Articles

Rhodium(II) Perfluorobutyrate Catalyzed Silane Alcoholysis. A Highly Selective Route to Silyl Ethers

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Rhodium(II) perfluorobutyrate, $Rh_2(pfb)_4$, is an effective catalyst for the alcoholysis of trialkylsilanes at room temperature. Primary alcohols react with triethylsilane approximately 5 times faster than do secondary alcohols, and tertiary alcohols are virtually inert. Enhanced selectivity is achieved with *tert*-butyldimethylsilane. Hydrosilylation of olefinic alcohols is relatively unimportant even with terminal alkenes, but $Rh_2(pfb)_4$ does promote hydrogenation of 3-phenyl-2-propen-1-ol. Selected diols have been silylated with complete regioselectivity in $Rh_2(pfb)_4$-catalyzed reactions with either triethylsilane or *tert*-butyldimethylsilane. Methanolysis of (*S*)-(−)-1-naphthylphenylmethylsilane occurs with nearly complete inversion of configuration at silicon, and spectral analysis of the catalytic reaction suggests a mechanism for silane alcoholysis in which the rhodium(II) catalyst coordinates with the silicon hydride to activate silicon for backside nucleophilic attack by the alcohol.

The alcoholysis of hydrosilanes is potentially a highly selective process for the protection of specific alcohol functionalities.[1] Several transition metal compounds have been reported to catalyze this transformation (eq 1),[1-9] but

$$R'OH + R_3SiH \xrightarrow{\text{catalyst}} R'OSiR_3 + H_2 \quad (1)$$

few of them are active for trialkylsilanes, and an even smaller number can be used effectively at room temperature.[4-7] Crabtree's $[IrH_2(THF)_2(PPh_3)_2]SbF_6$ is the most active,[7] but its rates for aliphatic alcohols are virtually independent of structure. Wilkinson's catalyst, $Rh(PPh_3)_3Cl$, is effective in refluxing benzene,[8] but olefin hydrosilylation is a competitive process under these conditions.[9] A simple and highly selective catalyst for the preparation of silyl ethers is not evident in these formulations, but, as we now report, rhodium(II) perfluoroborate ($Rh_2(pfb)_4$, pfb = perfluorobutyrate) possesses all of the qualifications of a conveniently employed, air stable,[10] highly effective, and exceptionally selective catalyst for the alcoholysis of hydrosilanes.

Results and Discussion

The treatment of cholesterol at room temperature and under nitrogen with 1.2 equiv of triethylsilane for 12 h in anhydrous dichloromethane containing 1.0 mol % of $Rh_2(pfb)_4$ resulted in the formation of the corresponding triethylsilyl ether in quantitative yield without any evident competition from olefin hydrosilylation. Similar treatment of a selection of alcohols with emphasis on those that contain a carbon–carbon double bond gave the results reported in Table I. Of the alcohols listed in the table (−)-menthol and (−)-borneol underwent silyl ether formation at the slowest rate, but a significant decrease in the reaction time for quantitative hydrosilylation was achieved by increasing to 5.0 mol % of $Rh_2(pfb)_4$ and excess silane. Simple alcohols that included the primary and secondary butyl and pentyl alcohols underwent quantitative alcoholysis of triethylsilane but are not included in the table. Tertiary alcohols did not react with triethylsilane under the same conditions or even in refluxing dichloromethane. In most cases $Rh_2(pfb)_4$ remained intact and could be recovered following completion of the reaction.

A wide variety of catalysts are reported to be effective for the alcoholysis of organosilanes,[1-9,11-17] but few studies

Table I. Product Yields from $Rh_2(pfb)_4$-Catalyzed Reactions of Selected Alcohols with Triethylsilane[a]

alcohol	reaction time, h	yield,[b] % triethylsilyl ether
benzyl alcohol	2	88
1-octanol	3	96
2-octanol	14	94
3-buten-1-ol	3	86
trans-3-phenyl-2-propen-1-ol	0.5	92
cholesterol	12	99
glycidol	9	91
(−)-nopol	6	90[c]
phenol	20	92
(−)-menthol[d]	22	94
(−)-borneol[d]	19	95

[a] Reactions were performed in dichloromethane at room temperature using 1.0 mol % of $Rh_2(pfb)_4$ and 1.1–1.3 molar equiv of triethylsilane. [b] Weight yield of product (>95% pure by ^1H NMR and/or GC analyses) prior to distillation or recrystallization. [c] Includes 3% of the hydrogenation product. [d] Reaction performed with 5.0 molar equiv of triethylsilane and 5.0 mol % of $Rh_2(pfb)_4$.

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have described reactions with alcholols that are as complex as those in Table I.[8a] Heterogeneous catalysts, particularly those of platinum,[11,12] are suitable for reactions with monofunctional alcohols, but competing reactions with other functional groups, especially the carbon–carbon double bond, limit their applicability for synthesis. With homogeneous catalysts the same problems are apparent in many cases, but with $Rh_2(pfb)_4$ they are negligible or they can be overcome.

Silyl ether formation occurred without significant competition from hydrosilylation of olefins when equimolar amounts of alcohol and silane were employed. However, when excess silane was added to olefinic alcohols, hydrosilylation occurred after alcoholysis was complete or nearly complete, except with compounds like cholesterol or (-)-nopol (6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-ethanol) that possess trisubstituted double bonds and gave no evidence of hydrosilylation even after extended reaction times. 3-Buten-1-ol was the most reactive toward hydrosilylation but underwent triethylsilane addition to the carbon–carbon double bond at a rate that was 10 times slower than alcoholysis.

trans-Cinnamyl alcohol was unique among the olefinic alcohols examined in its ability to undergo hydrogenation of the carbon–carbon double bond under alcoholysis conditions. When $Rh_2(pfb)_4$-catalyzed reactions between triethylsilane and cinnamyl alcohol were performed in a closed vessel to contain the liberated hydrogen, reduction of the carbon–carbon double bond occurred along with silane alcoholysis (eq 2), presumably from $Rh_2(pfb)_4$-cat-

$$PhCH{=}CHCH_2OH + Et_3SiH \xrightarrow[CH_2Cl_2]{Rh_2(pfb)_4} PhCH_2CH_2CH_2OSiEt_3 \quad (2)$$

alyzed hydrogenation,[18,19] and the corresponding (3-phenyl-1-propoxy)triethylsilane was formed along with only a trace amount (<3%) of the cinnamyl silyl ether. A similar competitive hydrogenation was recently reported for the alcoholysis of *tert*-butyldimethylsilane by allylic alcohols catalyzed by 10% palladium on carbon (5 mol %).[13] However, when $Rh_2(pfb)_4$ catalysis of the same reaction was performed at short reaction times in an open vessel, or under a flow of nitrogen, competition from hydrogenation was minimal, and the alcoholysis product could be obtained in 92% yield.

Rhodium(II) perfluorobutyrate was much more active than rhodium(II) acetate for silane alcoholysis. For comparison, the $Rh_2(OAc)_4$-catalyzed reaction between 1-octanol and an equimolar amount of triethylsilane was only 30% complete at 4 h in refluxing dichloromethane, but with $Rh_2(pfb)_4$ all of the 1-octanol was converted to silyl ether within 3 h at room temperature. Only after 18 h in refluxing dichloromethane was the $Rh_2(OAc)_4$-catalyzed reaction complete.

Table II. Relative Reactivities for Triethylsilane Alcoholysis Catalyzed by Transition Metal Compounds

	relative reactivity		
alcohol	$Rh_2(pfb)_4$[a]	$IrH_2(THF)_2(PPh_3)_2]SbF_6$[b]	$Ru(PMe_3)_2(CO)_2Cl_2$[c]
1-butanol	4.9	0.37	7.0
1-pentanol	4.7	0.35	3.3
1-hexanol	4.6	0.34	2.4
2-methyl-1-propanol	5.7	–	–
2,2-dimethyl-1-propanol	6.2	–	–
2-butanol	1.00	1.00	1.00
2-methyl-2-propanol	<0.01	0.22	0.086
cyclohexanol	2.2	0.023	0.21
phenol	0.03	0.005	no reaction

[a] Reactions performed in dichloromethane at 25 °C. [b] Data taken from ref 7. Reactions performed in dichloromethane at 25 °C. [c] Data taken from ref 6. Reactions performed in tetrahydrofuran at 18 °C.

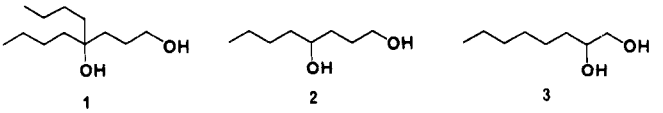
Table III. Relative Reactivities for $Rh_2(pfb)_4$-Catalyzed Alcoholysis of Representative Silanes

	relative reactivity[a]		
alcohol	Et_3SiH	t-$BuMe_2SiH$	Me_2PhSiH
1-butanol	1.00	1.00	1.00
2-methyl-1-propanol	1.09	0.62	1.23
2-butanol	0.26	0.01	0.35

[a] Reactions performed in refluxing dichloromethane.

Relative reactivities for alcoholysis of triethylsilane were examined to determine the potential of this methodology for selective reactions with di- and polyhydroxy compounds. Reactions were performed with a 10-fold excess of each of two alcohols over triethylsilane using 1.0 mol %, based on silane, of $Rh_2(pfb)_4$, and the results are described in Table II together with those for reactions catalyzed by $[IrH_2(THF)_2(PPh_3)_2]SbF_6$[7] and $Ru(PMe_3)_2(CO)_2Cl_2$.[6] Comparative data have been taken from reported turnover rates rather than actual relative rates which were found with $[IrH_2(THF)_2(PPh_3)_2]SbF_6$ to be only about half of the values determined from individual alcoholysis rate data.[7] Among these three catalysts, $Rh_2(pfb)_4$ stands out as offering the highest degree of selectivity, especially between primary or secondary alcohols and tertiary alcohols but not between primary and secondary alcohols. Further enhancement of this selectivity could be achieved with the use of *tert*-butyldimethylsilane but not with dimethylphenylsilane (Table III). Indeed, these results suggest that triethylsilane will offer complete regiocontrol for silylation of primary alcohols in the presence of tertiary alcohols and that *tert*-butyldimethylsilane will provide similar regiocontrol for silation of primary alcohols in the presence of secondary alcohols.

Diols **1–3** were reacted with triethylsilane or *tert*-butyldimethylsilane in the presence of a catalytic amount of $Rh_2(pfb)_4$ to determine the effectiveness of this methodology for regioselective formation of silyl ethers, and these



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results are reported in Table IV. As indicated by relative reactivities obtained with triethylsilane for simple alcohols (Table II), the primary alcohol of **1** is at least 100 times more reactive than the tertiary alcohol in the same molecule, and complete regioselectivity is achieved. Although results obtained from reactions between triethylsilane and

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Table IV. Regioselectivity in $Rh_2(pfb)_4$-Catalyzed Reactions of Trialkylsilanes with Diols[a]

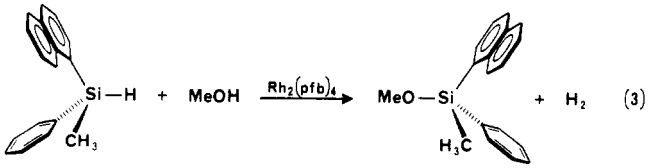
diol	R_3SiH	$[R_3SiH]/[diol]$	reaction time, h	isolated yield, %	relative yield, % 1°	2°	3°	di[b]
1	Et_3SiH	1.1	17	92	>99	–	<1	0
2	Et_3SiH	1.2	20	91	67	12	–	21
2	t-$BuMe_2SiH$	1.0	24	98	99	1	–	0
3	Et_3SiH	1.0	13	95	78	7	–	15
3	t-$BuMe_2SiH$	1.0	24	52	98	2	–	0

[a] Reactions generally performed at 25 °C with 1.0 equiv of the organosilane and 1.0 mol % of $Rh_2(pfb)_4$. [b] Disilylated product.

2 or 3 show a complex mixture of the two monosilylated diols and the disilated diol after all of the silane has reacted, at short reaction times, when the disilylated diol is not formed to any appreciable extent, the ratio of primary to secondary monosilylated diols corresponds to those predicted from the relative reactivities of the model compounds in Table II. As expected, then, the use of *tert*-butyldimethylsilane provides nearly complete regiocontrol in monosilylation of diols 2 and 3. However, longer reaction times in refluxing dichloromethane were required to achieve the reported results in these cases, and with 3 competitive reduction of $Rh_2(pfb)_4$ rendered the catalyst ineffective prior to completion of the reaction.

trans-1,2-Cyclohexanediol was also treated with triethylsilane in the presence of $Rh_2(pfb)_4$. With 1.0 molar equiv of the silane this diol formed 89% of the monosilylated product and 11% of the disilylated diol, but in only 12% yield. The use of 2.0 equiv of triethylsilane in refluxing dichloromethane resulted in the formation of 71% monosilylated diol and 29% disilylated diol in 70% isolated yield. With 3.0 equiv of triethylsilane in a reaction performed in refluxing chloroform, an 81% yield of a 57:43 mixture of mono- and disilylated diols was obtained. Unlike 1,4-diols, the 1,2-diols appear to cause deactivation of the catalyst prior to completion of the alcoholysis reaction. Attempts to prepare the silyl ketal of *trans*-1,2-cyclohexanediol by reaction with diphenylsilane were not successful.

With chloroplatinic acid methanolysis of α-naphthylphenylmethylsilane occurs with racemization, although heterogeneous catalysts give exclusive or predominant inversion.[11] In contrast, $Rh(PPh_3)_3Cl$-catalyzed methanolysis of this optically active silane proceeds with predominant retention of configuration when this reaction is performed in benzene, but predominant inversion of configuration is observed in methanol.[9] Rhodium(II) perfluorobutyrate catalyzed methanolysis of (*S*)-(−)-α-naphthylphenylmethylsilane in dichloromethane at 25 °C yielded the corresponding methoxysilane with complete inversion of configuration at silicon (eq 3) whereas per-



(3)

forming the same reaction in methanol as the solvent gave racemic α-naphthylphenylmethylmethoxysilane. Control experiments established that the enantiomeric methoxysilane underwent racemization in methanol which contained $Rh_2(pfb)_4$.

Spectroscopic methods previously employed to examine olefin coordination with $Rh_2(pfb)_4$[10] were used to determine the mechanistic features of the $Rh_2(pfb)_4$-catalyzed silane alcoholysis. Treatment of $Rh_2(pfb)_4$ in dichloromethane with an equivalent amount of triethylsilane caused an immediate shift in the distinct absorption for the dirhodium compound at 440 nm to a shoulder at 427 nm, but there was no shift in the absorption with λ_{max} at 630 nm as had been previouly observed from olefin coordination. No further change in the spectrum was observed. Addition of 2-methyl-2-propanol, chosen because this alcohol does not react with triethylsilane, resulted in an immediate shift of the λ_{max} at 630 nm to 595 nm and a shift in the absorption at 427 nm to 462 nm, and this spectrum did not change over 1 h. This spectrum is the same as that produced by addition of 2-methyl-2-propanol to $Rh_2(pfb)_4$ in the absence of triethylsilane.

Proton NMR analysis of triethylsilane in deuteriochloroform showed a downfield shift for the hydrogen bound to silicon from δ 3.61 to 4.36 upon addition of $Rh_2(pfb)_4$ with diamagnetic broadening of this heptet. A downfield shift for the methylene groups of triethylsilane from δ 0.59 to 0.77 was also observed. Treatment of this solution with *tert*-butyl alcohol returned the chemical shift values for triethylsilane to within 0.1 δ unit of their original positions in the absence of $Rh_2(pfb)_4$.

These spectral results and the observed inversion of configuration at silicon suggest a mechanism for silane alcoholysis (Scheme I) in which the rhodium(II) catalyst

Scheme I

$$R'OH + Rh_2L_4 \rightleftharpoons Rh(L)_4Rh(R'OH) \quad (4)$$

$$R_3SiH + Rh_2L_4 \rightleftharpoons Rh(L)_4Rh(H\text{-}SiR_3) \quad (5)$$

$$Rh(L)_4Rh(H\text{-}SiR_3) + R'OH \rightarrow [Rh(L)_4Rh\text{-}H]^- + R_3\overset{+}{S}iO(H)R' \quad (6)$$

$$[Rh(L)_4Rh\text{-}H]^- + R_3\overset{+}{S}iO(H)R' \rightarrow Rh_2L_4 + H_2 + R_3SiOR' \quad (7)$$

activates the silane (eq 5) for backside nucleophilic attack by the alcohol at silicon resulting in the formation of a dirhodium hydride complex and the protonated silyl ether (eq 6). Subsequent protonation of the hydride (eq 7) releases the dirhodium catalyst and forms the observed products, molecular hydrogen and the alkoxysilane. Alcohol inhibits this transformation by coordination with the active site of the rhodium(II) catalyst. This mechanism is consistent with the stereochemical and spectral results and also with the low catalytic reactivity of the less electrophilic rhodium(II) acetate. The selectivity observed in these reactions corresponds to those previously established for substitution reactions at silicon.[20] A similar silane adduct is proposed by Crabtree for alcoholysis with $[IrH_2(THF)_2(PPh_3)_2]SbF_5$,[7] but with this catalyst it is the metal-bound alcohol (replacing THF) that reacts with the organsilane coordinated to iridium rather than backside displacement of hydride by "free" alcohol that occurs with $Rh_2(pfb)_4$. The mechanism of the $(Ph_3P)_3RhCl$-catalyzed reaction is reported to be that of oxidative addition of the

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organosilane to rhodium(I) followed by displacement of the bound trialkylsilyl group with a coordinated alcohol (retention of configuration) or with an uncoordinated alcohol (inversion of configuration).[9]

In summary, $Rh_2(pfb)_4$ is an effective and selective catalyst for silane aloholysis that may also be applicable to hydrogenation of selected alkenes. Silane activation by this rhodium(II) carboxylate occurs through coordination of the Si–H bond to rhodium in a manner that may be similar to that recently reported for the association of organosilanes with $(\eta\text{-}C_6H_6)(CO)_2Cr$.[21] We are continuing to explore the scope and mechanistic details of these rhodium-catalyzed processes.

Experimental Section

General Methods. ^1H NMR spectra were obtained at 300 MHz, and mass spectra were run on a quadrupole instrument at 70 eV. Optical rotations were determined from measurements on a Perkin-Elmer 241MC spectropolarimeter. Analytical gas chromatographic analyses were performed with use of either or both methylsilicone or SP-2330 columns. Rhodium(II) perfluorobutyrate was synthesized from rhodium(II) acetate according to the established procedure,[22] and rhodium(II) acetate was prepared from rhodium(III) chloride.[23] Dichloromethane was distilled from P_2O_5 prior to use. Optically pure (*S*)-(−)-1-naphthylphenylmethylsilane was prepared according to the procedure of Corriu and Moreau.[24]

Silane Alcoholysis. General Procedure. Triethylsilane (1.1–1.3 equiv) was added to the alcohol of interest (1.0 equiv) and 0.6–1.0 mol % of $Rh_2(pfb)_4$ in 5.0 mL/mmol alcohol of anhydrous CH_2Cl_2. Gas evolution was observed in the light blue solution, and stirring was continued at room temperature for the time specified in Table I. Generally, the color of the solution remained unchanged during the course of reaction. The presence of water in the reaction solution resulted in the production of triethylsilanol and/or hexaethyldisiloxane. The reaction solution was then added to water, the organic layer was separated, and the water layer was extracted with ether. The combined organic solution was dried over $MgSO_4$, and the solvent and excess triethylsilane were removed under reduced pressure. The resulting material was weighed and then subjected to NMR and/or GC analyses to ascertain purity. Subsequent distillation, crystallization, or chromatographic purification afforded the alkoxysilane. In this way the triethylsilyl ether of 1-octanol was isolated by Kugelrohr distillation (120 °C, 0.5 Torr) in 86% yield, and the triethylsilyl ether of benzyl alcohol was obtained (140 °C, 0.5 Torr) in 80% yield, when these reactions were performed with 1.2 and 2.7 mmol of the respective alcohols. The triethylsilyl ether of cholesterol, mp 104 °C (lit[25] mp 88–90 °C), was isolated in 77% yield, following column chromatography on neutral alumina with CH_2Cl_2 as the eluent, when this reaction was performed on a 1.0-mmol scale; the absence of the hydroxyl group was conformed by IR spectroscopy. The triethylsilyl ether of glycidol was purified by column chromatography on neutral alumina. The triethylsilyl ether of (−)-nopol was obtained in 85% yield after Kugelrohr distillation (120 °C at 0.7 Torr).

(−)-Menthol (0.158 g, 1.00 mmol) was treated with 5.0 equiv of triethylsilane (0.584 g) in 5.0 mL of CH_2Cl_2 containing 0.053 g (0.050 mmol) of $Rh_2(pfb)_4$, and the blue reaction solution was allowed to stir at room temperature under nitrogen for 22 h. At the end of this time the reaction solution was light green. Following removal of solvent and excess silane, Kugelrohr distillation (150 °C, 0.1 Torr) afforded (−)-menthoxytriethylsilane in 87% yield. (−)-Borneol was reacted with triethylsilane under the same conditions, and Kugelrohr distillation provided the purified triethylsilyl ether in 81% yield.

Reaction of (*E*)-3-Phenyl-2-propen-1-ol with Triethylsilane. Triethylsilane (0.24 g, 2.06 mmol) was added to (*E*)-3-phenyl-2-propen-1-ol (0.200 g, 1.49 mmol) and 0.016 g of $Rh_2(pfb)_4$ (0.015 mmol, 1.0 mol %) in 4.0 mL of dry CH_2Cl_2. Gas evolution was observed from the initial light blue solution. After 15 h at room temperature the reaction solution was added to water, and the water layer was extracted with ether. The combined organic solution was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was analyzed by GC which showed 96% (3-phenyl-1-propoxy)triethylsilane and only 4% of the triethylsilyl ether of (*E*)-3-phenyl-2-propen-1-ol. Kugelrohr distillation (150 °C, 0.1 Torr) afforded 0.276 g (1.10 mmol, 74% yield) of 97% pure (3-phenyl-1-propoxy)triethylsilane.

(*E*)-3-Phenyl-2-propen-1-yl triethylsilyl ether: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.42–7.18 (m, 5 H), 6.60 (d, J = 15.9 Hz, 1 H), 6.30 (dt, J = 15.9, 15.1 Hz, 1 H), 4.35 (dd, J = 5.1, 1.8 Hz, 2 H), 1.00 (t, J = 7.9 Hz, 9 H), and 0.66 (q, J = 7.9 Hz, 6 H); mass spectrum m/e (rel abundance) 248 (8, M), 220 (12, M − 28), 219 (59, M − 29), 135 (5), 118 (10), 117 (100), 116 (11), 115 (32), 103 (11), 91 (15).

3-Phenyl-1-propyl triethylsilyl ether: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.32–7.15 (m, 5 H), 3.64 (t, J = 6.5 Hz, 2 H), 2.60 (t, J = 7.7 Hz, 2 H), 1.85 (quin, 2 H), 0.96 (t, J = 7.8 Hz, 9 H), and 0.60 (q, J = 7.8 Hz, 6 H); mass spectrum m/e (rel abundance) 222 (15, M − 28), 221 (72, M − 29), 118 (29), 117 (49), 103 (14), 101 (5), 91 (73).

Relative Reactivities for Silane Alcoholysis. To 1.00 mmol of the organosilane and 10.0 mmol of each of two alcohols was added 0.010 mmol of $Rh_2(pfb)_4$ (1.0 mol %) in 5.0 mL of anhydrous CH_2Cl_2. The resulting solution was maintained under nitrogen at 25 °C with stirring for at least 12 h. After evaporating the solvent and passing the residue through a short column of neutral alumina with CH_2Cl_2 washings to remove insoluble rhodium species, the resulting solution was subjected to GC analyses. Reproducability from duplicate runs was ±5%.

Selective Silation of Diols. Reactions were performed as described in the General Procedure. With diol **3** reactions with *tert*-butyldimethylsilane were performed under a variety of conditions, and that providing the highest conversion (52%) involved the addition of silane (3.7 equiv) and $Rh_2(pfb)_4$ (2.0 mol %) over 3 h to the diol in refluxing $CHCl_3$. With *trans*-1,2-cyclohexanediol reactions that were performed in refluxing $CHCl_3$ reached completion in one-tenth the time required for reactions performed in refluxing CH_2Cl_2. 1,2-Diols caused catalyst destruction, as evidenced by the color change in the reaction solution from the initial blue color to yellow-brown, during the course of the reaction, and this change occurred on a time scale that was competitive with silane alcoholysis. Similar catalyst inactivation was not evident with 1,4-diols. Reaction products were analyzed by GC, and their structures were confirmed by NMR (chemical shift differences between monosilylated diol and diol) and mass spectral analyses.

Methanolysis of (*S*)-(−)-α-Naphthylphenylmethylsilane. To optically pure (*S*)-(−)-α-naphthylphenylmethylsilane (0.248 g, 1.00 mmol) and methanol (0.048 g, 1.50 mmol) in 5.0 mL of anhydrous CH_2Cl_2 was added 0.011 g of rhodium(II) perfluorobutyrate (0.010 mmol, 1.0 mol %), and the reaction solution was stirred for 16 h at room temperature. Solvent and excess methanol were removed, and the resulting solid was purified by chromatographic separation on a neutral alumina column using CH_2Cl_2 as the eluent (96% recovery). The extent of methanolysis was 73%, and polarimetric analysis of the mixture gave, after subtraction of the contribution of unreacted silane, a rotation corresponded to $[\alpha]^{22}_D = +16.1°$ for the methoxysilane (lit.[26] for pure (*R*)-enantiomer, $[\alpha]^{22}_D = +17.0°$) or 95% inversion of configuration. When the same reaction was performed in methanol for the same time, methanolysis of the optically active organosilane was complete, and the observed rotation was 0.000°. When methanolysis was allowed to continue to 90% completion in a reaction performed with equimolar amounts of (*R*)-(+)-α-naphthylphenylmethylsilane and methanol, polarimetric analysis

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of the isolated products (93% recovery) gave $[\alpha]^{21}_D = -10.8°$ or 64% inversion, suggesting that continued reaction in the presence of methanol caused racemization. Indeed, addition of methanol to (*S*)-(+)-α-naphthylphenylmethylmethoxysilane in the presence of $Rh_2(pfb)_4$ caused 80% racemization within 20 h at room temperature.

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Registry No. 1, 1186-14-7; 1 (triethylsilyl ether), 129541-15-7; 2, 51916-47-3; 2 (triethylsilyl ether), 129541-16-8; 2 (*tert*-butyldimethylsilyl ether), 126680-66-8; 3, 1117-86-8; 3 (triethylsilyl ether), 129541-17-9; 3 (*tert*-butyldimethylsilyl ether), 129541-18-0; $Rh_2(pfb)_4$, 73755-28-9; Et_3SiH, 617-86-7; *t*-$BuMe_2SiH$, 29681-57-0; 1-octanol, 111-87-5; benzyl alcohol, 100-51-6; cholesterol, 57-88-5; glycidol, 556-52-5; (−)-nopol, 35836-73-8; (−)-menthol, 2216-51-5; (*E*)-3-phenyl-2-propen-1-ol, 4407-36-7; 2-octanol, 123-96-6; 3-buten-1-ol, 627-27-0; propen-1-ol, 4407-36-7; phenol, 108-95-2; (−)-borneol, 464-45-9; 1-butanol, 71-36-3; 1-pentanol, 71-41-0; 1-hexanol, 111-27-3; 2-methyl-1-propanol, 78-83-1; 2,2-dimethyl-1-propanol, 75-84-3; 2-butanol, 78-92-2; cyclohexanol, 108-93-0; (3-phenyl-1-propoxy)triethylsilane, 2290-40-6; (*E*)-3-phenyl-2-propen-1-yl triethylsilyl ether, 129541-12-4; (*S*)-(−)-α-naphthylphenylmethylsilane, 1025-09-8; (*R*)-(+)-α-naphthylphenylmethylsilane, 1025-08-7; (S)-(+)-α-naphthylphenylmethylmethoxysilane, 16544-83-5; 1-octyl triethylsilyl ether, 17957-36-7; benzyl triethylsilyl ether, 13959-92-7; cholesterol triethylsilyl ether, 7604-85-5; glycidol triethylsilyl ether, 17865-33-7; (−)-nopol triethylsilyl ether, 129541-13-5; (−)-menthoxytriethylsilane, 129541-14-6; (−)-borneol triethylsilyl ether, 129645-73-4; 2-octyl triethylsilyl ether, 17957-35-6; 3-buten-1-yl triethylsilyl ether, 13411-57-9; phenyl triethylsilyl ether, 5888-66-4; (*R*)-(−)-α-naphthylphenylmethylmethoxysilane, 3553-88-6.

Supplementary Material Available: ^1H NMR spectral data and ^1H NMR spectra for the triethylsilyl ethers shown in Tables I and IV (30 pages). Ordering information is given on any current masthead page.

[4 + 3] Cycloaddition Reaction of Some Silyl Enol Ethers Having a Conjugated Carbonyl Functionality

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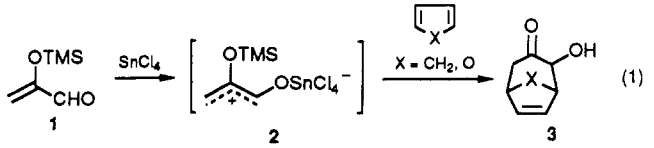
The Lewis acid catalyzed [4 + 3] cycloaddition reactions of 2-(trimethylsiloxy)propenal (**1**), with cyclopentadiene and furan were investigated. The vinylogous 4-(trimethylsiloxy)-2,4-pentadienal (**5**) reacted with cyclopentadiene in the presence of $SnCl_4$ at −78 °C to give 2-(formylmethyl)-substituted bicyclo[3.2.1]oct-6-en-3-one (**11**). This [4 + 3] cycloadduct arose as a result of the perispecific reaction at C_3 and C_5 rather than at C_2 and C_3 where the Diels–Alder reaction is normally expected to occur. With a homologous system, (1-(trimethylsiloxy)vinyl)oxirane (**7**, R = H) underwent a similar [4 + 3] cycloaddition reaction to give a 2-(hydroxymethyl)-substituted bicyclic product. In this case, trimethylsilyl triflate was a useful catalyst. The silyl enol ether **9**, conjugated with a 1,1-cyclopropanedicarboxylate was also reactive; thus, a catalyzed ring opening followed by the cycloaddition reaction gave a bicyclic diester. These cycloaddition reactions may be explained by the formation of a key oxyallyl cation-like intermediate and provide a method for constructing a functionalized bicyclo[3.2.1]octane system.

[4 + 3] Cycloaddition reactions have been extensively studied as a method for the formation of seven-membered rings.[1] Among the reliable 3C components in these reactions is the oxyallyl cation,[2] which was developed by Hoffmann.[3] Synthetic applications have been discussed in a recent review.[4]

Y= alkyl, silyl, metal, etc.

This type of intermediate is known to be accessible by an S_N1-like ionization in an allylic system by the reductive elimination of halogens from a halogenated ketone (in some cases directly from electronically equivalent cyclopropanone and alleneoxide).[3] An alternative approach was demonstrated in our previous work; 2-(trimethylsiloxy)-propenal (**1**) underwent cycloaddition to a diene as a 3C component rather than as a 2C dienophile, leading to a [4 + 3] cycloadduct **3**.[5,6] In this case, the activation of the carbonyl group by a Lewis acid lent positive character to the neighboring silyl enol ether, which gave rise to the key silyl oxyallyl cation intermediate **2** (eq 1).[5,6]



1 2 3 (1)

TMS = trimethylsilyl

It seemed reasonable to extend this [4 + 3] cycloaddition reaction to a silyl enol ether which is properly conjugated

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