When the irradiation was repeated in chloroform instead of dichloromethane, the reaction gave similar results to those reported above.

Dark Reaction of Selenosulfonate 1 with Diazomethane. Selenosulfonate 1 (156 mg, 0.50 mmol) was dissolved in 2 mL of dichloromethane and excess ethereal diazomethane was added. The reaction mixture was allowed to stand for 17 h at room temperature in an apparatus completely wrapped in aluminum foil to exclude light. After removal of volatile material in vacuo, NMR analysis of the resulting oil indicated the presence of three components with signals at δ 5.52 (d, J = 10 Hz) and 5.18 (d, J = 10 Hz), δ 4.24 (s) and 3.44 (s), attributed to 4 (CH_2), 3 (CH_2), and 5 (OCH_3), respectively, as well as the expected aromatic and aryl methyl resonances. The integrated intensities of these signals provided yields of 21%, 52%, and 27% for 3, 4 and 5, respectively. A 110-mg portion of this mixture was separated by preparative TLC in 25% ethyl acetate–hexane to afford, in increasing order of R_f, 26 mg of the α-(phenylseleno) sulfone 3, identical (TLC, IR, NMR) with an authentic sample (vide infra), 60 mg of a mixture of sulfinate esters 4 and 5, and 15 mg of diphenyl diselenide, identical (TLC, IR, NMR) with an authentic sample. The mixture of 4 and 5 could not be further separated. The presence of 5 was confirmed by comparing the mixture with an authentic sample (IR, NMR, GC–mass spectra); that of 4 was inferred from the NMR spectrum.[9] Finally, the mixture of 4 and 5 gave a mass spectrum showing m/e 326 and 324 at probe temperatures over 100 °C (M^+ of 4, ^{80}Se and ^{78}Se, respectively) and m/e 170 (M^+ of 5) at room temperature.

(Phenylseleno)methyl *p*-Tolyl Sulfone (3). Methyl *p*-tolyl sulfone (170 mg, 1.00 mmol) and sodium hydride (30 mg, 1.25 mmol) were refluxed 1 h in 5 mL of toluene under nitrogen. The mixture was then added to a solution of benzeneselenenyl chloride (239 mg, 1.25 mmol) in 5 mL of toluene. After being stirred for 30 min at room temperature, the solution was washed with water (2×), dried over anhydrous $MgSO_4$, and evaporated to dryness under vacuum. The residue was separated by preparative TLC in 25% ethyl acetate–hexane to afford 91 mg (28%) of the title compound: mp 79–81 °C; IR (film of melted product) 1317, 1303, 1145 cm^{-1}; NMR δ 7.70 (d, J = 9 Hz, 2 H), 7.5–7.0 (complex, 7 H), 4.24 (s, 2 H), 2.40 (s, 3 H); mass spectrum, m/e 326 (M^+, ^{80}Se), 324 (M^+, ^{78}Se). Anal. Calcd for $C_{14}H_{14}O_2SSe$: C, 51.69; H, 4.34; S, 9.86. Found: C, 51.79; H, 4.33; S, 10.14.

Attempted Reaction of Sulfone 3 with Diazomethane. Sulfone 3, prepared in the preceding procedure, was dissolved in 1 mL of dichloromethane. Excess ethereal diazomethane was added and the solution was irradiated as in the case of selenosulfonate 1. After 1 h, volatile material was removed in vacuo and the remaining residue consisted of unchanged 3 (melting point, NMR).

Registry No. 1, 68819-94-3; 2, 79665-09-1; 3, 79665-10-4; 4, 79665-11-5; 5, 672-78-6; methyl *p*-tolyl sulfone, 3185-99-7; benzeneselenyl chloride, 5707-04-0.

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[9] The AB quartet observed for the diastereotopic methylene protons in 4 closely resembles those in similar sulfinate esters such as benzyl *p*-toluenesulfinate: Wilt, J. W.; Wagner, W. J. *Chem. Ind.* (*London*) 1964, 1389.

Synthesis of Adamantane Derivatives. 56. Reaction of 1-Adamantyl Chloride with Trimethylsilyl Pseudohalide

Tadashi Sasaki,* Akira Nakanishi, and Masatomi Ohno

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

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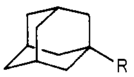
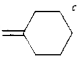
It is well documented that α- and β-unsaturated organosilanes are useful synthons as mild and stable nucleophiles, acting formally as the corresponding organometallics.[1] Their selective reactivity originating from the less electropositive nature of silicon sometimes gives advantages over other metals under the right conditions. Substitution at the adamantane bridgehead is a typical example. While nucleophilic attack of alkali organometallics at the bridgehead is severely restricted due to the intrinsic structure of adamantane, displacement under electrophilic conditions is easily realized with unsaturated organosilanes; we have reported that allylsilane and its analogues are reactive with 1-adamantyl chloride (1, Chart I) in the presence of Lewis acids.[2] In continuation of synthetic studies of adamantane derivatives we attempted the titanium tetrachloride catalyzed reactions of 1 with reagents represented as $Me_3SiX{\equiv}Y$ and $-X{=}Y{=}Z$ (X, Y, Z = C, N, O, or S). The reactions of these reagents with a typical tertiary alkyl halide are not precedented, although those with carbonyl functions are reported frequently. In fact, it was found that trimethylsilyl pseudohalide reacted smoothly. Notably, ambident cyanide 2 and isothiocyanate 6 showed nucleophilic behavior at the nitrogen and sulfur ends, respectively.

Chart I



Me_3SiR

1, R = Cl
3, R = NC
4, R = NHCHO
7, R = SCN
8, R = NCS
9, R = Br
12, R = NCO
13, R = NHCONH-*t*-Bu
14, R = N(Me)CN
16, R = N_3

2, R = CN
5, R = $CH{=}C{=}CH_2$ [a]
6, R = NCS
10, R = NCO
11, R = N=C=NMe [b]
15, R = N_3
17, R = N=C=  [c]
18, R = CHN_2 [d]

[a] G. Merault, P. Bourgeois, and J. Dunogues, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 274, 1857 (1972). The reagent obtained by this procedure is contaminated with a small amount of propargylsilane. See ref 4 for the preparation of pure 5. [b] I. Ruppert, *Tetrahedron Lett.*, 1987 (1977). [c] *tert*-Butyldimethylsilyl group was used in this case: D. S. Watt, *Synth. Commun.*, 4, 127 (1974). [d] D. Seyferth, A. W. Dow, H. Menzel, and T. C. Flood, *J. Am. Chem. Soc.*, 90, 1080 (1968).

As for the reaction with $Me_3X{\equiv}Y$, we already have reported the system where X and Y are carbons.[2] Another possible combination is the case of trimethylsilyl cyanide (2). Treatment of 2 with an equal amount of titanium tetrachloride and 1 in methylene chloride at 0 °C for 150 min gave the isonitrile 3 in 78% yield after liberation from the complex with pyridine. Decomposition with water resulted in the formation of the formamide 4 (61%) together with 3 (12%). An interesting feature is that the adamantyl cation attacked 2 at nitrogen to give the product 3 directly, whereas the reaction of a heteroatom-stabilized carbonium ion with 2 is reported to lead to the formation of nitrile derivatives.[3]

The reactions of (trimethylsilyl)cumulens toward 1 were next studied. Attempted reaction of 5, a prototype of

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[1] (a) T. H. Chan and I. Fleming, *Synthesis*, 761 (1979). (b) I. Fleming in "Comprehensive Organic Chemistry", Vol. 3, D. N. Jone, Ed., Pergamon Press, Oxford, 1979, Part 13.

[2] T. Sasaki, A. Usuki, and M. Ohno, *J. Org. Chem.*, 45, 3559 (1980).

[3] V. Asher, C. Becu, M. J. O. Antenius, and R. Callens, *Tetrahedron Lett.*, 22, 141 (1981). We have also observed that the $AlCl_3$-catalyzed reaction of 16 with 2 was mediated by azahomoadamantyl cation, affording 3-cyano-4-azahomoadamantane: T. Sasaki, S. Eguchi, and T. Okano, *J. Org. Chem.*, in press. See also the case of oxirane: W. Lidy and W. Sundermeyer, *Tetrahedron Lett.*, 1449 (1973).

cumulene, did not undergo the desired propargylation with **1** as observed with ketones[4] under the various conditions.[5] However, all of the systems, $Me_3SiN{=}C{=}Z$ where Z is O, N, and S, underwent substitution reactions with **1** under similar catalyzed conditions. Trimethylsilyl isothiocyanate (**6**) reacted even at −78 °C to give the thiocyanate **7** in 64% yield. This S-adamantylation is in contrast to the reported reaction of potassium thiocyanate with 1-adamantyl bromide (**9**), which produced the isomeric isothiocyanate **8**.[6] When the reaction was conducted at 0 °C, a mixture of **7** and **8** was obtained in a ratio of 6:4. As the control experiment exhibited, **7** isomerized catalytically to **8** at 0 °C, the formation of the kinetic product (**7**) may be explained by considering the preferential attack of the adamantyl cation on the γ-heteroatom (allylsilane type reaction[7]) or alternatively on the α-heteroatom in the equilibrated form, $X{\equiv}YZSiMe_3$ (ipso substitution). On the other hand the reactions of **10** and **11** proceeded more slowly and yields were low: **12** in 20% yield as its *tert*-butylurea derivative (**13**), at 0 °C for 5 h, and **14** in 19% yield, at room temperature for 12 h, respectively. In both cases about half of the starting **1** was recovered, and prolonged reaction times never improved the yield. Trimethylsilyl azide (**15**) as a system where X, Y, and Z are all nitrogens was treated with **1** at 0 °C for 2 min to give the azide **16** in 73% yield. A prolonged reaction time caused a decrease of the yield because of product decomposition. A similar type of substitution reaction for thioketals has recently been demonstrated.[8] Nevertheless, the other analogues, ketenimine (**17**) and diazomethane (**18**),[9] did not react with **1** under the above conditions.

The structural proof is based on the spectral and chromatographic comparisons with the authentic samples for the known compounds **3**, **4**, **7**, **13**, and **16** and on the independent synthesis for **14**, which was previously unknown.

In summary, these results indicate that successful substitution at the adamantane brideghead is achieved with trimethylsilyl pseudohalides having sufficient nucleophilicity, and this constitutes a simple and mild method for preparing some 1-adamantyl pseudohalides; for example, preparation of **7** otherwise requires several steps from **9**.[10]

Experimental Section

The organosilanes employed were purchased from Petrarch Systems Inc. or prepared according to the reported procedures for **5**, **11**, **17**, and **18**. Chromatographic separation in this experiment was performed on silica gel (Mallinckrodt, 100 mesh; elution with the solvent noted). Physical and spectral data were obtained as described in our previous paper.[2]

1-Adamantyl Isocyanide (3). To a solution of **1** (170 mg, 1 mmol) and $TiCl_4$ (190 mg, 1 mmol) in methylene chloride (4 mL) was added **2** (120 mg, 1.2 mmol) in methylene chloride (2 mL) at 0 °C, and the mixture was stirred for 150 min at this temperature. Evaporation of the solvent by using an aspirator gave a yellow residue to which pyridine (0.5 mL) in ether (5 mL) was added. After agitation, the solvent was again evaporated, and the product was extracted with hexane. Concentration of the solution gave **3** as a white crystalline solid (125 mg, 78%), identical with the compound obtained by our earlier method.[11] When the reaction mixture was poured into ice–water containing Na_2CO_3, followed by extraction with methylene chloride, **4** was isolated as a major product (110 mg, 61%) by chromatography (elution with chloroform) in addition to **3** (20 mg, 12%).

1-Adamantyl Thiocyanate (7). To a solution of **1** (170 mg, 1 mmol) and $TiCl_4$ (1900 mg, 1 mmol) in methylene chloride (4 mL) was added **6** (160 mg, 1.2 mmol) in methylene chloride (2 mL) dropwise at −78 °C, and after being stirred for 15 min, the reaction mixture was poured into ice–water containing Na_2CO_3. After an insoluble solid was filtered off through Celite, the organic layer was separated and dried over Na_2SO_4. Evaporation of the solvent left a solid, which was recrystallized from hexane to give **7** as a white crystalline solid: 125 mg (64%); mp 66–68 °C (lit.[10] mp 66–67 °C). When **1** was treated as above at 0 °C for 3 h, the same workup and chromatographic separation (elution with hexane) gave **8** (35 mg, 23%) as the first fraction and **7** (65 mg, 34%) as the second fraction. Isomerization of **7** to **8** was qualitatively accomplished by TLC (R_f 0.51 for **8** and 0.11 for **7**; Wakogel B-5, hexane) and IR (2100 cm^{-1} for NCS and 2155 cm^{-1} for SCN; the former band is stronger and broader) when **7** was mixed with an equal amount of $TiCl_4$ in methylene chloride at 0 °C for 3 h.

***N*-(1-Adamantyl)-*N*′-*tert*-butylurea (13).** To a solution of **1** (170 mg, 1 mmol) and $TiCl_4$ (190 mg, 1 mmol) in methylene chloride (4 mL) was added **10** (140 mg, 1.2 mmol) in methylene chloride (2 mL), and the mixture was stirred at room temperature for 5 h. The reaction mixture was poured onto ice, and the organic layer was separated quickly and dried over Na_2SO_4. Evaporation of the solvent left a solid which had an IR band at 2250 cm^{-1}. This solid was dissolved in dry ether (10 mL) and treated with *tert*-butylamine (80 mg, 1.1 mmol) overnight. After removal of the solvent and excess amine, the resulting solid was recrystallized from ether to give **13**: 50 mg (20%); mp 254–259 °C (lit.[12] mp 240–260 °C). From the mother liquor was recovered 85 mg of **1**.

***N*-(1-Adamantyl)-*N*′-methylcyanamide (14).** A mixture of **1** (170 mg, 1 mmol), $TiCl_4$ (190 mg, 1 mmol), and **11** (150 mg, 1 mmol) was stirred at room temperature for 12 h. A workup as for **3** and chromatography (elution with chloroform) gave recovered **1** (80 mg) as well as **14**: 35 mg (19%); mp 51–53 °C. The structure was confirmed by the following independent synthesis. *N*-Methyladamantanamine (300 mg, 1.8 mmol) in ether (3 mL) was added to a solution of cyanogen bromide (95 mg, 0.9 mmol) in ether (5 mL) at room temperature, and the mixture was stirred for 20 min. Removal of precipitates by filtration and subsequent chromatography (elution with chloroform) gave a white crystalline solid, **14**: 80 mg (46%); IR (KBr) 2200 cm^{-1}; NMR ($CDCl_3$) 2.78 (s, 3 H, CH_3), 1.53–2.30 (m, 15 H, ring proton). Anal. Calcd for $C_{12}H_{18}N_2$: C, 75.74; H, 9.54; N, 14.72. Found: C, 75.58; H, 9.42; N, 14.72.

1-Adamantyl Azide (16). To a solution of **1** (170 mg, 1 mmol) and $TiCl_4$ (190 mg, 1 mmol) in methylene chloride (4 mL) was added an ice-cooled solution of **15** (140 mg, 1.2 mmol) in methylene chloride (2 mL) at once at 0 °C. After being stirred for 2 min, the reaction mixture was poured into ice–water containing Na_2CO_3, and the product was extracted with ether and dried over Na_2SO_4. The solvent was evaporated to leave a solid, which was chromatographed through a short column (hexane elution) to give white crystalline solid **16** (130 mg, 73%), identical with the compound obtained by our earlier method.[13]

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[4] R. L. Danheiser and D. J. Carini, *J. Org. Chem.*, **45**, 3925 (1980).

[5] This reaction was conducted in the presence of Lewis acids such as $TiCl_4$, $AlCl_3$, $ZnCl_2$, and $SnCl_4$ in the temperature range −78 to +20 °C, but none of the expected 1-propargyladamantane was isolated though **1** was actually consumed. A referee suggested that the reactivity differences of **5** with **6**, for instance, might be explained in terms of the orbital differences between them: the lone pair on nitrogen may participate directly in the reaction of the sulfur atom of **6** with an electrophile. The resulting charge on nitrogen in the transition state may be directly stabilized by the adjacent silyl moiety. This is clearly somewhat different than the stabilization available to **5** as mentioned in footnote 4 of ref 4.

[6] H. Stetter and C. Wulff, *Chem. Ber.*, **95**, 2302 (1962).

[7] Reference 1b, p 631.

[8] B. M. Trost, M. Vaultier, and M. L. Santiago, *J. Am. Chem. Soc.*, **102**, 7929 (1980). For acetal, see H. Paulsen, Z. Gyoergydeak, and M. Friedman, *Chem. Ber.*, **107**, 1568 (1974).

[9] Shioiri reported BF_3-catalyzed reaction of **18** with ketones: N. Hashimoto, T. Aoyama, and T. Shioiri, *Tetrahedron Lett.*, **21**, 4619 (1980).

[10] A. Booerma-Markerink, J. C. Jagt, H. Meyer, J. Wilderman, and A. M. van Leusen, *Synth. Commun.*, **5**, 147 (1975).

[11] T. Sasaki, S. Eguchi, and T. Katada, *J. Org. Chem.*, **39**, 1239 (1974).

[12] W. Walter and G. Randou, *Justus Liebigs Ann. Chem.*, **722**, 52 (1969).

[13] T. Sasaki, S. Eguchi, T. Katada, and O. Hiroaki, *J. Org. Chem.*, **42**, 3741 (1977).

Registry No. **1**, 935-56-8; **2**, 7677-24-9; **3**, 22110-53-8; **4**, 3405-48-9; **6**, 2290-65-5; **7**, 39825-84-8; **8**, 4411-26-1; **10**, 1118-02-1; **11**, 62139-68-8; **13**, 25348-10-1; **14**, 79664-52-1; **15**, 4648-54-8; **16**, 24886-73-5; *N*-methylodamantanamine, 3717-38-2; cyanogen bromide, 506-68-3.

Communications

New Sigmatropic Sequences Based on the [2,3] Wittig Rearrangement of Bis-Allylic Ethers. Regiocontrolled Joining Reactions of Two or Three Allylic Moieties Leading to Unsaturated Carbonyl Compounds

Summary: Three new sigmatropic sequences based on the [2,3] Wittig rearrangement of bis-allylic ethers are described which provide unique, regiocontrolled methods for the synthesis of a variety of unsaturated carbonyl compounds possessing interesting molecular frameworks.

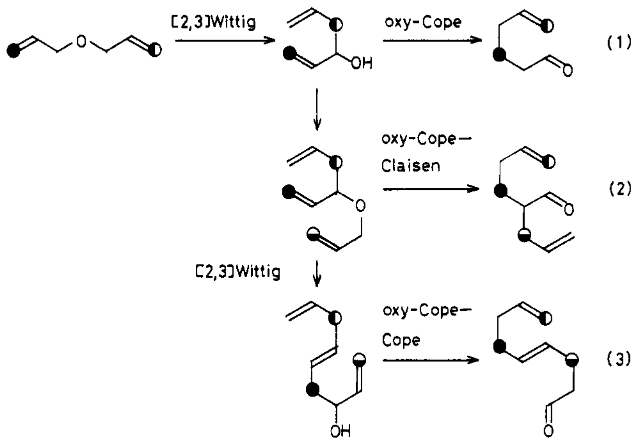
Sir: Recently we have found that the [2,3] Wittig rearrangement of unsymmetrical bis-allylic ethers **1** is exceedingly useful for regio- and stereoselective preparations of 1,5-dien-3-ols **2**.[1] To expand further the synthetic potential of the rearrangement, our efforts have now been directed toward development of new sigmatropic sequences triggered by the [2,3] Wittig variant. While a number of tanden [3,3]-[3,3] sigmatropic sequences such as the Claisen-Cope[2] and the Cope-Claisen rearrangements[3] have currently been developed and have found substantial utility in the methodology for organic synthesis, only a few [2,3] sigmatropic rearrangements have been exploited in tandem or in series for effecting carbon-carbon bond formations.[4]

Herein we describe three new sigmatropic sequences based on the [2,3] Wittig rearrangement which provide unique, facile methods for the synthesis of various kinds of unsaturated carbonyl compounds possessing interesting molecular frameworks. The overall bond organizations are shown in Scheme I. Significantly, the net effect of these sequences allows two or three allylic moieties initially linked by a readily formed ether bond(s) to be recombined by a newly created carbon-carbon bond(s) in a regiospecific fashion.

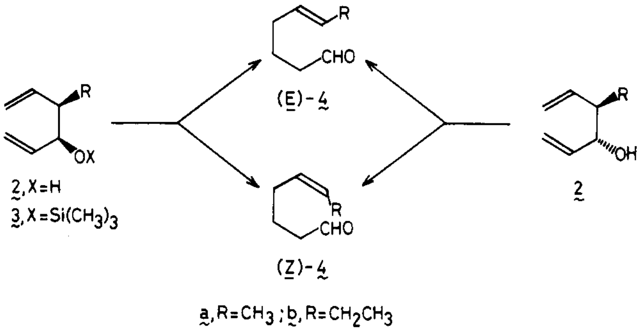
First, the accessibility of diastereomerically defined 1,5-dien-3-ols by virtue of the [2,3] Wittig rearrangement[1] has prompted us to investigate the unresolved stereochemistry of the *acyclic* oxy-Cope rearrangement.[5] Thus we carried out the rearrangement of both erythro- and threo-rich mixtures[6] of **2a** and **2b** (Scheme II) by applying the four current procedures: the anionic oxy-Cope[7] and the siloxy-Cope[8] modifications and thermolysis in *N*-methylpyrrolidone (NMP)[9] and in refluxing decane.

The experimental results thus obtained[10] reveal stereochemical features of the acyclic oxy-Cope rearrangement

Scheme I



Scheme II



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[1] Nakai, T.; Mikami, K.; Taya, S.; Fujita, Y. *J. Am. Chem. Soc.*, in press.

[2] Thomas, A. F. *J. Am. Chem. Soc.* **1969**, *91*, 3281. Thomas, A. F.; Ohloff, G. *Helv. Chim. Acta* **1970**, *53*, 1145. Frâter, G. *Ibid.* **1975**, *58*, 442. Frâter, G. *Chimia* **1975**, *29*, 528. Wilson, S. R.; Myers, R. S. *J. Org. Chem.* **1975**, *40*, 3309. Bowden, B.; Cookson, R. C.; Davis, H. A. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2634. Cookson, R. C.; Rogers, N. R. *Ibid.* **1973**, 2741. Fujita, Y.; Onishi, T.; Nishida, T. *Synthesis* **1978**, 523. Thio-Claisen-Cope: Tamaru, Y.; Harada, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1980**, *102*, 2392. Claisen-aza-Cope: Holmes, B. N.; Leonard, N. J. *J. Org. Chem.* **1976**, *41*, 568.

[3] Ziegler, F. E.; Piwinski, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 1611; **1980**, *102*, 880. Raucher, S.; Burks, J. E., Jr.; Hwang, K.-J.; Svedberg, D. P. *Ibid.* **1981**, *103*, 1853.

[4] (a) *S*-Ylide [2,3]-Cope: Labuschange, A. J. H.; Meyer, C. J.; Spies, H. S. C.; Schneider, D. F. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2129 and references therein. (b) *N*-Ylide [2,3]-Cope: Jemison, R. W.; Laird, T.; Ollis, W. D.; Sutherland, I. O. *Ibid.* **1980**, 1436; Büchi, G.; Wüest, H. *J. Am. Chem. Soc.* **1974**, *96*, 7573. (c) *N*-Oxide [2,3]-Claisen: Thyagarajan, B. S.; Hillard, J. B.; Reddy, K. V.; Majumdar, K. C. *Tetrahedron Lett.* **1974**, 1999. (d) *S*-Oxide [2,3]-Claisen: Majumdar, K. C.; Thyagarajan, B. S. *Chem. Commun.* **1972**, 83. (e) [2,3] Wittig-oxy-Cope: Garbers, C. F.; Scott, F. *Tetrahedron Lett.* **1976**, 507.

[5] Recent reviews include: Marvell, E. N.; Whalley, W. In "Chemistry of the Hydroxy Group"; Patai, S., Ed.; Interscience: New York, 1971; Vol. 2, Chapter 13. Bennett, G. B. *Synthesis* **1977**, 589.

[6] Two diastereomeric mixtures of **2a** (88% erythro and 79% threo) and a mixture of **2b** (80% threo) were used as substrates.

[7] The potassium alkoxide (prepared with KH) was heated in DME at 85 °C. Cf.: Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765. Evans, D. A.; Nelson, J. V. *Ibid.* **1980**, *102*, 774.

[8] The silyl ether **3** was heated in refluxing decane. Cf.: Thies, R. W. *Chem. Commun.* **1971**, 237. Thies, R. W.; Wills, M. T.; Chin, A. W.; A. W.; Schick, L. E.; Walton, E. S. *J. Am. Chem. Soc.* **1973**, *95*, 5281.

[9] Alcohol **2** was heated in NMP at 202 °C. Cf.: Fujita, Y.; Onishi, T.; Nishida, T. *Synthesis* **1978**, 612. Fujita, Y.; Amiya, S.; Onishi, T.; Nishida, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1983.

[10] For details of the experimental results, see the supplementary material.

0022-3263/81/1946-5447$01.25/0