

TRIMETHYLSILYL IODIDE. PREPARATION FROM AND CATALYTIC BEHAVIOR
WITH PHENYLSELENOTRIMETHYLSILANE

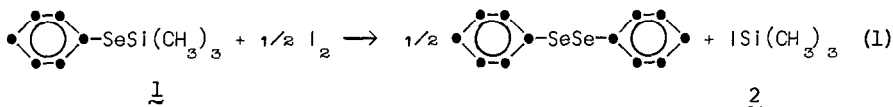
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Abstract - Trimethylsilyl iodide (TMSI) and diphenyldiselenide are produced by the addition of iodine to phenylselenotrimethylsilane. TMSI generated in this manner cleaves a variety of C-O bonds and catalyzes 1,2 and 1,4 additions of phenylselenotrimethylsilane to various carbonyl compounds.

Trimethylsilyl iodide is a useful reagent for effecting a variety of transformations in organic synthesis including dealkylations of ethers,¹ esters,² carbamates,³ and ketals,⁴ deoxygenations of sulfoxides and N-oxides,⁵ and conversion of alcohols into the corresponding iodides. The sensitivity of the reagent to moisture has prompted a number of methods for the in situ generation of trimethylsilyl iodide.^{1b,7} We wish to report a facile synthesis of the reagent that is adaptable for both preparative runs and in situ generation.

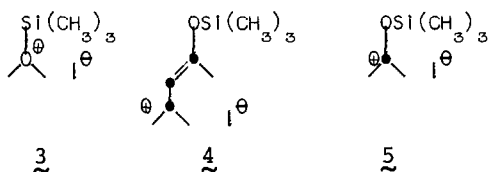
The addition of iodine to phenylselenotrimethylsilane (1)⁸ gives a mildly exothermic reaction in which diphenyldiselenide and trimethylsilyl iodide (2)



are produced as the only detectable products (eq 1). Presumably, a molecule of iodine reacts with a molecule of 1 to give 2 and phenylselenenyl iodide. The latter species must react rapidly with a second molecule of 1 to give 2 or disproportionate to iodine and diphenyldiselenide.⁹ The trimethylsilyl iodide can be isolated¹⁰ in 80-90% yield as an air- and light-sensitive, colorless oil (bp 103-107°) or can be generated in situ in a variety of solvents including methylene chloride, chloroform, and carbon tetrachloride.¹¹ The major advantage of this method of preparation of 2 is that quantities of the reagent can be prepared within 6 h in 60-70% overall yield in 3 steps from diphenyldiselenide, trimethylsilyl chloride, sodium, and iodine.

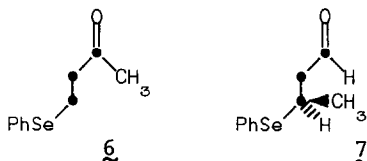
Table I contains several examples of C-O bond cleavage by trimethylsilyl iodide generated in situ by this method.¹² In a typical procedure, the substrate

and 1.05 molar equivalents of 1 are treated with 0.50 molar equivalent of iodine in 3 mL of solvent per mmol of substrate. No iodine color is visible. Workup consists of a thorough washing of the reaction mixture with sodium bicarbonate solution. The diphenyldiselenide can be removed by fractional crystallization, chromatography, or, for volatile products, as a distillation pot residue. The slight excess of 1 employed may well act as a hydrogen iodide scavenger to give benzeneselenol and trimethylsilyl iodide.



Presumably, the C-O cleavages occur by nucleophilic attack by iodide on a carbon of a silyl dialkyl onium species, such as 3, following initial electrophilic attack of silicon on oxygen.^{1,7} We felt that the electrophilic nature of 2 might be further exploited synthetically as a catalyst for the 1,4-additions of phenylselenotrimethylsilane to enones (via 4) and for 1,2-additions to aldehydes and ketones (via 5).^{8,13} Regeneration of the catalyst would occur by nucleophilic attack of iodide ion on 1 to give phenylselenide anion and 2. The 1,2-addition of 2 to aldehydes¹⁴ and the 1,4-addition of 2 to enones¹⁵ have been reported perhaps indicating the intermediacy of 4 and 5.

When the substrates in Table II were treated with 2.5 mole% of iodine and 1.05 equivalents of 1, a mildly exothermic reaction ensued to give the indicated products within 15 min. Benzaldehyde and *p*-methoxybenzaldehyde showed 90% conversion to the 1,2-adducts shown.¹⁶ Addition of water returned the aldehydes quantitatively.¹² Methyl vinyl ketone gave essentially complete conversion to a 68:32 mixture of the *E* and *Z* adducts indicated and small amounts (~5%) of the hydrolysis product 6.¹⁶ Hydrolysis of the reaction mixture gave 6 in 90% yield.¹² Crotonaldehyde was somewhat unusual in that a 3:1 mixture of both the 1,4-adducts and the 1,2-adduct was obtained.¹⁶ The *E* and *Z* isomers appeared to be present in nearly equal amounts. Hydrolysis of the adducts gave 7 in 70% yield and crotonaldehyde in 20% yield.¹² Identical results were obtained by adding 5 mole% of 2 directly to a solution of substrate and 1. Similarly, the addition of 5 mole% of potassium iodide and 18-crown-6 to an equimolar solution of methyl vinyl ketone and 1 in THF gave complete reaction within 0.5 h at room temperature to give a 72:28 mixture of the *E* and *Z* 1,4-adducts.



An interesting comparison can be made between 1 and phenylthiotrimethylsilane (8) and methylthiotrimethylsilane (9).¹⁷ Although 1 reacts readily with iodine, 8 and 9 give no detectable reaction after 24 h. Similarly, potassium iodide is a poor catalyst for initiating the 1,2- and 1,4-additions of 8 to aldehydes and enones. This is perhaps indicative that the silicon-sulfur bond is significantly stronger than the silicon-selenium bond.

REFERENCES AND NOTES

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(b) T.-L. Ho and G. A. Olah, Synthesis, 417 (1977).
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9. Various attempts to trap phenylselenenyl iodide with cyclohexene failed.
10. In a typical preparation, iodine (1.20 g, 4.72 mmol) was added in one portion to a stirred solution of 1 (2.29 g, 10.0 mmol) and 1 mL of m-xylene. The iodine color disappeared immediately upon addition. Distillation under N_2 gave 1.62 g of a colorless oil, bp 103–107°.
11. Solvents were dried by passing through alumina (activity I) prior to use.
12. All products gave satisfactory ^1H NMR, IR, and mass spectra.
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16. Product analysis by 90 MHz ^1H NMR. Isolation gave considerable hydrolysis.
17. D. A. Evans, K. G. Grimm, and L. K. Truesdale, J. Am. Chem. Soc., 97, 3230 (1975); D. A. Evans, L. K. Truesdale, K. G. Grimm, and S. L. Nesbitt, ibid., 99, 5009 (1977).

Table I. C-O Bond Cleavage with Phenylselenotrimethylsilane and Iodine.



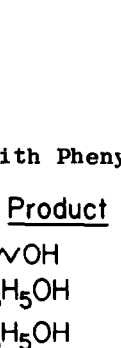
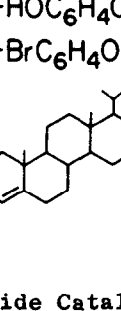

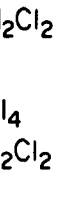

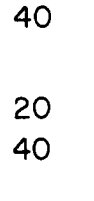

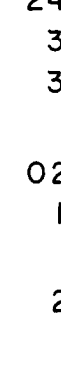

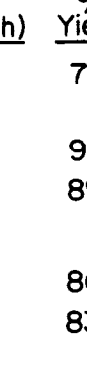

Substrate	Product	Solvent	Temp°C	Rx Time (h)	% Yield
THF		THF	40	05	78
C ₆ H ₅ OCH ₃	C ₆ H ₅ OH	CH ₂ Cl ₂	40	24	5
C ₆ H ₅ OCH ₂ C ₆ H ₅	C ₆ H ₅ OH	CH ₂ Cl ₂	20	3	90
4-BrC ₆ H ₄ OCH ₂ C ₆ H ₅	4-BrC ₆ H ₄ OH	CH ₂ Cl ₂	40	3	89
	4-HOC ₆ H ₄ OH	CCl ₄	20	02	86
4-BrC ₆ H ₄ OTHP	4-BrC ₆ H ₄ OH	CH ₂ Cl ₂	40	1	83
		CH ₂ Cl ₂	20	2	95

Table II. Trimethylsilyl Iodide Catalyzed Additions of Phenylselenotrimethylsilane

Substrate	Product	Solvent	Time (min)	% Conversion	E/Z Ratio
		CDCl ₃	5	90	—
		CDCl ₃	5	90	—
		CCl ₄	15	100	68:32
	 + 	CCl ₄	15	95	55:45

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