and concentrated by rotary evaporation to give 0.831 g (86%) of **4**, mp 127–9 °C; TLC (1:1 ether/hexane) R_f = 0.4; IR ($CHCl_3$) 3360, 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.20 (m, 2 H), 4.26 (broad m, 1 H), 2.3–3.0 (complex, 5 H), 1.0–2.0 (complex, 6 H).

3-Phenyltricyclo[5.2.1.0^{2,6}]dec-8-en-*endo*-3-ol (6). To a solution of 0.831 g (5.54 mmol) of **4** in 50 mL of CH_2Cl_2 with stirring was added 1.795 g of PCC (8.33 mmol), 15 drops of HOAc, and 3.6 g of Celite. The reaction slurry was stirred at rt under N_2 for 22 h, then diluted with ether, and passed through a column of neutral alumina (10 × 2.2 cm) with exhaustive ether washing. The combined ether solution (200 mL) was concentrated to a small volume and used directly in the next step.

To a stirred solution of the ketone **5** in 40 mL of dry ether at 0 °C was slowly added via syringe 2.7 mL of 3.0 M PhMgBr (8.1 mmol) in ether. The reaction mixture was stirred at 0 °C for 1 h ($CaCl_2$ drying tube) then for an additional 1 h at rt. Again at 0 °C, 10 mL of saturated Na_2SO_4 was slowly added with continued stirring. The mixture was gravity filtered with ether washing, dried, filtered, and evaporated to yield 0.892 g of a pale yellow oil. This crude product was purified by chromatography on a column of silica gel (2.8 × 24 cm) prepared in and eluted with 10% acetone in hexane, collecting 10-mL fractions. Fraction numbers 7–13 were evaporated to give crystalline **6**, mp 66–71 °C, 0.517 g (45%): IR (film) 3430, 1635, 1595, 1575, 1490, 1440 cm^{-1}; EIMS (*m/e*, base peak) 226 (M^+) (4.6), 208 (4.6), 165 (5.5), 142 (100), 115 (20.2), 105 (12.8), 91 (12.8), 77 (24.8), 66 (40); ^1H NMR ($CDCl_3$) (in part) δ 7.4 (complex, 5 H), 6.33 (m, 2 H).

PCC Oxidation of 6. A solution of a 0.208 g sample of **6** (0.923 mmol) in 20 mL CH_2Cl_2 was stirred at rt as 0.571 g of PCC (2.65 mmol), five drops of HOAc, and 1.8 g of Celite were added in succession. This suspension was stirred and refluxed for 4 h under N_2 then stirred at rt overnight. The reaction was worked up as described above to give the β keto ether **7**, 0.155 g (70%). The solid material was recrystallized from ether/petroleum ether, mp 95.5–97.5 °C: IR (film) 1760 cm^{-1} (no OH); EIMS (*m/e* base peak): 240 (M^+) (56), 212 (53), 183 (21), 155 (24), 143 (100), 128 (20), 115 (25), 105 (7.7), 91 (20), 77 (25); ^1H NMR ($CDCl_3$) δ 7.5–7.20 (m, 5 H, ArH), 4.10 (d, *J* = 5.4 Hz, 1 H, H-9), 3.2–2.90 (m, 3 H), 2.55 (d, *J* = 3.8 Hz, 1 H), 2.30 (m, 3 H), 2.10 (m, 1 H), 2.0–1.80 (q, *J* = 12.8 Hz 2 H). Anal. Calcd for $C_{16}H_{16}O_2$: C, 80.00; H. 6.67. Found: C, 79.88; H.6.76.

4- and 5-(2-Oxo-2-phenylethyl)-2-cyclopentenones (10 and 12).[4] To a solution of 0.304 g (1.63 mmol) of **8** in 20 mL of CH_2Cl_2 were added 1.04 g (4.82 mmol) of PCC and 2.0 g of Celite. This slurry was charged further with six drops of acetic acid, and the resulting mixture was stirred and refluxed under N_2 for 4 h then stirred overnight at rt. The reaction slurry was diluted with ether and passed through a column of neutral alumina (10.3 × 2.2 cm) with exhaustive ether washing. The total ether filtrate was evaporated to give the crystalline product (0.201 g, 63%), one spot on TLC (R_f 0.7, 5% acetone in ether), mp 84–6 °C, positive 2,4-DNP test: IR ($CHCl_3$) 1710, 1685, 1600, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.96 (m, 2 H, ortho H), 7.74 (dd, *J* = 2.5, 5.6 Hz, 1 H, H-3), 7.66–7.40 (complex, 3 H, ArH), 6.29 (m, 0.37 H, H-2, isomer **10**), 6.22 (dd, *J* = 2.0, 5.6 Hz, 0.62 H, H-2, isomer **12**), 3.60 (1 H, methine); the spectrum between δ 3.2–2.0 was very complex due to the presence of **12**/**10**, but consistent with the structural assignments; UV λ_{max} 239 (COPh), 220 (sh) nm; EIMS (*m/e*, base peak): 200 (42) (M^+), 105 (100), 95 (24), 77 (50). Anal. Calcd for $C_{13}H_{12}O_2 \cdot 0.2\ H_2O$; C, 76.62; H, 6.09. Found: C, 76.64; H, 5.92.

The ^{13}C NMR spectrum shows more than 13 signals due to the presence of the **12** (major)/**10** (minor) isomeric mixture: δ 209.9, 198.4 (C=O), 168.1, 164.5 (H-3), 137.2, 135.2, 134.4, 134.2, 129.6, 129.5, 128.8 (H-2, aromatic) 44.0, 42.2, 41.9, 41.6, 37.8, 37.3 (CH_2, CH). An attached proton test (APT) was performed which is consistent with the structural assignments. Particularly, in the δ 44.0–37.0 region, the six signals were revealed as 2 × CH_2 and 1 × CH, each with a corresponding minor signal associated with it, representing the accompanying isomer. All other carbon signals also behaved as expected.

4- and 5-(2-Oxo-2-hexyl)-2-cyclopentenone (11 and 13). The identical procedure [4] was followed for **9** to give the product as a clear oil (0.218 g, 73%), one spot on TLC (R_f 0.75, 5% acetone in ether)(trace starting material): IR (neat) 1710, 1590 cm^{-1}; UV λ_{max} 219 nm(cyclopentenone); EIMS (*m/e*, base peak): 180 (96)(M^+), 138 (59), 123 (71), 95 (100), 85 (73), 81 (23), 67 (33), 57 (51); ^1H NMR ($CDCl_3$) δ 7.74 (m, 0.37 H) 7.67 (dd, *J* = 2.4, 5.6 Hz, 0.62 H, H-3), 6.23 (m, 0.37 H), 6.17 (dd, *J* = 2.2, 5.8 Hz, 0.62 H, H-2), 3.40 (m, 1 H), 3.00 (m, 1 H), 2.50 (complex, 3 H), 1.92 (dd, *J* = 1.9 Hz, 1 H), 1.58 (complex, 2 H), 1.32 (complex, 2 H), 0.90 (2 t, 3 H, CH_2CH_3).

The above procedure run on tertiary alcohol **9** but without PCC gave 84% recovered starting material. In another control experiment, this procedure run on **18**[10] gave 82% recovered starting material.

***endo*-2-Phenylbicyclo[2.2.1]hept-5-en-*exo*-2-ol(14) was** synthesized according to the method of Brown and Peters[14] and reacted with PCC as described above. The product (75% yield) was a mixture of **12** (major) and **10** (minor).

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Novel Preparation of Highly Electrophilic Species for Benzenetellurenylation or Benzenesulfenylation by Nitrobenzenesulfonyl Peroxide in Combination with Ditelluride or Disulfide. Application to Intramolecular Ring Closures

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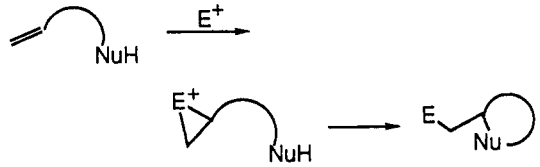
Taking advantage of the strong electrophilicity of nitrobenzenesulfonyl peroxide (NBSP), various synthetic reactions have been developed.[1-4] Though NBSP is known to attack the π-bond of simple olefins electrophilicially,[1,2] intramolecular cyclization did not occur with 4-penten-1-ol using *p*-nitrobenzenesulfonyl peroxide (*p*-NBSP) or *m*-nitrobenzenesulfonyl peroxide (*m*-NBSP) as an electrophilic promoter for the cyclization. However, we found that the electrophilic intramolecular ring closures of unsaturated alcohols and acids were effected by NBSP in combination with diphenyl diselenide in excellent yields.[5] Ring closures proceeding by intramolecular capture of the cationic intermediate initiated by suitable electrophilic reagents (represented by eq 1) are useful methods for the



(1)

synthesis of natural products.[6] In the course of our studies

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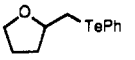
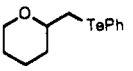
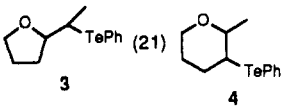
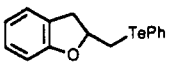
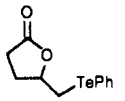
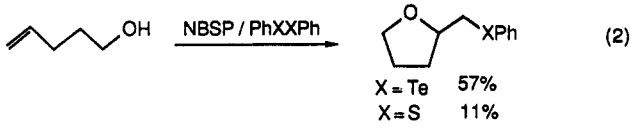
Table I. Electrophilic Intramolecular Ring Closures of Unsaturated Hydroxy and Carboxyl Compounds Using the Combination of *p*-NBSP/Diphenyl Ditelluride

run	olefin (mmol)	solvent	products	(yield, %)[a]
1	4-penten-1-ol (1.1)	CH_3CN		(57)
2	4-penten-1-ol (3.0)	CH_3CN		(74)
3	4-penten-1-ol (1.1)	CH_3NO_2	1	(62)
4	4-penten-1-ol (3.0)	CH_3NO_2		(75)
5	5-hexen-1-ol (1.1)	CH_3CN		(63)
6	5-hexen-1-ol (3.0)	CH_3CN		(71)
7	5-hexen-1-ol (1.1)	CH_3NO_2		(55)
8	5-hexen-1-ol (3.3)	CH_3NO_2	2	(66)
9	4-hexen-1-ol (1.1)	CH_3CN		(29)
			3 (21) 4	
10	2-allylphenol (1.1)	CH_3CN		(81)
			5	
11	4-pentenoic acid (3.0)	CH_3CN		(52)
			6	

[a] Yields were determined by GC based on benzenetellurenyl sulfonate evaluated from NBSP (0.5 mmol)/diphenyl ditelluride (0.5 mmol).

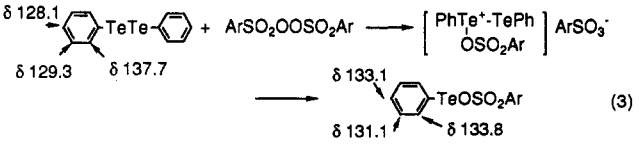
we revealed the electrophilic intramolecular ring closure using the combination of NBSP and diphenyl ditelluride or diphenyl disulfide.

When 4-penten-1-ol was added to a solution of *p*-NBSP with diphenyl ditelluride or diphenyl disulfide at 0 °C, intramolecular phenylsulfo- or phenyltelluroetherification occurred, respectively.



(2)

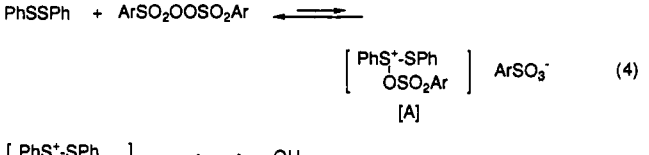
These results indicate the formation of a reactive electrophilic species by the reactions of NBSP with disulfide or ditelluride. In our previous paper, we proposed the formation of benzeneselenenyl nitrobenzenesulfonate ($PhSeOSO_2Ar$) by the reaction of diphenyl diselenide with NBSP.[4,5] So the formation of benzenetellurenyl nitrobenzenesulfonate ($PhTeOSO_2$ Ar)[7] and benzenesulfenyl nitrobenzenesulfonate ($PhSOSO_2Ar$)[8] are presumed. To verify the formation of the first of these species diphenyl ditelluride was treated with *p*-NBSP while the ^{13}C NMR spectrum was monitored. The signals of diphenylditelluride disappeared completely and those to be assignable to benzenetellurenyl *p*-nitrobenzenesulfonate immediately appeared (eq 3). The assignment of these signals was



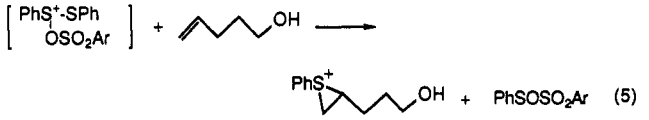
(3)

confirmed by a comparison with the chemical shifts observed in the reactions of diphenyl ditelluride with *m*-NBSP (δ 133.9 (C-2,6), 130.5 (C-3,5), and 133.1 (C-4)) and di(4-methoxyphenyl) ditelluride with *p*-NBSP (δ 135.9 (C-2,6), 115.8 (C-3,5), and 163.2 (C-4)). Thus, in the reaction of diphenyl ditelluride with NBSP, benzenetellurenyl nitrobenzenesulfonate is formed and is active enough to react with the carbon–carbon double bond in 4-penten-1-ol to afford a cyclic ether as was in the case of diphenyl diselenide with NBSP. The electrophilic species has the weakly nucleophilic nitrobenzenesulfonate as a counter anion. Reagents composed of reactive electrophiles and weak nucleophiles are expected to have the particular advantage of being applicable for cyclofunctionalization.

Similarly, NBSP was added to a solution of diphenyl disulfide, and the ^{13}C NMR was monitored. In this case, however, diphenyl disulfide remained unchanged. Probably, the disulfide is in equilibrium with the sulfonium ion A as shown in eq 4, and the equilibrium lies far to the disulfide. The sulfonium ion may act as an active electrophile and react with the carbon–carbon double bond of 4-penten-1-ol (eq 5).[9]



(4)



(5)

Some examples of electrophilic intramolecular ring closure of unsaturated hydroxy and carboxylic compounds effected by the combination of NBSP/ditelluride are shown in Table I.

Phenyltelluroetherification of 4-penten-1-ol and 5-hexen-1-ol proceeded in moderate yields and regiospecifically to afford 2-[(phenyltelluro)methyl]tetrahydrofuran (1) and 2-[(phenyltelluro)methyl]tetrahydropyran (2), respectively, and no signals for the regioisomers were detected (Table I, runs 1–8). In the phenylselenoetherification of 4-pen-

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(7) It has been reported that the oxidative cleavage of diphenyl ditelluride by benzoyl peroxide affords benzenetellurenyl benzoate, which is converted to benzenetellurenyl *p*-toluenesulfonate by the reaction with *p*-toluenesulfonic acid: Harabayashi, Y.; Ishihara, H.; Manami, H.; Mazuda, S.; Morita, Y.; Fujiwara, T. *Nippon Kagakukai Shi* **1987**, 1479.

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ten-1-ol under similar conditions, both 2-[(phenylseleno)methyl]tetrahydrofuran and 2-(phenylseleno)-tetrahydropyran were formed.[5] In the present case phenyltelluro group seems to be added in the less hindered terminal carbon of 4-penten-1-ol and 5-hexen-1-ol. In internal olefin, 4-hexen-1-ol, the corresponding tetrahydrofuran **3**, and pyran **4** were obtained in 21% and 29% yields, respectively (Table I, run 9). The cycloetherification in *o*-allylphenol occurred in a good yield (Table I, run 10). Phenyltellurolactonizations proceeded only with 4-pentenoic acid in 51% yield to afford **6** (Table I, run 11), but not in 5-hexenoic and 6-heptenoic acids. Also, the intermolecular acetoxytellurenylation of 1-octene was unsuccessful. The reactions of benzenetellurenyl sulfonate with olefins may be reversible with the equilibrium lying to the starting materials which makes reactions with weak nucleophiles difficult.

In the sulfo analogue, lactonizations in 4-pentenoic and 5-hexenoic acids proceeded in 52% and 49% yields to give 5-[(phenylthio)methyl]dihydrofuran-2-one (**7**) and 6-[(phenylthio)methyl]tetrahydropyran-7-one (**8**), respectively (eq 6), but cycloetherification in 5-hexen-1-ol did not

(6)

7 : n = 2 (52%)
8 : n = 3 (49%)

occur. Electrophilic benzenesulfenyl species prepared from NBSP/disulfide may react with the hydroxy group to give alkenyl sulfenate in preference to reaction at the carbon–carbon double bond.[10]

Although cyclofunctionalization using tellurium species have been reported,[11,12] effective electrophilic tellurium reagents toward olefins have not yet been well established. In the present study, we found a novel method for electrophilic benzenetellurenylation using the combination of diphenyl ditelluride and NBSP. The reactivity of electrophilic telluro species thus formed to olefins is lower than the seleno analogue; however, higher chemo- and regioselectivities were observed. We also found that electrophilic benzenesulfenyl species could be readily prepared from diphenyl disulfide by treatment with NBSP and can be used for phenylsulfolactonizations of unsaturated carboxylic acids.

Experimental Section

^{1}H NMR spectra were taken with a JEOL JNM PMX60SI (60-MHz) spectrometer. ^{13}C NMR spectra were taken with a JEOL FX90Q FTNMR spectrometer. IR spectra were recorded on a Hitachi 260-10 spectrometer. Gas chromatography was performed by a Hitachi 263-30 gas chromatography with SE-30 (2-m) stainless-steel column. Gel permeation chromatography was performed by means of a JAI Model LC-08 liquid chromatography equipped with two JAIGEL-1H columns (20 mm × 600 mm) with chloroform as eluent. Mass spectra were obtained with a JEOL JMS DX-300 spectrometer by an electron-impact (EI) ionization technique at 70 eV.

Materials. Diphenyl disulfide was obtained from Wako Chemical Co. Ltd. and recrystallized from hexane prior to use. Diphenyl ditelluride was synthesized by the reaction of phenyllithium with tellurium powder according to the literature (mp 62–64 °C (lit.[13] 64–65 °C)). Di(4-methoxyphenyl) ditelluride was synthesized from *p*-bromoanisole and tellurium powder by the Grignard reaction (mp 55–57 °C (lit.[13] 57–59 °C)). Nitrobenzenesulfonyl peroxides were synthesized from nitrobenzenesulfonyl chloride and 30% hydrogen peroxide according to the literature (*p*-NBSP: mp 124 °C dec (lit.[14] 127 °C dec; *m*-NBSP: mp 107 °C dec (lit.[14] 112 °C dec)). Unsaturated alcohols and carboxylic acids were purified by distillation prior to use. Acetonitrile was refluxed over calcium hydride and distilled prior to use. Nitromethane was dried over phosphorus pentaoxide and distilled prior to use.

General Procedures for the Reactions of Unsaturated Alcohol and Carboxylic Acid with Diphenyl Ditelluride. To a solution of diphenyl ditelluride (0.5 mmol) in freshly distilled acetonitrile (20 mL) was added solid NBSP (0.5 mmol) in small portions at 0 °C, and the solution was allowed to stir for 10 min. 4-Penten-1-ol or 5-hexen-1-ol (1.1 mmol) was added, and the resulting solution was allowed to react for 2 h at 0 °C. The reaction mixture was then poured into water (10 mL) and extracted with ether (10 mL × 3). The organic layer was washed with an aqueous solution of 5% $NaHCO_3$ (10 mL) and saturated NaCl (10 mL) and then dried over anhydrous $MgSO_4$. The solvent was evaporated to give a yellow oil, which was subjected to column chromatography on silica gel (Wakogel C-200; eluted by hexane/chloroform (1:2)). The separated 2-[(phenyltelluro)-methyl]tetrahydrofuran (**1**)[12] and 2-[(phenyltelluro)methyl]-tetrahydropyran (**2**)[12] were further purified by GPC. Similarly, 2-[(phenyltelluro)methyl]-2,3-dihydrobenzofuran (**5**)[12] was obtained from 2-allylphenol.

In 4-hexen-1-ol, the regioisomers 2-[(1-(phenyltelluro)ethyl]-tetrahydrofuran (**3**) and 2-methyl-3-(phenyltelluro)tetrahydropyran (**4**) were obtained, and they could be separated from each other by GPC. In order to identify the structure, they were reduced with triphenyltin hydride 2-ethyltetrahydrofuran and 2-methyltetrahydropyran, which ^{1}H and ^{13}C NMR and retention time of GC were compared with those of authentic samples.

2-[1-(Phenyltelluro)ethyl]tetrahydrofuran (3): pale yellow oil; IR (neat, cm^{-1}) 3060, 2970, 2860, 1570, 1470, 1430, 1375, 1075, 1050, 1020, 920, 750, 730, and 690; ^{1}H NMR ($CDCl_3$) δ 1.33–2.14 (m, 4 H), 1.63 (d, J = 3.6 Hz, 3 H), 3.29–4.08 (m, 4 H), 7.00–7.32 (m, 3 H), and 7.58–7.89 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.45, 26.27, 29.80, 30.72, 68.58, 84.35, 111.87, 127.74, 128.99, and 140.15; MS, m/z 306 (M$^+$, ^{130}Te). Anal. Calcd for $C_{12}H_{16}OTe$: C, 47.42; H, 5.31. Found: C, 46.94; H, 4.97.

2-Methyl-3-(phenyltelluro)tetrahydropyran (4): pale yellow oil; IR (neat, cm^{-1}) 3050, 2920, 2830, 1570, 1470, 1425, 1375, 1310, 1210, 1080, 1060, 1030, 860, 730, and 685; ^{1}H NMR ($CDCl_3$) δ 1.20–2.45 (m, 4 H), 1.29 (d, J = 3.3 Hz, 3 H), 3.05–3.72 (m, 2 H), 3.76–4.15 (m, 1 H), 7.01–7.31 (m, 3 H) and 7.60–7.88 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.11, 24.11, 33.15, 40.74, 68.58, 77.14, 112.03, 127.64, 129.10, and 139.34; MS m/z 306 (M$^+$, ^{130}Te). Anal. Calcd for $C_{12}H_{16}OTe$: C, 47.42; H, 5.31. Found: C, 47.72; H, 5.58.

4-Pentenoic, 5-hexenoic, or 6-heptenoic acid (1.1 mmol) was added to the resulting solution of diphenyl ditelluride (0.5 mmol) and NBSP (0.5 mmol) and allowed to stir for 2 h at 0 °C, and the reaction mixture was similarly treated. In the reaction of 4-pentenoic acid, 5-[(pehnyltelluro)methyl]dihydrofuran-2-one (**6**) and diphenyl ditelluride were isolated by column chromatography (Wakogel C-200, eluent: hexane/chloroform (3:1)) and GPC. The reactions of 5-hexenoic and 6-heptenoic acids with diphenyl ditelluride were also investigated; however, corresponding lactones were not obtained and diphenyl ditelluride was recovered.

5-[(Phenyltelluro)methyl]dihydrofuran-2-one (6): pale yellow oil; IR (neat, cm^{-1}) 3070, 2980, 2930, 1770, 1570, 1470, 1430, 1160, 1020, 970, 910, 730, and 690; ^{1}H NMR ($CDCl_3$) δ 1.50–2.77 (m, 4 H), 2.91–3.39 (m, 2 H), 4.41–4.87 (m, 1 H), 7.00–7.28 (m, 3 H), and 7.53–7.82 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.27, 29.15, 29.25, 80.99, 110.68, 128.29, 129.48, 138.96, and 176.39; MS m/z 306 (M$^+$, ^{130}Te); exact MS m/z 305.9851, calcd for $C_{11}H_{12}O_2{}^{130}Te$ 305.9899, 303.9867, calcd for $C_{11}H_{12}O_2{}^{128}Te$ 303.9882.

General Procedures for the Reactions of Unsaturated Alcohol and Carboxylic Acid with Diphenyl Disulfide and NBSP. Diphenyl disulfide (1.0 mmol) was treated with NBSP

(10) As a product alkenyl sulfinate was obtained. Probably, the sulfenate was further oxidized to sulfinate.

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(0.5 mmol) in freshly distilled acetonitrile at 0 °C, and then 4-penten-1-ol or 5-hexen-1-ol (1.1 mmol) was added. After 2 h the reaction mixture was poured into water and extracted with ether (10 mL × 3). The organic layer was washed with aqueous solutions of 5% $NaHCO_3$ (10 mL) and saturated NaCl (10 mL) and then dried over anhydrous $MgSO_4$. In the reaction of 4-penten-1-ol, 2-[(phenylthio)methyl]tetrahydrofuran[15] was isolated by column chromatography (Wakogel C-200, eluent; chloroform-/hexane (3-1)) and GPC. In the reaction of 5-hexen-1-ol, cycloetherifications did not occur.

In the reactions of unsaturated carboxylic acids, the following two methods were employed. Method A. 4-Pentenoic or 5-hexenoic acid (1.1 mmol) was added to the resulting solution of diphenyl disulfide (1.0 mmol) and NBSP (0.5 mmol) in acetonitrile (20 mL), and the solution was allowed to stir for 2 h at 0 °C. Method B. NBSP (0.5 mmol) was added to the solution of diphenyl disulfide (1.0 mmol) and 4-pentenoic or 5-hexenoic acids (1.1 mmol) in acetonitrile (20 mL). 5-[(Phenylthio)methyl]dihydrofuran-2-one (7)[15] was isolated from the reaction mixture by column chromatography (Wakogel C-200, eluent, hexane/chloroform (3:1)) and GPC. 6-[(Phenylthio)methyl]tetrahydropyran-2-one (8)[16] was also obtained by column chromatography (Wakogel C-200, hexane/chloroform (1:1)) and GPC.

Registry No. 1, 113345-02-1; 2, 122823-50-1; 3, 137542-98-4; 4, 137542-99-5; 5, 122823-57-8; 6, 137543-00-1; 7, 108078-64-4; 8, 108078-67-7; *m*-NBSP, 6209-71-8; *p*-NBSP, 6209-72-9; $PhTeOSO_2C_6H_4$-*p*-NO_2, 137542-97-3; PhTePh, 32294-60-3; $MeOC_6H_4$-*p*-$(Te)_2$-*p*-C_6H_4OMe, 35684-37-8; $Ph(S)_2Ph$, 882-33-7; $HO(CH_2)_3CH{=}CH_2$, 821-09-0; $HO(CH_2)_4CH{=}CH_2$, 821-41-0; $HO(CH_2)_3CH{=}CHCH_3$, 6126-50-7; $H_2C{=}CHCH_2C_6H_4$-*o*-OH, 1745-81-9; $HO(CH_2)_3CH{=}CH_2$, 591-80-0; $HO_2C(CH_2)_3CH{=}CH_2$, 1577-22-6.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of compound 6, for which elemental analyses were not performed (2 pages). Ordering information is given on any current masthead page.

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Stereoselective Alkene Synthesis via (α-Chloroalkyl)dimethylphenylsilanes and α-Dimethylphenylsilyl Ketones

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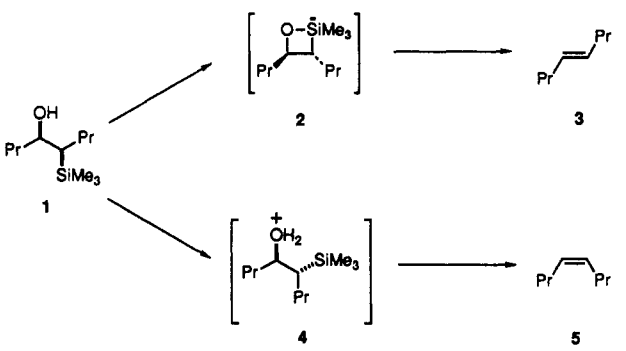
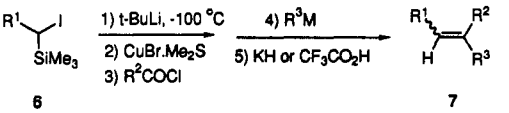
Introduction

The acid or base elimination of a diastereoisomerically pure β-hydroxy silane 1 (the Peterson olefination reaction[1]) provides one of the very best methods for the stereoselective formation of alkenes. Either the *E* or *Z* isomer may be prepared with excellent geometric selectivity from a single precursor (Scheme I). Thus, elimination of the syn diastereoisomer 1 under basic conditions proceeds via a syn manifold and the corresponding pentacoordinate silicate 2. This reaction provides the *E* isomer 3. In contrast, elimination under acid conditions takes place via the anti elimination of the conjugate acid 4 to produce the *Z* isomer 5. There is, however, a major problem that has prevented

Scheme I



Scheme II



the widespread use of the Peterson olefination reaction in synthesis. Unfortunately, there are few experimentally simple methods available for the formation of diastereoisomerically pure β-hydroxy silanes.[2,3] One reliable route is the Cram controlled addition of nucleophiles to α-silyl ketones,[3] but such an approach is complicated by difficulties in the preparation of α-silylalkyllithium species or the corresponding Grignard reagents. In large part, these difficulties would be resolved by the development of a simple method for the preparation and reductive acylation of (α-haloalkyl)silanes. We therefore set out to develop a simple convergent method for the synthesis of α-silyl ketones from aldehydes and acyl chlorides.

Recently, we reported a method for the preparation of both di- and trisubstituted alkenes via the reductive acylation of (α-iodoalkyl)trimethylsilanes 6, the addition of nucleophiles to the resultant α-trimethylsilyl ketones, and elimination.[4] The reductive acylation was carried out by reaction of 6 with *tert*-butyllithium at low temperature (Et_2O, −100 °C), conversion to the organocopper species, and reaction with an acid chloride (Scheme II). However, there are limitations with this methodology. The (α-iodoalkyl)trimethylsilanes 6 were prepared from aldehydes by the addition of hexamethyldisilane in the presence of tetrabutylammonium fluoride, followed by reaction of the resultant (α-hydroxyalkyl)trimethylsilanes with methyltriphenoxyphosphonium iodide. Unfortunately, the intermediate α-hydroxy silanes were formed in only modest yields due to competitive Brook rearrangement.[5] In addition, the conditions for halogen/lithium exchange were inconvenient. Subsequent to this initial publication, we have made significant improvements in this methodology. Herein we report that (α-chloroalkyl)dimethylphenylsilanes and α-dimethylphenylsilyl ketones are useful in-

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