

Table II. Quaternary Ammonium Fluoride Monohydrates^a Prepared in this Study

compound	dec, ^b °C	yield, %	Cl/F ratio ^c
(CH ₃) ₄ NF ^a	180	95	3.77
(C ₂ H ₅) ₄ NF ^a	80	83	7.21
(<i>n</i> -C ₃ H ₇) ₄ NF ^a	140	86	12.40
(<i>n</i> -C ₄ H ₉) ₄ NF ^a	151-3	87	15.80
(<i>n</i> -C ₆ H ₁₃) ₄ NF	153-5	89	24.10
(<i>n</i> -C ₈ H ₁₇) ₄ NF	156-8	89	30.80
(<i>n</i> -C ₈ H ₁₇) ₃ N(CH ₃)F	168-71	93	36.20
(<i>n</i> -C ₁₆ H ₃₄)N(CH ₃) ₃ F	246-9	93	18.40

^aThe salts were prepared as monohydrates but are relatively unstable in this form and tend to decompose unless absorb more water of hydration to form higher hydrates. ^bMeasured by thermal gravimetry using a TA-3000 Mettler Thermoanalyzer. ^cBased on experimental elementary analysis.

salts. Following the exchange step, the methanol is gradually evaporated under vacuum at room temperature. The precipitation of potassium chloride formed during the evaporation is filtered and removed several times in the course of the operation. The products obtained are 95-7% pure anhydrous quaternary ammonium fluoride salt in 83-95% yield. Since these materials, particularly those with ethyl, propyl, and butyl groups, are extremely unstable, it is recommended to add several equivalents (2-4) of water at the very last step of the evaporation to yield the corresponding hydrates which are stable at room temperature. Table II presents a list of products synthesized in the course of this work with their temperature of decomposition (all the salts in the form of monohydrate). The purity of the products was verified by elementary analysis.

Experimental Section

Materials. Quaternary ammonium chlorides or bromides were purchased from Aldrich and were used without further purification.

Conductometric Assay of Fluoride Anion. The method is based on the potentiometric method reported by Linge.¹¹ The reagent is a mixture of 1.0 g of lanthanum acetate and 0.5 mL of glacial acetic acid dissolved in 1.0 of double-distilled water. The titration is conducted in methanol-water mixture containing 40 wt % methanol; 100-mg samples are dissolved in 30 mL of this solution and titrated by the reagent with continuous monitoring of the conductivity using El-Hamma TH-230 conductometer and electrode. The endpoint is determined graphically.

This method is applicable to both aqueous and organic samples which are soluble in the water-methanol mixture. In samples containing a nonsoluble solvent (e.g. toluene), the solvent should be evaporated prior to the test.

Chloride anion was determined by argentometric titration.

Preparation of Tricaprylmethylammonium Fluoride. A mixture of 9.15 g of aliquat 336, 40 mL of absolute methanol, and 2.2 g of potassium fluoride containing 4% by weight of water is stirred at room temperature for 15 min. The mixture is filtered, to the solution is added another fraction of 2.2 g of potassium fluoride, and the mixing is continued for an additional 15 min. After filtration 25% of the methanol is evaporated under vacuum at room temperature, the mixture is filtered again, and this procedure is repeated four times until all the methanol is removed. The oily product (8.7 g, 94% yield) was found by titration and elementary analysis to contain 96.5% tricaprylmethylammonium fluoride and 3.5% chloride.

The other quaternary fluorides were prepared in identical procedures.

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Electrochemical Synthesis of (α -Halobenzyl)silanes and Benzal Disilanes

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Electrochemical reduction of a series of substituted benzal chlorides (4) in dimethylformamide containing excess chlorotrimethylsilane affords (α -chlorobenzyl)trimethylsilanes (5) or benzal (geminal) disilanes (6), depending upon experimental conditions. Benzal bromide (13) is reduced to (α -bromobenzyl)trimethylsilane (14) cleanly and in high yield without subsequent conversion to the geminal disilane 6a, apparently because of electrode passivation by bromide ion. The reactions are conveniently carried out at constant current in an undivided cell containing a stainless steel cathode and sacrificial magnesium anode.

α -Halosilanes (1) and geminal disilanes (2) are versatile synthetic intermediates,¹ but their widespread use in organic and organosilicon chemistry has been limited by the lack of convenient methods for their preparation. For example, a recent report described an improved method of preparation of bis(trimethylsilyl)methane (3),² yet this method involves the use of lithium at -50 °C, conditions which would be cumbersome at best and possibly hazardous for the synthesis of large amounts of 3, and in addition, it generates 3 in only 55% yield. The conversion

of benzal chloride (4a) to either (α -chlorobenzyl)trimethylsilane (5a) and benzal trimethylsilane (6a) is another case in point. The literature synthetic route to these substances involves reaction between 4a, chlorotrimethylsilane, and an active metal such as magnesium in hexamethyl phosphorous triamide.³ The reaction presumably involves formation of the Grignard reagents corresponding to 4a and 5a, which then react with the halosilane to form a mixture of 5a and 6a. It is relatively difficult in such cases to obtain good yields of the monohalide, since halides 4a and 5a tend to be about equally

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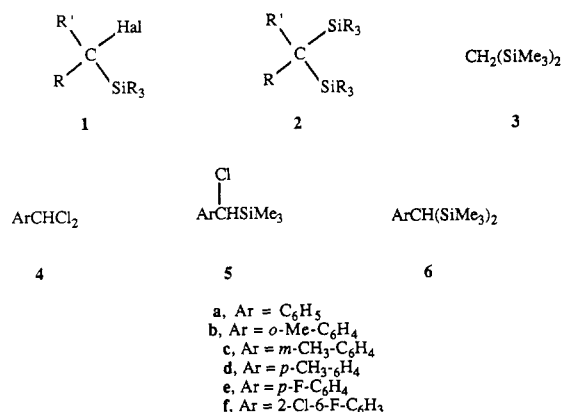
Table I. Electrochemical Reduction of Benzal Halides in the Presence of Trimethylchlorosilane

dihalide	α -halosilane, %	midpoint of electrolysis			
		4	9	6	other
4a	93	0	0	7	0
4b	94	1	1	3	1 ^b
4c	57	10	1	31	0
4d	81	7	0	12	0
4e	73	7	tr	20	tr ^c
4f	68	18	1	2	11 ^d
13	98	0	0	0	2 ^e

dihalide	geminal disilane (6), %	end of electrolysis			
		10	11	12	other
4a	74	10	16	0	0
4b	88	8	0	0	4 ^b
4c	78	18	5	0	0
4d	87	6	6	0	1 ^b
4e	91	8	1	1	1 ^b
4f	72	13	7	0	3, 5 ^f

^a Electrolyses carried out in DMF/0.5 M LiClO₄. ^b Unidentified. ^c 12a and 10a. ^d (*o*-Fluoro- α -chlorobenzyl)trimethylsilane (5) (Ar = *o*-F-C₆H₄). ^e 12b. ^f (*o*-Fluorobenzyl)trimethylsilane (10, Ar = *o*-F-C₆H₄) and *o*-fluorobenzyl trimethylsilane (6, Ar = *o*-F-C₆H₄), respectively.

reactive toward the metal used to initiate the process. We report herein a selective, efficient, and experimentally convenient electrochemical process for synthesizing (α -halobenzyl)silanes and benzal disilanes in yields which are considerably higher than by previous methods.

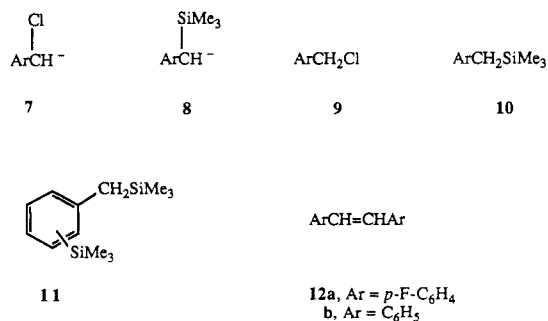


Electrochemical reduction of alkyl halides in the presence of chlorotrimethylsilane has been reported to afford alkyltrimethylsilanes.⁴ Since geminal dihalides are generally easier to reduce than the corresponding monohalides,⁵ we felt that it should be possible to silylate a geminal dihalide in stepwise fashion by proper control of experimental conditions. We have found that this is indeed possible. Constant-current electrochemical reduction of substituted benzal chlorides (4a-f) in dimethylformamide (DMF) containing chlorotrimethylsilane can be carried out to afford either the α -halosilane (5) or the corresponding benzal (geminal) disilane (6), depending simply on how long current is passed through the solution (Table I). As others have previously observed,⁴ current efficiencies for the reductive silylation process were found

to be rather low (50–70%) in DMF.⁶ For this reason, the progress of electrolysis was generally followed by periodic GC analysis of the electrolysis mixture. As anticipated, the reduction potentials of 4 and 5 are sufficiently different (4a, -2.23 V; 5a, -2.79 V vs Ag/0.1 M AgNO₃) that formation of 6 does not begin until 4 has been almost completely converted into 5. Electrolysis can be interrupted at this point to afford the α -chlorosilane (5) where desired.

These electrolytic silylation reactions can be carried out with a relatively simple experimental setup. It had been observed previously that yields of benzyltrimethylsilanes from the electrochemical reduction of benzyl halides in the presence of chlorotrimethylsilane are somewhat diminished if the electrolysis is conducted in an undivided cell.^{4b} Presumably this is because of concomitant oxidative destruction of the product silanes at the anode of the undivided cells.⁷ We found that an undivided cell, which is experimentally much more convenient, can be employed if a sacrificial magnesium anode⁸ is employed. The yields of 5 and 6 are also better at a stainless steel cathode than at carbon and when relatively concentrated solutions are electrolyzed.

These reactions presumably occur via carbanionic intermediates.⁵ The first electrochemical step involves conversion of 4 to an α -chlorobenzyl anion (7), which is then trapped by the chlorosilane to afford 5. A second reduction sequence then converts 5 to 6 via the α -silyl anion 8. Side products formed during the electrolyses are consistent with 7 and 8 as intermediates in these reactions. Thus, when the electrolysis of a given benzal chloride was monitored as a function of time, it was possible to observe not only the disappearance of the starting dichloride and formation of a mixture consisting of largely 5 but also the appearance of traces of the benzyl chloride 9, which then slowly disappears and is replaced by the benzyltrimethylsilane 10. Chloride 9 is presumably formed by protonation of 7 by an adventitious proton source, presumably water. A second reductive silylation then converts 9 to 10. Although chlorotrimethylsilane and water are both competing for anion 7, the ratio of reaction of 7 with the chlorosilane to that with water must be upwards of 50 or more in most cases, inasmuch as yields of 9 rarely exceed 1%. This is not just because a substantial molar excess of the chlorosilane is present in solution; electrolyses in THF, which is unquestionably considerably drier than DMF under our conditions, afford 9 (and ultimately 10) in yields of upwards of 10%. The low efficiency of water as a carbanion trap in these reactions is no doubt associated with its well-known tendency to associate strongly with DMF and thereby to become a very poor proton donor in this solvent.⁹



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(6) Current efficiencies approach 100% in THF.

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After the yield of **5** had built to a maximum, continued electrolysis caused it to disappear and geminal disilane **6** to appear. Geminal silanes **6** were accompanied in most cases by small amounts of isomeric substances, presumably bearing one of the silyl groups on the aromatic ring (**11**). The two types of compound exhibited distinctly different mass spectra. The geminal disilylated substances **6** generally exhibit a low-intensity molecular ion (*M*), together with weak peaks corresponding to *M* - 15 and *M* - 43 and an intense peak at *M* - 88, which is usually the largest peak in the spectrum. The ring silylated materials **11** generally fail to exhibit a molecular ion; the most prominent feature in the mass spectrum of these substances is always a strong peak at *M* - 89. In several instances, the assignment of the major isomer as **6** was confirmed by separating it in pure form by preparative GC and measuring its 400-MHz NMR spectrum (see the Experimental Section). Disilanes **6** and **11** arise from a common intermediate, the benzylic carbanion **8**.^{5,10} Ambident anion **8** can react with chlorotrimethylsilane either at the benzylic carbon to form **6** or at a ring carbon to afford **11** (after rearomatization). Disilanes **11** were not formed when electrolyses of **4** were carried out in tetrahydrofuran (THF). Benzylsilane **10** is also formed in the latter stages of electrolysis, that is, it appears to be formed from **5** as well as from **4**. In fact, the final electrolysis solution contains **10** in amounts which considerably exceed the sum of **9** and **10** present in the early stages. This is probably because the trimethylsilyl group in anion **8** offers steric hindrance toward introduction of a second such group at the same atom.

We were originally concerned that **7** might decompose to a carbene by ejection of chloride ion before it could be trapped by the chlorosilane. In general this did not prove to be a problem, although traces of *p,p'*-difluorostilbene (**12a**), presumably formed via an intermediate carbene,¹¹ could be detected by GC-mass spectrometry among the electrolysis products from **4e**. Fortunately, silylation appears to be faster than ejection of chloride ion from **7**. It was gratifying to note the low efficiency toward carbene formation even in the reduction of benzal bromide (**13**), where the better leaving group ability of bromine might have been expected to bias the reaction more strongly toward carbene formation; in fact only about 2% stilbene (**12b**) was formed in this electrolysis. On the other hand, this particular reaction exhibited a surprising feature not observed with the benzal chlorides **4**. Electrolysis stopped abruptly upon formation of (α -bromobenzyl)trimethylsilane (**14**); no further reduction of **14** was observed even after a substantial (2-fold) excess of current had been passed. It appears from this experiment that the stainless steel cathode is passivated either by a bromide ion or by an intermediate in the reaction.



Although ejection of chloride ion from **7** to afford carbene products was not a significant problem in these electrolyses, a related reaction was observed with the ring-halogenated benzal chlorides **4e** and **4f**. Analysis by GC-mass spectrometry of samples taken during the course of electrolysis of **4e** demonstrated the formation of traces of **10a**. Similar experiments on **4f** indicated the initial

buildup and decay of (*o*-fluoro- α -chlorobenzyl)trimethylsilane (**5**, Ar = *o*-F-C₆H₄) and the final formation of both (*o*-fluorobenzyl)trimethylsilane (**10**, Ar = *o*-F-C₆H₄) and *o*-fluorobenzal trimethylsilane (**6**, Ar = *o*-F-C₆H₄). Formation of these dehalogenated materials is intriguing, in view of the well-known difficulty of reducing alkyl and aryl chlorides and fluorides electrochemically.⁵ It may be that dehalogenation occurs by a path other than direct electrochemical reduction of the ring halogen atom, for example, by a path involving ejection of chloride or fluoride ion from an intermediate benzylic anion (**7** and/or **8**).

Summary

Electrochemical reduction of substituted benzal chlorides (**4**) in the presence of chlorotrimethylsilane affords either (α -chlorobenzyl)trimethylsilanes (**5**) or benzal (geminal) disilanes (**6**), depending on the amount of current passed in the electrolysis. The reactions are carried out in DMF, in a simple undivided electrolysis cell containing a stainless steel cathode and a sacrificial magnesium anode. We are exploring the scope of these reactions further as a synthetic route to other α -halosilanes and geminal di- and trisilanes.^{2,3,12}

Experimental Section

Analytical and preparative gas chromatography were carried out using a Gow-Mac 550P instrument equipped with a 1-m SE-30 column. Products were identified by mass spectrometry and/or NMR spectra. The latter were measured on a Varian XL-400 spectrometer on samples isolated by preparative gas chromatography. Mass spectrometric measurements were carried out by using a Hewlett-Packard Model 5988 gas chromatograph-mass spectrometer.

Benzal chloride (**4a**) and the halogenated benzal halides **4e** and **4f** were purchased from the Aldrich Chemical Co. The methyl-substituted benzal halides **4b-d** were synthesized by reaction between the appropriate aromatic aldehyde (Aldrich) and phosphorus pentachloride.¹³ Dimethylformamide was distilled at aspirator pressure from calcium hydride and used immediately. Lithium perchlorate was dried overnight in an Abderhalden apparatus at 110 °C before use. Trimethylchlorosilane was distilled from calcium hydride into a flask containing poly(4-vinylpyridine).¹⁴

Voltammetry. A Princeton Applied Research Model 174A polarographic analyzer was employed for voltammetry. Voltammetric measurements were carried out at a glassy carbon disk in 0.14 M LiClO₄/DMF. Potentials were measured relative to a Ag/0.1 M AgNO₃ reference electrode (This electrode is +0.35 V vs SCE).

Electrolyses. A 4.5 × 15 cm cylindrical stainless steel cloth cathode (W. P. Smith Co., Franklin Park, IL) was placed in a 180-mL Kimax electrolytic beaker containing a magnetic stirring bar. The beaker was sealed with a cork stopper wrapped with Teflon tape and containing four short lengths of glass tubing. The central tube, the largest, was of sufficient diameter to permit placement of a 15 mm diameter × 60 mm magnesium rod (Alfa) used as the anode. The other three were capped with septa and used as ports for introduction of nitrogen, electrical connection to the cathode, addition of reagents, and removal of samples. The cell was chilled in an ice bath, 40 mL of a 0.5 M LiClO₄/DMF solution were added, and the cell was flushed with nitrogen for 5 min. Chlorotrimethylsilane (5 mL) and the benzal halide (5 mmol) were then added, and a constant current of 0.4 A was applied by a Kepco (Flushing, NY) power supply. The progress of the reaction was monitored at intervals corresponding to uptake of 5 mF each by removing 1-mL samples for analysis by gas chromatography after treatment with aqueous NaHCO₃ (see the following). At the conclusion of electrolysis, the mixture was

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poured into saturated aqueous NaHCO_3 and extracted several times with hexane. The hexane extracts were washed once with saturated NaHCO_3 and twice with water and dried over MgSO_4 , and the solvent was then evaporated. The resulting product could be purified by distillation or preparative GC. ^1H NMR spectra (400 MHz) of compounds isolated by the latter method include the following. **5a**: δ 0.2 (s, 9 H), 4.5 (s, 1 H), 7.4 (m, 5 H) [lit.^{3b} δ 0.1 (s, 9 H), 4.31 (s, 1 H), 7.27 (s, 5 H)]. **6a**: δ -0.03 (s, 18 H), 1.46 (s, 1 H), 6.90 (d, 2 H), 7.01 (t, 1 H), 7.15 (t, 2 H) [lit.¹² (60 MHz) δ 0.04 (s, 18 H), 1.50 (1 H), 7.1 (m, 5 H)]. **6b**: ^1H NMR δ 0.01 (s, 18 H), 1.52 (s, 1 H), 2.18 (s, 3 H), 6.95 (d, 2 H), 7.1 (m, 2 H). **6d**: ^1H NMR δ -0.02 (s, 18 H), 1.41 (s, 1 H), 2.24 (s, 3 H), 6.79 (d, 2 H), 6.96 (d, 2 H).

Preparative-Scale Electrolysis of 6a. A mixture of 4.0426 g (25 mmol) of **4a** and 15 mL (12.8 g, 118 mmol) of

chlorotrimethylsilane was reduced as described previously, at a constant current of 0.5 A. GC analysis indicated the yield of **6a** to be maximal at 5.4 h (ca. 100% current efficiency). Workup and distillation afforded **6a** as a water-white liquid, 4.6420 g (19.7 mmol, 78% yield), bp 112–114 °C/18 mm (lit. bp 166 °C/99 mm^{3a} and 45 °C/0.5 mm¹²). Quantitative gas chromatographic analysis (pentadecane as internal standard) indicated an 84% yield of monosilane **5a** at the midpoint of the electrolysis.

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Oxidative Grob Fragmentation of γ -Tributylstannyl Alcohols with a Combination of Iodosylbenzene, Dicyclohexylcarbodiimide, and Boron Trifluoride

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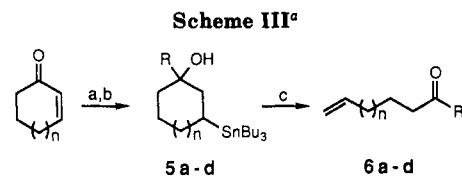
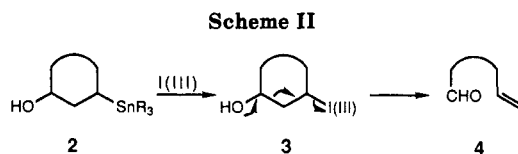
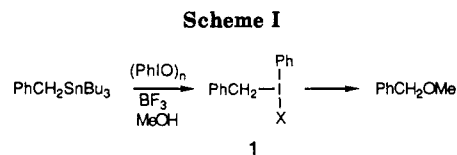
Exposure of cyclic γ -stannyl alcohols, prepared from cyclic vinyl ketones, to a combination of iodosylbenzene, dicyclohexylcarbodiimide, and boron trifluoride-diethyl ether in dichloromethane undergoes an oxidative Grob fragmentation to give unsaturated carbonyl compounds. The dicyclohexylcarbodiimide in this reaction apparently activates iodosylbenzene and decreases Lewis acidity of boron trifluoride. The fact that the iodine(III)-mediated Grob fragmentation proceeds stereospecifically suggests the fragmentation is concerted. The fragmentation, combined with conjugate addition of (tributylstannyl)lithium and reduction or alkylation, offers an efficient procedure for the reductive and alkylative ring opening of cyclic vinyl ketones. Since *cis*-benzyl ether **36**, after quenching of the reaction mixture with aqueous NH_4Cl , afforded the chlorostannane **37**, the reaction mechanism involving the formation of iodine(III) species **32** with two oxygen ligands at iodine was proposed.

In contrast to organolithiums, magnesiums, and aluminums, tetraorganotin demonstrate only limited reactivity toward electrophiles. This is due, at least in part, to significant covalent bond character of the C–Sn bond (According to Pauling,¹ the electronegativity of Sn(IV) is 1.9 vs 2.5 for C). On the other hand, the high polarizability of this bond² allows for organotins to participate as versatile carbanion equivalents in ionic reactions.

Recently, we reported reactivity umpolung of organotins as well as organosilicons involving the conversion of the corresponding organoiodine(III) and organothallium(III) species. They act as carbocation equivalents and react with a variety of nucleophiles.^{3–5} For example, reaction of benzyltributylstannane with iodosylbenzene (ISB) and boron trifluoride-diethyl ether in methanol affords benzyl methyl ether in 86% yield via the formation of the reactive benzyl iodine(III) species **1** (Scheme I).

γ -Trialkylstannyl alcohols have been shown to be useful intermediates in organic synthesis. The 1,3-cyclization of acyclic analogues provides an efficient route to substituted cyclopropanes.^{6,7} Chromic anhydride oxidation of a cyclic γ -stannyl alcohol constitutes a key step in alkylative enone transposition.⁸

Based on the results described above, we have designed an oxidative Grob fragmentation of cyclic γ -stannyl alcohols **2** that yields unsaturated carbonyl compounds **4**. This may involve in situ generation of γ -hydroxy iodine(III) species **3** as a key intermediate by the reaction with ISB



- a: R = Ph, n = 0
 b: R = Ph, n = 1
 c: R = n-C₁₀H₂₁, n = 1
 d: R = Ph, n = 2

^a Reagent: (a) Bu_3SnLi , THF; (b) PhLi or $n\text{-C}_{10}\text{H}_{21}\text{Li}$, THF; (c) DCC, ISB, $\text{BF}_3\text{-Et}_2\text{O}$, CH_2Cl_2 .

activated by Lewis acids (Scheme II).^{9–11} We report herein the results in detail.

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