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1,2-*Bis*-(Trialkylsilyl)ethanes: Synthons For Vicinal Dications?

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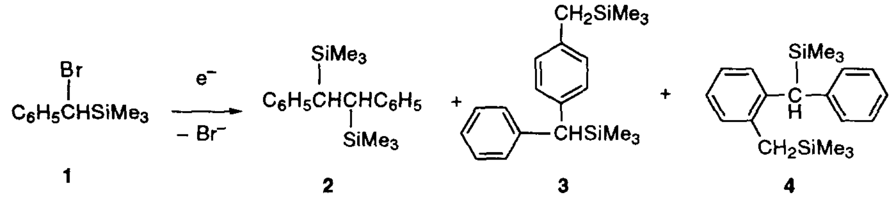
Abstract: Anodic oxidation of 1,2-*bis*-(trimethylsilyl)-1,2-diphenylethane in methanol affords a 65:35 mixture of 1,2-dimethoxy-1,2-diphenylethane (*dl:meso* = 10:1 and diphenylacetaldehyde dimethylacetal. The results can be interpreted in terms of a 1,2-diaryl-2-methoxyethyl cation, which can undergo either nucleophilic attack by solvent or rearrangement to a 2,2-diaryl-1-methoxyethyl cation. Experiments testing the generality of the reaction are described.

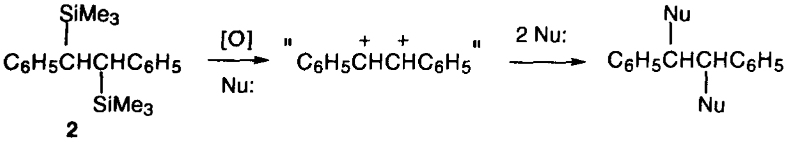
In the course of a study of the electrochemical formation and dimerization of a series of *alpha*-substituted benzyl radicals, we had occasion to carry out the electrochemical reduction of *alpha*-trimethylsilylbenzyl bromide (**1**).[1] The reaction produced the corresponding benzyl radical, which then coupled to afford a series of dimers **2**, **3**, and **4** in quantitative yield in the ratios 72:19:9, respectively (eq 1). We were intrigued by the juxtaposition of two highly electropositive trimethylsilyl groups on adjacent carbon atoms in **2**.



(1)

We were aware that several investigators had shown that benzyl silanes (**5**) are readily electrochemically oxidized to the corresponding benzyl carbocations (**6**), which then suffer attack by nucleophilic constituents of the electrolysis medium (eq 2).[2,3] 1,2-disilanes such as **2** might therefore be regarded as potential synthons for 1,2-dications (eq 3). We report here experiments which test and confirm this hypothesis but also show its limitations.

$$\underset{\mathbf{5}}{C_6H_5CH_2SiMe_3} \xrightarrow[\text{Nu:, }-\text{NuSiMe}_3]{-2e^-} \underset{\mathbf{6}}{C_6H_5CH_2^+} \xrightarrow{\text{Nu:}} \underset{\mathbf{7}}{C_6H_5CH_2Nu} \qquad (2)$$

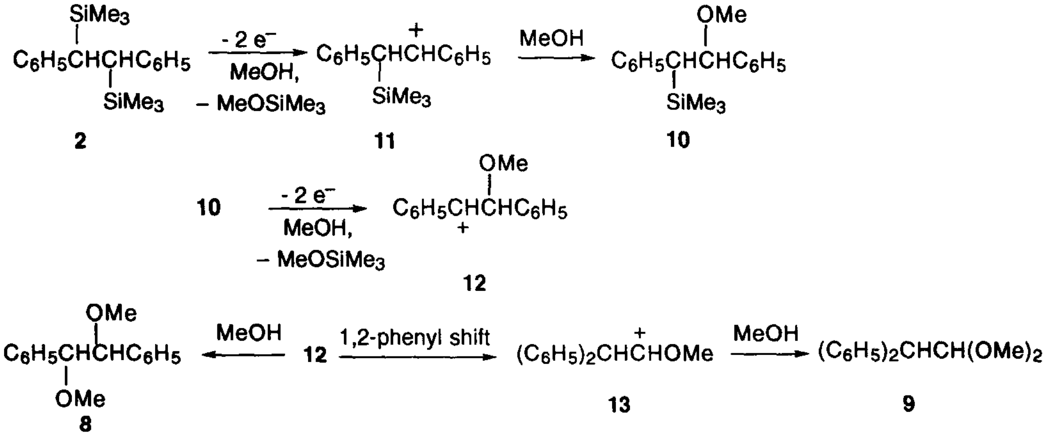


$$\underset{\mathbf{2}}{C_6H_5\overset{SiMe_3}{\overset{|}{C}}H\underset{\underset{SiMe_3}{|}}{C}HC_6H_5} \xrightarrow[\text{Nu:}]{[O]} "C_6H_5\overset{+}{C}H\overset{+}{C}HC_6H_5" \xrightarrow{2\text{ Nu:}} C_6H_5\overset{Nu}{\overset{|}{C}}H\underset{\underset{Nu}{|}}{C}HC_6H_5 \qquad (3)$$

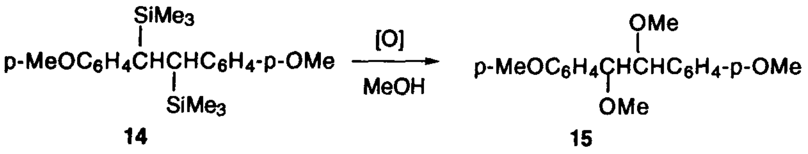
Our original synthesis[1] was inconvenient for preparation of multigram quantities of **2**. Although **2** could be prepared in larger quantities by reductive dimerization of **1** using zinc and catalytic amounts of dicyclopentadienyltitanium(IV) chloride,[4,5] the product was still contaminated by **3** and **4**. Reductive *bis*-

silylation of stilbene[6] with lithium and Me_3SiCl in HMPA [$(Me_2N)_3PO$] proved to be a more convenient route. The major product is the less soluble *meso*-diastereomer of **2**, which crystallizes in pure form from the crude product; it is readily prepared in 20 g quantities by this procedure. *Meso*- and *dl*-**2** exhibit cyclic voltammetric anodic peak potentials at +0.97 and +1.17 V (vs. Ag/0. 1 M $AgNO_3$),[7] respectively, at a glassy carbon electrode in CH_3CN containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) as supporting electrolyte. Controlled-potential electrochemical oxidation of either diastereomer of **2** at a carbon cloth anode in MeOH/0.1 M TBAHFP containing excess $NaHCO_3$ consumed 4.1 Faradays/mol of **2** and afforded a mixture of 1,2-dimethoxy-1,2-diphenylethane (**8**)[8] (*dl*:*meso* = 10:1) (65%) and diphenylacetaldehyde dimethylacetal (**9**) (35%) (Scheme 1). The stereochemistry of **8** was established by methylation of authentic *meso*-hydrobenzoin (KOH, MeI, DMSO, 5 min, r.t.); the product of this reaction corresponded to the minor (longer gc retention time) isomer of **8** from the electrolysis. Monitoring of the reaction during electrolysis showed that as **2** is consumed, a new substance, the methoxysilane **10**, is formed and then rapidly consumed by further electrolysis. If $NaHCO_3$ is omitted from the electrolysis medium, the electrolysis mixture becomes highly acidic as electrolysis proceeds, and degradation products of **8** and **9** are produced. Formation of **8** and **9** presumably involves a sequence involving oxidation to a benzylsilane radical cation. Nucleophilic removal of the silyl group and oxidation of the resulting benzyl radical afford cation **11**, which is stabilized not only by the phenyl group on the carbon to which it is attached, but also by the potent β-silicon effect[9] exerted by the remaining trimethylsilyl group. Reaction of **11** with the nucleophilic solvent and oxidation of the resulting **10** affords cation **12**; this species has two modes of reaction, reaction with methanol to afford **8** or rearrangement by phenyl migration to afford a new oxygen-stabilized cation (**13**); reaction of **13** with methanol affords acetal **9**.

Scheme 1

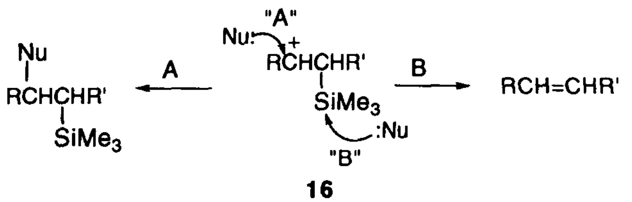


This mechanistic scheme is susceptible to experimental test. Stabilization of **12** against rearrangement should result in an increased proportion of products of type **8**. The *p,p'*-dimethoxy disilane **14** was prepared by reductive silylation of the corresponding stilbene, which in turn was prepared by the Wittig reaction. It was expected that the *p*-methoxy group should stabilize the intermediate corresponding to **12**. Indeed, the 1,2-dimethoxy compounds *meso*- and *dl*-**15** (1:1 *dl*:*meso* ratio) were the *only products* formed upon anodic oxidation of **14** (eq 4). The structure and stereochemistry of **15** were assigned by 4,5-*trans*-oxazaborolidine-catalyzed reduction[10a] of anisoin to afford the corresponding *meso* diol, mp 163-168° (lit[10b] mp 168-170°), followed by methylation of the latter with methyl iodide and KOH in dimethylsulfoxide. The product of this reaction corresponded (NMR spectrum) with the isomer of **15** of longer gc retention time from the electrolysis. No trace of the acetal analogous to **9** was detectable by GC-MS or NMR spectroscopy. Continued electrolysis past the point at which 4 Faraday/mole of **14** had been consumed, followed by aqueous hydrolysis, caused successive conversion of **15** into, first, *p*-methoxybenzaldehyde, and finally *p*-methoxybenzoic acid.



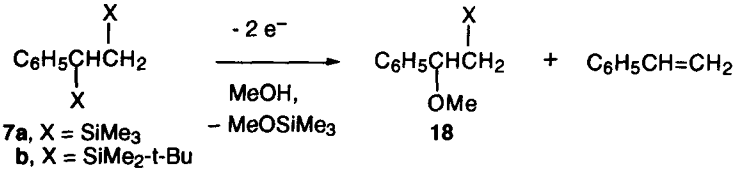
$$\underset{\mathbf{14}}{\text{p-MeOC}_6\text{H}_4\overset{\text{SiMe}_3}{\text{C}}\text{H}\underset{\text{SiMe}_3}{\text{C}}\text{HC}_6\text{H}_4\text{-p-OMe}} \xrightarrow[\text{MeOH}]{[\text{O}]} \underset{\mathbf{15}}{\text{p-MeOC}_6\text{H}_4\underset{\text{OMe}}{\overset{\text{OMe}}{\text{C}}}\text{HCHC}_6\text{H}_4\text{-p-OMe}} \quad (4)$$

Scheme 2



16

Nucleophilic attack on *beta*-silyl carbocation **16** can take place at two sites (Scheme 2). Our results described above show that attack at carbon (path A) is the primary mode of reaction with diaryl species (R = R' = aryl) in methanol. A different mode of reaction is observed with the unsymmetrical disilane **17a**, which was prepared by the reaction of lithium on styrene in the presence of trimethylchlorosilane.[11] Controlled-potential oxidation of **17a** at +0.8 V afforded a 7:1 mixture of styrene and methoxysilane **18a** (eq 5). [**18a** is stable at the electrolysis potential; continued electrolysis did however result in anodic conversion of styrene to a mixture of monomeric and dimeric methoxylated substances.[12,13]] The ratio of path A to path B thus appears to depend on the degree of aryl substitution. Indeed, when R = R' = alkyl, path B is the exclusive path.[14]



$$\underset{\substack{\mathbf{17a},\ \text{X = SiMe}_3\\ \mathbf{b},\ \text{X = SiMe}_2\text{-t-Bu}}}{\text{C}_6\text{H}_5\underset{\text{X}}{\overset{\text{X}}{\text{C}}}\text{HCH}_2} \xrightarrow[\text{MeOH, - MeOSiMe}_3]{-2\,e^-} \underset{\mathbf{18}}{\text{C}_6\text{H}_5\underset{\text{OMe}}{\overset{\text{X}}{\text{C}}}\text{HCH}_2} + \text{C}_6\text{H}_5\text{CH=CH}_2 \quad (5)$$

X = SiMe$_3$	13	87
X = SiMe$_2$-t-Bu	> 99.5	< 0.5

It seemed likely that this side reaction could be minimized or eliminated[15] by varying the groups attached to silicon. It is known that the ratio of path A to path B is sensitive to steric effects. In one study, attack was exclusively at silicon for R = trimethylsilyl, 60% at silicon and 40% at carbon for R = triphenylsilyl, and exclusively at carbon for R = t-butyldimethylsilyl or triisopropylsilyl.[15] Similarly, attack of acetonitrile on benzyltrimethylsilane radical cation is retarded 10,000-fold by bulky groups on silicon.[16] Gratifyingly, anodic oxidation of the *bis*-t-butyldimethylsilyl derivative **17b** in methanol was found to afford a >199:1 ratio of **18** to styrene, in contrast to the 1:7 ratio observed with the trimethylsilyl derivative. Thus it appears that steric effects can indeed be used to force the anodic behavior of these 1,2-disilanes into the path A channel.

We have also explored the reactions of **2** with several other electrophilic reagents. *Meso-* and *dl*-**2** each was found to react instantly with bromine in $CHCl_3$ at room temperature to afford in quantitative yield a single stereoisomer of 1,2-dibromo-1,2-diphenylethane (**19**), shown by ^1H NMR spectroscopy to be the *meso* isomer.[1,17] Unfortunately, **2** was found to be unreactive toward a number of other reactive electrophiles, e.g., nitronium tetrafluoroborate or acetic anhydride/BF_3-Me_2S. In each case the disilane could be recovered unchanged, although in a few reactions substances were formed in low yield which were produced by electrophilic substitution on one of the arene rings of **2** without disruption of the 1,2-disilyl moiety. Bromine apparently does not act as an electrophile toward **2**; rather, it apparently acts as an oxidizing agent, removing an electron from **2** to afford a radical cation, which then suffers desilylation to a neutral radical and attack by bromine (or oxidation of the radical to a carbocation followed by attack by bromide to afford **19** after a second such sequence). In other words, the reaction of **2** with Br_2 is apparently closely related to its anodic oxidation.

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REFERENCES

(1) Fry, A. J.; Porter, J. M.; Fry, P. F. *J. Org. Chem.* **1996**, *61*, 3191.
(2) Yoshida, J.-i.; Murata, T.; Isoe, S. *Tetrahedron Lett.* **1986**, *27*, 3373.
(3) Koizumi, T.; Fuchigami, T.; Nonaka, T. *Bull. Chem. Soc. Japan* **1989**, *62*, 219.
(4) Mayers, B., Fry, A. J., unpublished research.
(5) Yanlong, Q.; Guisheng, L.; Huang, Y.-Z. *J. Organomet. Chem.* **1990**, *381*, 29.
(6) Dunogues, J.; Calas, R.; Duffaut, N.; Lapouyade, P.; Gerval, J. *J. Organomet. Chem.* **1969**, *20*, P20.
(7) This reference electrode is +0.35 V vs sce.
(8) (a) Fischer, H. O. L.; Taube, C. *Chem. Ber.* **1926**, *59*, 851; (b) Irvine, J. C.; Weir, J. *J. Chem. Soc.* **1907**, *91*, 1390.
(9) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496.
(10) (a) Prasad, K. R. K.; Joshi, N. N. *J. Org. Chem.* **1996**, *61*, 3888; (b) Buck, J. S.; Jenkins, S. S. *J. Am. Chem. Soc.* **1929**, *51*, 2163.
(11) Weyenberg, D. R.; Toporcer, L. H.; Bey, A. E. *J. Org. Chem.* **1965**, *30*, 4096.
(12) Schäfer, H.; Steckhan, E. *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 518.
(13) Steckhan, E.; Schäfer, H. *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 472.
(14) Yoshida, J.-I., private communication.
(15) Hagen, G.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 4954.
(16) Dockery, K. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. *J. Am. Chem. Soc.* **1997**, *119*, 1876.
(17) McCullough, J. D. *J. Am. Chem. Soc.* **1940**, *62*, 480.

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