Anal. Calcd for $C_{14}H_{11}ClO_2$: C, 68.16; H, 4.50. Found: C, 68.31; H, 4.59.

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Registry No. 2, 68099-35-4; **3**, 78143-54-1; **4a**, 68099-15-0; **4b**, 68099-22-9; **5a**, 68099-31-0; **5b**, 78143-55-2; **6**, 29682-41-5; **7a**, 68099-13-8; **7b**, 68099-16-1; **8a**, 78143-56-3; **9a**, 78163-67-4; **12a**, 78185-42-9; **13a**, 78185-84-9; **13b**, 78143-57-4; **14a**, 78143-58-5; **15a**, 68099-37-6; **16a** (X = Br), 68125-11-1; **16a** (X = Cl), 78143-59-6; **17a**, 68099-36-5; **18a**, 68099-34-3; **19a**, 78143-60-9; **20**, 51274-68-1; **21**, 51274-67-0; **23a**, 78143-61-0; **25a**, 78143-62-1; **26a**, 78143-63-2; **27a**, 78143-64-3; **28a**, 78143-65-4; **29**, 78143-66-5; **30**, 78143-67-6; 2,5-dichloroaniline, 95-82-9; 2-cyclohexen-1-one, 930-68-7; 2,5-dichloro-4'-hydroxybiphenyl, 53905-28-5; 3-bromo-4-hydroxy-2',5'-dichlorobiphenyl, 78143-68-7; 2,5-dibromo-4-hydroxy-2',5'-dichlorobiphenyl, 78143-69-8; 2,5-dibromo-3-hydroxy-2',5'-dichlorobiphenyl, 78143-70-1; 3-acetoxy-2,5,2',5'-tetrachlorobiphenyl, 78143-71-2; 4-acetoxy-2,5,2',5'-tetrachlorobiphenyl, 78143-72-3; 2,5-dichloro-3'-chloro-4'-hydroxybiphenyl, 78143-73-4; 1-chloro-4-iodobenzene, 637-87-6; 4-chloro-4'-hydroxybiphenyl, 28034-99-3; 4-chlorobiphenyl, 2051-62-9; 4-acetoxy-4'-chlorobiphenyl, 57396-87-9; 3-bromo-4-acetoxy-4'-chlorobiphenyl, 78143-74-5; 1,1-dichloro-3-(2,5-dichlorophenyl)cyclohexane, 78143-75-6; 1-chlorocyclohexene, 930-66-5; benzeneselenyl chloride, 931-59-9; 1-phenylseleno-2,2-dichlorocyclohexane, 78143-76-7; 1-phenylseleno-1,2-dichlorocyclohexane, 78143-77-8; 3,3-dichloro-1-cyclohexene, 78143-78-9; 2,3-dichlorocyclohexene, 40099-06-7; 1,2-epoxy-3,3-dichlorocyclohexane, 78143-79-0; 1,2-epoxy-1,3-dichlorocyclohexane, 78143-80-3.

Supplementary Material Available: Experimental details for the preparation of compounds **8a**, **9a**, **23a**, **26a**, **27a**, **29**, **30**, 3,3-dichlorocyclohexene, 2,3-dichlorocyclohexene, 1,2-oxy-3,3-dichlorocyclohexane, and 1,2-epoxy-1,3-dichlorocyclohexane (5 pages). Ordering information is given on any current masthead page.

Synthetic Methods and Reactions. 103.[1] Preparation of Alkyl Iodides from Alkyl Fluorides and Chlorides with Iodotrimethylsilane or Its in Situ Analogues

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We have previously exploited the strong affinity of silicon for oxygen to carry out a number of synthetic transformations with iodotrimethylsilane.[2] These reactions included the cleavage of esters[3] and ethers[4] and the reduction of sulfoxides[5] and sulfonyl halides.[6] Silicon also forms an exceptionally strong bond with fluorine. Utilizing this property, we considered it feasible that the displacement of fluorine by iodine in fluoroalkanes could be achieved with iodotrimethylsilane, despite the reverse stability of the involved carbon–halogen bond (C–F > C–I).

Table I. Synthesis of Iodoalkanes

$$RF + Me_3SiI \longrightarrow RI + Me_3SiF$$

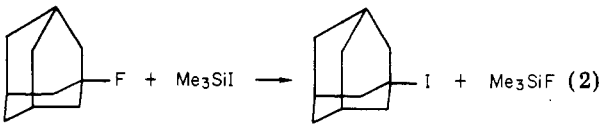
substrate R	reaction conditions: time, h	reaction conditions: temp, °C	yield,[a] %
1-hexyl	48	25	81[b]
1-decyl	24	61	*c*
benzyl	48	25	78
cyclohexyl	16	25	72
1-adamantyl	16	25	87
1-adamantyl	16	25	97[d]
1-adamantyl	16	25	92[e]
2-norbornyl	48	25	76
1-adamantyl	16	61	94[f]
2-methyl-2-propyl	16	61	90[f]

[a] Yield of the isolated, purified product. All products were >98% pure by GLC and had satisfactory physical and spectral data. [b] A mixture of 2- and 1-iodohexanes (55:45) was obtained. [c] Reaction incomplete even after 24 h in refluxing chloroform. [d] Reaction performed with $I_2/Me_3SiSiMe_3$ reagent. [e] Reaction performed with $Me_3SiCl/NaI/CH_3CN$ reagent. [f] The corresponding chlorides were the starting materials. The reaction was performed in refluxing chloroform.

Indeed, when tertiary and secondary alkyl fluorides are reacted with iodotrimethylsilane in a suitable inert solvent such as methylene chloride, the corresponding alkyl iodides are obtained in high yield (Table I, eq 1).

$$RF + Me_3SiI \rightarrow RI + Me_3SiF \quad (1)$$

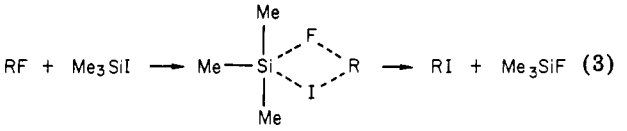
In a typical reaction, 1-fluoroadamantane was treated with iodotrimethylsilane (1.1 equiv) at room temperature under a dry nitrogen atmosphere. 1-Iodoadamantane was obtained in almost quantitative yield. An equivalent amount of fluorotrimethylsilane is formed in the reaction (eq 2).



(2)

The reaction proceeds readily for tertiary fluoroalkanes. Secondary fluoroalkanes react slower but generally without rearrangements. Thus, for example, fluorocyclohexane was transformed to iodocyclohexane without formation of any 1-iodo-1-methylcyclopentane. The reaction with primary fluoroalkanes is sluggish and generally leads to a mixture of iodoalkanes. For example, the conversion of 1-fluorohexane to 1-iodohexane is incomplete even after 24 h at room temperature.

The halogen exchange reaction probably proceeds via an intermediate pentacoordinate silicon species (eq 3).



(3)

The fluoride–iodide halogen exchange can also be accomplished with in situ reagents, such as chlorotrimethylsilane/sodium iodide or hexamethyldisilane/iodine.

It is interesting to note that tertiary chlorides such as 1-chloroadamantane and 2-chloro-2-methylpropane can also be transformed into the corresponding iodoalkanes, albiet at a much slower rate. However, secondary and primary chloroalkanes are not affected under the reaction conditions.

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The easy synthesis of fluoroalkanes from alkenes, alcohols, and other precursors with HF or with our HF/pyridine reagent[7] makes the present method an attractive route to iodoalkanes through the corresponding fluoroalkanes.

Experimental Section

General Procedure. Iodotrimethylsilane (2.21 g, 11 mmol) was added to a stirred solution of the alkyl fluoride (chloride) (10 mmol) in dichloromethane (25 mL), and the reaction mixture was stirred under a dry nitrogen atmosphere for 16 h. The reaction mixture was quenched with aqueous sodium bicarbonate solution and extracted with dichloromethane. The organic extract was washed with water and dried over anhydrous sodium sulfate. The solvent was evaporated and the product isolated by distillation or crystallization.

Reaction with hexamethyldisilane/iodine or with chlorotrimethylsilane/sodium iodide was performed as described previously.[6]

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No. Iodotrimethylsilane, 16029-98-4; 1-hexyl fluoride, 373-14-8; 1-decyl fluoride, 334-56-5; benzyl fluoride, 350-50-5; cyclohexyl fluoride, 372-46-3; 1-adamantyl fluoride, 768-92-3; 2-norbornyl fluoride, 694-95-1; 1-adamantyl chloride, 935-56-8; 2-methyl-2-propyl chloride, 507-20-0; 1-iodohexane, 638-45-9; 2-iodohexane, 18589-27-0; benzyl iodide, 620-05-3; cyclohexyl iodide, 626-62-0; 1-adamantyl iodide, 768-93-4; 2-norbonyl iodide, 55924-26-0; 2-methyl-2-propyl iodide, 558-17-8.

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Azetidinium Intermediate in the Reaction of 2-[(Dimethylamino)methyl]cyclopent-1-yl Mesylate with 3,4-Dichloroaniline

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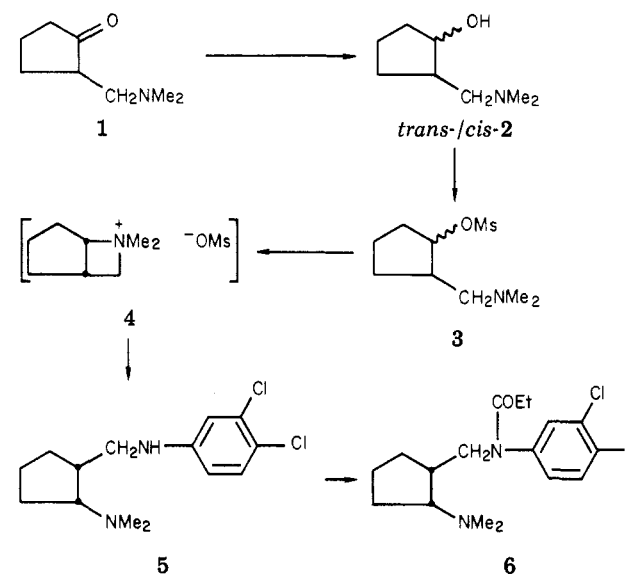
There have been many examples of aziridinium intermediates reported in the literature[1] but comparatively few examples of azetidinium intermediates.[2] While conducting a search for biologically active agents, we encountered an interesting example of the latter intermediate.

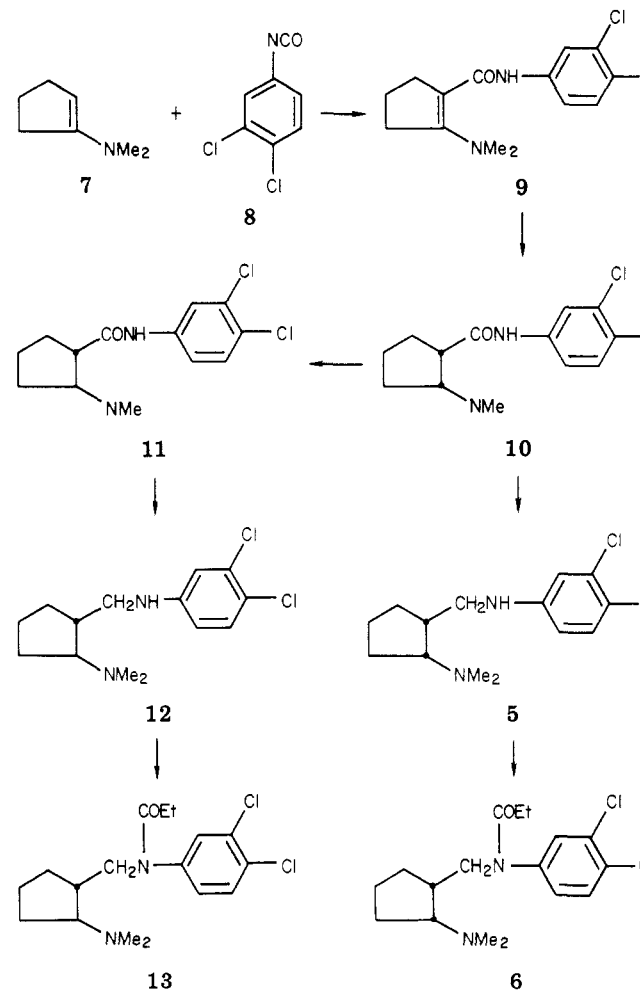
Treatment of the isomeric mixture of amino alcohols **2**,[3] obtained by lithium aluminum hydride reduction of Mannich base **1**, with sodium hydride and methanesulfonyl chloride and subsequent reaction of the resulting unstable mesylate **3** with 3,4-dichloroaniline produced diamine **5** as the only aniline-containing product (Scheme I). The structure of the product was established by comparison of the propionanilide **6**, obtained by acylation with propionic anhydride, with material produced in an alternate synthesis.

Reaction of 1-(dimethylamino)cyclopentene (**7**) with 3,4-dichlorophenyl isocyanate (**8**) in benzene[4] followed by PtO_2 hydrogenation gave cis amide **10**[5] (Scheme II).

Scheme I



Scheme II



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