J. Am. Chem. Soc. **1988**, *110*, 7737-7745 7737

carbons to be >CH's, and the remainder to be >CH_2's.

Stability of 22a$^+$ in the Presence of Triethylamine. A solution of 40 mg (0.01 mmol) of complex **22a**$^+$ in 0.5 mL of CH_2Cl_2 was combined with 0.06 mL of triethylamine at −78 °C and maintained at that temperature of 2 h. The solvent was removed, and the residue was washed with pentane; none dissolved. The ^1H NMR ($CDCl_3$) spectrum of the pentane-insoluble portion showed it to be unreacted starting material **22a**$^+BF_4^-$.

Acknowledgment. We thank our colleague Prof. Dan Reger for many helpful discussions throughout the course of this work, our colleague Dr. Ron Garber for his invaluable help and advice with the variable-temperature NMR experiments, Prof. Chuck Casey and his group with whom we spent a delightful and informative 7 months just prior to the initiation of this work, the National Institutes of Health, which provided the Department of Chemistry under Instrumentation Grant 1-510-RR02849 the VG Analytical, Ltd., 70SQ high-resolution, double-focusing mass spectrometer and VG 11/250 data system, and the National Science Foundation whose financial support, initially in the form of an EPSCOR grant to the University of South Carolina and later as a research grant to the principle investigator, made possible the work reported here.

Fluorodestannylation. A Powerful Technique To Liberate Anions of Oxygen, Sulfur, Selenium, and Carbon[1]

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Abstract: Fluoride ions smoothly destannylate organotin chalcogenides to liberate nucleophilic chalcogenide ions; hence the first nucleophilic oxide (O^{2-}) and selenide (Se^{2-}) transfer agents are reported where the tin atom serves as a "group 16 (VIB) transfer agent". In the presence of crown ethers or ammonium salts, this process results in a new way to generate "naked" nucleophiles. Ethers and selenides are formed in good to excellent yield. In addition, a useful C–C bond-forming reaction has been developed by using alkyltins with aldehydes and acid chlorides in the presence of fluoride ion. Aspects concerning reactivity and mechanism are presented. Finally, the generality of the fluorodestannylation procedure and the differences with parallel silicon chemistry are detailed.

Considerable effort has been focused on desilylation reactions over the past decade;[2] far less attention has been accorded parallel work on organotin compounds. In 1985, Pearlman reported that fluoride ion could induce the formation of exocyclic double bonds from stannylated and hindered *sec*-alkyl sulfones.[3] The next year Danishefsky and Hungate published a fluorodestannylative procedure applied to a cyclic stannylene of use in an intramolecular O-alkylation.[4] Later in 1987, Ohno described selective O-monoalkylations of an *O*-stannylene acetal derived from a tartrate ester, using fluoride ion to promote the reaction.[5] None of the above procedures were extended beyond their specific synthetic context.

Our own work during this period involved the discovery of a fluorodestannylation reaction of organotin sulfides (**1**), permitting the preparation of a host of organosulfides in high yield under mild and neutral conditions[1] (eq 1). In addition, we found that cyanide ion performed comparably (cyanodestannylation).

$$\underset{\mathbf{1}}{R_3Sn{-}S{-}SnR_3} + 2R'{-}Br \xrightarrow[\text{(or CN}^-)]{F^-} R'{-}S{-}R' + 2R_3Sn{-}F \qquad (1)$$

We wish to report that fluoride ion combines with organotin oxides, -sulfides, and -selenides and organotins in general to liberate the corresponding anion (Scheme I, Table I). In the presence of appropriate electrophiles, ethers, thioethers, organic selenides, and carbon–carbon bonds are produced. Most of these reactions take place in neutral media, in contrast with many known procedures using strong bases.[6] The generality of these fluoride and cyanide effects demonstrates a significant new dimension in organotin chemistry.

Scheme I

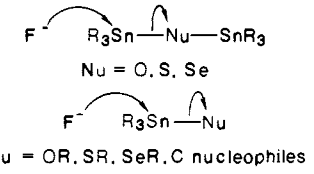

Table I. Tin Substrates under Investigation[a]

oxides	sulfides	selenides	organostannanes
$R_3Sn{-}O{-}SnR_3$	$R_3Sn{-}S{-}SnR_3$	$R_3Sn{-}Se{-}SnR_3$	R''_4Sn
$R_3Sn{-}OR'$	$R_3Sn{-}SR'$	$R_3Sn{-}SeR'$	$Bu_3Sn{-}R''$
	R_2SnS		$Bu_3Sn{-}C{\equiv}CH$

[a] R = aryl, alkyl; R′ = alkyl; R″ = allyl.

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(6) Among them with sulfur: use of *t*-BuOK: Wilson, K. D.; Beak, P. *J. Org. Chem.* **1987**, *52*, 218; use of $NaBH_4$: Hopkins, P. B.; Holler, T. P.; Spaltenstein, A. *J. Org. Chem.* **1987**, *52*, 2977. Among them with oxygen: use of NaOH: Gokel, G. W.; Hernandez, J. C.; Viscariello, A. M.; Arnold, K. A.; Campana, C. F.; Echegoyen, L.; Fronczek, F. R.; Gandour, R. D.; Morgan, C. R.; Trafton, J. E.; Miller, S. R.; Minganti, C.; Eiband, D.; Schultz, R. A.; Tamminen, M. *J. Org. Chem.* **1987**, *52*, 2693; use of *t*-BuOK: Gupta, R. C.; Slawin, A. M. Z.; Stoodley, R. J.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1986**, 668; use of Grignard reagent: Marshall, J. A.; Lebreton, J.; DeHoff, B. S.; Jenson, T. M. *Tetrahedron Lett.* **1987**, *28*, 723. Among them in the formation of selenide ion (Se^{2-}): use of $NaBH_4$: Klayman, D. L.; Griffin, S. T. *J. Am. Chem. Soc.* **1973**, *95*, 197; use of $LiBHEt_3$: Gladysz, J. A.; Hornby, J. L.; Garbe, J. E. *J. Org. Chem.* **1978**, *43*, 1204; use of NH_2NH_2/NaOH: Syper, L.; Mlochowski, J. *Synthesis* **1984**, 439.

Table II. Formation of Symmetrical Ethers

entry	substrate[a]	organotin	solvent[b]	*T*, °C	time, h	fluoride[c]/CN^-	product	yield,[d] %
1	$PhCH_2Br$	$(Bu_3Sn)_2O$	A	20	6	$TBAF\cdot 3H_2O$	$(PhCH_2)_2O$	41[g]
2	$PhCH_2Br$	$(Bu_3Sn)_2O$	A	50	2	$TBAF\cdot 3H_2O$	$(PhCH_2)_2O$	50[g]
3	$PhCH_2Br$	$(Bu_3Sn)_2O$	A	55	7	CsF·18C6	$(PhCH_2)_2O$	71
4	*n*-hexyl iodide	$(Bu_3Sn)_2O$	A	90	36	CsF·18C6	$(n\text{-Hex})_2O$	25[g]
5	*n*-hexyl iodide	$(Bu_3Sn)_2O$	B	52	5	CsF·18C6	$(n\text{-Hex})_2O$	50[e]
6	*n*-hexyl iodide	$(Bu_3Sn)_2O$	B	20	96	CsF	$(n\text{-Hex})_2O$	53[g]
7	*n*-hexyl iodide	$(Bu_3Sn)_2O$	C	52	5	CsF·18C6	$(n\text{-Hex})_2O$	54[g]
8	*n*-hexyl iodide	$(Bu_3Sn)_2O$	C	20	16	CsF·18C6	$(n\text{-Hex})_2O$	50[g]
9	*n*-hexyl iodide	$(Bu_3Sn)_2O$	E	20	9	CsF·18C6	$(n\text{-Hex})_2O$	5[e]
10	*n*-hexyl iodide	$(Bu_3Sn)_2O$	C	20	144	TBACN[f]	$(n\text{-Hex})_2O$	nil
11	*n*-hexyl iodide	$(Me_3Si)_2O$	B	50	28	CsF·18C6	$(n\text{-Hex})_2O$	nil
12	*n*-decyl iodide	$(Bu_3Sn)_2O$	A	80	24	CsF·18C6	$CH_3(CH_2)_7CH{=}CH_2$	90

[a] The molar ratio of substrate to organotin is 2.00:1.05. [b] A = acetonitrile; B = DMF; C = *N*-methyl-2-pyrrolidinone; D = DMSO; E = DMF/TMEDA; cesium fluoride was used in (1.3–1.5)-fold excess unless otherwise noted; TEAF = tetraethylammonium fluoride. [d] Isolated yields unless otherwise noted. [e] GC yield. [f] Tetrabutylammonium cyanide. [g] Benzyl alcohol or 1-hexanol as side product was observed by NMR and GC.

Tin is a larger atom than silicon and while being considered hard, it should be softer than silicon.[7] Hence, like silicon, it has a tendency to associate with the hardest atom, namely, fluoride. While the analogy with fluorodesilylation is very close, experimentally, different results and reactivities from organotin to silicon analogues encouraged us to develop this general concept. For example, we found that hexamethyldisilathiane (**2**) when treated with fluoride ion in the presence of 1-bromohexane formed a 2.3:1 mixture of monosulfide *and* disulfide (eq 2), whereas the tin analogue gave a near-quantitative yield of pure monosulfide (eq 3).

$$2CH_3(CH_2)_5Br + \underset{\mathbf{2}}{Me_3Si\text{-}S\text{-}SiMe_3} \xrightarrow{F^-} \text{-S-} + \text{-S-S-}\ (2.3{:}1) \qquad (2)$$

$$2CH_3(CH_2)_5Br + \underset{\mathbf{1}}{Me_3Sn\text{-}S\text{-}SnMe_3} \xrightarrow{F^-} \text{-S-}\ (99\%) \qquad (3)$$

In addition, hexamethyldisiloxane (**3**) does not generate a significant amount of ether in the presence of fluoride ion and simple organic halides, whereas the tin analogue does (eq 4 and 5).

$$2CH_3(CH_2)_5I + \underset{\mathbf{3}}{Me_3Si\text{-}O\text{-}SiMe_3} \xrightarrow{F^-} \text{-O-}\ (\text{trace}) \qquad (4)$$

$$2CH_3(CH_2)_5I + \underset{\mathbf{4}}{Bu_3Sn\text{-}O\text{-}SnBu_3} \xrightarrow{F^-} \text{-O-}\ (54\%) \qquad (5)$$

We will present a new, general concept for generating in situ synthetic equivalents of cesium and quaternary ammonium salts containing oxygen, sulfur, and selenium ions as "naked" nucleophiles; their effective nucleophilicities will be discussed. Finally, a possible mechanism for the fluorodestannylation reaction will be proposed as a working hypothesis.

Results and Discussion

Comparison of Fluorodestannylation with Fluorodesilylation. As indicated above, fluorodestannylation can be applied to a host of organotin derivatives (Table I). Thus, tin can carry chalcogens as the synthetic equivalent of O^{2-}, S^{2-}, Se^{2-}, RO^-, RS^-, and RSe^-. These organotins act as general "group 16 (VIB) transfer agents" when combined with fluoride ion. The physical properties of most of these chalcogen-containing organotins are suitable for the synthetic chemist; they are usually high-boiling liquids or solids with definite melting points. Their stability permits them to be manipulated without special precaution (e.g., bis(triphenyltin) selenide (**5**) is stable to the ambient atmosphere for several days without turning red).[8] Their solubility in many organic solvents makes then excellent substitutes for their chalcogens salt analogues (e.g., Na_2S, Na_2Se, etc.).

The general reactivity of organotins differs significantly from that of organosilicons due to the different bond energies of tin and the various chalcogens compared with that of silicon. Although the Sn–F bond energy is not known for triaralkyltin fluorides, a comparison can be made between some values obtained for the tin tetrahalide series (including SnF_4).[9,10] The poor overlap of orbitals between large chalcogens like selenium and sulfur with silicon makes these compounds extremely unstable; tin, however, accommodates these chalcogens much better. Also, oxygen strongly prefers to be bound with silicon rather than tin (although the latter type of compound is sufficiently stable). A qualitative explanation is provided by application of the concept of HSAB theory[7a] or the recent density functional theory.[7b]

Several exchange reactions with a variety of silicon, germanium, and tin derivatives lead to the qualitative evaluation of their bond energies and affinities toward some ligands containing oxygen and sulfur moieties.[11] These reactions help to rationalize the relative stability of Sn–O, Sn–S, and Sn–Se bonds as compared to the Si–O, Si–S, and Si–Se bonds. From these results, it has been demonstrated that tin is softer than silicon in trialkyltin mercaptides or oxides even though the tin compounds used here should be considered as hard Lewis acids.

Sulfur. We have already demonstrated the efficacy of the fluoro- and cyanodestannylation procedure as applied to organotin sulfides **1**.[1] At moderate temperatures (20–80 °C) under essentially neutral solvent conditions, using CsF, CsF with 18-crown-6 (18C6), tetrabutylammonium fluoride (TBAF), or cyanide (TBACN) with **1**, a variety of aliphatic halides can be converted in excellent overall yields (averaging over 90%) to the corresponding acyclic and cyclic sulfides. In sharp contrast, the silicon analogue hexamethyldisilathiane (**2**) gives *di*sulfide as a significant product, showing the higher lability of the silicon–sulfur bond.[12]

Oxygen. Although the methodology is still evolving, our results indicate that bis(tributyltin) oxide (**4**) combined with fluoride ion

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[7] (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561.

[8] Most of the organotins containing three organic ligands (alkyl or aryl) are often used as biocides: Schweinfurth, H. *Tin Its Uses* **1985**, *143*, 9. Caution! It is advisable to handle them with gloves in a fume hood.

[9] For tin tetrahalides, see: Shaw, C. F.; Allred, A. L. *Organomet Chem. Rev. A* **1970**, *5*, 96. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 375. The Sn–halogen average bond energies evaluated are (in kcal/mol) as follows: Sn–Cl, 82; Sn–Br, 65; Sn–I, 45. Huheey, J. E. *Inorganic Chemistry, Principles of Structure and Reactivity*; 2nd ed.; Harper and Row: New York, 1978; p 848: Sn–F, 99; Sn–Cl, 77; Sn–Br, 65; Sn–I, 49.

[10] The average Sn–halogen bond energies for the trimethyltin halide series are (in kcal/mol) as follows: Sn–Cl, 75; Sn–Br, 61; Sn–I, 45. Thus a comparison between the magnitude and the trend showed in the tin tetrahalides versus the trimethyltin halide series leads us to approximate the Sn–F bond energy of trimethyltin fluoride at ca. 99 kcal/mol (close to the Sn–F energy of SnF_4) according to Huheey.[9] We emphasize that this value is an average bond energy and does not correspond to the value obtained by an homolytic cleavage of the Sn–F bond.

[11] Armitage, D. A.; Sinden, A. W. *J. Organomet. Chem.* **1975**, *90*, 285. Sukhani, O.; Gupta, V. D.; Mehrotra, R. C. *Organomet. Chem.* **1967**, *7*, 85.

[12] The most probable pathway for the latter reaction likely involves attack of an alkanethiolate on the sulfur atom of unreacted hexamethyldisilathiane (**2**); with fluoride ion this dithio derivative would generate RSS^-, which could be alkylated to give disulfide.

Table III. Formation of Unsymmetrical Ethers

entry	substrate[a]	organotin	solvent[b]	T, °C	time, h	fluoride	product	yield,[c] %
1	allyl bromide	$PhCH_2OSnBu_3$	A	100	2	CsF·18C6	$PhCH_2O$-allyl	90
2	*n*-hexyl iodide	$PhCH_2OSnBu_3$	A	75	2	AgF·24C8[d]	$PhCH_2O$-*n*-Hex	17
3	*n*-butyl iodide	$PhCH_2OSnBu_3$	A	80	24	CsF·18C6	$PhCH_2O$-*n*-Bu	20
4	*n*-hexyl iodide	$PhCH_2OSnBu_3$	NMP	20	24	CsF·24C8	$PhCH_2O$-*n*-Hex	69

[a] The molar ratio of substrate to organotin is 1.00:1.05. [b] A = acetonitrile; NMP = *N*-methyl-2-pyrrolidinone. [c] Isolated yields, not optimized. [d] 24C8 = dibenzo-24-crown-8.

Table IV. Formation of Organic Selenides

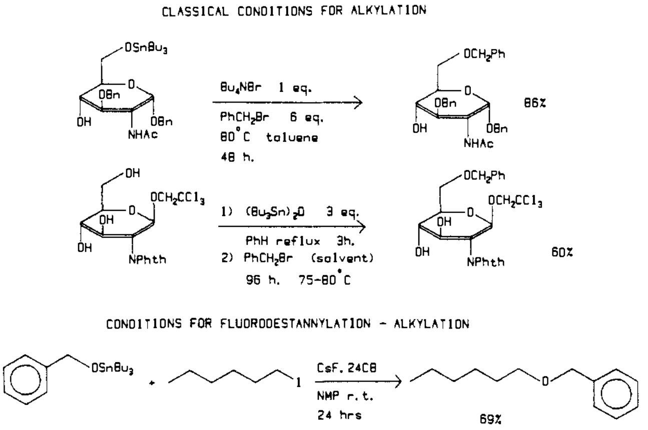
entry	substrate[a]	organotin	solvent[b]	T, °C	time, h	fluoride[c]	product	yield,[d] %
1	$PhCH_2CH_2Br$	$(Ph_3Sn)_2Se$	A	40	1.0	CsF·18C6	$(PhCH_2CH_2)_2Se$	89
2	$PhCH(CH_3)Br$	$(Ph_3Sn)_2Se$	A	40	40	CsF·24C8	$(PhCH(CH_3))_2Se$	67
3	$CH_3COO(CH_2)_3Br$	$(Ph_3Sn)_2Se$	A	36	2.0	CsF·24C8	$(CH_3COO(CH_2)_3)_2Se$	97
4	$CH_3(CH_2)_5Br$	$(Ph_3Sn)_2Se$	A	48	1.5	CsF·18C6	$(CH_3(CH_2)_5)_2Se$	96
5	$CH_3(CH_2)_5OTs$	$(Ph_3Sn)_2Se$	A	20	3.0	CsF·18C6	$(CH_3(CH_2)_5)_2Se$	70[e]
6	$CH_3(CH_2)_5Br$	$(Ph_3Sn)_2Se$	A	55	48	TBACN[f]	$(CH_3(CH_2)_5)_2Se$	nil

[a] The molar ratio of substrate to organotin is 2.00:1.05. [b] A = acetonitrile:THF (8:3). [c] A 5-fold excess was used. [d] Isolated yields, not optimized. [e] 30% of diselenide was formed. [f] Tetrabutylammonium cyanide.

can deliver[13] the equivalent of O^{2-}, thus providing a useful alternative to the well-known Williamson ether synthesis.[14] In addition, using this fluorodestannylation procedure, we are able to generate in situ a synthetic equivalent of cesium oxide (Cs_2O) complexes with a crown ether. With hexamethyldisiloxane (**3**), the reaction failed; presumably the energy of the silicon–oxygen bond is too strong to displace the oxide ion. To our knowledge, only trimethylsilanolate salts of lithium, sodium, and potassium (see compound **13**) have been described as being synthetic equivalents of "O^{2-}" in the literature. This was, however, in a different context involving the conversion of carboxylic acid derivatives into their corresponding anhydrous acid salts.[15]

Thus, we present the first "O^2-transfer agent" (**4**) involved in substitution reactions. This commercial reagent possesses significant nucleophilicity to counter balance many elimination processes usually observed in the Williamson reaction. To test the basicity of the medium, we employed several iodo compounds (well-known for giving a high degree of elimination under basic conditions[14c]) as shown in Tables II and III. In contrast to the report of Danishefsky and Hungate[3] showing the neutrality of the process in an intramolecular O-alkylation using an organostannylene, we found that tributylstannyl oxide provoked some elimination as indicated by the alcoholic and alkene side products isolated or observed by gas chromatography. This basicity increases when the solvent was changed to DMSO or CH_3CN. A slow addition of the organotin oxide or variation in the number of equivalents of cesium fluoride did not change the results; in the same way, the addition of crown ethers increased the rate of the reaction but gave the same yield of ether.

Scheme II



Synthetic Equivalent of "O^{2-}"

$$2PhCH_2Br + \underset{\mathbf{4}}{Bu_3Sn\text{-}O\text{-}SnBu_3} \xrightarrow[71\%]{F^-} PhCH_2\text{-}O\text{-}CH_2Ph + 2Bu_3Sn\text{-}F \quad (6)$$

$$2n\text{-}CH_3(CH_2)_5\text{-}I + \underset{\mathbf{4}}{Bu_3Sn\text{-}O\text{-}SnBu_3} \xrightarrow[54\%]{F^-} [n\text{-}CH_3(CH_2)_5]_2O + 2Bu_3Sn\text{-}F \quad (7)$$

In addition to symmetrical aliphatic ethers that were formed in modest yield (ca. 50%, Table II), unsymmetrical ethers have been prepared in better yield by using this method (Table III). In general, ethers can be prepared under mild conditions at room temperature. Furthermore, we have demonstrated a new strategy for directly introducing a benzyl ether group starting from an organic halide. In conclusion, the fluorodestannylation–alkylation procedure makes it possible to employ substrates having β-hydrogens without causing too much elimination; in contrast, the Williamson conditions are usually reserved for phenols or compounds having no β-hydrogens[14c] due to the strong basicity of the medium.

Considering the pioneering work of Ogawa and Veyrieres[16] in their regioselective stannylation–alkylation process on carbohydrate substrates, we thought it appropriate to give a clear representation of the reaction conditions found here compared to the usual or

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(13) The oxide anion has been the subject of discussion about its basicity: Smith, D. W. *J. Chem. Educ.* **1987**, *64*, 480. However, in this context, the oxygen should not exist doubly charged but in the form of a stannolate; otherwise the medium would be highly basic and provoke much more elimination. We are still verifying the limit associated with the basicity of the medium. It has been recently reported that regioselective mono-O-*p*-toluenesulfonylation of nucleosides can be effected under phase-transfer conditions with dibutyltin oxide and ammonium quaternary fluoride, chloride, and bromide: Grouiller, A.; Essadiq, H.; Najib, B.; Molière *Synthesis* **1987**, 1121.

(14) For the classic Williamson reaction, see: (a) March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: 1977; pp 357–8. (b) Vogel, A. *Textbook of Practical Organic Chemistry*, 4th ed.; Longman: New York, 1981; pp 413, 753–4. (c) Feuer, H.; Hooz, J. In Patai, S. *The Chemistry of the Ether Linkage*; Interscience: New York, 1967, pp 446–468. (d) Naemura, K.; Ebashi, I.; Matsuda, A.; Chikamatsu, H. *J. Chem. Soc., Chem. Commun.* **1986**, 666. (e) Merz, A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 846. Phase-transfer catalysis using tetraalkylammonium salts has also been employed: (f) Nouguier, R. M.; Mchich, M. *J. Org. Chem.* **1987**, *52*, 2995. See Gokel, et al. in ref 6. Nouguier, R.; Medani, C. *Tetrahedron Lett.* **1987**, *28*, 319. Jones, R. A. *Aldrichim. Acta* **1976**, *9*, 35–45 and references cited therein. (g) Freedman, H. H.; Dubois, R. A. *Tetrahedron Lett.* **1975**, 3251. (h) Dockx, J. *Synthesis* **1973**, 447. The Williamson reaction in the synthesis of oxygenated crown ethers, among them: (i) Gokel, G. W.; Cram, D. J.; Liotta, C. L.; Harris, H. P.; Cook, F. L. *J. Org. Chem.* **1974**, *39*, 2445. (j) Christiansen, J. J.; Eathough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351. (k) Gokel, G. W.; Durst, H. D. *Synthesis* **1976**, 168. (i) Pedersen, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 391.

(15) Laganis, E. D.; Chenard, B. L. *Tetrahedron Lett.* **1984**, *25*, 5831.

(16) (a) Ogawa, T.; Nukada, T.; Matsui, M. *Carbohydr. Res.* **1982**, *101*, 263. (b) Sugawara, F.; Nakayama, H.; Ogawa, T. *Carbohydr. Res.* **1982**, *108*, C5. (c) Ogawa, T.; Nakabayashi, S.; Sasajima, K. *Carbohydr. Res.* **1981**, *96*, 29. (d) Veyrieres, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1626. (e) Veyrieres, A.; Alais, J. *J. Chem. Soc., Perkin Trans. 1* **1981**, 377.

Table V. C–C Bond Formation

entry	substrate[a]	organotin	solvent[b]	*T*, °C	time, h	fluoride	product	yield,[c] %
1	PhCH(Me)CHO	$(allyl)_4Sn$	DMF	20	3	CsF (5.1)	PhCH(OH)(allyl)	85
2	PhCH(Me)CHO	$Bu_3Sn(allyl)$	DMF	85	72	CsF (4.6)	PhCH(OH)(allyl)	7
3	PhCH(Me)CHO	$Bu_3SnC{\equiv}CH$	NMP	44	90	CsF (3.7)	$PhCH(OH)C{\equiv}CH$	nil
4	$PhCH_2COCl$	$(allyl)_4Sn$	NMP	20	20	CsF (2.3)	$PhCH_2CH_2CH{=}CH_2$	76
5	$PhCH_2COCH_3$	$(allyl)_4Sn$	A	55	200	CsF (4.5)	$PhCH_2C(CH_3)(OH)(allyl)$	16
6	cyclo-$(CH_2)_{12}CO$	$(allyl)_4Sn$	DMF	55	24	CsF (4.9)	cyclo-$(CH_2)_{12}C(OH)(allyl)$	2

[a] The molar ratio of organotin to carbonyl compounds is 1.05:1.00. [b] A = acetonitrile:DMF (5:1); NMP = *N*-methyl-2-pyrrolidinone. [c] Isolated yields, not optimized.

Scheme III. Demonstration of Reaction Neutrality for the Preparation of Bis(1-phenethyl) and Bis(2-phenethyl) Selenides

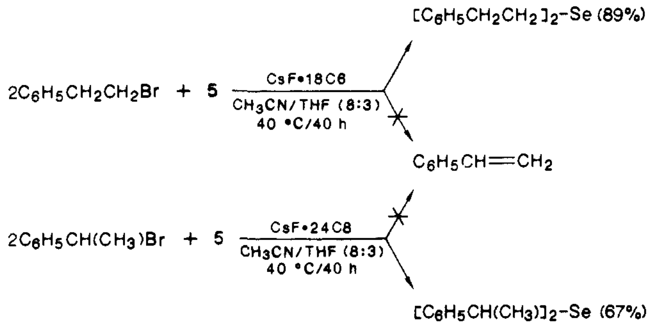

Table VI. List of Synthetic Equivalents of Various Salts of Cesium and Quaternary Ammonium Ions[a]

cesium		quaternary ammonium			
Cs_2O	CsOR	$(TBA)_2O$	TBAOR	$(TEA)_2O$	TEAOR
Cs_2S	CsSR	$(TBA)_2S$	TBASR	$(TEA)_2S$	TEASR
Cs_2Se		$(TBA)_2Se$			

[a] TBA = tetrabutylammonium; TEA = tetraethylammonium.

Scheme IV. Formation of Synthetic Equivalents of Cesium and Tetrabutylammonium Salts[a]

$$R_3Sn{-}X{-}SnR_3 + 2CsF{\bullet}18C6 \longrightarrow 2R_3Sn{-}F + \text{"}Cs_2X\text{"}{\bullet}18C6$$

$$R_3Sn{-}X{-}SnR_3 + 2TBAF \longrightarrow 2R_3Sn{-}F + \text{"}(TBA)_2X\text{"}$$

$$R_3Sn{-}X{-}R' + CsF{\bullet}18C6 \longrightarrow R_3Sn{-}F + 18C6{\bullet}Cs^{+\,-}XR'$$

$$R_3Sn{-}X{-}R' + TBAF \longrightarrow R_3Sn{-}F + TBA^{+\,-}XR'$$

[a] X = O, S, Se.

classical procedures.[16] As shown in Scheme II, the reaction time is diminished to 2–3 h when an organotin oxide is treated with fluoride ion in DMF or NMP (*N*-methyl-2-pyrrolidinone) in the presence of benzyl bromide. This is in sharp contrast to the few examples of parallel alkylations on simple monosaccharides.[16] These conditions require heating (80 °C) for 2–3 days with reactive halides such as benzyl bromide. This suggests that our conditions can successfully be applied with monosaccharides; we are presently investigating this aspect in our laboratories.[17]

Selenium. For the preparation of organoselenides, up to now, the most prominent methods in the literature are certainly those developed by Gladysz[18] using lithium triethylborohydride with metallic selenium or the procedure of Klayman[19] using sodium borohydride with selenium pellets. However, in both cases the supersaturated selenide salt formed must be used immediately, as it tends to precipitate in time, losing its reactivity. Yields of organoselenides are ca. 50–60% with nonactivated halides such as 1-bromohexane.[18,19] The silicon carrier of Se^{2-}, hexamethyldisilaselenane[20] (**8**), is a highly reactive and difficult substance to work with; H_2Se is immediately liberated upon contact air.

In contrast, organotin selenides are relatively stable; bis(triphenyltin), selenide (**5**) is not significantly odorous, can easily be prepared in substantial quantities (40 g, 83% yield), and can be stored in a refrigerator for up to 1 year without any appreciable decomposition (verified by ^{119}Sn NMR). In the presence of alkyl halides this material is smoothly destannylated under neutral solvent conditions and mild reaction temperatures (ca. 40 °C) (Table IV) to deliver organoselenides in excellent isolated yield.

Our method takes place in totally neutral, anhydrous conditions, whereas the two cited procedures have a tendency to be basic by the slight excess of hydride reagent used or the difficulty associated with the titration or the weighing of such hydrides. This latter problem of standardization of hydride can also give rise to some undesired organic diselenides as byproducts. As shown in Scheme III, the neutrality of the medium appears responsible for the high-yield preparation of bis(1-phenethyl) and bis(2-phenethyl)phenethyl selenide (entries 1 and 2 in Table IV) without the formation of styrene. In the case of 1-phenethyl bromide, it is a clear demonstration that hindered secondary organic selenides are readily obtainable (in this case as a *dl*/meso mixture).

Carbon. Our preliminary results indicate that the reactivity of organotins in the presence of fluoride ion is slightly less than with the corresponding silicon analogues with aldehydes.[21] Since the strength of the Sn–F bond is unclear in the literature (ca. 99 kcal/mol),[10] it is presently difficult to quantify and to compare accurately the thermodynamic effects in these systems.[22] However, the importance of carbon–carbon bond formation in organic synthesis lead us to explore the use of fluorodestannylation in this field. Tetraallyltin without fluoride assistance has been successful for that purpose as demonstrated in 1980 by Daude and Pereyre.[23] However, long reaction times were required and only poor to good yields were obtained with ketones and some aldehydes (often less than 60% yield). With allyltributyltin, poor yields and strong heating were required to react with aldehydes.

As shown in Table V, we are able to transfer allylic groups to aldehydes and an acid chloride using fluoride ion to promote the coupling (entries 1 and 4). For example, with tetraallyltin (**9**) and fluoride ion, the reaction time decreased to 3 h at room temperature (85% yield) compared to 18 h at room temperature (82% yield) with the method of Daude and Pereyre.[23] In the reaction with allyltributyltin, a poor yield with aldehyde (Table V, entry 2) was obtained. Some reactions were carried out with commercial ethynyltributyltin (entry 3) with limited success. Ketones were less effective in the coupling reaction, giving low yields (entries 5 and 6).

This method gives an alternate way to make C–C bonds without involving strong Lewis acids (such as BF_3, $TiCl_4$, or $SnCl_4$) as is often characteristic with organostannanes.[24]

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(17) Gingras, M.; Chan, T. H.; Harpp, D. N., unpublished results.

(18) Gladysz, J. A.; Hornby, J. L.; Garbe, J. E. *J. Org. Chem.* **1978**, *43*, 1204.

(19) Klayman, D. L.; Griffen, T. S. *J. Am. Chem. Soc.* **1973**, *95*, 197.

(20) Detty and Seidler (Detty, M. R.; Seidler, M. D. *J. Org. Chem.* **1982**, *47*, 1354) described this compound as air-sensitive and found that it could be stored for only 1 month under nitrogen at −20 °C.

(21) We are currently verifying the difference in reactivity between Sn–allyl and Si–allyl groups with fluoride ions. A recent report outlines further work on fluorodesilylation reactions of this type: Kira, M.; Kobayashi, M.; Sakurai, H. *Tetrahedron Lett.* **1987**, *28*, 4081.

(22) Qualitative bond energy calculations indicate that both fluorodesilylation and fluorodestannylation favor cleavage of the Si (Sn)–C bonds although the Si–C cleavage is predicted to be more exothermic according to some values of Si–C bond energy obtained by: Davis, D. D.; Gray, C. E. *J. Org. Chem.* **1970**, *35*, 1303.

(23) Daude, G.; Pereyre, M. *J. Organomet. Chem.* **1980**, *190*, 43.

(24) For leading references without Lewis acid or fluoride, see: Ytagai, H.; Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 4548. Abel, E. W.; Rowley, R. J. *J. Organomet. Chem.* **1975**, *84*, 199. Servens, C.; Pereyre, M. J. *J. Organomet. Chem.* **1972**, *35*, C20.

In Situ Formation of Synthetic Equivalents of Cesium and Quaternary Ammonium Salts: A New Pathway to "Naked Nucleophiles". The concept of "naked anions" is not new; it was explored extensively[25] following Pedersen's landmark discovery of crown ethers in 1967.[26] Also, quaternary ammonium or phosphonium salts have been found to enhance the nucleophilicity of several anions in phase-transfer catalysis.[25] With these concepts in mind, we used several fluoride and cyanide sources to liberate the corresponding ligand bound to tin. As can be seen in Scheme IV and in Table VI, a number of synthetic equivalents of cesium and quaternary ammonium salts were investigated.

Experimentally, we have demonstrated[1,27] that cesium ions complex effectively with crown ethers. Consequently, cesium fluoride in the presence of 18C6 is a much more potent nucleophile than NaF or KF with 18C6. Indeed, we came to that conclusion while comparing various reaction rates under similar conditions with cesium ion and the ions mentioned above (see Table VI).

This constitutes a real improvement over the usual salts of sodium or potassium complexes with crown ethers. It should be noted that cesium salts like Cs_2S and Cs_2Se are found in the literature, however, with no clear application to organic synthesis.[28] Cs_2O has been used extensively in ceramics, in glass additives, in conductivity materials, and as a cocatalyst in aromatization.[29] We present the first real application of it as a reagent in organic synthesis as well as for Cs_2Se and Cs_2S.

Although the magnitude of the nucleophilicity of several anions is enhanced, it is possible that these anions coordinate somewhat with the organotin fluoride formed in the medium (organotin halides usually tend to increase their coordination sphere to five ligands[30]). For this reason, we feel that comparison of the expected nucleophilicity for a pure "naked" anion to the experimental one obtained differs somewhat. Fortunately, to alleviate this negative effect, an excess of fluoride ions competes with the anion formed for the fifth coordination site on tin. Since organotin fluoride prefers to form "polymers" with pentacoordinated tin,[31] this competition for the fifth ligand favors fluoride ion rather than the "naked" anion.

Another important factor to consider here should be the "α-effect" of the tin. For instance, if we assume that the reaction pathway proceeds with intermediates **10**, **11**, and **12**, the metal effect on the displacement reaction is not entirely clear. A silicon analogue **13** of the tin oxide has been used recently as a synthetic equivalent of hydroxide or "O^{2-}".[15] This salt demonstrated good solubility in organic solvents. It seems that trimethylsilanolates prefer to attack directly a carbomethoxy or an acyl chloride rather than abstracting α-protons. This supports the idea that the α-effect on tin should enhance the nucleophilicity of the charged oxygen atom, thus favoring S_N2 reaction.

$R_3Sn{-}O^-$	$R_3Sn{-}S^-$	$R_3Sn{-}Se^-$	$Me_3Si{-}O^-$
10	**11**	**12**	**13**

Fluoride Ion Study. As a general rule with transfer reagents **1** (R = Bu, phenyl), **4**, and **5**, we found that tetrabutylammonium fluoride trihydrate ($TBAF{\cdot}3H_2O$) is the most reactive source of fluoride ion but its water content limits its use only with activated electrophiles such as α-bromo ketones. Benzyl bromide appears to be the limiting case where the $TBAF{\cdot}3H_2O$ fluoride source can be used without too much formation of thiol[32] with reagent **1** (or alcohol with **4**) as side products. With nonactivated alkyl halides such as 1-bromohexane, the preferred method for S^{2-} transfer employs our anhydrous fluorinating system: cesium fluoride complexes with a catalytic amount of 18-crown-6.[1]

This overall system appears to be general and very effective with activated alkyl halides. A qualitative scheme of reactivities associated with fluoride can be summarized as $TBAF{\cdot}3H_2O >$ $CsF{\cdot}18C6 > CsF$. This trend was determined with organotin oxides, organotin sulfides, and organotin selenides; we are studying this effect with organostannanes containing labile C–Sn bonds.

Cyanide Study. Tetrabutylammonium cyanide (TBACN) was investigated mostly with activated organic halides such as benzyl bromide; we found that its reactivity did not permit us to use it with nonactivated electrophiles without involving some forcing conditions as compared to the fluoride case. For example, treatment of benzyl bromide and bis(tributyltin) sulfide (**14**) in the presence of TBACN gives only a 42% yield of dibenzyl sulfide. The same reaction with $TBAF{\cdot}3H_2O$ gave sulfide in 85% yield.[1] Finally, TBACN did not initiate alkylation either in the reaction of bis(tributyltin) oxide (**4**) with 1-iodohexane or in the reaction of bis(triphenyltin) selenide (**5**) with 1-bromohexane.

Solvent Effects and Complexation on Tin. While studying the organotin sulfides,[1] were observed that these kinds of reactions were highly sensitive to the solvent used. We established an order of reactivity associated with the choice of the solvents involved.[33] From this study, we found that nonpolar and noncomplexing solvents work poorly, whereas those having high dielectric constants (associated with a high level of complexing ability on tin) were the best to use.[1] These findings parallel our work with the organotin oxides and selenides; however, organotin oxides are more sensitive to the solvent used than the other systems studied. For example, both acetonitrile and DMF work very well with organotin sulfides (**1**) but the yield is halved (using more forcing conditions) in alkylating with organotin oxide (**4**) when DMF ($E^\circ = 38.8$)[34] was replaced by acetonitrile ($E^\circ = 36.7$)[34] (compare entries 4 and 5 in Table II).

Even if both solvents have about the same dielectric constant, it seems that the complexation of DMF on organotin oxides is strongly required. It has been reported that this system is sensitive to the solvent used, and DMF was found in many instances as the best solvent with organotin oxides[35] (especially in alkylations). In general, we found that the efficiency of the solvents in these systems (organotin oxides, sulfides, and selenides as well as organostannanes) follows roughly the following trend: $NMP \geqslant DMF \gg CH_3CN \gg EtOAc \sim CH_2Cl_2$.

We have shown by a ^{119}Sn NMR study[36] with organotin sulfides that fluoride ion complexes to a modest degree on tin at room temperature. However, at lower temperatures (−50 to −60 °C), we were able to detect several new ^{119}Sn signals from TBAF and bis(triphenyltin) sulfide (**1**, R = phenyl) and can conclude that a complexation on tin had taken place. A labile complex is proposed at room temperature based on the broad signal observed.[35]

Effect of Substituents on Tin. In general, triorganotins containing group 16 as a ligand do not show a significant variation

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[25] Among the leading references: Dehmlow, S. S.; Dehmlow, E. V. *Phase Transfer Catalysis*; Verlag Chemie: Deerfield Beach, FL, 1983. Starks, C. M.; Liotta, C. *PTC, Principles and Techniques*; Academic, Don Mills: Ontario, Canada, 1978. Weber, W. P.; Gokel, G. W. *PTC in Organic Synthesis*, Springer-Verlag: New York, 1977. See Jones in ref 14f and Dockx in ref 14h.

[26] Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, 89, 7017.

[27] Gingras, M.; Harpp, D. N. *Tetrahedron Lett.*, in press. For the complexation of cesium acetate, see: Torisawa, Y.; Hiromitsu, T.; Ikegami, S. *Chem. Lett.* **1984**, 1555.

[28] A full structure search with CAS ONLINE gave 12 answers for Cs_2Se and 23 for Cs_2S.

[29] Aromatization: Dadashov, B. A.; Abbasov, S.; Gasymova, S. A. *Uch. Zap. Azerb. Un-t., Ser. Khim.* **1973**, *3*, 86; *Chem. Abstr.* **1973**, *83*(12), 103883*h*.

[30] Davies, A. G.; Smith, P. J. *Comprehensive Organometallic Chemistry*; Pergamon: New York, 1982; p 562.

[31] Leibner, J. E.; Jacobus, J. *J. Org. Chem.* **1979**, *44*, 449.

[32] Under certain conditions, alkyl halides and **1** (R = Bu) with fluoride ion can be converted to thiols in good yield; this will be reported separately.

[33] $DMF \sim NMP > CH_3CN \gg EtOAc > CH_2Cl_2$; NMP = *N*-methyl-2-pyrrolidinone (*N*-methylpyrrolidinone).

[34] Taken from: Nilles, G. P.; Schuetz, R. D. *J. Chem. Educ.* **1973**, *50*, 267.

[35] (a) Hanessian, S.; David, S. *Tetrahedron* **1985**, *41*, 646. (b) David, S.; Thieffry, A.; Forchioni, A. *Tetrahedron* **161**, 2647.

[36] The shielding effect on the ^{119}Sn signal gives only a shift of <0.5 ppm upfield with $TBAF{\cdot}3H_2O$ or TBACN at 20 °C (the ^{119}Sn spectral window is about 300 ppm). At −60 °C in CD_2Cl_2, we observed the disappearance of bis(triphenyltin) sulfide (**1**, R = phenyl) at −55 ppm and the presence of a new doublet at −228 ppm when TBAF was added. We will report more data in another publication. A shift of ~150–170 ppm has been observed for stable complex formation; see ref 30, p 527. The broadening of the signal at room temperature could come from a labile complex formation; this signal broadening has also been observed with complexing solvents; see ref 35b.

in reaction rates with different substituents on tin. We already demonstrated this feature in a previous article on organotin sulfides **1**.[1] However, it appears that organotin oxides are more sensitive to the substituents. Qualitatively, we found significant differences in reactivity from phenyl to butyl groups on tin, the butyl group being more reactive. Selenides should follow the same tendency as sulfides. Generally, for common alkyl halides involved in an S_N2 reaction, the substituent effects on tin are negligible compared to the fluoride and cyanide effects. Finally, the solvent effect usually takes priority over the substituent effects.

Substituent effects can be important where solubility problems slow the reaction rate, e.g., using bis(triphenyltin) selenide (**5**) in acetonitrile as solvent.[37] Steric hindrance combined with electronic effects can be an important consideration as demonstrated in the case of tetraallyltin (**9**). This is an unstable molecule and decomposes to a white solid at ambient atmosphere, whereas allyltributyltin is sufficiently stable to be manipulated without special precautions. As mentioned earlier, bis(triphenyltin) selenide (**5**) does not decompose easily to elemental selenium when exposed to the atmosphere for several hours or days but when the substituents offer less steric bulk, selenium formation is more rapid. Finally, the general mechanism of these reactions does not seem to be influenced by the substituents on tin.

Mechanistic Considerations. It is clear that fluorodestannylation is different from fluorodesilylation and we are investigating the characteristics of the former and trying to understand the general mechanism. From our results on sulfide formation[1] we suggested that the organotin sulfide is ionized to some extent prior to attack by fluoride and that this ionization facilitates the rate and extent of reaction. This speculation derives from a solvent and a ^{119}Sn NMR study of complexation on tin at room temperature and that a trace of water catalyzes the reaction.[1] Further support for ionization of organotins has already been described.[38]

In organosilicon chemistry, a hypervalent silicon species has been implicated where fluoride attacks the silicon first, prior to the ionization of the Si–X bond.[39] Thus, from a mechanistic point of view, fluorodestannylation could proceed by a different pathway. It seems that the ionization process for tin could be generalized for organotin oxides and organotin selenides since the bond energy of these latter compounds are considered to be equal or lower for selenium and definitely lower for oxygen, compared to the tin–sulfur bond. This ionization could also provoke an increase in hardness for tin compounds and favor a better attack of fluoride or cyanide ion.

We propose a solvent ionization process where an intermediate cationic triorganotin is formed and is temporarily stabilized by the solvent. Subsequently, fluoride ion could attack this positively charged intermediate; this pathway qualitatively explains the strong coordinative solvent effect observed. The counterion effect observed (from cesium to tetrabutylammonium) is also consistent with this mechanism.[1]

On the other hand, we recently found some spectroscopic evidence for a complex formation between TBAF and bis(triphenyltin) sulfide (**1**) at low temperature.[36] Thus, we cannot exclude the existence of some negatively charged organotin fluoride complexes, in low concentration, acting as initiators of the reaction instead of the ionization mechanism. The exact structure of these organotin fluoride complexes is unknown.

Bis(tributyltin) oxide (**4**) and bis(tributyltin) sulfide (**14**) reacted with benzyl bromide in the presence of TBAF·3H_2O to produce tributylstannyl benzyl ether (**15**) and tributylstannyl benzyl sulfide (**16**), respectively. Their presence in the reaction mixture was confirmed (^{1}H NMR and ^{119}Sn NMR) by comparison with authentic samples independently prepared.[40]

$Bu_3Sn{-}O{-}CH_2Ph$ $Bu_3Sn{-}S{-}CH_2Ph$

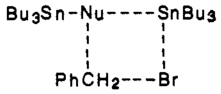
15 **16**

Scheme V. Suggested Mechanism[a]

$$Bu_3Sn{-}Nu{-}SnBu_3 \rightarrow Bu_3Sn{-}Nu^- + [Bu_3Sn{\bullet}solvent]^+$$
$$[Bu_3Sn{\bullet}solvent]^+ + F^- \rightarrow Bu_3Sn{-}F$$
$$Bu_3Sn{-}Nu^- + PhCH_2Br \rightarrow PhCH_2{-}Nu{-}SnBu_3$$
$$PhCH_2{-}Nu{-}SnBu_3 \rightarrow PhCH_2{-}Nu^- + [Bu_3Sn{\bullet}solvent]^+$$
$$[Bu_3Sn{\bullet}solvent]^+ + F^- \rightarrow Bu_3Sn{-}F$$
$$PhCH_2{-}Nu^- + PhCH_2Br \rightarrow PhCH_2{-}Nu{-}CH_2Ph$$

[a] Nu = O, S, Se; solvent = DMF, CH_3CN; Bu_3SnF = "polymer".

Scheme VI. Concerted Mechanism



Scheme VII. Doubly Charged Anion (Direct Attack of F^-)

$$Bu_3Sn{-}Nu{-}SnBu_3 + F^- \rightarrow Bu_3Sn{-}Nu^- + Bu_3Sn{-}F$$
$$Bu_3Sn{-}Nu^- + F^- \rightarrow Nu^{2-} + Bu_3Sn{-}F$$

Assuming that bis(triphenyltin) selenide (**5**) will follow the same reaction pathway, we then propose as a working hypothesis that the chalcogen atom is released in a stepwise manner. Two consecutive displacement steps should constitute the most probable mechanism, and one of them should involve the nucleophile corresponding to a tributyltin chalcogenide ion (Scheme V). This stepwise mechanism is also consistent with the predominant formation of thiols from bis(tributyltin) sulfide (**14**), 1-bromohexane, and TBAF·3H_2O in the presence of water, the intermediate tributylstannyl hexyl sulfide (**17**) being trapped or hydrolyzed.

The nondependence of the substituents on tin on the reaction rate can be interpreted if the second alkylation step is the rate-determining step. This step proceeds in the absence of tin substituents and without the help of an "activating effect" from the adjacent tin atom. It is consistent with the predominant formation of thiols under aqueous conditions. As the concentration of the triaralkyltin thiolate intermediates increases, because of the slower rate of the second alkylation, the intermediates are readily hydrolyzed. However, the slight dependence of the substituent on organotin oxides seems to justify a more complex mechanism with oxygen as nucleophile.

A concerted mechanism appears unlikely because of the solvent polarity effect observed on the rate of the reaction (Scheme VI) and the fluoride effect. Furthermore, this mechanism, without the use of fluoride, has been ruled out by Kozuka and Ohya.[41]

A mechanism involving a doubly charged anion (Scheme VII) analogous to the findings in a recent paper by Steliou, Corriveau, and Salama[42] (MeLi + $Me_3SiSSiMe_3 \rightarrow Li_2S$) is less likely in this case because of the formation of products **15** and **16** in the presence of excess fluoride ion. In addition, the Sn–F bond (99 kcal/mol) is not as strong as the Si–F bond (139 kcal/mol). Thus, a second attack of fluoride ion on the organotin $Bu_3Sn{-}Nu^-$ should be more difficult. The increase of the softness of tin with a negative charge in the α-position and the natural repulsion of two

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(37) We failed to obtain a reaction with 1-bromohexane and bis(triphenyltin) selenide (**5**) in the presence of CsF/18-crown-6 in pure acetonitrile. In a mixture of THF/CH_3CN (8.3), the reaction proceeded rapidly.

(38) In analogy with trialkyltin chlorides that are known to exist in the form of a diaquo cationic trialkyltin, it seems reasonable to extend this property to organotin oxides, sulfides, and selenides based on the Sn–O, Sn–S, and Sn–Cl bond energies; see ref 30, p 557. A recent ^{119}Sn NMR study demonstrated the formation of a stable stannonium cation at −78 °C using HSO_3F: Wasylishen, R. E.; Leighton, K. L. *Can. J. Chem.* **1987**, *65*, 1469.

(39) Support of this mechanism comes from: Fujita, M.; Hiyama, T. *Tetrahedron Lett.* **1987**, *28*, 2263.

(40) Spectral characteristics: tributylstannyl benzyl sulfide (**16**) prepared independently: ^{1}H NMR ($CDCl_3$) 3.76 ppm (CH_2 signal); ^{119}Sn NMR ($CDCl_3$) 75.64 ppm. Observed in the reaction mixture: ^{1}H NMR ($CDCl_3$) 3.78 ppm (CH_2 signal); ^{119}Sn NMR ($CDCl_3$) 74.67 ppm. Tributylstannyl benzyl ether (**15**) prepared independently: ^{1}H NMR ($CDCl_3$) 4.80 ppm (CH_2 signal); ^{119}Sn NMR ($CDCl_3$) 110.16 ppm; observed in the reaction mixture: ^{1}H NMR ($CDCl_3$) 4.82 ppm (CH_2 signal); ^{119}Sn NMR ($CDCl_3$) 110.41 ppm.

(41) Kozuka, S.; Ohya, S. *J. Organomet. Chem.* **1978**, *149*, 161. Kozuka, S.; Ohya, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2651.

(42) Steliou, K.; Salama, P.; Corriveau, J. *J. Org. Chem.* **1985**, *50*, 4969.

negative charged species such as F^- and Bu_3Sn-Nu^- should also discourage this mechanism. A solvent-assisted ionization process for making a doubly charged nucleophile (Nu^{2-}) seems to us less likely than the two proposed mechanisms.

Comments about the Purification. The difficulty associated with the purification of products in some reactions involving organotin compounds has been accorded special attention[31,43] (especially with tributyltin hydride as reagent). The usual purification consists of treating the organotin formed as byproduct with fluoride ion to generate the "polymeric" organotin fluoride, insoluble in many solvents. However, in our hands this method failed to remove completely the organotin byproducts. Here, we determined with the aid of ^{119}Sn NMR that the usual treatment of a reaction mixture with fluoride ion containing organotin bromide quantitatively forms polymeric organotin fluoride but the problem remained as these "polymeric" organotin fluorides are partially soluble in organic solvents. We found that a simple filtration through a short column of silica gel using only ethyl acetate as eluent gave satisfactory results to remove polymeric organotin fluoride. A strong advantage of this methodology is a kind of "autopurification" of the mixture with fluoride ion. As the reaction proceeds, fluoride ion removes the tin moiety as a precipitate, directly eliminating this extra step as is often done in the purification of organotins.[31]

Conclusion

We have demonstrated that fluoride ion can attack organotin chalcogenides to liberate powerfully nucleophilic chalcogenide ions. This process provides a new way to form "naked" nucleophiles; using this concept, one can generate ethers, sulfides, and selenides smoothly under essentially neutral conditions. This method appears to be among the best in the literature considering factors such as yield, temperature, and short reaction time. The most important parameters found in these reactions were the fluoride or cyanide effects followed by a strong solvent effect. An order of reactivity has been established for the various fluoride sources used. Two general mechanisms have been postulated based on ^{119}Sn NMR and ^1H NMR. Organotins can act as general "group 16 (VIB), transfer agents"; further, a new way for making carbon–carbon bonds has been demonstrated here by use of fluorodestannylation.

Experimental Part

Chemicals. All of the organotin compounds, organic halides, aldehydes, ketones, TBAF·$3H_2O$, CsF, selenium, and crown ethers were purchased from Aldrich Chemical Co. and used as such unless noted otherwise. Reagent grade acetonitrile, DMF, and *N*-methyl-2-pyrrolidinone (NMP) were distilled over calcium hydride. THF was dried over metallic sodium wire using the benzophenone ketyl radical as an indicator. When some water was involved in the medium, spectroscopic grade DMF and acetonitrile were used without purification. Diethyl ether, hexane, and ethyl acetate involved in the purification steps were reagent grade solvents. All of the reactions were carried out under a nitrogen atmosphere except when using TBAF·$3H_2O$. Cesium fluoride was dried under vacuum (2–5 mmHg) at 110 °C (pistol dryer) for 1–2 days.

Instrumentation. ^{119}Sn, ^{13}C, and ^1H NMR spectra were recorded on a Varian XL-200 or XL-300, and the chemical shifts (in ppm) are reported in reference to tetramethyltin, chloroform, and tetramethylsilane, respectively. All of the samples were dissolved in deuteriated chloroform. For ^{119}Sn and ^{13}C NMR, a 10-mm B.B. or 5-mm B.B. probe was used and the spectra were recorded with a decoupler. In the description of NMR spectra, the abbreviations s, d, t, q, and m signify singlet, doublet, triplet, quartet, and multiplet, respectively. The uncorrected melting points were recorded in capillary tubes on a Gallenkamp apparatus. Infrared spectra were recorded on an Analect AQS-20 FTIR spectrometer using neat liquid between two blank sodium chloride cells or in solution with 0.1-mm sodium chloride cells with chloroform as solvent. Low-resolution electron impact mass spectra were taken on a Du Pont 21-492B mass spectrometer with a direct insertion probe (70 eV at 250 °C). Chemically induced (CI) mass spectra were recorded with a source of 70 eV at 210 °C with isobutane on a Hewlett-Packard 5980A mass spectrometer.

Gas chromatography was performed on a Hewlett-packard Model 5890 combined with a Hewlett-Packard integrator Model 3390A or a Varian GC Model 3700. A FID detector was employed on both instruments. A capillary column with methylsilicone as adsorbent on the Hewlett-Packard GC was used to monitor some reactions, to check purity, and specifically to evaluate the yield of some reactions involving organotin oxide. The progress of the reactions and the purity of final products were monitored by TLC on an aluminum sheet precoated with 0.2-mm silica gel 60 F254 (E. Merck 5554). Most of the thin-layer chromatograms were visualized with iodine absorbed on silica gel, with a molybdic acid solution, or with a UV lamp. Flash chromatography was carried out with silica gel from E. Merck (Kieselgel 60 no. 9385, particle size 0.040–0.063 mm).

Fluorodesilylation with Hexamethyldisilathiane (2). 1-Bromohexane (409 mg, 2.48 mmol), dried cesium fluoride (1.88 g, 12.4 mmol), a catalytic amount of 18-crown-6 (65 mg, 0.25 mmol), and dried acetonitrile (10 mL) were combined in a 25-mL flask. Commercial hexamethyldisilathiane (Petrarch Systems Ltd., 232 mg, 1.30 mmol, 0.27 mL) was injected over 10 min with a syringe (fume hood, odor). Upon addition at room-temperature, a blue color persisted, and when the rate of addition increased, a green color appeared. After 2 h, the solvent was evaporated, and 20 mL of *n*-hexane plus 10 mL of water was added. The organic layer was evaporated to give 266 mg of a mixture of di-*n*-hexyl sulfide and di-*n*-hexyl disulfide in a ratio of 2.3:1.0 as determined by ^1H NMR: sulfide, 2.52 ppm (t, CH_2SCH_2); disulfide, 2.70 ppm (t, CH_2SSCH_2).

Fluorodesilylation with Hexamethyldisiloxane (3). In a 50-mL flame-dried flask were placed 1-iodohexane (1.00 g, 4.72 mmol), 18-crown-6 (150 mg, 0.58 mmol), cesium fluoride (2.00 g, 13.2 mmol), and DMF (15 mL). Hexamethyldisiloxane (**3**, 0.766 g, 4.72 mmol, 1.00 mL) was added slowly over 15 min at 50 °C, and the mixture was stirred vigorously. The formation of di-*n*-hexyl ether was followed by GC. Only traces of the desired ether were detected (2–3% yield) after 28 h. The retention time of the product was identical with that of authentic di-*n*-hexyl ether under several conditions.

Formation of Symmetrical Ethers. Dibenzyl Ether with TBAF·$3H_2O$ (General Procedure). Freshly distilled benzyl bromide (504 mg, 2.95 mmol), bis(tributyltin) oxide (**4**, 1.04 g, 1.74 mmol), tetrapropylammonium iodide (230 mg, 0.73 mmol; this reagent can be omitted without drastically changing the results), and acetonitrile (12 mL) were placed in a flask closed with a stopper. After the mixture was stirred for 5 min, tetrabutylammonium fluoride trihydrate (1.11 g, 3.50 mmol) was added in one portion. The reaction was stirred for 6 h at room temperature; the mixture became cloudy, indicating the presence of tributyltin fluoride. Evaporation of the solvent and addition of ethyl acetate may result in the formation of a precipitate that can be filtered on Celite. Filtration of the residue through a short column of silica gel (using pure ethyl acetate) followed by a solvent gradient of 100% hexanes to 10% EtOAc/hexanes gave 120 mg of dibenzyl ether (0.61 mmol, 41% yield): ^1H NMR (60 MHz) 7.27 (s, 10 H), 4.52 (s, 4 H); MS (*m*/*z* (relative intensity) 107 (17), 105 (13), 93 (10), 92 (100), 91 (62), 90 (7), 89 (9), 79 (18), 77 (10), 65 (14), 51 (11), 39 (95); IR ($CHCl_3$) 3000, 2860, 1495, 1450, 1355, 1085, 1065, 690.

Dibenzyl Ether with Cesium Fluoride. To a 100-mL flask were added freshly distilled benzyl bromide (1.00 g, 5.84 mmol), bis(tributyltin) oxide (**4**, 1.74 g, 2.92 mmol), a catalytic amount of 18-crown-6 (80 mg, 0.30 mmol), and acetonitrile (24 mL). An excess of cesium fluoride (2.0 g, 13.2 mmol) was added in one portion. The reaction mixture was stirred vigorously at 55 °C for 7–9 h; ^1H NMR showed >95% conversion. After cooling at room temperature, the solvent was evaporated. Ethyl acetate (50 mL) and a saturated solution of potassium fluoride (25 mL) were added, and the mixture was stirred for 45 min at room temperature. Finally, the organic layer was washed with water (~25 mL) and dried over Na_2SO_4. A simple filtration on silica gel (short column) using pure ethyl acetate afforded pure dibenzyl ether (408 mg, 2.06 mmol, 71% yield). The spectral data were the same as above.

Di-*n*-hexyl Ether (General Procedure). A flask was charged with 1-iodohexane (1.00 g, 4.72 mmol), bis(tributyltin) oxide (**4**, 1.48 g, 2.48 mmol), 18-crown-6 (150 mg, 0.57 mmol), and *N*-methyl-2-pyrrolidone (15 mL). An excess of cesium fluoride (3.0 g, 19.7 mmol) was added in one portion while stirring vigorously at 52 °C for 5 h. The reaction progress was monitored by GC. After cooling, diethyl ether (40 mL) and water (40 mL) were added, the aqueous layer was discarded, and the ethereal phase was washed with water (4 × 20 mL) and dried over $Na_2SO_4/MgSO_4$. The precipitate of tributyltin fluoride was filtered on Celite. The ether was evaporated and the residue was dissolved in pure ethyl acetate. A simple filtration on a short column using the latter solvent removed the remaining tributyltin fluoride. Flash chromatogra-

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(43) In our hands, organotin fluoride was incompletely removed by this procedure (cited in ref 30). Lengthy, but alternate procedures are given by: McKean, D. R.; Parrinello, G.; Renaldo, A. F.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 422. Russell, G. A.; Herold, L. L. *J. Org. Chem.* **1985**, *50*, 1037.

phy using 5% ethyl acetate/hexane ensures the removal of hexyl alcohol formed as side product. Di-*n*-hexyl ether was obtained as a colorless liquid (236 mg, 1.27 mmol, 54% yield): ^{1}H NMR 3.40 (t, 4 H), 1.58 (m, 4 H), 1.30 (m, 12 H), 0.90 (t, 6 H). The sample was found to be identical with authentic material by GC under several conditions of operations (high and low temperature of the capillary column).

The procedure was extended to 1-tosylhexane, 1-bromohexane, and 1-iodohexane while using acetonitrile or DMF instead of 1-methyl-2-pyrrolidinone with the conditions specified in Table II. In some instances, cesium fluoride was used in an equivalent amount compared to organotin oxide or the crown ether was omitted.

Formation of Unsymmetrical Ethers. Allyl Benzyl Ether with Cesium Fluoride. In a high-pressure metal cylinder were placed tributylstannyl benzyl ether (**14**, 1.00 g, 2.50 mmol),[44] allyl bromide (393 mg, 3.25 mmol), 18-crown-6 (200 mg, 0.76 mmol), an excess of cesium fluoride, and acetonitrile (15 mL). The mixture was stirred at 100 °C in the cylinder for 2 h. After cooling at room temperature, the mixture was transferred to a flask and the solvent was evaporated. Ethyl acetate (25 mL) was added and stirring was continued for 5 min. A simple filtration through silica gel afforded 401 mg of an impure liquid product (a second, more polar spot was detected by TLC). Flash chromatography afforded 330 mg of pure material ($PhCH_2OCH_2CH{=}CH_2$, 90%): ^{1}H NMR 7.35 (m, 5 H, Ph), 5.98 (m, CH), 5.32 (d, $=CH_2$), 5.22 (d, $=CH_2$), 4.55, 4.05 (d, CH_2).

***n*-Hexyl Benzyl Ether with Silver(I) Fluoride.** A flask was charged with 1-iodohexane (348 mg, 1.65 mmol), tributylstannyl benzyl ether (**15**, 590 mg, 1.48 mmol), silver(I) fluoride (dried at 50 °C overnight under vacuum, 0.5 mm Hg), dibenzo-24-crown-8 (95 mg, 0.21 mmol), and acetonitrile (15 mL). The flask was heated at 75 °C for 2 days. The solvent was removed and the mixture was filtered on a short column of silica gel using pure ethyl acetate as eluent. An impure product (366 mg) was flash chromatographed with 10% EtOAc/90% hexane. Finally, 47 mg of slightly impure *n*-hexyl benzyl ether (as determined by ^{1}H NMR) was obtained. ^{1}H NMR revealed the major signals of *n*-hexyl benzyl ether: 7.36 (m), 4.5 (s), 3.47 (t), 1.6 (m), 1.3 (m), 0.90 (t).

***n*-Hexyl Benzyl Ether with Cesium Fluoride.** Cesium fluoride (856 mg, 5.64 mmol) was flame-dried under high vacuum in a flask and cooled at room temperature under a stream of argon. Dibenzo-24-crown-8 was added in a catalytic amount (19 mg, 0.042 mmol) followed by 1-methyl-2-pyrrolidinone (15 mL) and tributylstannyl benzyl ether (**15**, 1.00 g, 2.52 mmol); 1-iodohexane (588 mg, 2.77 mmol, 0.41 mL) was injected in the flask with a syringe. After stirring at room temperature, a yellow color appeared within 10–15 min. Stirring was continued for 24 h. Finally, ether (100 mL) and water (100 mL) were added; the ethereal phase was washed further with 3 × 30 mL of water. If needed, a filtration on Celite could be carried out to remove insoluble organotin fluoride. The organic phase was dried with $Na_2SO_4/MgSO_4$. Filtration through a short column of silica gel using EtOAc as eluent was carried out followed by flash chromatography using a gradient of hexane (100%) increasing to 10% EtOAc. The product can be visualized on TLC while heating using a spray mixture developed in our laboratory: 30% H_2SO_4/5% HNO_3 in water. ^{1}H NMR 7.34 (m, 5 H), 4.51 (s, 2 H), 3.48 (t, 2 H), 1.62 (quintuplet, 2 H), 1.31 (m, 6 H), 0.89 (t, 3 H).

Formation of Symmetrical Selenides. Preparation of Bis(triphenyltin) Selenide (5). A 250-mL flask flamed and cooled under a nitrogen stream was charged with a commercial solution of lithium borohydride 1.0 M in THF (105 mL, 0.105 mol). The flask was placed in an ice bath, and finely crushed selenium pellets (3.95 g, 0.050 mol) were added in small portions. A brown-red color appeared upon addition, and hydrogen was liberated to finally give a white milky mixture. The reaction mixture was stirred for 5 min and then warmed to room temperature. Stirring was continued for 2.5 h. To this stage, this procedure is essentially that reported by Gladysz.[18] Triphenyltin chloride (36.62 g, 0.095 mol) was added in one portion followed by anhydrous THF (90 mL). The flask was wrapped with aluminum foil to prevent light-induced reactions and the reaction mixture was stirred vigorously overnight. This sequence is similar to that reported by Detty with some silicon analogues.[45] *n*-Hexane (100 mL) was added in order to precipitate lithium chloride; the mixture was filtered on a pad of Celite (under a vigorous flow of nitrogen from a funnel). Caution! Highly toxic H_2Se is immediately liberated in contact with air. The solvent evaporation was carried out in a fume hood. The crude bis(triphenyltin) selenide (**5**) was dissolved in THF (60 mL), and absolute ethanol (200 mL) was added slowly to crystallize the white product. Filtration under atmospheric conditions afforded white crystalline (not highly odorous) bis(triphenyltin) selenide (**5**, 28.33 g, 0.036 mol): mp 147.0–147.5 °C (lit. mp 148 °C[45]); ^{119}Sn NMR 79.13 (s); ^{13}C NMR 139.00, 136.54, 129.29, 128.52. The mother liquors were evaporated to dryness and triturated with absolute ethanol to give 2.32 g of additional bis(triphenyltin) selenide (**5**); combined yield: 83%.

Di(2-phenethyl) Selenide.[46] A 50-mL flask was charged with (2-bromoethyl)benzene (153 mg, 0.83 mmol), bis(triphenyltin) selenide (**5**, 345 mg, 0.44 mmol), 18-crown-6 (50 mg, 0.19 mmol), tetrahydrofuran (3.0 mL), and acetonitrile (8.0 mL). The mixture was stirred for 5–10 min, cesium fluoride was added in one portion (1.0 g, 6.6 mmol), and the reaction mixture in the foil-wrapped flask was stirred vigorously for 1 h at 40 °C. The solvent was evaporated and the mixture was taken up in pure ethyl acetate. The insoluble impurities were filtered on Celite. Flash chromatography using 5% EtOAc in hexane gave a colorless liquid corresponding to di(2-phenethyl) selenide (107 mg, 0.37 mmol, 89% yield) homogeneous on TLC (5% EtOAc/hexane): ^{1}H NMR 7.23 (m, 10 H), 2.88 (A_2B_2 system, 8 H); MS (CI based on ^{80}Se) *m/z* 291 (M + 1); ^{13}C NMR 141.35, 128.57, 128.46, 126.43, 37.30, 25.10; TLC showed one major spot (R_f 0.70 in 10% acetone/90% hexane).

Di-*n*-hexyl Selenide from 1-Bromohexane. 1-Bromohexane (347 mg, 2.10 mmol), 18-crown-6 (30 mg, 0.11 mmol), cesium fluoride (1.26 g, 8.29 mmol), and acetonitrile (16 mL) were placed in a 50-mL flask. A solution containing bis(triphenyltin) selenide (**5**, 779 mg, 1.00 mmol) and tetrahydrofuran (6.0 mL) was injected slowly over 45–50 min using a glass syringe. The reaction mixture was heated at 48 °C during the addition. To ensure maximum conversion, the reaction mixture was stirred for an additional 45 min. Evaporation of the solvent followed by filtration through a short column of silica gel using pure ethyl acetate as eluent afforded 239 mg of a colorless liquid corresponding to di-*n*-hexyl selenide (96% yield): ^{1}H NMR 2.53 (t, 4 H), 1.65 (quintuplet, 4 H), 1.30 (m, 12 H), 0.87 (t, 6 H); MS *m/z* (relative intensity) 250 (^{80}Se, M$^+$, 15), 248 (^{78}Se, M$^+$, 4) 166 (19), 165 (24), 164 (7), 163 (8), 85 (31), 84 (25), 83 (22), 69 (14), 57 (34), 56 (34), 55 (31), 44 (7), 43 (100), 42 (17), 41 (43), 39 (16), 32 (24), 29 (47), 28 (61), 27 (45). TLC showed one major spot (R_f 0.85 in 5% EtOAc/95% hexane).

Bis(4-acetoxybutyl) Selenide from 4-Bromobutyl Acetate. This is essentially the same procedure as described for di-*n*-hexyl selenide from 1-bromohexane but using the following chemicals: 4-bromobutyl acetate (400 mg, 2.05 mmol), bis(triphenyltin) selenide (**5**, 779 mg, 1.00 mmol), cesium fluoride (1.04 g, 6.85 mmol), and acetonitrile (15 mL). Dibenzo-24-crown-8 (90 mg, 0.20 mmol) was used as phase-transfer catalyst. The slow addition of the organotin selenide reagent dissolved in THF (6.0 mL) took 70 min at 36 °C, and the reaction mixture was further stirred for 50 min to ensure maximum conversion of the starting material. Bis(4-acetoxybutyl) selenide was obtained as a colorless liquid after filtration through a short column of silica gel (300 mg, 97% yield). ^{1}H NMR 4.07 (t, 4 H), 2.58 (t, 4 H), 2.05 (s, 6 H), 1.73 (m, 8 H); MS *m/z* (relative intensity) 136 (13), 135 (10), 115 (17), 85 (4), 73 (8), 71 (15), 61 (5), 57 (5), 56 (17), 55 (35), 54 (10), 43 (100), 41 (15), 39 (11), 29 (17), 28 (24), 27 (10); ^{13}C NMR 170.98, 63.79, 28.78, 27.14, 23.29, 20.91; TLC on silica gel using 10% acetone/90% hexane showed one major spot (R_f 0.25).

Di-*n*-hexyl Selenide from 1-(*p*-Toluenesulfonyl)-*n*-hexane. A dried 50-mL flask was charged with bis(triphenyltin) selenide (**5**, 922 mg, 1.18 mmol), 1-(*p*-toluenesulfonyl)-*n*-hexane (607 mg, 2.37 mmol) prepared in the standard way,[47] 18-crown-6 (30 mg, 0.11 mmol), acetonitrile (16 mL), and THF (6.5 mL). Cesium fluoride was added in one portion (546 mg, 3.59 mmol), giving a bright yellow color. After the mixture was stirred for 3 h at room temperature, the solvent was evaporated, and ethyl acetate (30 mL) was poured into the flask. Stirring was continued for a few more minutes at room temperature, and the mixture was filtered through Celite and then passed through a short column of silica gel using ethyl acetate as eluent. Flash chromatography on silica gel using 3% EtOAc/97% hexane afforded 90 mg (0.27 mmol) of di-*n*-hexyl diselenide (^{1}H NMR 2.92 (t, 4 H), 1.73 (quintuplet, 4 H), 1.32 (m, 12 H), 0.90 (t, 6 H); MS *m/z* (relative intensity) 166 (17), 164 (4), 85 (30), 84 (20), 69 (20), 57 (53), 56 (49), 55 (37), 43 (100), 42 (44), 41 (67), 39 (35), 32 (22), 29 (63), 28 (85), 27 (56)) and di-*n*-hexyl selenide in 70% yield based on the ^{1}H NMR signal at 2.52 ppm compared to the diselenide signal at 2.92 ppm.

Di(1-phenethyl) Selenide from (1-Bromoethyl)benzene. Cesium fluoride (582 mg, 3.83 mmol) was added to a flask and the latter was flame-dried and cooled under a stream of argon. Dibenzo-24-crown-8 was added in a catalytic amount (39 mg, 0.087 mmol), followed by

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[44] Davies, A. G.; Kleinschmidt, D. C.; Palan, P. R.; Vasishtha, S. C. *J. Chem. Soc. C* **1971**, 3972.

[45] For physical properties on bis(triphenyltin) selenide (**5**), see: Sawyer, A. K. *Organotin Compounds*; Marcel Dekker: New York, 1971; p 491 and references cited therein.

[46] Higuchi, H.; Otsubo, T.; Ogura, F.; Yamaguchi, H.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 182; see ref 18.

[47] Vogel, A. (revised by B. S. Furniss et al.) *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Longman: New York, 1978; p 654 (pyridine method).

acetonitrile (16 mL) and the injection of (1-bromoethyl)benzene (379 mg, 2.05 mmol, 0.28 mL). With the use of a syringe pump, a solution of bis(triphenyltin) selenide (779 mg, 1.00 mmol) in THF (6.0 mL) was added over 1 h. The mixture was heated to 40 °C during this addition and then for 40 h; 70 min after the addition of the bromide, a sample taken from the mixture indicated a 42% conversion of starting material by ^{1}H NMR. After 40 h, the solvent was evaporated and pure ethyl acetate was added. The residue was passed through a short column of silica gel using only ethyl acetate as eluent. ^{1}H NMR indicated 67% conversion into di(1-phenethyl) selenide as a pair of diastereoisomers: ^{1}H NMR 7.26 (m, phenyl), 3.89 (q, Se–CH), 3.84 (q, Se–CH), 1.72 (d, CH_3), 1.60 (d, CH_3).

C–C Bond Formation. *d,l*-2-Phenylpropionaldehyde with Tetraallyltin (9). *d,l*-2-Phenylpropionaldehyde (538 mg, 4.01 mmol), DMF (10 mL), and cesium fluoride (3.38 g, 22.3 mmol) were placed in a 50-mL flask. Tetraallyltin (**9**, 1.25 g, 4.35 mmol, 1.04 mL) was injected with a syringe within 5 min. After the mixture was stirred for 3 h at room temperature, TLC (20% EtOAc/80% hexane) showed almost complete conversion. After 3.7 h, diethyl ether (60 mL) and brine (45 mL) were added, the precipitate formed was filtered through Celite, and the ethereal phase was washed further with water (3 × 20 mL) and dried with Na_2SO_4. Flash chromatography on silica gel (using 20% EtOAc/80% hexane) afforded pure 4-phenyl-1-penten-3-ol (602 mg, 3.42 mmol) in 85% yield based on the aldehyde as a pair of diastereoisomers (determined by ^{1}H NMR): homogeneous on TLC; ^{1}H NMR 7.27 (m, 5 H), 5.83 (m, 1 H), 5.15 (m, 2 H), 3.75 (m, 1 H), 2.80 (q, 1 H), 2.13 (m, 2 H), 1.38 and 1.32 (two pairs of doublets (2.4:1.0), 3 H); MS *m/z* (relative intensity) 176 (M^+, 1), 135 (24), 117 (21), 107 (24), 106 (100), 105 (66), 104 (9), 103 (9), 92 (10), 91 (60), 79 (35), 78 (27), 77 (36), 71 (23), 65 (6), 57 (29), 51 (32), 43 (89), 41 (27), 39 (41), 29 (24), 28 (72), 27 (23).

1-Phenyl-2-methyl-4-penten-2-ol from Phenylacetone and Tetraallyltin.[48] A flask was charged with cesium fluoride (1.20 g, 7.90 mmol) and then flame-dried under high vacuum. After cooling with a stream of argon, acetonitrile (9.5 mL) and DMF (0.5 mL) were added. Then freshly distilled phenylacetone (216 mg, 1.61 mmol, 0.22 mL) was injected followed by tetraallyltin (500 mg, 1.77 mmol, 0.42 mL). The reaction mixture was heated at 55–60 °C for 8 days under argon. Acetonitrile was evaporated and DMF was removed under high vacuum. Ethyl acetate was added to the residue, which was then filtered through a short column of silica gel. Flash chromatography using 10% acetone/90% hexane provided *d,l*-1-phenyl-2-methyl-4-pent-2-ol (45 mg, 16% yield based on phenylacetone): IR (neat) 3600–3250, 3060, 3030, 2975, 2930, 2900, 1640, 1495, 1450, 1010, 1000, 910, 760, 700; ^{1}H NMR 7.27 (m, 5 H), 5.95 (m, 1 H), 5.20–5.10 (m, 2 H), 2.77 (d, 2 H), 2.25 (d, 2 H), 1.15 (s, 3 H); MS *m/z* (relative intensity) 176 (M^+, 0.2), 158 (0.3), 135 (40), 117 (26), 115 (16), 107 (20), 106 (100), 105 (59), 104 (37), 103 (26), 92 (29), 91 (87), 79 (24), 78 (36), 77 (44), 71 (26), 65 (17), 57 (41), 51 (24), 43 (76), 41 (43), 39 (30), 29 (25), 28 (20), 27 (28). TLC gave a single spot using acetone/hexane or ethyl acetate/hexane systems as eluents.

1-Phenyl-4-pentyn-3-ol from *d,l*-Phenylpropionaldehyde and Ethynyltributyltin. Cesium fluoride (885 mg, 5.83 mmol) and NMP (8.0 mL) were placed in a 25-mL flask. Ethynyltributyltin (500 mg, 1.59 mmol) and *d,l*-phenylpropionaldehyde (200 mg, 1.49 mmol, 0.20 mL) were added by syringe in one portion. The mixture was stirred at 44 °C for 90 h. A bright yellow color appeared first and turned to orange over time. Ether (50 mL) and water (50 mL) were finally added. The ethereal phase was washed with 3 × 15 mL of water and dried on Na_2SO_4. Flash chromatography using 20% ethyl acetate in hexane gave no significant amount of the desired alcohol as determined by ^{1}H NMR. Several fractions revealed the presence of the tributyltin moiety as well as the consumption of the aldehyde; however, no attempt was made to hydrolyze the possible intermediate tin oxide.

1-Phenyl-4-penten-2-one from Phenylacetyl Chloride and Tetraallyltin. Cesium fluoride (613 mg, 4.04 mmol) was placed in a 25-mL flask and flame-dried and cooled under vacuum. Then 1-methylpyrrolidinone (8.0 mL) was added, followed by phenylacetyl chloride (0.21 mL, 249 mg, 1.61 mmol) and tetraallyltin (0.42 mL, 500 mg, 1.77 mmol). The reaction was stirred vigorously at room temperature for 20 h. A milky appearance denoted the formation of organotin fluoride after a few hours. Ether (100 mL) was added followed by brine (75 mL). The ethereal phase was washed further with brine (3 × 25 mL) and dried on $Na_2SO_4/MgSO_4$. Flash chromatography on silica gel using 15% acetone in hexane as eluent gave pure 1-phenyl-4-penten-2-one (196 mg, 76% yield) existing mainly as the enol form: IR (neat) 3560–3400, 3075, 3030, 2920, 1640, 1495, 1455, 1365, 1080, 1030, 1000, 914, 700; ^{1}H NMR 7.29 (m, 5 H), 5.87 (m, 1 H), 5.2–5.1 (m, 2 H), 2.80 (s, 2 H), 2.24 (d, 2 H); MS *m/z* (relative intensity) 160 (M^+, 8), 129 (1), 105 (15), 92 (28), 91 (100), 77 (12), 69 (23), 41 (41); ^{13}C NMR 137.18, 133.79, 130.73, 128.23, 126.54, 118.86, 73.49, 45.41, 43.50; single spot on TLC using acetone/hexane or ethyl acetate/hexane systems as eluent.

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Registry No. 2, 3385-94-2; **3**, 107-46-0; **4**, 56-35-9; **5**, 4324-23-6; **14**, 33868-53-0; $H_3C(CH_2)_7CH{=}CH_2$, 872-05-9; $Ph(CH_2)_2Br$, 103-63-9; $PhCH(CH_3)Br$, 585-71-7; $H_3CCO_2(CH_2)_3Br$, 592-33-6; $H_3C(CH_2)_5Br$, 111-25-1; $H_3C(CH_2)_5OTs$, 3839-35-8; $(PhCH_2CH_2)_2Se$, 65027-51-2; $((PhCH(CH_3))_2Se$, 116747-64-9; $(CH_3CO_2(CH_2)_3)_2Se$, 116747-65-0; $(CH_3(CH_2)_5)_2Se$, 7732-99-2; PhCH(Me)CHO, 93-53-8; $PhCH_2COCl$, 103-80-0; $PhCH_2COCH_3$, 103-79-7; $Bu_3SnC{\equiv}CH$, 994-89-8; decyl-I, 2050-77-3; allyl-Br, 106-95-6; hex-I, 638-45-9; butyl-I, 542-69-8; $PhCH_2O$-allyl, 14593-43-2; $PhCH_2O$-hex, 61103-84-2; $PhCH_2O$-butyl, 588-67-0; cyclo-$(CH_2)_{12}CO$, 832-10-0; PhCH(OH)-allyl, 936-58-3; Ph-$(CH_2)_2CH{=}CH_2$, 768-56-9; $PhCH_2C(CH_3)(OH)$-(allyl), 39615-80-0; cyclo$(CH_2)_{12}C(OH)$-(allyl), 116747-66-1; Bu_3Sn(allyl), 24850-33-7; dihexyl sulfide, 6294-31-1; dihexyl disulfide, 10496-15-8; benzyl bromide, 100-39-0; dibenzyl ether, 103-50-4; dihexyl ether, 112-58-3; dihexyl diselenide, 52056-08-3; triphenyltin chloride, 639-58-7; tetrallyltin, 7393-43-3.

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[48] See ref 23. Butsugan, Y.; Kadosaka, I.; Araki, S. *Chem. Lett.* **1979**, *5*, 527. Esafov, V. I. *Zh. Obshch. Khim.* **1963**, *33*, 3755.