) yield of the title compound. IR (neat): 2940 (s), 2860 (s), 1450 (m), 1410 (w), 1310 (w), 1290 (m), 1250 (s), 1210 (w), 1190 (w), 1140 (w), 1130 (w), 1110 (w), 1070–1030 (br, m), 1000 (w), 970 (m), 910 (s), 880 (m), 850 (s), 800 (s), 790 (s), 690 (m), 680 (m), 620 (m) cm^{-1}. ^1H NMR ($CDCl_3$): 2.29 (2 H, s, H_1, H_4), 1.56–1.43 (4 H, m, H_5, H_6), 1.31–1.11 (4 H, m, H_2, H_3, H_7), 0.83 (1 H, t, H_2, $J = 8.6$ Hz), 0.34 (6 H, s, methyl) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 37.7, 37.4, 36.6, 33.8, 31.8, 31.2, 30.9, 29.4, 28.6 (C_2), 0.04 (methyl) ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): 30.1 ppm.

Relative Rates. In a typical relative rate experiment, a 25-mL three-necked flask equipped with a spin bar, heating mantle, and nitrogen inlet atop a reflux condenser was charged with 0.164 g (1.0 mmol) of Ib, 0.210 g (1.0 mmol) of Ic, 4.0 mL of toluene, and 0.100 g of *o*-dichlorobenzene as internal standard. The mixture was warmed to 80 °C, and 0.020 g (0.21 mmol) of dimethylchlorosilane and 0.9 μmol of platinum catalyst were added. The course of the reaction was followed by GC. After 30 min, all of the silane had been consumed, and the product distribution was determined by GC. The data are summarized in Table III.

Supplementary Material Available: High-resolution mass spectral data (1 page). Ordering information is given on any current masthead page.

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