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Communications

Diastereoselective Addition of Carbon Electrophiles to Styrylsilanes: The Dimerization of β-(*E*)-(Halosilyl)styrenes[1]

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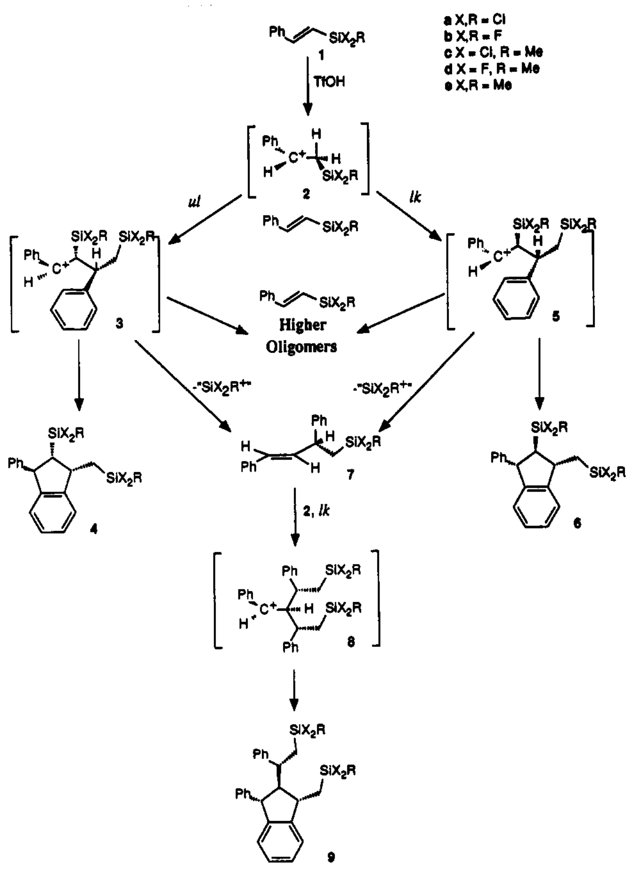
Summary: β-(Halosilyl)styrenes undergo dimerization and trimerization reactions leading to 1,2,3-trisubstituted 1*H*-dihydroindenes with high diastereoselectivity.

Organosilyl groups are known to hyperconjugatively stabilize carbocations in the β-position (the β-effect).[4] This stabilization has been extensively used in organic synthesis for regiocontrolled carbon–carbon bond formation.[5] Vinylsilanes are very versatile educts for use in stereoselective olefin formation via a substitution reaction with electrophiles controlled by the β-effect. In such reactions, however, the directing effect provided by the silyl group is lost after the formation of only one C–C bond.

Addition reactions to vinylsilanes, during which the silyl group is not lost, are rare, particularly if carbon electrophiles are used.[6] By moderating the leaving-group ability of the silyl group, we have found that such addition reactions of carbon electrophiles can occur diastereoselectively and, furthermore, that the nature of the ligands on silicon affects the stereochemical outcome of the reaction.

Scheme I



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[1] Presented at the IX International Silicon Conference, Edinburgh, Scotland, July 1990, Abstract 4.7.

[2] Natural Sciences and Engineering Research Council of Canada University Research Fellow, 1985–1995.

[3] Taken, in part, from the M.Sc. thesis of T.S., McMaster University, 1990.

[4] Bassindale, A. R.; Taylor, P. G. *Activating and Directive Effects of Silicon.* In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1989; Part 2, Chapter 14. Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496. Lambert, J. B.; Wang, G.; Finzel, R. B.; Teramura, D. H. *Ibid.* **1987**, *109*, 7838.

[5] Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer: Berlin, 1983. Fleming, I. Organosilicon Chemistry. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 3, Chapter 13.

[6] Halogen electrophiles: Eisch, J. J.; Foxton, M. W. *J. Org. Chem.* **1971**, *36*, 3520. Koenig, K. E.; Weber, W. P. *Tetrahedron Lett.* **1973**, 2533. Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1978**, *43*, 4424. Miller, R. B.; McGarvey, G. *Ibid.* **1979**, *44*, 4623. Andrianov, K. A.; Zhdanov, A. A.; Odinets, V. A. *J. Gen. Chem. U.S.S.R.* **1961**, *31*, 3764. Carbon electrophiles: Overman, L. E.; Castenada, A.; Blumenkopf, T. A. *J. Am. Chem. Soc.* **1983**, *108*, 1303. Fleming, I.; Pearce, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2485.

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We report herein β-effect controlled dimerization and trimerization reactions of β-(trihalosilyl)- and β-(dihalomethylsilyl)styrenes that lead to 1,2,3-trifunctionalized indans containing three or four contiguous chiral centers.

In the presence of trifluoromethanesulfonic acid (triflic acid), β-(trichlorosilyl)styrene[7,8] (**1a**) undergoes an oligomerization reaction.[9] By use of the appropriate dilution conditions (2.8 M in $CDCl_3$) and low temperature (−55 °C),[10] it was possible to form mainly the dimer **4a** (Scheme I; **4a**:**6a** = 92:8, yield ca. 55% by ^{1}H NMR);[11] the remaining products were higher oligomers. In contrast, the reaction of (dichloromethylsilyl)styrene[8] (**1c**) under the same conditions led to a mixture that contained mostly desilylated trimer **9c** contaminated with dimer **6c** (Scheme I; **9c**:**6c** = 7:2, yield ca. 50% by ^{1}H NMR).[11] The remaining products in these reactions were also higher oligomers.

The formation of dimers **4** and **6** can be rationalized in the manner shown in Scheme I. The leaving-group ability of the trichlorosilyl and dichloromethylsilyl groups is poor. Therefore, after protonation of **1** to form cation **2**, protiodesilylation[12] does not occur and a reaction occurs with the only viable nucleophile in solution, another styrene. Intermediate **3** arises from an *ul*-addition process, whereas **5** arises from a *lk*-addition of another monomer. In either case, the cationic center can then be attacked by the phenyl ring in an intramolecular Friedel–Crafts reaction on the face anti to the silyl group to form **4** or **6**, respectively.

The product arising from *ul*-addition is the kinetic product; warming the reaction of **1a** to 0 °C leads to a 50:50 mixture of **4a**/**6a**.[13] The preference for *ul*-addition under conditions of kinetic control with Lewis acid catalysis has often been observed.[14] With a more electron-rich silyl group ($MeSiCl_2$ compared with $SiCl_3$) and a correspondingly increased β-effect,[15] the stabilized cations **2c**, **3c**, and **5c** can undergo equilibration leading eventually to the thermodynamic product **6**. In the case of the less stabilized cation **3a**, kinetic trapping of the cation occurs in an intramolecular Friedel–Crafts reaction.

The mechanism of formation of **9** is more difficult to rationalize as the key intermediate is presumably **7** in which one of the chiral centers has been lost; it could arise from either **3** or **5**. *lk*-Addition of **2** to **7** would give symmetrical **8**, which can cyclize to **9** in a Friedel–Crafts reaction, again on the least hindered face (Scheme I).

The dimerization of styrenes under acidic conditions, leading to indans, is a well-documented reaction[16] and has been shown to occur to give highly substituted indans in special cases.[17] A stereoselective example with *p*-quinone methides was recently reported by Angle et al.[18] The dimerization reaction reported is of interest not only because of the observed stereocontrol resulting from the substitution on silicon but from the fact that the chlorosilyl groups provide a handle for further synthetic elaboration. We are currently examining related reactions in which other carbon electrophiles annelate onto the silylstyrene to determine the synthetic potential of such a strategy.

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Supplementary Material Available: Experimental procedures for the preparation of **4**, **6**, and **9**; spectroscopic data (mp; IR; MS; ^{1}H; ^{13}C, ^{29}Si NMR) for **4e**, **6e**, and **9e**; ORTEP diagrams from the X-ray crystal structure analysis of **4e** and **9e** (4 pages). Ordering information is given on any current masthead page.

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[7] The starting materials **1a**,**c** are readily prepared by the H_2PtCl_6-catalyzed hydrosilation of phenylacetylene with $HSiCl_3$ or $HSiMeCl_2$, respectively, in THF. Tamao, K.; Yoshida, J.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Takahashi, M.; Kurita, A.; Murata, M.; Kumada, M. *Organometallics* **1982**, *1*, 355 and references cited therein. **1b**,**d** are prepared by the fluorination of **1a** and **1c**, respectively, using ZnF_2.

[8] Similarly, (trifluorosilyl)styrene (**1b**) led primarily to **4b** and (difluoromethylsilyl)styrene to a mixture of **6d** and **9d**, respectively. However, reactions with the fluorinated compounds were notoriously difficult to work with and were accompanied by extensive degradation or formation of side products.

[9] Brook, M. A.; Hülser, P.; Sebastian, T. *Macromolecules* **1989**, *22*, 3814.

[10] Changing the concentration of the reaction or the temperature of the reaction only increased the amount of higher oligomers and/or desilylated product.

[11] The structure of the compounds could not be directly assigned. Therefore, they were first converted to the corresponding air-stable trimethylsilyl derivatives by reaction with MeMgBr (0 °C, Et_2O). The structures of **4e**, **6e**, and **9e** (yield after purification from **1**, **4e** 38%, **6e** 7%, **9e** 24%) were determined by NOE measurements and confirmed for **4e** and **9e** by X-ray crystal structure determination. Frampton, C. S.; Brook, M. A.; Jueschke, R.; Sebastian, T. *Acta Crystallogr., Sect. C* submitted for publication.

[12] The normal reaction course with (trimethylsilyl)styrene and acid is protiodesilylation to form styrene: Weber, W. P.; Koenig, K. E. *J. Am. Chem. Soc.* **1973**, *95*, 3416.

[13] One of the reviewers was concerned that the 50:50 mixture of isomers **4a**/**6a** could arise from equilibration of the two at the higher temperature. To discount this possibility, a 90:10 mixture of **4a**/**6a** (prepared at −55 °C) was submitted to triflic acid catalysis at higher temperature (0–25 °C overnight). No change in the ratio of stereoisomers was observed.

[14] Brook, M. A.; Seebach, D. *Can. J. Chem.* **1987**, *65*, 836. Seebach, D.; Goliński, J. *Helv. Chim. Acta* **1981**, *64*, 1413.

[15] Brook, M. A.; Hadi, M.; Neuy, A. *J. Chem. Soc., Chem. Commun.* **1989**, 957. Brook, M. A.; Neuy, A. *J. Org. Chem.* **1990**, *55*, 3609.

[16] Moreau, M.; Matyjaszewski, K.; Sigwalt, P. *Macromolecules* **1987**, *20*, 1456. Higashimura, T.; Hiza, M.; Hasegawa, H. *Macromolecules* **1979**, *12*, 217. *Ibid.* **1979**, *12*, 1058. Kunitake, T.; Takarabe, K. *Ibid.* **1979**, *12*, 1061. Hiza, M.; Hasegawa, H.; Higashimura, T. *Polymer J.* **1980**, *12*, 379. MacMillan, J.; Martin, I. L.; Morris, D. J. *Tetrahedron* **1969**, *25*, 905.

[17] Marcuzzi, F.; Melloni, G. *J. Chem. Res., Miniprint* **1979**, 2287.

[18] Angle, S. R.; Arnaiz, D. O. *J. Org. Chem.* **1990**, *55*, 3708.

Stereocontrolled Oxaspirocyclization of Conjugated Dienes via Palladium Catalysis

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Summary: Mild palladium-catalyzed spirocyclizations of 1-(3-hydroxyalkyl)- and 1-(4-hydroxyalkyl)-1,3-cycloalkadienes (**5a**, **5b**, **5d**, and **5e**) have been developed. The reactions proceed via a spirocyclic π-(allyl)palladium intermediate and result in the 1,4-addition of the hydroxy function and a chloride or an acetate. The stereochemistry of the reactions can be controlled to give either cis or trans 1,4-addition across the double bond.