New Stereoselective Synthesis of (Z)-α-Iodovinylsilanes via One-Pot Iododesilylation/Isomerization of 1,1-Bis(silyl)alk-1-enes

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Received 18 June 2008; revised 12 August 2008

SYNTHESIS 2008, No. 22, pp 3687–3691

Abstract: Synthetically useful (Z)-2-aryl-1-iodo-1-silylethenes were prepared in good to excellent yields via one-pot monoiododesilylation/isomerization of readily accessible 2-aryl-1,1-bis(silyl)ethenes using N-iodosuccinimide or bis(pyridine)iodonium tetrafluoroborate under mild conditions.

Key words: halogenation, iododesilylation, vinylsilanes, organometallic reagents, stereoselective synthesis

Stereodefined α-halovinylsilanes represent a class of compounds that has attracted significant attention in recent years as important intermediates in organic and organometallic synthesis. In particular, substituted α-iodovinylsilanes can serve as precursors for the stereoselective preparation of 1-lithio-1-silylalkenes, trisubstituted olefins, secondary amides as well as a variety of important organosilicon intermediates such as silyl-substituted alk-1-enes, (Z,E)-1,3- and 1,4-dienes or α-bromovinylsilanes (Scheme 1).

Although β-substituted (E)-α-iodovinylsilanes can be produced in high isomeric purities and yields by iodination of the monohydroalumination or monohydrozirconation products derived from the reaction of substituted silylacetylenes with diisobutylaluminum hydride (DIBAL-H) or hydrozirconocene, respectively, the direct synthesis of their Z-isomers remains a formidable challenge. As the double bond geometry of the α-metalated vinylsilanes can be controlled by the proper choice of conditions in the hydroalumination reaction, the treatment of alkynylsilanes with DIBAL-H in nonpolar solvents can provide an access to Z-configured α-iodovinylsilanes, however, this process seems to be not general. (Z)-α-Iodovinylsilanes can be also obtained by isomerization of their E-isomers through intermediacy of 1-lithiovinylsilanes formed by addition of catalytic amounts of tert-butyllithium. Since the trifunctional α-iodovinylsilane moiety represents a uniquely constituted synthon for stereoselective syntheses of substituted olefins and dienes, the development of new, direct and straightforward synthetic methods for (Z)-α-iodovinylsilane preparation is of great significance.

1,1-Bis(silyl)alk-1-enes constitute an important class of organometallic reagents, which are currently widely used as potential intermediates in the organic and organometallic syntheses. Although the utility of the 2-aryl-1,1-bis(silyl)ethenes as intermediates in the stereoselective

Scheme 1 Synthetic utility of substituted α-iodovinylsilanes
synthesis of functionalized organosilicon compounds is well documented,10 the reactivity of geminally silylated alkenes towards halogen electrophiles lags far behind mainly due to the complexity of their synthesis.

Recently, we have developed a new efficient protocol for the synthesis of 2-aryl-1,1-bis(silyl)ethenes from easily available starting materials using a sequential procedure: ethylene glycol silylation – one-pot silylative coupling cyclization10/Grignard reagent treatment – Heck coupling10a (Scheme 2), and reported their application to the preparation of synthetically useful 2-aryl-1,1-dibromoethenes via NBS-based double bromodesilylation11 (Scheme 3). Mild conditions, good functional group compatibility and simplicity of the experimental technique of this new bromodesilylation approach prompted us to explore the application of 2-aryl-1,1-bis(trimethylsilyl)ethenes to iododesilylation procedure.

We wish to report herein our results on the iododesilylation of 2-aryl-1,1-bis(trimethylsilyl)ethenes. Initial studies were carried out with the 1,1-bis(trimethylsilyl)-2-phenylethene as a substrate under analogous conditions; reversed the stereoselectivity, leading to formation of (Z)-1-iodo-2-(2-methylphenyl)-1-phenylethene as a single product within 24 hours (Scheme 4). This result clearly points to the strong preference of the trimethylsilyl group in vinylsilane to occupy the sterically more favorable trans-position, which agreed with the observations reported by Zweifel et al.2a

Such E → Z isomerization of α-halovinylsilanes has been previously observed for chloro- and bromo-substituted vinylsilanes upon UV irradiation in the presence of bromine, however, attempts to isomerize the (E)-iodovinylsilanes to their Z-isomers resulted in appreciable exchange of iodine by bromine.8 Although Zweifel and co-workers described the tert-butyllithium-catalyzed isomerization of alkyl-substituted (E)-α-iodovinylsilanes to (Z)-α-iodovinylsilanes through intermediary of 1-lithovinylsilanes, the spontaneous NIS-mediated isomerization of (E)-1-iodo-1-trimethylsilyl-2-phenylethene is unprecedented.

To investigate the generality of this reaction, a series of 2-aryl-1,1-bis(silyl)ethenes bearing various substituents in the aromatic ring was subjected to similar reaction conditions. For economical reasons, we decided to use for further synthetic investigation the cheaper NIS, and managed to decrease the necessary amount of the iodinating agent to 1.2 equivalents making the reaction even more economical. In a typical procedure, the 2-aryl-1,1-bis(silyl)ethene was dissolved in acetonitrile at room temperature and treated with 1.2 equivalents of NIS. In general, the reactions proceeded smoothly under mild conditions to give the corresponding (Z)-2-aryl-1-iodo-1-trimethylsilylthienes in good yield within 24 hours (Table 1), when substrates containing m- and p-substituted aryl groups were used. In contrast, the use of o-substituted 2-aryl-1,1-bis(silyl)ethene, that is, 1,1-bis(trimethylsilyl)-2-(2-methylphenyl)ethene as a substrate under analogous conditions reversed the stereoselectivity, leading to formation of (E)-1-iodo-2-(2-methylphenyl)-1-

**Scheme 2**  Synthesis of starting 2-aryl-1,1-bis(silyl)ethenes

**Scheme 3**  Synthesis of 2-aryl-1,1-dibromoethenes through double bromodesilylation of 2-aryl-1,1-bis(silyl)ethenes

**Scheme 4**  Sequential one-pot monoiododesilylation/isomerization of 1,1-bis(trimethylsilyl)-2-phenylethene

α-iodovinylsilane generates a stereodefined Z-isomer as single product within 24 hours (Scheme 4).
trimethylsilylethene as the predominant product (Table 1, compound 4).

All the iododesilylation reactions were also tested in the presence of four equivalents of (Py)2IBF4 under analogous conditions. Although the reactions occurred selectively with an excess of the iodinating agent to give monodesilylation Z-products within 24 hours with the exception of 1,1-bis(trimethylsilyl)-2-(4-methoxyphenyl)ethene, which unexpectedly formed the double-iodinated product, 1,1-diiodo-2-(4-methoxyphenyl)ethene (10), in 97% yield (Scheme 5).

As an extension to the present study we found that our method can be also applied to the iodination of tetrasilyl derivative of 1,4-divinylbenzene, easily obtained by Heck arylation of 1,1-bis(trimethylsilyl)ethene with 1,4-diiodobenzene11 (Scheme 6).

To test the synthetic utility of the obtained (Z)-2-aryl-1-iodo-1-trimethylsilylethenes, we pursued transformation of the selected product into synthetically useful bromoalkene derivatives. The treatment of (Z)-1-iodo-2-(4-methoxyphenyl)-1-trimethylsilylethene with n-BuLi and 2.5 equivalents of molecular bromine at −78 °C led to selective substitution of iodine by bromine to afford 1-bromo-2-(4-methoxyphenyl)-1-trimethylsilylethene in 89% yield. However, partial double bond isomerization occurred during this transformation to give a mixture of isomeric α-bromovinylsilanes (Z/E = 76:24) (Scheme 6). On the other hand, quenching of the stereodefined (Z)-1-iodo-2-(4-methoxyphenyl)-1-trimethylsilylethene with excess of N-bromosuccinimide (5 equiv) afforded 1,1-dibromo-2-(4-methoxyphenyl)ethene13 in 92% yield as a result of

### Table 1

<table>
<thead>
<tr>
<th>Ar</th>
<th>Product</th>
<th>Z/E</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>Ph</td>
<td>Ar</td>
<td>99:1</td>
<td>80</td>
</tr>
<tr>
<td>p-MeC6H4</td>
<td>Ar</td>
<td>99:1</td>
<td>86</td>
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<tr>
<td>m-MeC6H4</td>
<td>Ar</td>
<td>97:3</td>
<td>91</td>
</tr>
<tr>
<td>o-MeC6H4</td>
<td>Ar</td>
<td>11:89</td>
<td>94</td>
</tr>
<tr>
<td>m-MeOC6H4</td>
<td>Ar</td>
<td>96:4</td>
<td>88</td>
</tr>
<tr>
<td>p-MeOC6H4</td>
<td>Ar</td>
<td>99:1</td>
<td>97</td>
</tr>
<tr>
<td>p-ClC6H4</td>
<td>Ar</td>
<td>94:6</td>
<td>92</td>
</tr>
<tr>
<td>p-BrC6H4</td>
<td>Ar</td>
<td>99:1</td>
<td>87</td>
</tr>
<tr>
<td>p-NO2C6H4</td>
<td>Ar</td>
<td>99:1</td>
<td>88</td>
</tr>
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</table>

*Reactions were performed at a 1 mmol scale with 1.2 equivalents of NIS in 15 mL of MeCN at r.t.*

*Assigned by NOE measurements.*

*Isolated yields of chromatographically pure products.*

*Reaction performed with Py2IBF4 (4 equiv).*

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**Scheme 5** Synthesis of 1,1-diiodo-2-(4-methoxyphenyl)ethene (10)

**Scheme 6** Synthesis of (Z,Z)-1,4-bis(2-iodo-2-trimethylsilylvinyl)benzene

**Scheme 7** Synthetic utility of (Z)-1-iodo-1-trimethylsilyl-2-(4-methoxyphenyl)ethene
In conclusion, we have developed a highly flexible protocol based on sequential one-pot iododesilylation/isomerization of 2-aryl-1,1-bis(silyl)ethenes that allows the synthesis of configurationally pure (Z)-2-aryl-1-iodo-1-trimethylsilylthlenes under mild conditions. Synthetic applications of the resulting α-iodovinylsilanes are underway.

(1) N-Iodosuccinimide (Aldrich), and bis(pyridine)iodonium tetrfluoroborate (Aldrich) were used without further purification. The starting 2-aryl-1,1-bis(trimethylsilyl)ethenes were prepared by adaptation of a procedure described in literature. 10b

(Z)-2-Aryl-1-iodo-1-trimethylsilylthlenes; General Procedure

-1-Iodo-2-(4-methoxyphenyl)-1-trimethylsilylthene (6)
Yield: 0.31 g (92%); yellowish oil.
1H NMR (CDCl3): δ = 0.29 [s, 9 H, Si(CH3)3], 7.23 (s, 1 H, C=CH), 7.63 (d, J = 8.5 Hz, 2 H arom), 7.53 (d, J = 7.7 Hz, 2 H arom).
13C NMR (CDCl3): δ = –1.2, 112.8, 128.2, 129.7, 133.8, 144.0.
MS (EI): m/z (%): 332 (M+, 100), 205 (55), 73 (85).
HRMS: m/z calcd for C12H17IOSi: 332.0093; found: 332.0068.

(Z)-1-Iodo-2-(4-methoxyphenyl)-1-trimethylsilylthene (6)
Yield: 0.32 g (97%); yellowish oil.
1H NMR (CDCl3): δ = 0.29 [s, 9 H, Si(CH3)3], 7.23 (s, 1 H, C=CH), 7.63 (d, J = 8.5 Hz, 2 H arom), 7.53 (d, J = 7.7 Hz, 2 H arom).
13C NMR (CDCl3): δ = –1.2, 112.8, 128.2, 129.7, 133.8, 144.0.
MS (EI): m/z (%): 332 (M+, 100), 205 (55), 73 (85).
HRMS: m/z calcd for C12H17IOSi: 332.0093; found: 332.0068.

(Z)-1-Iodo-2-(4-methoxyphenyl)-1-trimethylsilylthene (6)
Yield: 0.32 g (97%); yellowish oil.
1H NMR (CDCl3): δ = 0.29 [s, 9 H, Si(CH3)3], 7.23 (s, 1 H, C=CH), 7.63 (d, J = 8.5 Hz, 2 H arom), 7.53 (d, J = 7.7 Hz, 2 H arom).
13C NMR (CDCl3): δ = –1.2, 112.8, 128.2, 129.7, 133.8, 144.0.
MS (EI): m/z (%): 332 (M+, 100), 205 (55), 73 (85).
HRMS: m/z calcd for C12H17IOSi: 332.0093; found: 332.0068.
1,1-Diiodo-2-(4-methoxyphenyl)ethene (10)

Bis(pyridine)iodonium tetrafluoroborate (1.49 g, 4.0 mmol) was added to a solution of 1,1-bis(trimethylsilyl)-2-(4-methoxyphenyl)ethene (0.53 g, 1.0 mmol) in MeCN (10 mL) and the suspension was stirred at r.t. for 24 h. The solvent was evaporated and the mixture was extracted with n-hexane (25 mL). The organic layer was concentrated and the product was purified by column chromatography on silica gel, eluting with n-hexane–EtOAc (40:1) to give 10; yield: 0.37 g (97%); yellow oil.

1H NMR (CDCl3): δ = 3.82 (s, 3 H, OCH3), 6.89 (d, J = 8.8 Hz, 2 Harom), 7.43 (d, J = 8.2 Hz, 2 Harom), 8.10 (s, 1 H, C=CH).
13C NMR (CDCl3): δ = 129.9, 130.8, 136.3, 137.4.
HRMS: m/z calcd for C12H17BrO: 284.0232; found: 284.0242.

1-Bromo-2-(4-methoxyphenyl)-1-trimethylsilylethene (12) Utilization of 1-Bromo-2-(4-methoxyphenyl)-1-trimethylsilylethene (0.52 g, 1.6 mmol) in pentane (20 mL) was added to a solution of 1,1-bis(trimethylsilyl)-2-(4-methoxyphenyl)ethene (0.28 g, 1.0 mmol) in MeCN (10 mL) and the suspension (Poland); Grant NN 204 238734 and PBZ KBN 118/T09 is thanked gratefully acknowledged.

Acknowledgment

Financial support from the Ministry of Science and Higher Education (Poland); Grant NN 204 238734 and PBZ KBN 118/T09 is gratefully acknowledged

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