

Silene Stereochemistry. 8. The Stereospecific Addition of Methanol to Silenes

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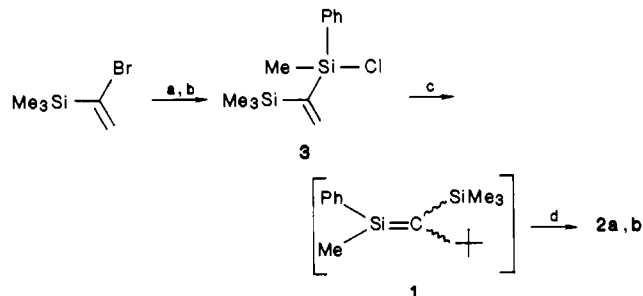
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Despite the large number of reports in recent years on the reactions of both transient and stable silenes,¹ relatively little is known about the stereochemistry or mechanisms of their reactions. We recently reported that the addition of alkoxy-silanes to silenes is a stereospecific syn addition.² Alcohols have been shown to be highly efficient, regio-specific silene traps.¹ Apparently nonstereospecific addition of methanol to certain silenes has been observed,³ and some discussion of a mechanism which could be nonstereospecific has appeared.⁴ In contrast, we wish to report the observation of stereospecific addition of methanol to a silene.

Previous work by our group has demonstrated the applicability of a thermal retro-Diels-Alder reaction for the stereospecific generation of silenes.^{2,5} In our studies involving methoxytrimethylsilane as a silene trap, we determined the relative stereochemistry of the diastereomers which correspond to the methanol adducts of (*E*)- and (*Z*)-1-phenyl-1-methyl-2-neopentyl-2-(trimethylsilyl)silene (**1**).² We therefore synthesized appropriate precursors to these silenes, their anthracene adducts **2a,b**, by the method outlined in Scheme I.

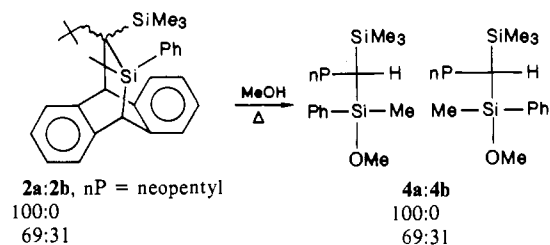
[α -(Trimethylsilyl)vinyl]methylphenylchlorosilane (**3**) was prepared in 62% isolated yield by the reaction of methylphenyldichlorosilane with (α -lithiovinyl)trimethylsilane.⁶ Treatment of a benzene solution of **3** and excess anthracene with *tert*-butyllithium at room temperature, followed by hydrolytic workup, gave a 77:23 mixture of **2a** and **2b**, isolated in 43% yield by column chromatography.⁷ Fractional crystallization of this mixture from hexane gave pure **2a** as colorless needles, leaving

Scheme I^a



^a (a) *tert*-Butyllithium, ethyl ether, -78 °C, 1 h; (b) MePhSiCl₂ (2 equiv), ethyl ether, -78 °C, inverse addition (62% isolated yield); (c) *tert*-butyllithium (1.5 equiv), benzene; (d) anthracene (2 equiv), room temperature, 14 h, workup with saturated NH₄Cl solution, (**2a/2b**, 77:23) 43% isolated yield.

Scheme II



a solution containing a 69:31 mixture of **2a,b**.

The anthracene adducts undergo a facile stereospecific decomposition under sealed tube conditions at temperatures as low as 190 °C to produce (*E*)- or (*Z*)-**1**, the mildest stereospecific route to a silene yet reported. When pure **2a** was subjected to sealed-tube thermolysis⁸ at 205 °C for 1 h in the presence of a 9-fold excess of methanol, the amount of anthracene recovered indicated that 69% decomposition of **2a** had occurred.⁸ The only other product detected was the (*R,R*),(*S,S*) methanol adduct **4a**,² produced in 98% yield based on percent decomposition. A control experiment, identical in every respect except that a 66-fold excess of methanol was used,⁹ gave essentially the same percent decomposition of **2a**, showing that **4a** does not arise through a bimolecular reaction of methanol with **2a**. In addition, heating a 69:31 mixture of **2a,b** with a 19-fold excess of methanol at 160 °C for 1 h gave no reaction. Similar experiments were carried out with the 69:31 mixture of **2a,b** over a temperature range of 190 to 250 °C. The percent decomposition ranged from 15% to 95%, but in all cases a 69:31 mixture of the diastereomeric adducts **4a,b** was obtained. As with the experiments using pure **2a** the percent decomposition of the anthracene adducts was independent of methanol concentration. The relative stereochemistry of the diastereomers was established by coinjection with authentic samples,² using capillary GLC techniques which resolve the diastereomers. These results are summarized in Scheme II.

These results show that, at least under our conditions, the reaction of methanol with silenes is stereospecific. As the addition of the polar σ -bond of alkoxy-silanes to the Si=C double bond has been shown to be stereospecific syn,² it seems likely that the addition of alcohols will show the same stereochemistry. The

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(6) Preparation of [α -(trimethylsilyl)vinyl]methylphenylchlorosilane (**3**). To a solution of 50.0 mmol of (α -bromovinyl)trimethylsilane^{6b} in 150 mL of dry ether stirred at -78 °C under a nitrogen atmosphere was added 52.0 mmol of *tert*-butyllithium in pentane dropwise. After stirring for an additional 2 h at -78 °C the solution was added over a period of 40 min to a solution of 100 mmol of methylphenyldichlorosilane in 200 mL of ether cooled to -78 °C. The mixture was held at -78 °C for an additional hour and then allowed to warm to room temperature overnight. The liquid portion of the mixture was decanted and combined with hexane washings of the precipitate. Solvents were removed by vacuum transfer and fractional distillation of the remaining oil gave 7.89 g, 62% yield, of **3**, bp 82-84 °C at 0.4 torr, as a colorless oil. MS, *m/z* (relative intensity) 254 (1), 239 (73), 155 (74), 145 (95), 121 (95), 73 (100); ¹H NMR (neat with D₂O external lock) δ -0.35 s, 9 H, 0.26 (s, 3 H), 6.06 (s, 2 H), 6.78-6.85 (m, 3 H), 7.09-7.20 (m, 2 H); ¹³C NMR (neat with CDCl₃ external lock) δ (multiplicity of proton off-resonance decoupled spectra) -0.58, (q), 1.37 (q), 127.53 (d), 129.74 (d), 133.38 (d), 134.94 (s), 144.18 (t), 149.51 (s). Anal. Calcd for C₁₂H₁₉Si₂Cl: C, 56.54; H, 7.51. Found: C, 56.35; H, 7.76. (b) Chan, T. H.; Mychajlowski, W.; Ong, B. S.; Harpp, D. N. *J. Org. Chem.* **1978**, *43*, 1526-1532.

(7) (a) The preparation of **2a,b** followed methods that we have previously reported for similar silene anthracene adducts.^{7b} Column chromatography on silica gel with hexane as the solvent permitted separation of the nonvolatile **2a,b** from the volatile components of the reaction mixture in 43% recovered yield. Fractional crystallization from hexane allowed separation of pure **2a** as isomerically pure colorless needlelike crystals, mp 180.8-181.9 °C dec. The ratio of **2a** to **2b** in mixtures was determined by integration of the proton NMR signals at δ 4.19 and 4.02, respectively, which are assigned as the protons on the bridgehead carbons adjacent to silicon. Anal. Calcd for C₃₀H₃₉Si₂: C, 79.23; H, 8.42. Found for a mixture of **2a** and **2b**: C, 78.94; H, 8.55. ¹³C NMR (CDCl₃) δ (**2a**) -0.14 (q, SiMe), 2.6-3.0 (br, SiMe₃), 23.87 (s, C-SiMe₃), 33.13 (q, C(CH₃)₃), 34.84 (s, C(CH₃)₃), 40.41 (d) and 52.06 (d) (bridgehead carbons), 47.69 (t, methylene C), 124-143 (Ar C) (**2b**) 0.29 (q, SiMe), 2.10 (q, SiMe₃), 24.61 (s, C-SiMe₃), 32.69 (q, C(CH₃)₃), 34.36 (s, C(CH₃)₃), 41.31 (d) and 52.42 (d) (bridgehead carbons), 49.89 (t, methylene carbon), 124-143 (aryl carbons). (b) Cheng, A. H.-B.; Jones, P. R.; Lee, M. E.; Roussi, P. *Organometallics* **1985**, *3*, 581-584.

(8) In typical experiments weighed samples of the silene precursors **2a,b** were combined with excess methanol in cyclohexane solvent with hexadecane as the internal standard, degassed, and sealed in 7 mm \times 12 cm Pyrex tubes under vacuum. The tubes were then placed in a vertical pyrolysis oven, preheated to the indicated temperatures for 1-2 h. The experiments testing the effect of the amount of methanol on the percent decomposition were carried out simultaneously. After cooling, the tubes were opened, benzene was added to dissolve the precipitated anthracene, and the product mixtures were analyzed by GLC using a capillary (22-m fused silica SE-54) column and FID detection. Yields and percent decompositions were calculated using response factors relative to the internal standard.

(9) The concentrations of the anthracene adduct **2a** in the experiments with the 9-fold and 66-fold excess of methanol were 0.046 and 0.043 M, respectively.

testing of this hypothesis requires establishing the stereochemistry of the silene precursors **2a,b**. Efforts aimed at the unambiguous determination of this stereochemistry are under way.

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Additivity in Split Cotton Effect Amplitudes of *p*-Phenylbenzyl Ethers and *p*-Phenylbenzoates

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We have been investigating micro methods to determine the site of oligosaccharide linkages^{1,2} on the basis of the exciton chirality method.^{3,4} During the studies we found that Cotton effect amplitudes or *A* values⁵ of the split CD curves of hexopyranoside tri- and tetra-*p*-bromobenzoates respectively, agreed with the sum of *A* values of the three and six dibenzoate units present.⁶ Namely, each benzoate chromophore on a pyranoside or any rigid system, e.g., trichothecenes,⁷ adopts a specific predictable conformation, uniquely defining its position relative to others. However, the lability of benzoates to methanolysis, hydrolysis, transacylation, etc. prevents their direct application to oligosaccharide linkage analysis. An additivity relation has herein been demonstrated for the more stable phenylbenzyl ether chromophores applicable to glycosidic linkage studies.

Preliminary results with *p*-(methoxycarbonyl)benzylates, the chromophores of which are the same as those of benzoates, suggested that additivity may hold.⁴ The *p*-phenylbenzyl chromophore best met the chromophoric criteria of strong UV ϵ , ease of formation, and stability; other chromophores which were abandoned after preliminary studies include *p*-cyanobenzyl and phenylpropynyl ethers. The PhBn ethers absorb at 253 nm and give split CD curves with extrema at 238 nm/260 nm (Figure 1). The Cotton effect *A* values of 15 tri- and tetra-PhBn hexopyranosides were calculated on the basis of additivity with very good agreement. These benzyl chromophores offer the further advantage of being oxidizable to corresponding *p*-phenylbenzoates, also exhibiting additivity, yet with a ca. 5-fold increase in *A* values.

Benzylations were carried out by stirring methyl glycosides, the OH groups of which were appropriately derivatized as methyl ethers, acetonides, etc., in DMF/THF (1:1) with NaH for 1 h, treating with PhBnBr in THF, and stirring 12 h, room temper-

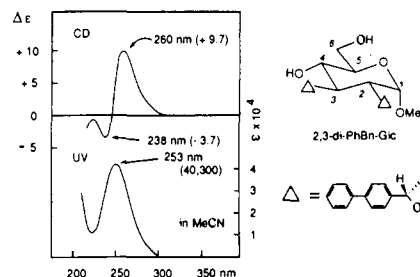
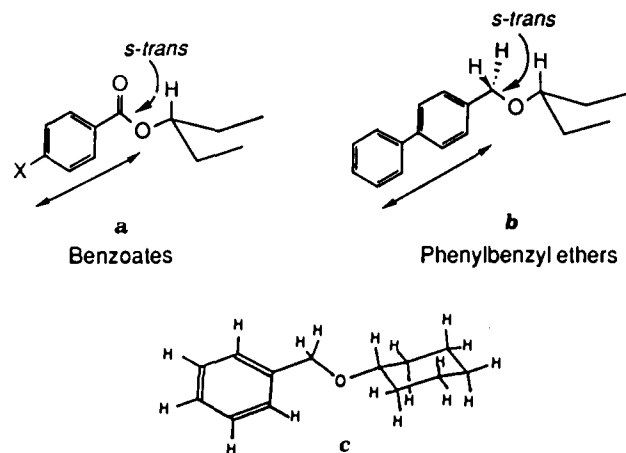


Figure 1. UV and CD of 2,3-di-*p*-phenylbenzyl ether of α -methyl glucoside, 15.4 μ g/mL (29.3 pmol), in CH_3CN .

ature, 70% yield. UV measurements of several PhBn ethers led to the following ϵ values which were used as constants for determining the concentration of UV and CD solutions: mono 20 300, di 40 300, tri 61 000, tetra 82 300.

As in the case of *p*-bromobenzoates⁶ all 18 di-PhBn ethers of α -methyl glucopyranoside, mannopyranoside, and galactopyranoside were prepared to provide the standard *A* values of bichromophoric units (Table I). The additivity relation was next tested by making all possible tri- and tetra-glucoside benzylates (Table II). Very good agreement is seen throughout between A_{obsd} and A_{calcd} in all 15 cases, despite the added possibility of conformational mobility, e.g., for **19**, A_{obsd} is -16.4, whereas A_{calcd} is +13.4 (for 2,3-, see **1**) - 25.4 (for 3,4-, **4**) - 5.0 (for 2,4-, **2**) = -17.0. Furthermore, the values are sufficiently different within each sugar class to be characteristic of the substitution pattern. This additivity relation suggests that, as in the case of benzoates (a), benzyl ethers favor an *s-trans* conformation around the C-O bond in Ph-CH₂-O-CH- (b) and that the 6-benzyl group with an additional C-C bond as well as other benzyl groups prefer specific conformations in each sugar.⁸ In Table I, conformations



of 6-PhBn groups are depicted to reflect the measured chirality signs of dibenzylate units involving this group. Conformation **b** is corroborated by molecular mechanics calculation (MM2) of (benzyloxy)cyclohexane which show that in its stablest conformation, **c**, the two benzyl methylene hydrogens flank the carbonyl hydrogen.

The 1(e),2(e)- and 1(e),2(a)-di-*p*-bromobenzoates with dihedral angles of 60° have absolute *A* values of ca. 62,⁶ but values for corresponding dibenzyl units vary from 3.9 (7, Table I) to 25.4 (4). One reason, although not the only one, is that the long PhBn chromophore extends further from the pyranose ring than the BrBz chromophore, resulting in a longer interchromophoric distance *R* in *ea* than in *ee* (it has been shown³ that *A* is inversely proportional to the square of *R*). Although differences exist, the benzylates and benzoates can thus be handled in a similar manner in exciton chirality problems.

The longer *R* in PhBn ethers in comparison to BrBz leads to considerably smaller *A* values, a typical case being mannoside

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(5) *A* (amplitude) values denote the difference in $\Delta\epsilon$ of split extrema; the sign is positive when the signs of first (longer wavelength) and second Cotton effects of the split CD curves are, respectively, positive and negative, and vice versa.

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