understand biological aspects of the iodides, especially their interactions with a thiol group of a protein.

Experimental Section

General Methods. Melting points were measured on a Yanagimoto melting point apparatus and were uncorrected. IR spectra were recorded on a Shimazu 400 spectrophotometer in KBr pellets. ^{1}H NMR spectra were obtained with JEOL PMX 60 (60 MHz) and FX 100 (100 MHz) spectrometers using tetramethylsilane as an internal standard. Mass spectra were measured on a Hitachi RMU-7 spectrometer. High-performance liquid chromatography (HPLC) was carried out on a Waters ALC/PGC 244 liquid chromatography equipped with a U6K injector and a differential refractometer detector, in which a reversed-phase μ-Bondapak C_{18} column (30 × 0.39 i.d. cm) and MeOH/H_2O were employed as the stationary and mobile phases, respectively.

[16-^{2}H]-16α- and 16β-Bromo-3β-hydroxy-5-androsten-17-ones (1-*16-d* and 2-*16-d*). Treatment of 1[1] with 0.12 equiv of NaOD for 30 min under the controlled conditions[1] gave a mixture of 1-*16-d* and 2-*16-d*, which were purified by HPLC (MeOH/H_2O, 7/3, v/v; flow rate 2.0 mL/min). 1-*16-d*: mp 176–178 °C (lit.[1] mp 177–178 °C); MS, 19% d_0, 81% d_1; t_R 4.5 min. 2-*16-d*: mp 171–174 °C (lit.[1] mp 171–173 °C); MS, 4% d_0, 96% d_1; t_R 5.5 min.

Reaction of 1, 1-*16-d*, 2, and 2-*16-d* with CH_3COSK. CH_3COSK was suspended in 5 mL of dry acetone, and 1, 1-*16-d*, 2, or 2-*16-d* (100 mg, 0.27 mmol) was added to the suspension, and then the mixture was stirred at room temperature for an appropriate time. After the same workup as previously reported, the residue (95–105 mg) was obtained.

16α-(Acetylthio)-3β-hydroxy-5-androsten-17-one (3). The residue obtained above from 2, using 1 equiv of CH_3COSK and a 20-min reaction time, was repeatedly recrystallized from ether to give 3 (78 mg, 79%) as colorless needles: mp 134–135 °C; HPLC t_R 4 min (MeOH/H_2O, 7/3, v/v); IR (KBr) 3350 (OH), 1740 and 1683 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (3 H, s, 18-CH_3), 1.03 (3 H, s, 19-CH_3), 2.38 (3 H, s, 16α-$SCOCH_3$), 3.49 (1 H, br m, 3α-H), 4.34 (1 H, dd, J = 2 and 8 Hz, 16β-H), 5.37 (1 H, m, 6-H). Anal. Calcd for $C_{21}H_{30}O_3S$: C, 69.58; H, 8.34; S, 8.84. Found; C, 69.25; H, 8.50; S, 8.71.

3 could not be obtained in pure form by preparative HPLC using the MeOH/H_2O system as the mobile phase, because of its partial epimerization to the 16β-isomer 4 during evaporation of the solvent.

2-*16-d* was converted similarly to 3-*16-d* in 75% yield: mp 134–135 °C; MS, 10% d_0, 90% d_1.

16β-(Acetylthio)-3β-hydroxy-5-androsten-17-one (4). Crystallization of the residue obtained above from 1, using 1 equiv of CH_3COSK and a 5-h reaction time, from acetone afforded 4 (85 mg, 87%) as colorless needles: mp 167–169 °C; HPLC t_R 5 min (MeOH/H_2O, 7/3, v/v); IR (KBr) 3480 (OH), 1740 and 1688 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (3 H, s, 18-CH_3), 1.03 (3 H, s, 19-CH_3), 2.38 (3 H, s, 16β-$SCOCH_3$), 3.44 (1 H, br m, 3α-H), 3.98 (1 H, dd, J = 2 and 8 Hz, 16α-H), 5.40 (1 H, m, 6-H). Anal. Calcd for $C_{21}H_{30}O_3S$: C, 69.58; H, 8.34; S, 8.84. Found; C, 69.43; H, 8.73; S, 8.50.

Similar treatment of 1-*16-d* as above gave 4-*16-d* in 83% yield: mp 167–170 °C; MS, 26% d_0, 74% d_1.

16β-(Acetylthio)-3β-acetoxy-5-androsten-17-one (5). 4 (50 mg, 0.14 mmol) was acetylated by Ac_2O and pyridine. Crystallization of the crude product from ether gave 5 (45 mg, 84%) as colorless needles: mp 148–152 °C; IR (KBr) 1743, 1725, and 1690 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83 (3 H, s, 18-CH_3), 1.02 (3 H, s, 19-CH_3), 2.03 (3 H, s, 3β-$OCOCH_3$), 2.37 (3 H, s, 16β-$SCOCH_3$), 4.98 (1 H, dd, J = 2 and 8 Hz, 16α-H), 4.93 (1 H, br m, 3α-H), 5.09 (1 H, m, 6-H).

Treatment of 4 with CH_3COOK in MeOD. A solution of 4 (50 mg, 0.14 mmol) and CH_3COOK (13.5 mg, 0.14 mmol) in MeOD (4 mL) was allowed to stand at room temperature for 1 h. After this time, the reaction mixture was poured into H_2O and extracted with AcOEt. After usual workup 4-*16-d* (mp 165–168 °C; 8% d_0, 92% d_1) was recovered (94%).

When 4 was subjected to the above treatment without CH_3COOK, 4-*16-d* (mp 166–169 °C; 26% d_0, 74% d_1) was isolated (100%).

16-*S*,17-*O*-Isopropylidene-16β-mercapto-5-androstene-3β,17β-diol (8). A solution of 4 (360 mg, 0.99 mmol) in 15 mL of anhydrous THF was added dropwise with stirring to a suspension of 180 mg of $LiAlH_4$ in 14 mL of anhydrous ether. The reaction mixture was heated under reflux for 7 h and then treated as usual. The reduction product, 16β-mercapto-5-androstene-3β,17β-diol (160 mg), was dissolved in a mixture of 14 mg of *p*-TsOH, 0.7 mL of anhydrous ether, and 7 mL of dried acetone, and the mixture was heated under reflux for 4 h. After an insoluble byproduct was filtered off, the filtrate was diluted with H_2O. The precipitate was collected by filtration, dried, and recrystallized from $CHCl_3$–MeOH to give 8 (178 mg, 57% from 4) as colorless leaflets: mp 211–214 °C; ^{1}H NMR ($CDCl_3$–CD_3OD) δ 0.93 (3 H, s, 18-CH_3), 1.03 (3 H, s, 19-CH_3), 1.60 and 1.72 (3 H, s, $OC(CH_3)_2S$), 3.48 (1 H, br m, 3α-H), 4.02 (1 H, br s, 17α-H), 5.37 (1 H, m, 6-H). Anal. Calcd for $C_{22}H_{34}O_2S$: C, 72.88; H, 9.45; S, 8.84. Found: C, 72.53; H, 9.46; S, 9.00.

3α-Acetoxy-16-*S*,17-*O*-isopropylidene-16β-mercapto-5-androsten-17β-ol (9). 8 (50 mg, 0.14 mmol) was acetylated by Ac_2O–pyridine. After usual workup, the crude product was recrystallized from $CHCl_3$–MeOH to give 9 (52 mg, 92%) as colorless leaflets: mp 151–154 °C; IR (KBr) 1740 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (3 H, s, 18-CH_3), 1.02 (3 H, s, 19-CH_3), 1.58 and 1.71 (3 H, s, $OC(CH_3)_2S$), 2.02 (3 H, s, 3β-$OCOCH_3$), 4.17 (1 H, br s, 17α-H), 4.60 (1 H, br m, 3α-H), 5.39 (1 H, m, 6-H). Anal. Calcd for $C_{24}H_{36}O_3S$: C, 71.25; H, 8.97; S, 7.92. Found: C, 71.13; H, 8.95; S, 8.10.

16α- and 16β-(Carboxymethylthio)-3β-hydroxy-5-androsten-17-one (6 and 7). Compounds 6 and 7 were separately synthesized from 2 and 1 according to Pelc and Holmes,[5] in 30% yield, respectively. 6: mp 195–198 °C (lit.[5] mp 196–200 °C, previously reported as mp of the 16β-thioether 7). ^{1}H NMR ($CDCl_3$) δ 1.02 (3 H, s, 18-CH_3), 1.05 (3 H, s, 19-CH_3), 3.36 and 3.74 (1 H, d, J = 15 Hz, -SCH_2-), 5.36 (1 H, m, 6-H). 7: mp 195–198 °C (lit.[5] mp 195–198 °C, previously reported as mp of the 16α-isomer 6); ^{1}H NMR (CD_3OD) δ 1.00 (3 H, s, 18-CH_3), 1.06 (3 H, s, 19-CH_3), 3.33 and 3.70 (1 H, d, J = 15 Hz, -SCH_2-), 5.34 (1 H, m, 6-H).

When 1-*16-d* and 2-*16-d* were subjected to the above reaction, 7-*16-d* (mp 196–198 °C; 22% d_0, 78% d_1) and 6-*16-d* (mp 195–198 °C; 8% d_0, 92% d_1) were obtained, respectively.

Treatment of 7 with KOH in MeOD. A solution of 7 (50 mg, 0.13 mmol) and KOH (11 mg, 0.20 mmol) in 5.7 mL of MeOD was allowed to stand at room temperature for 10 min. The reaction mixture was acidified by AcOH and then poured into H_2O. After extraction with AcOEt, the organic phase was washed with H_2O, dried (Na_2SO_4), and evaporated to give a solid. Crystallization of the solid from acetone–ether gave 7-*16-d*: mp 195–198 °C; MS 43% d_0, 57% d_1.

Acknowledgment. We thank Prof. Toshio Nambara and Dr. Kadzutake Shimada of Tohoku University for mass spectra and elemental analysis.

Registry No. 1, 1093-91-0; 1-*16-d*, 91191-05-8; 2, 74644-60-3; 2-*16-d*, 91191-06-9; 3, 91191-07-0; 3-*16-d*, 91191-08-1; 4, 91191-09-2; 4-*16-d*, 91191-10-5; 5, 91191-11-6; 6, 81354-95-2; 6-*16-d*, 91191-12-7; 7, 81354-96-3; 7-*16-d*, 91191-13-8; 8, 91191-14-9; 9, 91191-15-0; CH_3COSK, 10387-40-3; $KSCH_2CO_2H$, 34452-51-2; 16β-mercapto-5-androstene-3β,17β-diol, 91191-16-1.

Polystyryltri-*n*-butylphosphine[1]

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Received January 27, 1984

Diarylphosphine-functionalized polystyrene resins have been extensively utilized as polymeric ligands and reagents.[2] Surprisingly, analogous polymer-bound *trialkylphosphines* have not yet been reported. Because of their

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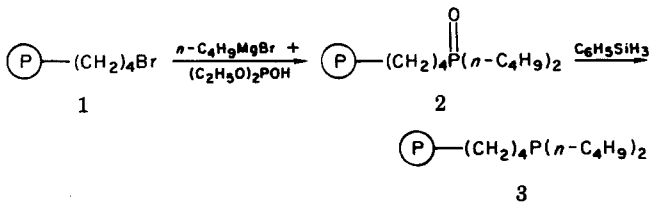
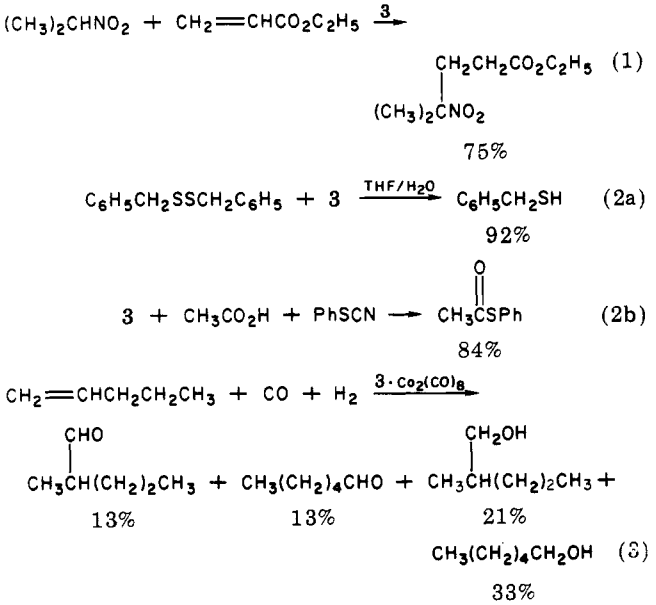
Scheme I



greater basicity and nucleophilicity, such phosphines exhibit substantially higher reactivity for a variety of synthetic transformations.[3] In this paper we report an efficient synthesis of the title polymer and demonstrate its utility as a catalyst, as a reagent, and as a ligand.

Suspension copolymerization of 4-bromobutylstyrene (60/40, meta/para) with 80 mol % styrene and 1 mol % divinylbenzene afforded a microporous resin, **1**, in a yield exceeding 90%.[4] Subsequent treatment with bromomagnesium di-*n*-butylphosphinite, prepared from *n*-butylmagnesium bromide plus diethyl hydrogen phosphite, yielded polystyryltri-*n*-butylphosphine oxide (**2**);[5] reduction with phenylsilane afforded the corresponding polymeric phosphine **3** (Scheme I).

Equations 1–3 represent three classes of reactions in which **3** has been successfully applied, as a catalyst, reagent, and ligand, respectively. Product yields and



reaction conditions compare favorably with analogous transformations carried out using soluble tri-*n*-butylphosphine.[7-10] Comparison of polystyryltri-*n*-butylphosphine with polystyryldiphenylphosphine as a catalyst for reaction 1 indicates substantially greater activity of the former. Thus, treatment of 1.07 g (12.0 mmol) of 2-nitropropane with 1.00 g (10.0 mmol) of ethyl acrylate in 3 mL of THF, in the presence of 0.079 g (0.1 mmol) of phosphine **3**, afforded a 90% yield (GLC) of the Michael adduct after 16 h; under similar conditions, 0.06 g (0.1 mmol) of polystyryldiphenylphosphine (2% cross-linked) produced a 7% yield. As is the case with most polymeric agents, the principal virtue of **3** is that the spent and unused polymer can be easily removed from product mixtures by simple filtration.

Experimental Section

General Methods. Unless stated otherwise, all reagents and chemicals were obtained commercially and were used without further purification. One percent cross-linked ω-bromobutylated polystyrene (gel type, 60/120 mesh) was prepared by using procedures similar to those previously described.[4] Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl under a nitrogen atmosphere. All ^{1}H NMR and IR spectra were recorded on Varian EM 360 and Beckman Acculab 7 spectrometers, respectively. Product mixtures were analyzed by GLC on a Hewlett-Packard Model 5830 flame-ionization instrument using a 6-ft × 0.125 in. 10% Carbowax 20 M on Chromosorb W column. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Polystyryltri-*n*-butylphosphine Oxide (2). Diethyl hydrogen phosphite (1.28 g, 9.76 mmol) was dissolved in 3 mL of dry ethyl ether and the resulting solution added to 20 mL of 1.5 M *n*-butylmagnesium bromide in ether under a nitrogen atmosphere. After refluxing the mixture for 1 h, 20 mL of anhydrous THF was added, followed by addition of 2.0 g of **1** (3.08 mmol of bromine). The mixture was refluxed for 36 h under nitrogen, cooled to 0 °C, and quenched by the dropwise addition of 20 mL of 8.0 M HCl. The polymer was recovered by filtration, washed with 200 mL of THF/H_2O (4:1), extracted continuously (Soxhlet) with THF/H_2O for 20 h, and dried (70 °C, 15 h (0.05 mm)). Bromine analysis indicated the complete elimination of bromine. Anal. Calcd P, 4.24. Found: P, 4.95.

Polystyryltri-*n*-butylphosphine (3). A mixture of **2** (5.0 g), phenylsilane (3.25 g, 30 mmol), and chlorobenzene (50 mL) was refluxed for 70 h under a nitrogen atmosphere. After cooling to room temperature, the polymer was recovered by filtration, washed successively with 400 mL of THF/ethanol (1:1) and 20 mL of THF, and dried (70 °C, 20 h (0.05 mm)). Quaternization of 0.24 g of the reduced polymer **3** with 4 mL of chlorobenzene containing 1.06 g (8.4 mmol) of benzyl chloride for 20 h at 100 °C, and subsequent chloride ion analysis,[6] indicated the presence of 1.27 mmol of reactive phosphine/g of dry polymer.

Polystyryltri-*n*-butylphosphine–$Co_2(CO)_8$. To a suspension of 4.0 g of **3** (5.1 mmol of phosphine), swollen in 70 mL of dry benzene, was added 37 mL of 0.26 M $Co_2(CO)_8$ in toluene. The resulting mixture was then stirred for 3 h at room temperature, and the resin was recovered by filtration, washed successively with 100 mL of toluene and 80 mL of petroleum ether, and stirred in 80 mL of dimethoxyethane at 70 °C for 24 h. Finally, the polymeric catalyst was filtered, washed successively with 20 mL of dimethoxyethane and 100 mL of petroleum ether, and dried (65 °C, 12 h (0.05 mm)), yielding a reddish brown product: IR (KBr) 2058, 1990, 1970, 1930, 1870 cm^{-1}. Anal. Calcd for a resin having a ratio of cobalt/phosphorus = 1.0: P, 3.72; Co, 7.08. Found: P, 3.46; Co, 7.36. Under hydroformylation conditions, the color of the polymer beads became deep red.

Addition of 2-Nitropropane to Ethyl Acrylate.[7] To a solution of ethyl acrylate (4.61 g, 46 mmol) and 2-nitropropane (4.95 g, 55.6 mmol) dissolved in 10 mL of THF was added 0.38 g (0.48 mmol of phosphine) of **3**. The mixture was stirred at room temperature for 19 h, filtered, and distilled (bp 114–116 °C, 7 mm) to give 6.5 g (75%) of the Michael adduct, having the expected ^{1}H NMR spectrum.[7]

Reduction of Benzyl Disulfide.[8] To a solution of benzyl disulfide (0.123 g, 0.50 mmol) dissolved in 5 mL of THF plus 0.25 mL of water was added 0.458 g (0.57 mmol) of phosphine of **3**. The mixture was stirred at room temperature for 5 h and analyzed by GLC after addition of *n*-pentanol (0.5 mmol) as an internal

(1) Supported by the Division of Basic Energy Sciences of the Department of Energy (Contract EG-77-S-02-4446).

(2) Lieto, J.; Milstein, D.; Albright, R. L.; Minkiewicz, J. V.; Gates, B. C. *CHEMTECH* **1983**, 46. "Polymer-Supported Reactions in Organic Synthesis"; Hodge, P., Sherrington, D. C., Eds.; Wiley: New York, 1980.
(3) Henderson, W. A.; Buckler, S. S. *J. Am. Chem. Soc.* **1960**, *82*, 5794.
(4) Tomoi, M.; Ogawa, E.; Hosokawa, Y.; Kakuicki, H. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3015.
(5) Kabachnik, M. I.; Mastryukova, T. A.; Shipov, A. E. *Zh. Obshch. Khim.* **1965**, *35*, 1574.
(6) Stewart, J. M.; Young, J. D. "Solid Phase Peptide Synthesis"; W. H. Freeman: San Francisco, CA, 1969; p 55.
(7) White, D. A.; Baizer, M. M. *Tetrahedron Lett.* **1973**, 3597.
(8) Humphrey, R. E.; Potter, J. L. *Anal. Chem.* **1965**, *37*, 164.
(9) Slaugh, L. H.; Mullineaux, R. D. *J. Organomet. Chem.* **1968**, *13*, 469.
(10) Grieco, P. A.; Yokoyama, Y.; Williams, E. *J. Org. Chem.* **1978**, *43*, 1283.

standard. Analysis after 5 h showed an 87% yield of benzyl mercaptan; extending the reaction time to 19 h increased the yield to 92%.

Hydroformylation of 1-Pentene.[9] A 75-mL stainless steel reaction vessel (Hoke bomb, Whitey, OH), equipped with a $^1/_8 \times ^1/_2$ in. Teflon-coated magnetic stirring bar, was charged with 0.13 g (0.145 mmol of cobalt) of the polymeric cobalt catalyst, 0.085 g (0.4 mmol) of *n*-pentadecane (internal standard), 10 mL of *n*-octane, and 0.63 g (9.0 mmol) of 1-pentene under a nitrogen atmosphere. After the vessel was sealed, a mixture of hydrogen and carbon monoxide (2/1) was introduced. The system was then heated to 180 °C by placing the vessel in an oil bath, and the mixture was stirred magnetically, using an external magnetic stirrer. The maximum pressure (480–510 psi at 180 °C) and equilibrium temperature were obtained in ca. 5 min. After 14 h, the pressure dropped a total of 110 psi, and the vessel was then cooled (0 °C) and vented and an aliquot analyzed by GLC. The product mixture consisted of 1-hexanal (13%), 1-hexanol (33%), 2-methylpentanal (13%), 2-methylpentanol (21%), pentane (7%), and pentenes (2%). Reuse of the catalyst gave identical results.

Benzenethiol Acetate.[10] To a mixture of 0.866 g (1.1 mmol of phosphine) of **3** and acetic acid (0.06 g, 1.0 mmol) in 7 mL of dry methylene chloride was added 0.135 g (1.0 mmol) of phenyl thiocyanate. The mixture was stirred under nitrogen for 5 h at 40 °C; analysis by GLC indicated an 84% yield of benzenethiol acetate.

Registry No. $(EtO)_2POH$, 762-04-9; BuMgBr, 693-03-8; $CH_3CH(NO_2)CH_3$, 79-46-9; $EtOCOCH{=}CH_2$, 140-88-5; $PhCH_2SSCH_2Ph$, 150-60-7; $(CH_3)_2C(NO_2)CH_2CH_2CO_2Et$, 23102-02-5; $PhCH_2SH$, 100-53-8; $CH_2{=}CHCH_2CH_2CH_3$, 109-67-1; $OHC(CH_2)_4CH_3$, 66-25-1; $HO(CH_2)_5CH_3$, 111-27-3; $OHCCH(CH_3)CH_2CH_2CH_3$, 123-15-9; $HOCH_2CH(CH_3)CH_2CH_2CH_3$, 105-30-6; CH_3CO_2H, 64-19-7; PhSCN, 5285-87-0; AcSPh, 934-87-2.

Trialkyl(2-nitro-1-alkenyl)silanes. Synthesis and Diels–Alder Reaction

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Received November 16, 1983

With the explosive development of organosilicon chemistry during the past 15 years, (1-alkenyl)trialkylsilanes **1**, or more commonly vinylsilanes, have become increasingly important in selective organic synthesis.[1] Whereas most of them react as nucleophiles, a few reports have appeared recently on electrophilic vinylsilanes possessing an electron-withdrawing group at the β-position.[2] Among these, trialkyl(2-nitro-1-alkenyl)silanes ((nitrovinyl)silanes) **2** are interesting in view of recent attention to the chemistry of nitroalkenes.[3]

In a previous report, we reported the synthesis of the simplest (nitrovinyl)silane **2a** via nitroselenenylation of vinylsilane **1a** and its reaction with organometallic compounds.[4] Recently Padwa has reported the cycloaddition reactions of **2a** prepared by an independent procedure.[5]

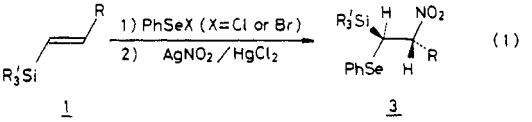
Table I. Synthesis of 2 and 3 via Nitroselenenylation of 1

	1		2	3
	R	R′	yield, %	yield,[c] %
a	H	Me	66[a]	89
b	C_4H_9	Et	37[b]	93
c	C_6H_{13}	Me	42[b]	94
d	C_6H_{13}	Et	40[b]	96
e	C_8H_{17}	Et	43[b]	96

[a] Benzeneselenenyl bromide was used. [b] Benzeneselenenyl chloride was used. [c] Isolated yield based upon **2**.

We now disclose our own results on the general synthesis of (nitrovinyl)silanes **2** and the Diels–Alder reaction of **2a** as a dienophile.[5]

Synthesis of **2** began with nitroselenenylation of vinylsilanes **1**, which involves treatment of **1**[6] with benzeneselenenyl halide (halogen = Cl or Br) followed by addition of silver nitrite in the presence of mercury(II) chloride (eq 1). Nitroselenides **3** were obtained in 37–66% isolated

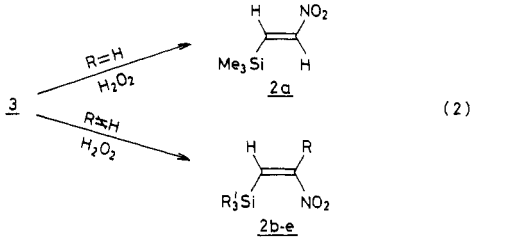


(1)

1 3

yield as shown in Table I. After a number of attempts, the best yields of **3** were obtained by using bezeneselenenyl chloride, except for the case of **1a**, where the use of benzeneselenenyl bromide afforded a significantly improved yield. Although the yields of nitroselenenylation were by no means excellent, both regio- and stereoselectivity are completely controlled: In each case there was obtained a single isomer. The regiochemistry is consistent with the intervention of a β-silyl cation generated by initial reaction of **1** with benzeneselenenyl halide.[7] The stereochemistry of addition across the C=C bond is most probably trans in light of the previous cases involving simple alkenes, where exclusive trans addition has been observed.[4]

Such a stereochemical assignment of **3** is in complete agreement with the stereochemical consequence of subsequent oxidation step which proceeds via syn elimination of benzeneselenenic acid (eq 2).[8] While oxidation of **3a**



(2)

with an excess of hydrogen peroxide provided *E* isomer **2a**, a thermodynamically more stable isomer, **3b–e** upon oxidation under similar conditions afforded *Z* isomers **2b–e** in excellent yields (Table I). Stereochemical assignment of **2** was unequivocally established by considering the anisotropic deshielding effect of the NO_2 group.[9] The

(1) Recent reviews: (a) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworth: London, 1981. (b) Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983.

(2) (a) Paquette. L. A.; Williams, R. V. *Tetrahedron Lett.* **1981**, *22*, 4643. (b) Pillot, J. P.; Dunogues, J.; Calas, R. *Bull. Soc. Chim. Fr.* **1975**, 2143; (c) Cunico, R. F.; Clayton, F. J. *J. Org. Chem.* **1976**, *41*, 1480.

(3) Recent reviews: (a) Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. *Chimia* **1979**, *3*, 1. We thank Professor Seebach for sending us a reprint of this review article.

(4) Hayama, T.; Tomoda, S.; Takeuchi, Y.; Nomura, Y. *Tetrahedron Lett.* **1983**, *24*, 2795.

(5) Padwa, A; MacDonald J. G. *J. Org. Chem.* **1983**, *48*, 3189.

(6) Vinylsilane (**1a**) was purchased from Chisso Co., a Petrarch Chem. Co. Agent in Tokyo. Other vinylsilanes **1b–e** were prepared by hydrosilylation of the corresponding alkynes using chloroplatinic acid as a catalyst: Stork, G.; Colvin, E. W. *J. Am. Chem. Soc.* **1971**, *93*, 2080.

(7) Reference 1a, p 62.

(8) Sharpless, K. B.; Young, M. W.; Lauer, R. F. *Tetrahedron Lett.* **1973**, 1979.

(9) The strong deshielding anisotropic effect of the nitro group has been discussed in (a) Yamaguchi, I. *Can. J. Chem.* **1962**, *40*, 105. (b) Fraser, R. R. *Ibid.* **1960**, *38*, 2226. We have observed substantial anisotropic effect of the nitro group on the chemical shifts of H-5 of 4-nitro-4-octenes (**4**): δ 5.67 for the *Z* isomer and δ 7.11 for the *E* isomer: Hayama, T; Tomoda, S; Takeuchi, Y; Nomura, Y, *Tetrahedron Lett.* **1982**, *23*, 4733.

0022-3263/84/1949-3235$01.50/0