

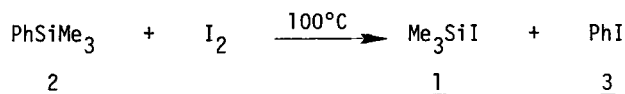
MILD METHODS FOR THE IN SITU GENERATION OF TRIMETHYLSILYL IODIDE

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We have shown that trimethylsilyl iodide 1 is a very useful reagent for a number of important organic transformations including: the dealkylative hydrolysis of ethers,² esters,³ carbamates,⁴ and ketals;⁵ the conversion of alcohols into the corresponding iodides;⁶ the simple formation of iodomethyl methyl ether;⁷ and the formation of aldehyde iodohydrin trimethylsilyl ethers and their further reactions.⁸ Other workers have also reported its utility in dealkylations^{9,10} and deoxygenations.¹¹ We have described a simple two-step procedure for the preparation of trimethylsilyl iodide 1 from trimethylsilyl chloride,¹² and the iodide is now commercially available from several suppliers. We now report very mild and convenient methods for the in situ generation of trimethylsilyl iodide 1 under completely neutral conditions.

Even though the silyl iodide is fairly easy to prepare pure, its extreme sensitivity to hydrolysis led Olah to prepare it in situ¹⁰ by the method of Whitmore.¹³ Namely, treatment of phenyltrimethylsilane 2 with iodine at 110°C affords an equimolar mixture of the silyl iodide 1

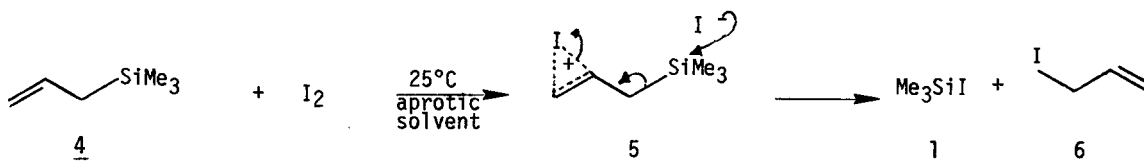


and iodobenzene 3. If one carries out this reaction in the presence of an alkyl carboxylate or alkyl phenyl ether, dealkylation is observed.¹⁰

We rejected this method of in situ generation of trimethylsilyl iodide 1 for two primary reasons. First, one must use very high temperatures, e.g., 110°C, in order to efficiently cleave phenyltrimethylsilane with iodine. Thus all of the inherent selectivity of the dealkylation process is lost. For example, at 110°C there is little difference in the reactivity of benzyl and methyl esters or ethers, whereas the difference is very great at room temperature or below,^{2,3} thus

allowing the selective removal of a benzyl group in the presence of methyl. This is not possible in this *in situ* generation method. Secondly, iodobenzene 3 is a necessary and unavoidable by-product in the generation of the silyl iodide 1 from the phenylsilane 2. Only in the case of acids and phenols can this by-product be easily removed. Its presence becomes a serious problem in the isolation of simple alcohols formed by dealkylation of the corresponding ethers. The only general solution for its removal is the time-consuming process of column or gas chromatography. For these two major reasons, we decided to avoid this method of *in situ* generation and develop others.

One would expect allylic silanes to react much more rapidly with iodine than aryl silanes to generate a β -silyl iodonium iodide, which would then eliminate the silyl iodide.¹⁴ This is indeed the case. Treatment of allyltrimethylsilane 4 with iodine in aprotic solvents affords trimethylsilyl iodide 1 and allyl iodide 6 very rapidly at room temperature or below. The reaction presumably proceeds via the iodonium iodide 5. If one carries out this reaction in the presence of



esters, ethers, or carbamates, the corresponding trimethylsilyl esters, ethers, and carbamates are produced (Table) in high yields. The only drawback to this procedure for the *in situ* preparation of 1 is the fact that allyl iodide is formed. Although it can be removed with heating on the rotary evaporator (b.p. 102°C), its high electrophilicity may make it incompatible with substrates containing nucleophilic groups, e.g. amines.

For this reason we sought a method of generation which would produce a totally unreactive and easily removable by-product. This was accomplished as follows. Treatment of benzene with lithium and trimethylsilyl chloride in tetrahydrofuran affords the 3,6-bis-trimethylsilyl-1,4-cyclohexadiene 7 in 55% yield.¹⁵ When this bis-allylic silane 7 is treated with iodine in aprotic solvents at 0°C to 25°C, there ensues a very rapid reaction which forms two equivalents of trimethylsilyl iodide 1 and one equivalent of benzene as the only products. The intermediates in this reaction are presumably the compounds 8 and 9.¹⁶ When this process is carried out in the presence of esters, ethers, or carbamates, clean dealkylation takes place in high yield (Table).

Therefore, compounds 4 and 7 are clearly superior reagents for the low-temperature *in situ* generation of trimethylsilyl iodide 1. Furthermore, one might expect from reports in the literature¹⁷ that these compounds would also be efficient scavengers for hydrogen iodide, producing the

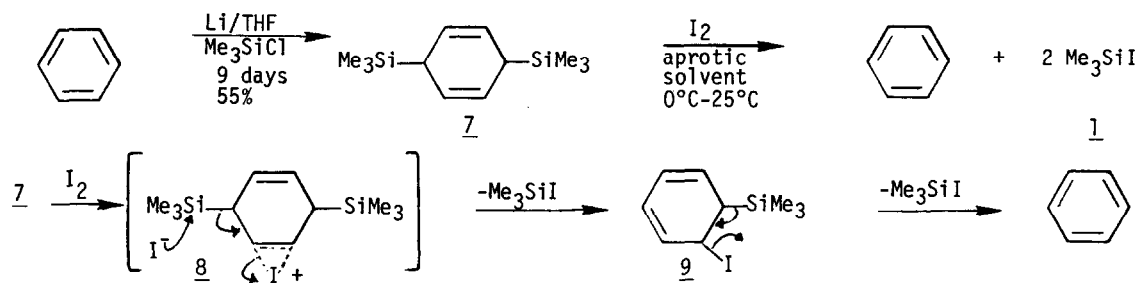
TABLE
Dealkylation with Allylic Silanes and Iodine^a



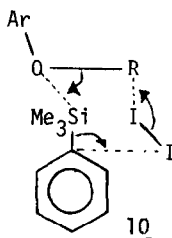
Compound	Temp (°C)	Time	Yield (%) ^b	Temp (°C)	Time	Yield (%) ^b
PhCOOtBu	25	15 min	100	25	15 min	100
PhCOOCH ₂ Ph	25	15 min	100 (83)	25	46 hr	100 (78)
CH ₃ COOCH ₂ Ph	25	15 min	100	25	3½ hr	100
PhCOOiPr	50	10 hr	100	50	78 hr	100
methyl mesitoate	50	6 hr	100	50	30 hr	100
PhCH ₂ OCH ₂ CH ₃	25	20 min	100	25	20 min	100
p-MeOC ₆ H ₄ OMe	25	2½ hr	100	25	6 hr	100
H ₂ NCOOCH ₂ Ph	25	15 min	100	25	15 min	100

a) In all cases a slight excess of the allylic silane versus iodine was used.

b) Yields were determined by integration of the pertinent peaks in the NMR spectra. Isolated yields are given in parentheses.



β -iodosilanes at low temperatures. As the times for dealkylation in the Table indicate, the bis-silyl cyclohexadiene **7** appears to scavenge hydrogen iodide very readily while the allylsilane **4** does not seem to be as effective in this regard.¹⁸ Thus, one can guarantee the absence of hydrogen iodide in the reaction mixture by the use of a very slight excess of the bis-silyl cyclohexadiene **7**. Finally, we believe that the dealkylation observed here proceeds by the mechanism we have previously suggested^{2,3} and not by the trimolecular six-centered transition state **10** proposed by Olah.¹⁰ Since one can observe the rapid formation of trimethylsilyl iodide **1** in the NMR prior to dealkylation, it



is obvious that the allylic silanes 4 and 7 generate 1 without being present in the transition state for dealkylation.

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18. Although the reaction vessel and solvents are carefully dried before using, there is always the possibility of adventitious water being present (and thus generating HI). There may be other reasons for the faster dealkylation with 4 but they have not yet been identified.

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