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Preparation of Vinylsilanes and Vinyl Halides Containing Alkene or Epoxide Functional Groups[1]

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In connection with an investigation of synthetic procedures in the vitamin D area we have prepared the vinyl halide epoxide 3 and converted it to the vinylsilane epoxide 4 (Scheme I). Our three-step procedure for the preparation of 4 constitutes a new approach to functionalized vinylsilanes which may have applicability beyond our immediate goal.

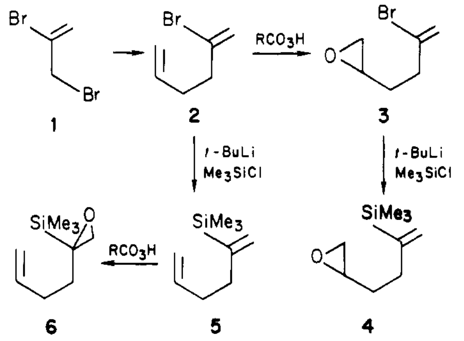
In regard to the preparation of 2-silylated-1-alkenes, exemplified by 4, the number of available methods is limited.[3] Their suitability for the preparation of epoxide 4 is hard to judge, in view of the intermediacy of strong base necleophiles and/or acids in the syntheses. Bond and co-workers[4a] and later Paquette et. al.[4b–d] have developed a synthesis applicable to such vinylsilanes based on the Shapiro reaction. The less substituted enolate of the lithiated sulfonylhydrazone of a ketone is allowed to react in the presence of Me$_3$SiCl. Since the dilithio intermediate is prepared in tetramethylethylenediamine rather than an ether solvent to avoid lithiation of the solvent, the prospects for the compatibility of the method with an epoxide functionality were doubtful. Similarly, it is not clear that a procedure involving hydrosilylation of silylated alkynes, followed by protonolysis,[5] would be applicable to the preparation of 4. Other routes to 2-silylated-1-alkenes involve metalation of expensive 1-bromo-1-(trimethylsily)ethene[6] and further reactions.

Here we describe the transformation of the coupled product 2 to vinylsilane 4. Related reactions carried out in the course of the study are given. From the outset we envisioned that the coupling of an allyl-Grignard reagent with a halo-substituted allyl halide would serve as the source of the six carbon fragment. Although the preparation of 2-bromoallyl bromide (1) was given,[2] a search of the literature revealed that 2-bromo-1,5-hexadiene (2), the expected coupling product of 1 with an allylmagnesium-Grignard reagent, *was unknown*. Likewise the chlorine analogue, 2-chloro-1,5-hexadiene (8), *was unknown*, although the potential precursor, 2,3-dichloropropene (7), is a very inexpensive commercial chemical. Below we report that the coupling reactions are readily carried out.

Description

The coupling reaction of 1 to give 2 was carried out by a variety of procedures. Although high yields were not obtained, whether or not CuI was added as recommended[7] for other allylic couplings, efficient distillation provided pure 2 in substantial amounts in one step from commercial chemicals. Although we used no catalyst in our better procedure, we assume that the the reaction course may be a function of transition metals present in the commercial allylmagnesium bromide. In contrast with our experience involving 2, the previously unprepared 8, the chloride analogue of 2, was obtained readily in high yield from the allylic chloride 7. However, 8 appeared not to undergo metalation and accordingly is not a potential source of 4 (see below).

Scheme I



In principle the desired vinylsilane epoxide 4 could be obtained from 2 via conversion to the vinyl bromide 3 followed by replacement of Br by trimethylsilyl or by the inverse procedure, conversion of 2 to 5 and then 5 to 4. Although the vinylsilane group is said to be mildly deactivating toward electrophilic attack, owing to electron-acceptor properties of d or antibonding orbitals,[4b] examination of reported epoxidation rates show that it is the replacement of *carbon* by silicon which results in deactivation. The silated double bond in 5 differs from the unsilylated one in that hydrogen has been replaced by silicon to give a more substituted double bond, possibly activated toward epoxidation to give 6, which was not our target.

Accordingly, it was likely that success would rest on the possibility of metalation of the vinylic bromine in 3 without reaction of the epoxide group with the metallated intermediate. Subsequent trimethylsilylation would then give 4. The vinyl bromide 2 was epoxidized to 3 and subjected to metalation with *tert*-butyllithium below −100 °C, conditions found by Seebach[8] to be effective for the metalation of terminal vinyl halides. Gratifyingly, the metalation of the nonterminal vinyl bromide 3 occured cleanly with survival of the epoxide group to give 4 (76%). Other examples of the preparation of an organolithium in the presence of epoxide groups have appeared.[9]

We also prepared the vinylsilane 5 and epoxidized it. In an early experiment conversion of 2 to a Grignard reagent[10] followed by trimethylsilylation, did not succeed. However, metal–halogen interchange with *tert*-butyllithium[8] gave the vinylsilane 5 in a moderate yield even though a dry ice bath was used instead of the the Trapp solvent mixture (−110 °C) used by Seebach. Epoxidation of 5 appeared to give 6 mixed with some 4, as indicated by the gas chromatographic area ratio, 7.7:1.

The vinyl halide 8 when subjected to reaction with *tert*-butyllithium under the Seebach conditions followed by reaction with Me$_3$SiCl gave the elimination product 9, which was readily isolated. No 5 was formed. This re-

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(1) Support by the National Institutes of Health is gratefully acknowledged. The 400-MHz spectra were taken at the NSF regional NMR facility at USC.

(2) *Organic Syntheses*; Gilman, H; Ed, John Wiley and Sons: New York, 1941; Collect. Vol. I, p 209.

(3) Colvin, E. *Silicon in Organic Synthesis*; Buttersworths: London, England, 1981.

(4) (a) Chamberlin, A. R.; Stremke, J. E.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 147. (b) Paquette, L. A., Fistad, W. E., Dime, D. S., Bailey, T. R. *J. Org. Chem.* **1980**, *45*, 3017. (c) Taylor, R. T.; Degenhardt, C. R.; Melega, W. P.; Paquette, L. A. *J. Org. Chem.* **1977**, *2*, 159. (d) Barth, W.; Paquette, L. A. *J. Org. Chem.* **1985**, *50*, 2438.

(5) Hudrlik, P. F.; Schwartz, R. H.; Hogan, J. C. *J. Org. Chem.* **1979**, *44*, 155.

(6) (a) Huynh, C.; Linstrumelle, G. *Tetrahedron Lett.* **1979**, *12*, 1073. (b) Knochel, P.; Normant, J. F. *Tetrahedron Lett.* **1984**, *25*, 4383. (c) Paquette, L. A.; Yan, T. H.; Wells, G. J. *J. Org. Chem.* **1984**, *49*, 3610.

(7) (a) Linstrumelle, G. *Tetrahedron Lett.* **1977**, 1181. (b) For a review, see: Benkeser, R. *Syntheses* **1971**, 347.

(8) Seebach, D; Neumann, H. *Tetrahedron Lett.* **1976**, 4839.

(9) Cooke, N. P., Jr.; Houpis, I. N. *Tetrahedron Lett.* **1985**, *26*, 3643, and references contained therein.

(10) Normant, H.; Dele'pin, M. *Compt. Rend.* **1954**, *239*, 1510.

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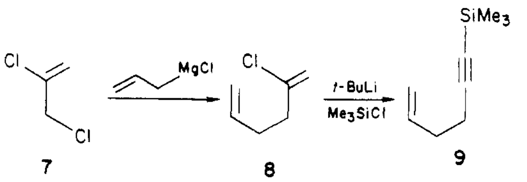
action provides a simple and inexpensive route to **9**, which previously has been prepared by a longer route involving vinyl bromide.[11]



We briefly investigated the reaction of dibromide **1** and its dichloro analogue **7** with *tert*-butyllithium, followed by chlorotrimethylsilane. The dibromide appeared to undergo metal–halogen interchange at the allylic carbon to give a poor yield of 2-bromo-3-(trimethylsilyl)propyne, difficult to separate from solvent. The dichloride gave many components, not studied further.

Experimental Section

2-Bromo-1,5-hexadiene (2) was prepared by adding a solution of allylmagnesium bromide (1 M in ethyl ether, 0.16 mol) by cannula to a dried three-neck flask equipped with a Friedrich condenser and drying tube, septum fitted addition funnel, and thermometer. The condenser temperature was set at −10 °C. 2,3-Dibromopropene (0.12 mol, 24 g) was added to the main flask at a rate which maintained rapid reflux. A vigorous reaction began immediately. After the addition, the solution was maintained at reflux for 2 h. An insoluble salt separated and a brown color developed. The solution was washed with HCl (15 mL, concentrated) in H_2O (90 mL) and was dried overnight over $CaCl_2$. The ether was removed by columm distillation. The desired 2-bromo-1,5-hexadiene (**2**), distilled at 43 °C, 28 torr, 11.4 g (60%). A higher boiling component, possibly 2,5-dibromo-1,5-hexadiene, was discarded. ^{1}H NMR ($CDCl_3$): δ 5.70 (m, 1, CH=); 5.58, 5.48 (peaks show small allylic coupling, CH_2=CBr); 5.10 (m, 2, =CH_2); 2.41 (m, 4, CH_2). Anal. Calcd for C_6H_9Br:C, 44.75; H, 5.63. Found: C 44.98; H, 5.62. ^{13}C NMR (CDC_3): δ 133.71 (=CBr), 121.06 (=CH), 116.74 (=CH_2), 115.65 (=CH_2), 40.61 (CH_2), 32.07 (CH_2).

2-Chloro-1,5-hexadiene (8) was prepared by a similar procedure using allylmagnesium bromide (1 M, 0.065 mol) and 2,3-dichloropropene (0.045 mol, 5 g). The product was distilled at 52–54 °C, 100 torr. No higher boiling component (cf. preceding preparation) was present. The yield was 4.1 g (78%). ^{1}H NMR ($CDCl_3$): δ 5.66 (m, 1, CH=), 5.15 (s, 2, CCl=CH_2), 5.03 (m, 2, CH_2=), 2.38 (m, 4, CH_2).

2-Bromo-5,6-epoxy-1-hexene (3). A solution of 2-bromo-1,5-hexadiene (**2**) (4.99 g, 0.031 mol) in methylene chloride was prepared. To it was added (at 150 dp/min) a nominal 35% excess of untitrated *m*-chloroperbenzoic acid (7.20 g, 0.042 mol) in 92 mL of CH_2Cl_2. After reaction overnight a gas chromatogram showed seven area percent of reactant remaining. A nominal 10 mol % of additional MCPBA was added. After 24 h, isolation in the manner described for the conversion of **5** to **6** and distillation through a Vigreaux column gave **3**, 3.47 g, 63%, bp 70–85 °C, 10 torr. ^{1}H NMR ($CDCl_3$): δ 5.82 and 5.71 (s, 2 H,=CH_2), in 2.95 (m, 1 H, HCO), 2.89 (m, 2 H, H_2CO), 2.77 (m, 2 H, CH_2), 1.95 and 1.86 (m, 2 H, CH_2). ^{13}C NMR: δ 133.15 (=CBr), 117.19 (=CH_2), 50.91 (CHO), 46.95 (CH_2), 37.89 (CH_2), 30.89 (CH_2). Anal. Calcd for C_6H_9Br:C, 40.70; H, 5.12. Found: C, 40.41; H, 5.29.

2-(Trimethylsilyl)-5,6-epoxy-1-hexene (4). A solution of 2-bromo-5,6-epoxy-1-hexene (**3**) (3.01 g, 17 mmol) in a Trapp solvent mixture (tetrahydrofuran/ether/pentane, 4:1:1) was cooled in a bath of methylcyclohexane/liquid N_2 until the bath temperature was below −100 °C. After several minutes *tert*-butyllithium in pentane (20 mL, 1.7 M) was added slowly by syringe. After 3 h at −100 °C, Me_3SiCl (1.83 g, 16.9 mmol) was added. After 10 min the mixture was removed from the cold bath and allowed to warm to room temperature. During this time the solution turned from yellow to clear with precipitation of a solid (presumably LiBr). To the mixture was added brine containing HOAc and CH_2Cl_2. After repeated extractions with brine the CH_2Cl_2 layer was subjected to rotary evaporation and distillation to give 2.04 g, 71%, of **4**, bp 82–86 °C, 18–21 torr. ^{1}H NMR ($CDCl_3$): δ 5.55 and 5.35 (s, 2 H, =CH_2), 2.95 (m, 1 H, CHO), 2.80 and 2.55 (m, 2 H, OCH_2), 2.30 (m, 2 H, CH_2), 1.6 (m, 2 H, CH_2), 0.21 (s, 9 H, $SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 151.01 (=CSi), 124.16 (=CH_2), 51.89 (CHO), 47.01 (CH_2O), 31.78 (CH_2), 31.69 (CH_2), −1.61 (Si-CH_3). Anal. Calcd for $C_9H_{18}OSi$: C, 63.47; H, 10.65. Found: C, 63.42; H, 10.99.

2-(Trimethylsilyl)-1,5-hexadiene (5) and Its Epoxidation. A solution of 2-bromo-1,5-hexadiene (3.91 g, 24 mmol) in a Trapp solvent mixture (THF, 70 mL; ether, 17 mL; pentane, 17 mL) was cooled under dry nitrogen to −68 °C in a dry ice acetone bath. *Tert*-Butyllithium in pentane (24 mL of 2 M, 48 mmol) was added slowly from a syringe. After 3 h, trimethylsilyl chloride (2.8 mL, 24 mmol) was added. After 10 min the reaction was slowly warmed to room temperature. The reaction was allowed to proceed overnight. A deep yellow color formed that disappeared upon washing with brine. The brine extraction was repeated and the solution was dried over $MgSO_4$. Solvent was removed by columm distillation. The compound was distilled to give 1.60 g (45%) at 49–52 °C, 15 torr. ^{1}H NMR ($CDCl_3$): 5.7 (m, 1 H, CH=), 5.45 (m, 2 H, =CH_2), 5.03 (m, 2 H, =CH_2), 2.20 (m, 4H, CH_2), 0.10 (s, 9 H, $SiCH_3$). ^{13}C NMR: δ 151.61 (=CSi), 136.66 (=CH), 123.69 (=CH_2), 114.38 (=CH_2), 35.22 (CH_2), 33.19 (CH_2), −1.52 ($SiCH_3$). Anal. Calcd for $C_9H_{18}Si$: C, 63.47; H, 10.65. Found: C, 61.63; H, 10.73.

Epoxidation of 40 mg, 0.26 mmol, of **5** was carried to approximately 80% of completion by a procedure similar to that for epoxidation of **3**. Cappillary gas chromatography showed some **4**, identical in retention time with that whose preparation is described above, and a major product having a slightly different retention time, presumed to be **6**, in a ratio of 1:7.7. Since we needed a preparation of **4**, no further characterization was done.

5-Hexen-1-ynyltrimethylsilane (9). A solution of 2-chloro-1,5-hexadiene (2.46 g, 0.021 mol) in THF (69 mL), ether (17 mL), and pentane (17 mL) was cooled in a dry ice–acetone bath to −68 °C under dry nitrogen. *tert*-Butyllithium (2 M, 21 mL) was added slowly by syringe. Four hours later trimethylsilyl chloride was added. The mixture turned deep red while reacting overnight. An insoluble salt formed. The color and salt disappeared when the solution was extracted with brine. The organic layer was dried overnight over $MgSO_4$ and the solvent was removed by columm distillation. The product was distilled to give 1.1 g (38%), bp 58–61 °C, 15 torr. ^{13}C NMR ($CDCl_3$): δ 136.73 (=CH), 115.54 (=CH_2), 106.60 (≡CSi), 84.79 (≡C), 32.89 (CH_2), 19.70 (CH_2), 0.10 (CH_3Si). The IR and ^{1}H NMR spectra closely matched those given in ref 11.

Registry No. **1**, 513-31-5; **2**, 101933-87-3; **3**, 101933-89-5; **4**, 101933-90-8; **5**, 101933-91-9; **6**, 101933-92-0; **7**, 78-88-6; **8**, 101933-88-4; **9**, 1578-50-3; allyl bromide, 106-95-6; chlorotrimethylsilane, 75-77-4.

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Baeyer–Villiger Oxidation of Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione

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Recent interest in Baeyer–Villiger oxidation of polycyclic ketones[1-5] prompts us to report on recent results obtained

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