(30 mL), and the organotin compounds were extracted with hexane (3 × 30 mL). NMR analysis of the acetonitrile portion revealed a 10:1 ratio of **63:27**. The products consisting of **63** (76%) and **27** (7%) were distilled to give **63**: IR (film) 3081, 2982, 2936, 2920, 1769 s (C=O), 1642 (CH=CH$_2$), 1170, 1026 cm^{-1}; ^{1}H NMR δ 1.48–1.59 (m, 1 H), 1.86–2.28 (m, 4 H), 2.35–2.46 (m, 1 H), 2.49–2.59 (m, 1 H), 4.15–4.24 (m, 1 H, CH*H*O), 4.36 (dt, *J* = 8.8, 2.6 Hz, 1 H, C*H*HO), 5.01–5.11 (m, 2 H, C=CH$_2$), 5.72–5.87 (tdd, *J* = 17, 10.4, 6.6 Hz, 1 H, C*H*=CH$_2$); mass spectrum *m/e* 140 (M$^+$, 0.5), 86 (100), 67 (12), 55 (33); exact mass calcd for C$_8$H$_{12}$O$_2$ *m/e* 140.0837, found *m/e* 140.0860.

3-But-3-enylspirocyclohexyl-1,5'-butyrolactone (64). Prepared by reaction of selenocarbonate **12** with allyltributyltin as described above for the preparation of **63**: IR (film) 3078, 2938, 2862, 1767 s (C=O), 1451, 1202, 1132, 951 cm^{-1}; ^{1}H NMR δ

1.26–1.75 (m, 13 H), 2.00–2.33 (m, 3 H), 2.65–2.78 (m, 1 H), 5.01 (d, *J* = 9.9 Hz, 1 H, *trans*-CH=CH*H*), 5.06 (d, *J* = 15.8 Hz, 1 H, *cis*-CH=CH*H*), 5.72–5.86 (m, 1 H, C*H*=CH$_2$); exact mass calcd for C$_{13}$H$_{20}$O$_2$ *m/e* 208.1463, found *m/e* 208.1585.

The Electrochemical Reductive Trimethylsilylation of Aryl Chlorides: A Good Route to Aryltrimethylsilanes and a Novel Route to Tris(trimethylsilyl)cyclohexadienes[†]

Michel Bordeau,* Claude Biran,* Pierrette Pons, Marie-Pierre Léger-Lambert, and Jacques Dunoguès*

Laboratoire de Chimie organique et organométallique (URA 35 CNRS) Université Bordeaux I, F-33405 Talence, France

The electroreductive trimethylsilylation of aryl chlorides R–C$_6$H$_4$Cl (R = H, *o*-Me, *m*-Me, *p*-Me) can be controlled so as to give, in good yields, either the corresponding aryltrimethylsilanes (products of the reduction of the carbon–chlorine bond) or mixtures of *cis*- and *trans*-tris(trimethylsilyl)cyclohexa-1,3(or 1,4)-dienes (products of the successive reduction of the carbon–chlorine bond and the partial reduction of the aromatic ring). Which of the two products is formed depends upon how much electricity is passed during the constant current electrolysis, in a one-compartment cell equipped with a sacrificial aluminum anode, of an aryl chloride in 80:20 THF/HMPA solution that also contains Et$_4$NBF$_4$ as the supporting electrolyte and excess Me$_3$SiCl. The electroreductive trimethylsilylation of phenyltrimethylsilane gave, in 62% yield, a mixture of three 3,5,6-tris(trimethylsilyl)-cyclohexa-1,3-dienes, of which the trans, pseudo a-a isomer constituted 89%. Such products cannot be obtained by the chemoreductive trimethylsilylation of phenyltrimethylsilane. The electroreductive trimethylsilylation of benzene and toluene produced the corresponding bis(trimethylsilyl)cyclohexa-1,4-dienes. The regio- and stereochemical outcomes of the electroreductive trimethylsilylation of the various substrates can be explained in terms of the electronic and steric effets of the substituents originally attached to the aromatic ring and the steric effects of the trimethylsilyl groups that are subsequently attached.

Introduction

In reporting the results of our studies of the use of organosilicon compounds in organic synthesis, we have described the application of allyl-, vinyl-, and phenylsilanes in the preparation of functionalized organic compounds.[1,2] We have since focused our efforts on developing electrochemical methods for silylating aryl halides R–C$_6$H$_4$–X (R = H, *o*-, *m*-, *p*-Me; X = Cl, Br), benzene, toluene, and phenyltrimethylsilane. Such methods would obviate the use of chemical reducing agents like metallic lithium or sodium.

Only a few reports of the electroreductive silylation of organic halides have so far appeared. Shono et al.[3] obtained benzyltrimethylsilanes and allyltrimethylsilanes by the electrolysis of benzyl chlorides and allyl halides, respectively, in the presence of chlorotrimethylsilane (Me$_3$SiCl). The electrolyses were performed in a two-compartment cell equipped with platinum electrodes. However, when the diaphragm that separated the anodic

and cathodic compartments was removed, both trimethylsilylation and chlorination took place. Yoshida et al.[4] succeeded in electroreductively silylating allyl chlorides, vinyl halides, and aryl iodides. However, attempts to electroreductively silylate aryl chlorides (the least expensive aryl halides) and alkyl halides failed. In any event, the method could not be easily modified so as to permit preparative-scale silylations.

As for our work, we have described a very selective electroreductive silylation of polychloromethanes[5] and have reported the first results of attempts to electroreductively silylate benzyl chloride, phenyl bromide, and phenyl

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(3) Shono, T.; Matsumura, Y.; Katoh, S.; Kise, N. *Chem. Lett.* 1985, 463.

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Table I. Synthesis of Aryltrimethylsilanes by the Electroreductive Trimethylsilylation of Aromatic Bromides and Chlorides[a]

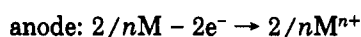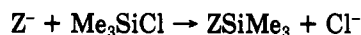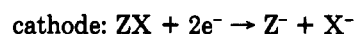| ArX		quantity of ArX (mmol)	[Me₃SiCl]/[ArX][b]	product arylsilane		yield (%)	
						by GLC	isolated
PhBr	1	14	6	PhSiMe₃	(5)	84	76
PhBr	1	14	8.3	PhSiMe₃	(5)	60[c]	50
PhCl	2	20	6	PhSiMe₃	(5)	75	70
o-CH₃C₆H₄Br	3o	13	8.6	o-CH₃C₆H₄SiMe₃	(6o)	72	63
o-CH₃C₆H₄Cl	4o	13	9.3	o-CH₃C₆H₄SiMe₃	(6o)	70	65
m-CH₃C₆H₄Cl	4m	13	9.3	m-CH₃C₆H₄SiMe₃	(6m)	80	76
p-CH₃C₆H₄Cl	4p	13	9.3	p-CH₃C₆H₄SiMe₃	(6p)	70	65

[a] Anode: Al. Solvent: 80:20 THF/HMPA. Supporting electrolyte: Et_4NBF_4 (sufficient to yield a 0.02 M solution). Constant current: 50 mA. Temperature: rt. Quantity of electricity passed: 2.2 $F \cdot mol^{-1}$. [b] Molar ratio. [c] Anode: Mg. Solvent: DMF. Supporting electrolyte: $MgCl_2$ (sufficient to yield a 0.02 M solution). Constant current: 50 mA. Temperature: rt. Quantity of electricity passed: 2.2 $F \cdot mol^{-1}$.

chloride.[6a] More recently, Fry[7] succeeded in silylating benzyl chlorides and bromides by a method similar to that which we describe below.

As a followup to two preliminary papers,[6b,c] herein we describe in detail a very practical method for the electroreductive trimethylsilylation of aryl chlorides and simple arenes.[5,6a,d] The electrolysis apparatus consisted of a one-compartment cell fitted with a sacrificial aluminum anode and a stainless steel grid or carbon-cloth cathode. Tetraethylammonium tetrafluoroborate (sufficient to yield a 0.02 M solution) served as the supporting electrolyte. The solvent was 80:20 THF/HMPA. The electrolyses were performed under conditions of constant current in the presence of excess Me₃SiCl. Using the work of Perichon et al.[8] as a model, we attempted to develop a method that had the potential to be used for industrial-scale syntheses.

In the electrolysis of organic halides, the carbanions that are generated by cathodic reduction are trapped by Me₃SiCl, a good electrophile that is present in excess in the reaction medium:

$$\text{cathode: } ZX + 2e^- \rightarrow Z^- + X^-$$

$$Z^- + Me_3SiCl \rightarrow ZSiMe_3 + Cl^-$$

$$\text{anode: } 2/nM - 2e^- \rightarrow 2/nM^{n+}$$

The reaction that is depicted is possible because Me₃SiCl is not electroreduced at cathodic potentials more positive than −3.0 V vs SCE.[9] Most alkyl and aryl halides are more easily reduced.[10] Moreover, because oxidation of the metal anode and concomitant formation of the corresponding metal halide prevents halogenation side reactions, the use of a diaphragm to separate the anodic and cathodic compartments is not necessary.

Results and Discussion

What the products of the electroreductive trimethylsilylation of aryl chlorides R–C₆H₄–Cl (R = H, o-Me, m-Me, p-Me) are is largely dependent upon how much
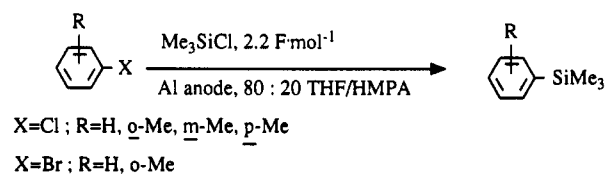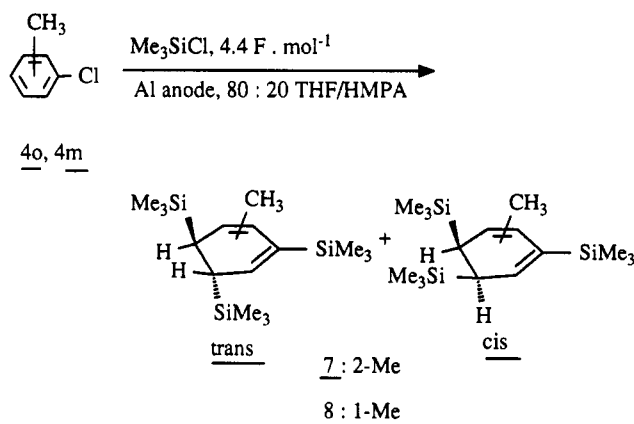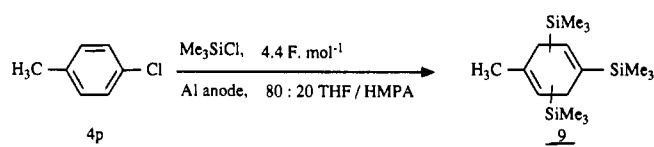
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Scheme I

X=Cl ; R=H, o-Me, m-Me, p-Me

X=Br ; R=H, o-Me

Scheme II

4o, 4m

trans   7 : 2-Me

cis   8 : 1-Me

Scheme III

4p

Table II. Results of Applying the Best-Known Chemical Methods for Synthesizing Aryltrimethylsilanes from Aromatic Chlorides and Bromides

ArX	ArSiMe₃	% yield of ArSiMe₃			
		Mg (i) or ArMgX (j)/Me₃SiCl (THF or Et₂O)[13–15]	Mg/ Me₃SiCl HMPA[16]	Na/ Me₃SiCl toluene[15–17]	ArLi/ Me₃SiCl THF[18]
1	5	76 (j)			67
2	5		87	90	
3o	6o				55
3m	6m	50–56 (j)			53
3p	6p	50–56 (j)			53
4o	6o		80	87	
4m	6m	77 (i)	85	85	
4p	6p	77 (i)	80	87	

electricity is used for the electrolysis. When an aluminum bar is used as the anode, passage of up to 2.2 $F \cdot mol^{-1}$ of electricity through a solution of an aryl chloride and excess Me₃SiCl in 80:20 THF/HMPA leads to the formation of the corresponding aryltrimethylsilane (the product of the reduction of the carbon–chlorine bond). Although highly negative cathodic potentials are required,[11] when up to 4.4
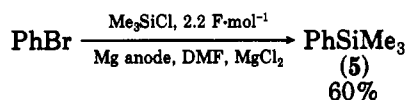
Table III. Electroreductive Trimethylsilylation of Aryl Chlorides and Simple Arenes[a]

starting material	electricity passed (F·mol^{-1})	products	yield[b] (%) by GC	yield[b] (%) isolated	no. of isomers (isomeric ratio)[c]
4o	4.4	7	84	71	2 (*trans:cis* = 92:8)
		6o	12		
4m	4.4	8	90	76	2 (*trans:cis* = 75:25)
		6m	8		
4p	4.4	9	34[d]		3
		6p	46[d]		
PhSiMe$_3$ (5)	2.0	10	62	48	3 (*trans* a–a:*cis* a–e:*cis* a–e = 89:6:5)
		11	14	9	2 (80:20 mixture)
		5	24		
PhH (12)	2.2	14	75	62	2 (*trans:cis* = 70:30)
PhCH$_3$ (13)	2.2	15	70	58	1 (*trans*)

[a] Quantity of starting material: 14 mmol ([Me$_3$SiCl]/[arene] = 11). Anode: Al. Solvent: 80:20 THF/HMPA. Supporting electrolyte: Et$_4$NBF$_4$ (sufficient to yield a 0.02 M solution). Constant current: 50 mA. Temperature: rt. [b] That the sum of the % yields is not 100 reflects the fact that trace amounts of bis(trimethylsilyl)arenes were also produced. [c] Determined by GC, MS, 270-MHz ^{1}H NMR, and 67.88-MHz ^{13}C NMR analysis. [d] A very complex reaction mixture was produced (see below).

F·mol^{-1} are passed, a mixture of *cis*- and *trans*-tris(trimethylsilyl)cyclohexadienes (products of the successive reduction of the carbon–chlorine bond and the partial reduction of the aromatic ring) is produced. In the mixture of products, the trans isomer predominates. What occurs is summarized in Schemes I–III.

It should be noted that when DMF was the solvent, only bromobenzene could be trimethylsilylated, using a magnesium bar as the anode and MgCl$_2$ as the supporting electrolyte, i.e.

$$\text{PhBr} \xrightarrow[\text{Mg anode, DMF, MgCl}_2]{\text{Me}_3\text{SiCl, 2.2 F·mol}^{-1}} \text{PhSiMe}_3$$
$$\text{(5)}$$
$$60\%$$

(11) The half-wave reduction potentials ($E_{1/2}$ vs SCE) of some aryl halides are as follows: PhBr, −2.53 V (Au cathode, DMF solution); PhCl, −2.71 V (Au cathode, DMF solution); and *m*-MeC$_6$H$_4$Cl, −2.80 V (Zn-coated stainless steel cathode, DMF solution. See: Rabemantsea, A. Thèse d'Université, Université Pierre et Marie Curie, Paris, 1986. Several values for the half-wave reduction potential of benzene have been reported. These are −3.42 V (by direct measurement, −60 °C in DME solution containing Bu$_4$NPF$_6$ supporting electrolyte),[12a] −3.38 V (by direct measurement, −90 °C in THF solution containing Bu$_4$NPF$_6$ supporting electrolyte),[12b] −3.31 V (by direct measurement, −90 °C in DME solution containing Bu$_4$NClO$_4$ supporting electrolyte),[12c] −3.31 V (by extrapolation from the reduction potentials of 20 hydrocarbons),[12d] and −3.5 V (by calculation from the reduction potential of naphthalene).[12e]
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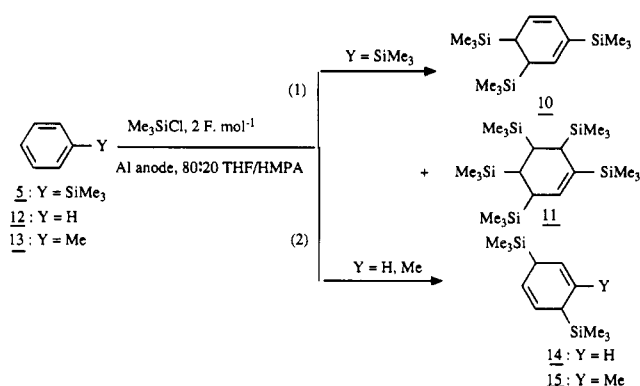
Scheme IV

Table I summarizes the results of attempts to synthesize aryltrimethylsilanes by passing 2.2 F·mol^{-1} of electricity through solutions of the appropriate aryl halides in 80:20 THF/HMPA.

In Table II are summarized for purposes of comparison the results of applying the best-known chemical methods for preparing aryltrimethylsilanes from chloro- and bromoarenes.

When the two sets of data are compared, it becomes clear that, except when PhCl is the starting material, both the electrochemical method described here and the various chemical methods give comparable yields of aryltrimethylsilanes. Furthermore, it should be possible to modify the former so as to make it economically competitive for large-scale syntheses.

Continued electrolysis (as much as 4.4 F·mol^{-1} of electricity were passed) of both *o*-chlorotoluene (4o) and *m*-chlorotoluene (4m) produced, relatively cleanly and in fairly high yield, mixtures of previously unknown *cis*- and *trans*-methyltris(trimethylsilyl)cyclohexa-1,3-dienes (7 and 8, respectively, cf. Scheme II and Table III). In the mixtures, the respective *trans*-isomers predominated.
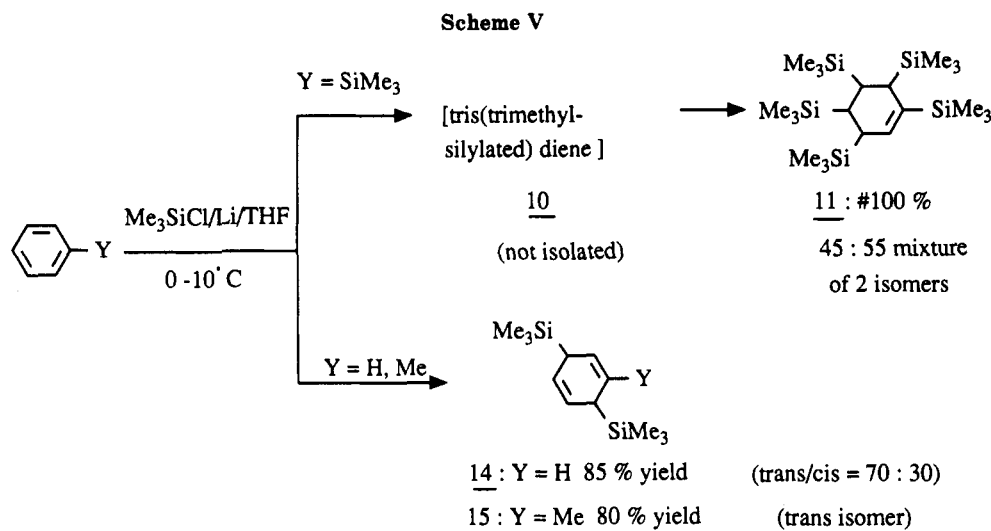
As the results of analysis by GLC, MS, 270-MHz ^{1}H NMR, and 67.88-MHz ^{13}C NMR showed,[19] 4o gave a 71% yield of a 92:8 mixture of *trans*- and *cis*-7, whereas 4m gave a 76% yield of a 75:25 mixture of *trans*- and *cis*-8.

Before the conditions for the electrolysis of 4o, 4m, and 4p were optimized, considerable aromatization of the tris(trimethylsilyl)cyclohexadienes was observed. However, except in the case of *p*-chlorotoluene (4p), that undesirable side reaction could be almost totally suppressed.

The electroreductive trimethylsilylation of *p*-chlorotoluene (4p) proved to be more difficult to achieve and gave a more complex mixture of products than did those of the other tolyl chlorides (Scheme III and Table III). Thus, 4p gave a 34% yield of a mixture of three methyltris(trimethylsilyl)cyclohexa-1,4-dienes 9 (not isolated) while 46% of the intermediate aryltrimethylsilane remained unconsumed. Undesired aromatic products, particularly bis(trimethylsilyl)toluenes, were formed even after the conditions of electrolysis were optimized. Continued electrolysis (as much as 8 F·mol^{-1} was passed) gave results which were too complex to be interpreted.

As expected, a mixture of *cis*- and *trans*-tris(trimethylsilyl)cyclohexa-1,3-dienes (10) was obtained in good yields by passing only 2 F·mol^{-1} of electricity through a solution of PhSiMe$_3$ (5) and excess Me$_3$SiCl in 80:20 THF/HMPA (Scheme IV, Table III). It thus is clear that not only can the electroreductive trimethylsilylation of aryl

(19) Bordeau, M.; Biran, C.; Pons, P.; Léger, M.-P.; Dunoguès, J. To be published.

Scheme V

$\underline{10}$
(not isolated)

$\underline{11}$: #100 %
45 : 55 mixture
of 2 isomers

$\underline{14}$: Y = H   85 % yield   (trans/cis = 70 : 30)
$\underline{15}$: Y = Me 80 % yield   (trans isomer)

halides be controlled, but also so can that of other arenes. In both cases, the reaction can be arrested at the stage where easily reducible conjugated dienes are the products. In the case of 5, the reaction was, again, highly stereoselective.

An 80:20 mixture of two 1,3,4,5,6-pentakis(trimethylsilyl)cyclohex-1-enes (11), products of the electroreductive trimethylsilylation of compounds 10, was also formed, but in only 14% yield. The spectra and other physical properties of compounds 11 and those of the pentakis(trimethylsilyl)cyclohexenes obtained by the chemoreductive trimethylsilylation of PhSiMe$_3$[20,21] are very similar or identical. No attempts were made to optimize the yields of compounds 11 because they could already be conveniently prepared by chemical methods.

On the other hand, the electroreductive trimethylsilylation of "simple" arenes like benzene (12) and toluene (13) yielded bis(trimethylsilyl)cyclohexa-1,4-dienes (Scheme IV, reaction (2) and Table III). Benzene gave a 70:30 mixture of trans-14/cis-14, whereas toluene gave only trans-15.

For purposes of comparison, the results of the chemoreductive trimethylsilylation of the same species[20-22] are shown in Scheme V.

The chemoreductive trimethylsilylation of chlorotoluenes by Me$_3$SiCl and Li in THF has never been studied. Thus, there exists no basis for comparison between it and the electroreductive trimethylsilylation of chlorotoluenes. However, a comparison of the results of the electroreductive trimethylsilylation of PhY (Y = H, Me, SiMe$_3$) and those of the chemoreductive trimethylsilylation of the same compounds is possible (cf. Schemes IV and V). From such a comparison it can be clearly seen that *the electroreductive trimethylsilylation of PhSiMe$_3$ can be relatively easily controlled so as to yield, selectively, tris(trimethylsilylated) conjugated dienes. Similar control of the chemoreductive trimethylsilylation of PhSiMe$_3$ cannot be exercised.* Consequently, only pentakis(trimethylsilyl)cyclohexenes are isolated.

The well-known Birch reduction of arenes involves solvated electrons that are generated by dissolving alkali or alkaline earth metals in liquid NH$_3$, amines, or HMPA.[23]

Scheme VI
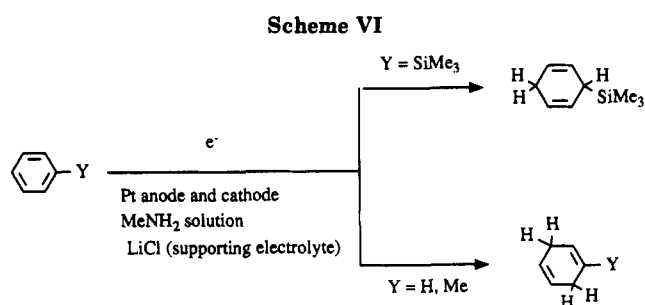
Mechanistically similar reductions have been effected by the electrolysis of arenes in solutions that also contain Li$^+$ or Na$^+$ electrolytes and a proton donor.[24-29] Cathodes of platinum, aluminum, graphite or vitreous carbon and solvents like liquid ammonia, methyl- or ethylamine, ethylenediamine, HMPA, or diglyme have been employed in such electrolyses. Under such conditions, the cathodic reaction generates solvated electrons, which are the actual reducing agents.

The electroreduction of arenes has also been effected at a mercury cathode in solutions that contain tetraalkylammonium salt electrolytes.[29,30]

The products of electroreduction are usually the corresponding cyclohexa-1,4-dienes. However, the regioselectivity of the successive protonations of the negatively charged intermediates depends on the nature of the substituent Y. For example, the electroreduction of toluene

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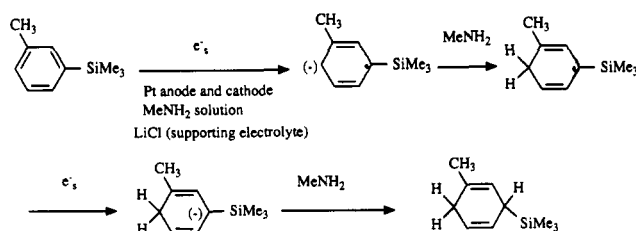
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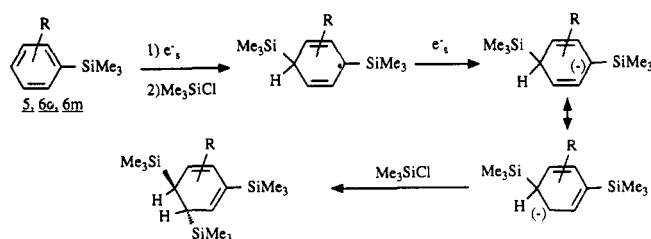
Scheme VII

Scheme VIII

at a Pt cathode, in an undivided cell, in $MeNH_2$ solution that also contained LiCl, provided 1-methylcyclohexa-1,4-diene whereas that of phenyltrimethylsilane gave 3-(trimethylsilyl)cyclohexa-1,4-diene[24,25] (Scheme VI).

The results can be explained in terms of a mechanism which resembles that of the Birch reduction. Thus, the transfer of a single electron to the arene would generate a radical anion. In the radical anion the negative charge would be expected to reside in the LUMO Ψ_4 when Y is an electron-releasing group and in the LUMO Ψ_5 when Y is an electron-withdrawing group. Thus, the protonation of the radical anion would occur at an ortho or meta position when the parent arene is an alkylbenzene and at the para position when the parent arene is phenyltrimethylsilane.[25] When both an alkyl group and a trimethylsilyl group are present, the site of protonation would reflect the net effect of the two groups.

Transfer of an electron to the cyclohexadienyl radical so formed would yield a cyclohexadienyl anion. Protonation of that species generally occurs of the position para to that of the first protonation, thus yielding the less thermodynamically stable of two possible products, i.e., the corresponding 1,4-diene, the product of a kinetically controlled reaction.[25] Thus, from *m*-tolyltrimethylsilane, for example, only the expected product was formed[25] (Scheme VII).

It can reasonably be assumed that the electroreductive trimethylsilylation of benzene, toluene, phenyltrimethylsilane, and the tolyltrimethylsilanes proceeds by way of a mechanism similar to that described above. The first step in the mechanism is the direct cathodic generation of solvated electrons (e⁻ (M) → e⁻$_s$), a so-called "primary process" which is favored in HMPA solution[28,31] and which is possible in the absence of dissolved alkali metal ions.[32] The transfer of an electron to the arene would generate a radical anion which, in the absence of a proton donor but in the presence of Me_3SiCl, would be trimethylsilylated. In the cases of the anion radicals generated from toluene, the trimethylsilyl group would be introduced into a position that is ortho or meta to the methyl group, and in the cases of phenyltrimethylsilane, *o*-tolyltrimethylsilane, and *m*-tolyltrimethylsilane, into a position that is para to trimethylsilyl group that is already present. The transfer of an electron to the trimethylsilylated cyclohexadienyl free radical so formed would yield the corresponding anion. In the cases of the anions derived from benzene and toluene, the second trimethylsilyl group would then be introduced into the position para to the first trimethylsilyl group to yield the corresponding bis(trimethylsilyl)cyclohexa-1,4-dienes. However, in the cases of the anions derived from the three aryltrimethylsilanes steric hindrance by a tri-

methylsilyl group prevents the introduction of a second trimethylsilyl group at the position para to that of the first trimethylsilylation. Rearrangement of the cyclohexa-1,4-dienyl anion to a cyclohexa-1,3-dienyl anion would generate a less sterically hindered anionic center. Trimethylsilylation would then yield the corresponding tris(trimethylsilyl)cyclohexa-1,3-dienes (Scheme VIII).

Finally, in the case of *p*-tolyltrimethylsilane, the electronic effects of the methyl and trimethylsilyl groups oppose rather than renforce each other, so it is difficult to predict what carbon atom would be the site of the first trimethylsilylation. To complicate matters still further, steric hindrance by the methyl group would retard trimethylsilylation of the carbon atom para to the trimethylsilyl group that was originally present. The experimental results do show that *p*-tolyltrimethylsilane is less reactive toward electroreductive trimethylsilylation than are the other tolyltrimethylsilanes and gives a more complex mixture of products.

The stereochemical outcomes of the electroreductive bis(trimethylsilylation) of **5**, **6o**, and **6m** can be explained in terms of the steric effect exerted by the first trimethylsilyl group to be introduced. Thus, because the ring of the aryl radical anion is nearly planar, the first attack by Me_3SiCl, at the position para to the trimethylsilyl group originally present, is equally likely from above or below the plane of the ring. However, in the second trimethylsilylation, that of the cyclohexadienyl anion, Me_3SiCl would attack from that direction which presents the minimum amount of steric hindrance. Such attack would probably yield the product of a kinetically controlled reaction, which in this case also happens to be the product of a thermodynamically controlled reaction. Similar product stereochemistry is generated by the chemoreductive tetra(trimethylsilylation) of phenyltrimethylsilane.[21]

C-Trimethylsilylated conjugated cyclohexadienes are suitable for use in Diels–Alder reactions.[33] Moreover, all such poly(trimethylsilylated)cyclohexadienes, upon aromatization with or without the loss of a trimethylsilyl group, give the corresponding trimethylsilylated arenes, which are valuable substrates for aromatic substitution reactions.[1,2,13,34]

Conclusion

By controlling the quantity of electricity that is used for electrolysis it was possible, for the first time, to effect the electroreductive trimethylsilylation of aryl halides so as to produce either aryltrimethylsilanes (the products of the reduction of the carbon–chlorine bond) or tris(trimethylsilyl)cyclohexadienes (products of the successive

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reduction of the carbon–chlorine bond and partial reduction of the aromatic ring). Conditions were found under which the yields of aryltrimethylsilanes from the electroreductive trimethylsilylation of aryl bromides were greatly improved. In contrast to chemoreductive trimethylsilylation, electroreductive trimethylsilylation could be controlled so as to permit the synthesis and isolation of tris(trimethylsilyl)cyclohexa-1,3(or 1,4)-dienes. The regio- and stereochemical outcomes of the electroreductive trimethylsilylation of phenyl-, o-tolyl-, and m-tolyltrimethylsilane could be explained in terms of the net electronic effect exerted by the substituents originally attached to the aromatic ring and the steric effects of the trimethylsilyl groups subsequently attached. In any event, electroreductive trimethylsilylation has been shown to be a convenient method for preparing attractive organosilicon synthons. Finally, as an alternative to chemoreductive trimethylsilylation, electroreductive trimethylsilylation possesses two very important advantages: it can be performed at room temperature, and obviously, it makes unnecessary the use of an alkali metal as the reducing agent.

Experimental Section

General Methods. The electrolysis of magnetically stirred solutions was performed under dry argon under conditions of constant current density ($J = 0.10 \pm 0.05$ A/dm^2) in a one-compartment cell fitted with a sacrificial anode of aluminum or magnesium rod and a cylindrical stainless steel grid or vitreous carbon-cloth cathode ("basket"). Constant current (current strength = 50 mA; quantity of electricity = 2.2 or 4.4 F·mol^{-1}) was provided by a Phillips 32-1 regulated DC power supply.

THF and HMPA were dried by distillation from sodium benzophenone ketyl and CaH$_2$, respectively. Anhydrous Et$_4$NBF$_4$ and MgCl$_2$ were purchased from Aldrich. The former was recrystallized from acetone and then was dried in vacuo. The latter was used without purification. Me$_3$SiCl, a generous gift from Rhône-Poulenc Co., was distilled from Mg powder immediately before use. Gas chromatography (GC) was performed with a temperature-programmable Perkin-Elmer 8410 gas chromatograph equipped with a 1.50-m × 3-mm stainless steel column packed with 5% OV 101 on Chromosorb GAW. IR spectra were recorded with a Perkin-Elmer 1420 spectrophotometer. The peak intensity is designated s (strong), m (medium), or w (weak). ^{1}H NMR spectra of CDCl$_3$ solutions were recorded at 250 or 270 MHz with a Bruker AC250 or WH 270 spectrometer. CHCl$_3$, ($\delta = 7.27$ ppm) served as the internal standard. ^{1}H NMR spectra of CCl$_4$ solutions were recorded at 60 MHz with a Hitachi-Perkin-Elmer R 24B spectrometer. CH$_2$Cl$_2$ ($\delta = 5.25$ ppm) served as the internal standard. The signals are designated s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). ^{13}C NMR spectra of CDCl$_3$ solutions were recorded at 67.88 MHz with a Bruker WH 270. CDCl$_3$ ($\delta = 77.70$ ppm) served as the internal standard. The signals are designated P (primary carbon), S (secondary), T (tertiary), or Q (quaternary). Electron-impact mass spectra were recorded at an ionization voltage of 70 eV with a VG Micromass 16 F mass spectrometer coupled with a gas chromatograph (Intersmat IGC 121 M) equipped with a capillary column.

The identities of previously described compounds were confirmed by comparing their physicochemical properties with those of authentic samples or those reported in the literature. The physicochemical properties of new compounds are reported below. In those cases where the product was a mixture of cis and trans isomers, the signals due to each isomer were identified by interpreting the various spectra in the light of the results of the GC and MS analysis of the mixture. The interpretation of complex ^{1}H NMR spectra was facilitated by the results of applying double irradiation techniques.

Electroreductive Trimethylsilylation of Benzene, Toluene, and Aryl Halides. General Procedure. The supporting electrolyte (an amount just sufficient to permit passage of an electrical current, i.e., enough to make a 0.02 M solution) and the solvent (50 mL) were introduced into the cell. The solution was

deaereted by bubbling Ar through it for 20 min, during which time the solution was irradiated with ultrasound. Then, a large excess of Me$_3$SiCl (six to nine times the theoretically required amount) was added. Any HCl that was produced by the reaction of Me$_3$SiCl with traces of water was removed by electrolyting the solution ($I = 100$ mA). The other hydrolysis product, (Me$_3$Si)$_2$O, is electrochemically inert. When evolution of H$_2$ had ceased, the substrate (14 mmol) was introduced by means of a syringe. Electrolysis ($I = 50$ mA) was then initiated and was continued until the theoretically required quantity of electricity had been passed. Water was then added to the reaction mixture, and the whole was extracted with Et$_2$O (3 × 50 mL). The combined extracts were dried (Na$_2$SO$_4$) and concentrated. The residue was analyzed by GC or distilled or both.

Compound **5** was identified as phenyltrimethylsilane by comparing its spectra and other physical properties with a commercially available authentic sample. Similarly, compounds **6o**, **6m**, and **6p** were identical to, respectively, independently synthesized[35] samples of o-tolyl, m-tolyl, and p-tolyl(trimethylsilane). Compounds **11** were identical to the products obtained by the chemoreductive tetrakis(trimethylsilylation) of **5**.[21]

2-Methyl-3,5,6-tris(trimethylsilyl)cyclohexa-1,3-diene (7). A mixture of the cis and trans isomers: bp 135 °C (2 mmHg); GC (temperature program: 70 °C for 5 min then to 200 °C at 5 °C/min), t_R = 25 (trans isomer) and 25.7 min (cis isomer), trans:cis = 92:8; MS m/e (rel intensity) 310 (3, M), 237 (3, M − 73), 149 (100, CH$_3$C$_6$H$_4$SiMe$_2$$^+$), 121 (5, 149 − 28; loss of C$_2$H$_4$, a fragmentation characteristic of compounds that bear vicinal CH$_3$ and SiMe$_3$ groups), 73 (93, Me$_3$Si$^+$), 45 (15), 43 (4); IR (liquid film), 3000 (w, HC=), 2945 (s), 2895 (m), 2845 (m), 1545 (m, C=C), 1445 (m), 1435 (m), 1400 (m), 1245 (s), 1180 (s), 1160 (m), 830 (s), 750 (m), 690 (m), 660 (w), 635 (w) cm^{-1}. Anal. Calcd for C$_{16}$H$_{34}$Si$_3$: C, 61.85; H, 11.03; Si, 27.12. Found: C, 61.84; H, 11.07; Si, 27.29.

trans-**7**: ^{1}H NMR (270 MHz, CDCl$_3$), δ 0.06, 0.08 (2s, 9 H and 9 H, Me$_3$SiC$_{allylic}$), 0.21 (s, 9 H, Me$_3$SiC$_{dienic}$), 1.67 (d, J = 6.7 Hz, 1 H), 1.82 (d, J = 6.7 Hz, 1 H), 1.86 (s, 3 H), 5.25 (d, J = 6.7 Hz, 1 H), 6.04 (d, J = 6.7 Hz, 1 H); ^{13}C NMR (67.88 MHz, CDCl$_3$), δ 139.2 (T), 135.7 (Q), 132.4 (Q), 121.8 (T), 28.6 (T), 26.0 (T), 23.6 (P), 0.9 (P), −2.4 (P).

MS analysis showed that *cis*-**7** constituted ca. 8% of the mixture of isomers (its fragmentation pattern is similar to that of *trans*-**7**). Although signals due to *cis*-**7** are present in the ^{1}H and, especially, the ^{13}C NMR spectra of the mixture, some are obscured by signals due to trace impurities. Consequently, not all of the signals due to *cis*-**7** could be identified.

1-Methyl-3,5,6-tris(trimethylsilyl)cyclohexa-1,3-diene (8). A mixture of the cis and trans isomers: bp 132 °C (2 mmHg); GC (temperature program: 70 °C for 5 min, then to 200 °C at 5 °C/min), t_R = 24.1 (*trans*-**8**) and 25.3 min (*cis*-**8**), trans:cis = 75:25; MS m/e (rel intensity) 310 (3, M), 221 (5, M − 73 − 16), 149 (100, CH$_3$C$_6$H$_4$SiMe$_2$$^+$), 73 (75), 45 (12), 43 (4); IR (liquid film) 3000 (w, HC=), 2950 (s), 2895 (s), 2850 (m), 1575 (shoulder C=C s-cis), 1556 (m, C=C s-trans), 1440 (m), 1410 (m), 1350 (w), 1315 (w), 1255 (shoulder), 1245 (s), 1190 (w), 1150 (m), 1115 (w), 1090 (w), 830 (s), 745 (m), 690 (m), 635 (w) cm^{-1}. Anal. Calcd for C$_{16}$H$_{34}$Si$_3$: C, 61.85; H, 11.03; Si, 27.12. Found: C, 61.88; H, 11.10; Si, 27.32.

trans-**8**: ^{1}H NMR (270 MHz, CDCl$_3$), δ 5.81 (d, J = 6.2 Hz, 1 H), 5.58 (s, 1 H), 1.85 (d, J = 6.2 Hz, 1 H), 1.80 (s, 3 H), 1.50 (s, 1 H), 0.18 (s, 9 H, Me$_3$SiC$_{dienic}$), 0.08, 0.05 (2s, 9 H and 9 H, Me$_3$SiC$_{allylic}$); ^{13}C NMR (67.88 MHz, CDCl$_3$), δ 134.39 (Q), 134.23 (T), 133.98 (Q), 122.0 (T), 31.07 (T), 29.37 (T), 25.32 (P), −0.8 (P), −2.6 (P).

cis-**8**: ^{1}H NMR (270 MHz, CDCl$_3$), δ 5.90 (s, 1 H), 5.19 (s, 1 H), 1.80 (s, 3 H), H$_{allylic}$ not assigned, 0.2–0 (3s, 3 × 9 H); ^{13}C NMR (67.88 MHz, CDCl$_3$), δ 141.12 (Q), 140.06 (Q), 135.44 (T), 118.20 (T), 39.46 (T), 32.96 (T), 25.15 (P), −1.5 (P), 0.2 (P).

3,5,6-Tris(trimethylsilyl)cyclohexa-1,3-diene (10). A mixture of the cis and trans isomers: bp 120 °C (2 mmHg); GC (temperature program: 50 °C for 5 min, then to 200 °C at 5 °C/min) t_R = 27.2 (*trans-a-a*-**10**), 29.3 (*cis-a-e*-**10**) and 30.9 min

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(*cis-e-a*-10). trans *a-a*:cis *a-e*:cis *e-a* = 89:6:5; MS *m/e* (rel intensity) 296 (2, M), 223 (1, M − 73), 207 (5, M − 73 − 16), 135 (86, M − 146 − 15, PhSiMe₂⁺), 73 (100), 45 (17), 43 (6); IR (liquid film) 3000 (w, HC=), 2930 (s), 2880 (m), 1585 (m, C=C), 1545 (w), 1430 (w), 1395 (w), 1250 (shoulder), 1240 (s), 1180 (w), 1150 (w), 825 (s), 740 (m), 680 (m), 620 (w) cm⁻¹. Anal. Calcd for C₁₅H₃₂Si₃: C, 60.73; H, 10.87; Si, 28.40. Found: C, 60.72; H, 10.91; Si, 28.45.

***trans-α,α*-10:** ¹H NMR (270 MHz, CDCl₃), δ 5.80 (d, *J* = 7.2 Hz, 1 H), 5.67 (d, *J₁* = 9.6 Hz, 1 H), 5.53 (dd, *J₁* = 9.6 Hz, *J₂* = 6.2 Hz, 1 H), 1.80 (d, *J* = 7.2 Hz, 1 H), 1.70 (d, *J* = 6.2 Hz, 1 H), 0.12 (s, 9 H, Me₃SiC_dienic), 0.09, 0.01 (2s, 9 H and 9 H, Me₃SiC_allylic).

3,6-Bis(trimethylsilyl)cyclohexa-1,4-dienes (14). A mixture of the cis and trans isomers: GC (temperature program: 40 °C for 5 min, then to 220 °C at 10 °C/min), *t*_R = 20.4 (*trans*-14) and 22.0 min (*cis*-14), trans:cis = 70:30; IR (liquid film) 1600 cm⁻¹ (m, C=C). ¹H NMR (250 MHz, CDCl₃): the spectrum of the mixture was very similar to this described in;²⁰ the spectra of both isomers (described below) are very close: for the *trans*-14 isomer, the Me₃Si singlet is 1.5 Hz downfield, the H_ethylenic multiplet is 2 Hz upfield and the H_allylic multiplet is 32 Hz upfield, trans:cis = 70:30; for the assignment, it was assumed that, in the trans isomer, the H_allylic, located in the perpendicular area of the Si–C bond, is shielded by the magnetic anisotropy of this bond. Such an effect was previously observed for the trans isomer of the 1,2-bis(trimethylsilyl)ethylene in which the H_ethylenic is 0.1 ppm shielded by the *cis*-Si–C bond.³⁶

***trans*-14:** crystallized, mp = 50 °C (EtOH); ¹H NMR (250 MHz, CDCl₃), δ 0.118 (s, 18 H, Me₃Si), 2.25 (m, 2 H), 5.52 (m, AB type, 4 H); ¹³C NMR (62.9 MHz, CDCl₃), δ 123.43 (T), 30.67 (T), −3.57 (P); ²⁹Si NMR (39.73 MHz, CDCl₃) δ 1.23. Anal. Calcd for C₁₂H₂₄Si₂: C, 64.20; H, 10.78; Si, 25.02. Found: C, 64.18; H, 10.85; Si, 25.06.

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***cis*-14:** liquid; ¹H NMR (250 MHz, CDCl₃) δ 0.112 (s, 18 H, Me₃Si), 2.37 (m, 2 H), 5.52 (m, AB type, 4 H); ¹³C NMR (62.9 MHz, CDCl₃), δ 122.75 (T), 30.41 (T), −2.98 (P); ²⁹Si NMR (39.73 MHz, CDCl₃) δ −0.58.

Cyclohexa-1,4-diene was shown to be almost planar;³⁷ 14 does not seem strictly planar because of the AB-type spectrum presented by the H_ethylenic of both isomers, but the weak difference for the ¹³C chemical shifts of the C_allylic of both isomers indicates a structure not far from planarity. Moreover, the presence, in the ¹H NMR spectrum of both isomers, of a single signal for the 2 H_allylic on the one hand and for the 2 SiMe₃ groups on the other hand, would indicate the existence of a rapid conformational isomerism at room temperature. This assumption was confirmed by their ¹³C and ²⁹Si NMR spectra also showing a single signal for the Me₃Si groups.

1-Methyl-3,6-bis(trimethylsilyl)cyclohexa-1,4-diene (*trans*-15): bp 96 °C (2.5 mmHg); ¹H NMR (250 MHz, CDCl₃) δ 0.07 (s, 9 H, Me₃SiC₆), 0.13 (s, 9 H, Me₃SiC₃), 1.71 (t, *J* = 1.5 Hz, 3 H), 2.19 (m, 2 H, H_allylic), 5.21 (m, 1 H, H₂), 5.54 (m, 2 H, H₄, H₅); ¹³C NMR (62.9 MHz, CDCl₃) δ 132.13 (Q, C₁), 125.64 (T, C₄ or C₅), 122.29 (T, C₄ or C₅), 117.46 (T, C₂), 35.79 (T, C₃), 30.74 (T, C₆), 24.78 (P, CH₃), −1.74 (P, Me₃SiC₃), −3.35 (P, Me₃SiC₆); IR (liquid film) 1610 cm⁻¹ (m, C=C). Anal. Calcd for C₁₃H₂₆Si₂: C, 65.46; H, 10.99; Si, 23.55. Found: C, 65.50; H, 10.91; Si, 23.65.

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Synthesis and Dimerization of Two Cross-Conjugated Trienes: 3-Methylene-1,4-pentadiene and 1,2,3-Trimethylenecyclohexane[1]

Walter S. Trahanovsky* and Kenneth A. Koeplinger

Ames Laboratory and the Department of Chemistry, Iowa State University, Ames, Iowa 50011

3-Methylene-1,4-pentadiene (8) and 1,2,3-trimethylenecyclohexane (10) are prepared in moderate to high yields in good purity by the flash vacuum pyrolysis of 1,5-diacetoxy-3-(acetoxymethyl)pentane (12) and 1,2,3-tris-(acetoxymethyl)cyclohexane (17), respectively. Triene 8 dimerizes cleanly at a moderate rate in benzene at 95 °C to give only one major product, [4 + 2] dimer 1,4,4-trivinylcyclohexene (13). Triene 10, the conformationally restricted all cisoid analog of 8, dimerizes more rapidly in benzene at 95 °C to give only one major dimer, a [4 + 2] dimer (21). It is concluded that the dimerization proceeds by a two-step mechanism: rate-determining attack at the middle methylene group to form a resonance-stabilized diradical intermediate followed by rapid closure of the diradical to give a [4 + 2] dimer.

Introduction

2,3-Dimethylene-2,3-dihydrofuran (1), the furan-based *o*-quinodimethane (*o*-QDM), has been studied extensively by our research group during the past decade.²⁻⁷ Much

of our work has focused on the mechanism of the dimerization of 1 which occurs readily in solution at temperatures above −30 °C. Of special interest is the fact that the dimerization gives almost quantitatively the head-to-head [4 + 4] dimer 2.² On the basis of a secondary deuterium kinetic isotope effect study, it was concluded that the

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