Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We also thank Daniel Marshall and Steven L. Westland, undergraduates, who did some exploratory work on eq 1 at College of DuPage and Professor P. Geneste (Montpellier, France) who provided us with some unpublished data.[16]

Registry No. 1a, 1483-82-5; **1b**, 932-87-6; **1c**, 501-65-5; **1d**, 536-74-3; **2a**, 39561-64-3; **2b**, 81423-90-7; **2c**, 81423-91-8; **2d**, 70445-87-3; **3b**, 81423-92-9; **3d**, 81423-93-0; (*E*)-**4**, 81423-94-1; **5b**, 55118-77-9; **5d**, 27183-55-7; **6**, 201-69-4; **7**, 1055-26-1; (*p*-methoxyphenyl)propiolic acid, 2227-57-8; SbF_5, 7783-70-2; SO_2, 7446-09-5.

Notes

Stereoselective Ketone Reductions: Reduction of 4-*tert*-Butylcyclohexanone by Alkylsilanes in the Presence of Rhodium(I) and Ruthenium(II) Catalysts

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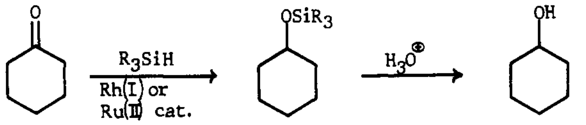
Received June 16, 1981

A number of years ago, it was established that ketones undergo facile reduction by alkylsilanes to afford silyl ethers in the presence of homogeneous rhodium(I) or ruthenium(II) catalysts (eq 1).[1–4] The reaction allowed, after



(1)

hydrolysis, the overall transformation of ketones to alcohols which could not be accomplished under mild conditions with molecular hydrogen and similar soluble catalysts.[5,6] In particular, commerically available tris(triphenylphosphine)rhodium(I) chloride and to a lesser extent tris(triphenylphosphine)ruthenium(II) dichloride were reported to be efficient catalysts, providing silyl ethers in high yields and under mild, neutral conditions. These attractive features notwithstanding, the reaction has rarely been used for the reduction of ketones and aldehydes.

A brief study of menthone and camphor showed remarkable stereochemical control.[1d] Bulky trialkylsilanes gave predominantly the more stable reduction product, and the mono- or dialkylsilanes gave predominantly the less stable reduction product. This limited set of data was suggestive of a powerful method for stereoselective reductions, where the product configuration could be varied by choosing the appropriate silane, but it has not been pursued.[7] Here we report an examination of the reduction of a standard test case, 4-*tert*-butylcyclohexanone, using di- and trialkylsilanes in an effort to define the optimum conditions for high stereoselectivity and the variables which influence selectivity.

Table I. Rh(I)-Catalyzed Hydrosilylation of 4-*tert*-Butylcyclohexanone[a]

entry	silane	temp, °C	time, h	Ax/Eq ratio[b]
1	Et_3SiH	25	144	33:67
2	Et_3SiH	45	20	23:77
3	Et_3SiH	80	3	11:89
4	Et_3SiH	110	1.5	12:88[c]
5	Ph_3SiH	25	64	19:81[e]
6	Ph_3SiH	80	24	12:88
7	$PhMe_2SiH$	80	12	29:71
8	$(EtO)_3SiH$	80	20	29:71[d]
9	Cl_3SiH	80	18	37:63[e]
10	Et_2SiH_2	25	0.25	46:54
11	Ph_2SiH_2	25	0.25	57:43

[a] Reactions were performed by using 2 mol % of tris(triphenylphosphine)rhodium(I) chloride, 1.5 equiv of the alkylsilane, and 1 equiv of 4-*tert*-butylcyclohexanone in benzene solution. [b] Ratios determined by GLC analysis of the derived alcohols after hydrolysis (catalyst *p*-TsOH·H_2O/aqueous MeOH/25 °C/1 h) of the crude silyl ethers. [c] Toluene solvent. [d] A major side reaction was the formation of the silyl enol ether. [e] Reaction was <20% complete.

Results and Discussion

(A) Tris(triphenylphosphine)rhodium(I) Chloride Catalyst. The results obtained from the reduction of 4-*tert*-butylcyclohexanone by various di- and trialkylsilanes in the presence of tris(triphenylphosphine)rhodium(I) chloride are shown in Table I. The reactions were conducted in benzene solution[8] by using 1.5 molar equiv of the alkylsilane and 2 mol % of the rhodium catalyst. In general, the reductions with trialkylsilanes (entries 1–7) required heating at 80 °C to obtain reasonable reaction rates. In most cases these reactions were incomplete (60–90% conversion), using only 2 mol % of the catalyst. Increasing the amount of catalyst to 5 mol % gave essentially complete consumption of starting ketone in the case of triethylsilane and dimethylphenylsilane. The addition

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(1) (a) Ojima, I.; Kogure, T.; Nihonyanagi, M.; Nagai, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3506. (b) Ojima, I.; Nihonyanagi, M.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1972**, 938. (c) Ojima, I.; Nihonyanagi, M.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Nakatsugawa, K.; Nagai, Y. *J. Organomet. Chem.* **1975**, *94*, 449. (d) Ojima, I., Nihonyanagi, M.; Nagai, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3722.

(2) Corriu, R. J. P.; Moreau, J. J. E. *J. Chem. Soc., Chem. Commun.* **1973**, 38.

(3) Eaborn, C.; Odell, K.; Pidcock, A. *J. Organomet. Chem.* **1973**, *63*, 93.

(4) Reviews: (a) Nagai, Y. *Org. Prep. Proced.* **1980**, *12*, 13. (b) Ojima, I.; Yamamoto, K., Kumada, M., *Aspects Homogeneous Catal.* **1977**, *3*, 186. (c) Lukevics, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. *Organomet. Chem. Rev.* **1977**, *5*, 1–180.

(5) Review: Birch, A. J.; Williamson, D. H. *Org. React.* **1976**, *24*, 1.

(6) For hydrosilylations of ketones with platinum catalysts see: (a) Hayashi, T.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1972**, *46*, C65. (b) Hayashi, T.; Yamamoto, K.; Kumada, M. *Ibid.*, **1976**, *112*, 253.

(7) An isolated report of the hydrosilylation of 4-*tert*-butylcyclohexanone by a rhodium catalyst has appeared although the stereochemistry of the product is not clear; see: Bottrill, M.; Green, M. *J. Organomet. Chem.* **1976**, *111*, C6.

(8) Ojima's work generally was performed without solvent.

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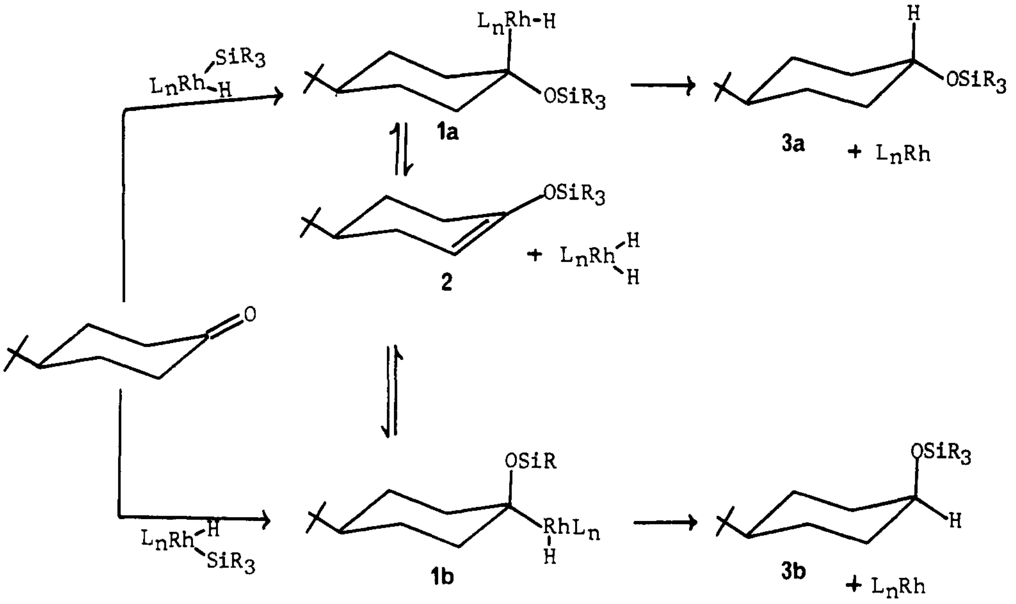
Scheme I



of polar solvents (e.g., 10% acetonitrile or nitromethane) gave slow reaction (<5% after 24 h at 80 °C) with triethylsilane. The reaction also proceeded slowly in 10% THF/benzene at 80 °C to give an axial/equatorial preference of 20:80 with triethylsilane. In contrast, the reductions with dialkylsilanes were rapid at 25 °C in benzene.

There is a definite *trend* in the stereoselectivity of the reduction as a function of steric bulk of the alkylsilane. Unfortunately the effect was not as dramatic as in the menthone example previously reported.[1d] Under optimum conditions the axial/equatorial preference varied from 57:43 with diphenylsilane to 11:89 with triethylsilane. The isolated yields of the silyl ethers with triethylsilane and diethylsilane were 92% and 97%, respectively (see Experimental Section).

Higher temperatures favored the more stable product, perhaps due to thermodynamic control through rapid equilibration. Control experiments, however, indicate the product silyl ethers **3a** and **3b** do not undergo equilibration when independently subjected to the reaction conditions. An alternate route for equilibration involves intermediate alkylrhodium species (**1a**,**b**[9] (Scheme I) which can undergo reversible β-hydride elimination and subsequent equilibration via silyl enol ether **2**.[10] Labeling studies involving the reduction of 2,2,6,6-tetradeuterio-4-*tert*-butylcyclohexanone with triethylsilane, however, indicated no proton incorporation β to the silyloxy group in the product silyl ether. The complementary experiment involving the reduction of 4-*tert*-butylcyclohexanone with triethylsilyl deuteride indicated no deuterium incorporation β to the silyloxy group in the product. In addition, attempted hydrogenation of silyl enol ether **2** with tris(triphenylphosphine)rhodium(I) chloride under the reaction conditions afforded only starting silyl enol ether **2**. Thus it appears that if equilibration is occurring, intermediate **2** is not involved.

(B) Tris(triphenylphosphine)ruthenium(II) Dichloride Catalyst. The results obtained from the reduction of 4-*tert*-butylcyclohexanone by various di- and trialkylsilanes in the presence of 2 mol% of tris(triphenylphosphine)ruthenium(II) dichloride are shown in Table II. The reactions were conducted under conditions similar to those for the rhodium-catalyzed reductions; however, longer reaction times and heating to 80 °C were necessary in all cases, including the dialkylsilanes. In general, the reactions proceeded only to 40–60% completion. Again a similar trend in stereoselectivity was observed as a function of steric bulk of the alkylsilane. Despite the sluggish nature of the reduction, excellent yields were achieved with triethylsilane by increasing the amount of catalyst to 5 mol %, adding 5 mol % of silver trifluoroacetate, and heating to 110 °C in toluene. Thus the silyl ether was obtained in 96% yield, and the axial/equatorial preference was 5:95 (see Experimental Section). The stereoselectivity represents an improvement on the analogous rhodium-catalyzed reduction and is comparable to the more widely used lithium aluminum hydride reduction which has been reported to afford axial/equatorial ratios of 11:89[11a] to 4:96.[11b]

Table II. Ru(II)-Catalyzed Hydrosilylation of 4-*tert*-Butylcyclohexanone[a]

entry	silane	time, h	Ax/Eq ratio[b]
1	Et_3SiH	8	08:92
2	Et_3SiH	20	05:95[c]
3	Ph_3SiH	24	07:93
4	$PhMe_2SiH$	10	12:88
5	Et_2SiH_2	12	41:59
6	Ph_2SiH_2	12	49:51

[a] Reactions were performed by using 2 mol % of tris(triphenylphosphine)ruthenium(II) dichloride and 1.5 molar equiv of the alkylsilane relative to 4-*tert*-butylcyclohexanone in benzene at 80 °C. [b] Ratios determined by GLC analysis of the derived alcohols from hydrolysis (*p*-toluenesulfonic acid hydrate/MeOH/25 °C/1 h) of the crude silyl ethers. [c] Reaction was performed in toluene at 110 °C with 2 mol % of silver trifluoroacetate added.

In summary, 4-*tert*-butylcyclohexanone undergoes reduction with triethylsilane in high yield to provide predominantly the more stable equatorial silyl ether in the presence of tris(triphenylphosphine)rhodium(I) chloride or tris(triphenylphosphine)ruthenium(II) dichloride/silver

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(9) This type of alkylrhodium intermediate has been proposed by Ojima (see ref 1d).

(10) Silyl enol ethers have been observed as byproducts in the reduction of aromatic ketones (see ref 2 and 3).

(11) (a) Brown, H. C.; Deck, H. R. *J. Am. Chem. Soc.* **1965**, 87,5620. 5620. (b) Lansbury, P. T.; MacLeay, R. E. *J. Org. Chem.* **1963**, *28*, 1940.

trifluoroacetate. An axial/equatorial preference of 5:95 was achieved.

Experimental Section

General Methods. Reactions were conducted under argon in a 25-mL two-necked flask fitted with a rubber septum. Liquids were transferred via argon-flushed syringes. Benzene and toluene were distilled from sodium/benzophenone ketyl; tris(triphenylphosphine)rhodium(I) chloride and tris(tripenylphosphine)ruthenium(II) dichloride were obtained from Alfa, Danvers, MA; alkylsilanes were obtained from Petrarch Systems, Bristol PA, and used without purification. An authentic mixture of *cis*- and *trans*-4-*tert*-butylcyclohexanol for GLC comparison was prepared by lithium aluminum hydride reduction of 4-*tert*-butylcyclohexanone in ether.[11] Triethylsilyl deuteride[12] and 2,2,6,6-tetradeuterio-4-*tert*-butylcyclohexanone[13] were prepared by literature methods.

GLC analyses were obtained on a Perkin-Elmer 3920 gas chromatograph fitted with a flame-ionization detector. Separations were provided by a 6 ft × $^1/_8$ in., 5% 2:1 FFAP/Bentone aluminum column.

Triethylsilane/Rhodium(I)-Catalyzed Reduction. To an orange homogeneous solution of 154 mg (1.00 mmol) of 4-*tert*-butylcyclohexanone and 45 mg (0.050 mmol) of tris(triphenylphosphine)rhodium(I) chloride in 5.0 mL of benzene was added 0.24 mL (1.5 mmol) of triethylsilane. The reaction mixture turned yellow and was heated at reflux for 1 h. The resulting deep red solution was concentrated by rotary evaporation. The residual oil was diluted with 5 mL of hexane, filtered, concentrated, and chromatographed on silica gel (3% ether–hexane) to afford 249 mg (92%) of *cis,trans*-[(4-*tert*-butylcyclohexyl)oxy]triethylsilane as a colorless liquid: IR (film) 2945, 1453, 1365, 1237, 1090, 1009, 843, 745 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.45–2.1 (br, ~q at 0.65, $J = 7$ Hz, and s at 0.85, 33 H), 3.45 (br s, ~1 H); mass spectrum, *m/e* (relative intensity) 270 (M^+, 1), 242 (22), 241 (100), 137 (23), 103 (93), 87 (11), 81 (16), 75 (66); exact mass calcd for $C_{16}H_{34}OSi$ *m/e* 270.2379, found 270.2381; GLC analysis, two major peaks (97% of total peak area) in an area ratio of 11:89, corresponding to the axial/equatorial isomers, respectively.

Diethylsilane/Rhodium(I)-Catalyzed Reduction. To an orange solution of 154 mg (1.00 mmol) of 4-*tert*-butylcyclohexanone and 9.0 mg (0.010 mmol) of tris(triphenylphosphine)rhodium(I) chloride in 5.0 mL of benzene was added dropwise 0.15 mL (1.1 mmol) of diethylsilane. The reaction was mildly exothermic and turned yellow. After 15 min the solution was concentrated by rotary evaporation, and the residual oil was diluted with 3 mL of hexane. The resulting slurry was filtered, concentrated, and evaporatively distilled [60 °C (0.10 torr)] to afford 235 mg (97%) of *cis,trans*-[(4-*tert*-butylcyclohexyl)oxy]diethylsilane as a colorless low melting solid: IR (film) 2960, 2102, 1463, 1371, 1240, 1090, 1057, 1012, 861, 830 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.60–2.4 (br, with s at 0.87, 28 H), 3.45 (br s, 0.5 H), 3.97 (m, 0.5 H), 4.38 (m, 1 H); mass spectrum *m/e* (relative intensity) 242 (m^+, 15), 213 (58), 177 (17), 143 (49), 138 (73), 137 (54), 123 (58), 99 (59), 83 (65), 82 (77), 81 (100), 80 (61), 75 (48); exact mass calcd for $C_{14}H_{30}OSi$ *m/e* 242.2066, found 242.2054; GLC analysis, two major peaks (99% of total peak area) in a 47:53 area ratio corresponding to the axial/equatorial isomers, respectively.

Triethylsilane/Ruthenium(II)-Catalyzed Reduction. To a solution of 154 mg (1.00 mmol) of 4-*tert*-butylcyclohexanone, 48 mg (0.05 mmol) of tris(triphenylphosphine)ruthenium(II) dichloride, and 11 mg (0.05 mmol) of silver trifluoroacetate[14] in 5.0 mL of toluene was added 0.24 mL (1.5 mmol) of triethylsilane. The reaction mixture was heated at reflux and turned purple after several min. After 20 h at reflux, the solution was concentrated by rotary evaporation, diluted with 3 mL of hexane, filtered, concentrated, and evaporatively distilled [70 °C (0.10 torr)] to yield 260 mg (96%) of *cis,trans*-[(4-*tert*-butylcyclohexyl)oxy]triethylsilane as a colorless liquid. GLC analysis: two major peaks (97% of the total peak area) in a 5:95 area ratio corresponding to the axial/equatorial isomers, respectively.

General Procedure for Hydrolysis of Silyl Ethers. A solution of the crude silyl ether and a few crystals of *p*-toluenesulfonic acid hydrate in 5 mL of 10% aqueous methanol was stirred at 25 °C for 1 h. An aliquot was removed for GLC analysis.

Registry No. 3a ($R_3 = Et_3$), 81256-40-8; **3a** ($R_3 = Et_2$, H), 81256-41-9; **3a** ($R_3 = Ph_3$), 81256-42-0; **3a** ($R_3 = Me_2$, Ph), 81256-43-1; **3a** ($R_3 = OEt_3$), 81256-44-2; **3a** ($R_3 = Cl_3$), 81256-45-3; **3a** ($R_3 = Ph_2$, H), 81256-46-4; **3b** ($R_3 = Et_3$), 81256-47-5; **3b** ($R_3 = Et_2$, H), 81256-48-6; **3b** ($R_3 = Ph_3$), 81256-49-7; **3b** ($R_3 = Me_2$, Ph), 81256-50-0; **3b** ($R_3 = OEt_3$), 81278-81-1; **3b** ($R_3 = Cl_3$), 81256-51-1; **3b** ($R_3 = Ph_2$, H), 81256-52-2; Et_3SiH, 617-86-7; Et_2SiH_2, 542-91-6; Ph_3SiH, 789-25-3; $PhMe_2SiH$, 766-77-8; $(EtO)_3SiH$, 998-30-1; Cl_3SiH, 10025-78-2; Ph_2SiH_2, 775-12-2; 4-*tert*-butylcyclohexanone, 98-53-3; tris(triphenylphosphine)rhodium(I) chloride, 14694-95-2; tris(triphenylphosphine)ruthenium(II) dichloride, 15529-49-4.

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[12] Doyle, M. P.; McOsker, C. C.; West, C. T. *J. Org. Chem.* **1975**, *41*, 1393.

[13] Geneste, P.; Lamaty, G. *Bull. Soc. Chim. Fr.* **1968**, 669.

[14] Janssen, D. E.; Wilson, C. V. "Organic Syntheses"; Rabjohn, N., Ed.; Wiley: New York, 1963, Collect. Vol. IV, p 547.

Conversion of 2,4,6-Trinitrobenzyl Chloride to 2,2′,4,4′,6,6′-Hexanitrostilbene by Nitrogen Bases

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Received November 3, 1981

In Shipp and Kaplan's report of the remarkably facile preparation of 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) from 2,4,6-trinitrotoluene (TNT) and alkaline hypochlorite, it was disclosed that 2,4,6-trinitrobenzyl chloride (TNBzCl) is obtainable in 85% crude yield by quenching the reaction after only 1 min, and is converted to HNS by reaction with sodium hydroxide.[1] The sequence in eq 1 and 2 was

$$\underset{\text{TNT}}{\text{PiCH}_3} \xrightarrow{\text{OH}^-} \text{PiCH}_2^- \xrightarrow[\text{OCl}^-]{[\text{Cl}^+]} \underset{\text{TNBzCl}}{\text{PiCH}_2\text{Cl}} \qquad (1)$$

$$\underset{\text{TNBzCl}}{\text{PiCH}_2\text{Cl}} \xrightarrow{\text{OH}^-} \text{PiCHCl}^- \xrightarrow{\text{PiCH}_2\text{Cl}} \text{PiC(Cl)HCH}_2\text{Pi} \xrightarrow[-\text{HCl}]{\text{OH}^-} \underset{\text{HNS}}{\text{PiCH}{=}\text{CHPi}} \qquad (2)$$

Pi = picryl = 2,4,6-trinitrophenyl

suggested to account for these transformations. HNS was reportedly obtained in yields up to 50% from TNBZCl and up to 42% from TNT. The yields cited, however, included coprecipitated byproducts, largely 2,2′,4,4′,6,6′-hexanitrobibenzyl, which are removable by washing with acetone. On attempting to duplicate the crude HNS yield of 50% using TNBzCl and sodium hydroxide in the prescribed mole ratio of 1,[2] we obtained a 46% yield. This was reduced to 40% on washing with acetone.[3]

We report here that HNS can be obtained from TNBzCl in substantially improved yields by using certain nitrogen bases in place of sodium hydroxide. Bases in the pK_B range of 2.8–8.8 have been examined and are listed in Table I together with the yields of HNS obtained from

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[1] Shipp, K. G.; Kaplan, L. A. *J. Org. Chem.* **1966**, *31*, 857.

[2] No HNS is obtained when the NaOH/TNBzCl molar ratio equals 2.[1]

[3] The yield on starting with TNT and alkaline hypochlorite was similarly decreased from 42% to 37%.

[4] (a) Dean, J. A., Ed. "Lange's Handbook of Chemistry", 12th ed.; McGraw-Hill: New York, 1979; p 5–14. (b) Hall, J. L.; Fisher, J. F. *Proc. W. Va. Acad. Sci.* **1962**, *34*, 85; *Chem. Abstr.* **1963**, *59*, 3748*d*. (c) "CRC Handbook of Chemistry and Physics", 60th ed.; CRC Press: Boca Raton, FL, 1979; p D-161.

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