Cross-Coupling of Organosilanes with Organic Halides Mediated by Palladium Catalyst and Tris(diethylamino)sulfonium Difluorotrimethylsilicate

Summary: In the presence of tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF) and allylpalladium chloride dimer as a catalyst, organosilicon compounds like vinyl-, ethynyl-, and allylsilanes react with such organic halides as aryl, vinyl, and allyl halides to give the corresponding coupled products in synthetically useful yields in a stereospecific and chemoselective manner.

Sir: The transition-metal-catalyzed cross-coupling reactions of organometallics with organic halides provide important, versatile methods of selective carbon–carbon bond formation.[1] Although various organometallics could be used as the coupling partners, in view of practicability, usable ones have been restricted to such conveniently available reagents as organomagnesium[2] and organocopper compounds.[3] However, these organometallics are reactive enough to frequently destroy some functional groups on both coupling partners and thus limit seriously the extent of synthetic application.

Organometallic compounds of zinc,[4] aluminium,[5] boron,[6] and zirconium[4b,5c,d] partly solve the problems of the lack of chemoselectivity but still are characterized by instability to atmospheric moisture and/or oxygen and also by less availability of the organometallic reagents. Recently, Stille and Migita have independently exploited the palladium-catalyzed cross-coupling reaction of organotin compounds with organic halides.[7] Low nucleophilicity of the organotin reagents as well as high stereo- and regiospecificity of the reaction offers several advantages over the conventional methods.

The homologous organosilicon compounds have been believed to be too stable to do the similar coupling reaction due to the much less polarized Si–C bonds.[5b] Although a few papers have appeared which partly succeeded in cross-coupling reaction using organosilanes, drastic reaction conditions are generally required and low yields of the products result owing to the poor reactivity of organosilanes.[8] Thus, without efficient activation of organosilanes, the transmetalation of an organic moiety from silicon to palladium catalyst seems to be hardly achieved. We report herein that the cross-coupling reaction of organosilicon compounds with organic halides indeed takes place in the presence of an allylpalladium chloride dimer catalyst[9] and tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF) to give rise cleanly to the desired coupling products. TASF is a good F^- source readily prepared from (diethylamino)sulfur trifluoride and diethyl(trimethylsilyl)amine[10] and recently recognized to be an excellent reagent for cleavage of Si–C,[11] Si–O,[12] Si–Si,[13] and Si–H bonds.[14]

$$R^1X + R^2SiMe_3 \xrightarrow[Pd]{F^-} R^1R^2$$

R^1 = aryl, alkenyl, allyl
R^2 = alkenyl, allyl, alkynyl

A representative procedure follows. A tetrahydrofuran (THF) solution of TASF (1.0 M solution, 0.40 mL, 0.40 mmol) was added to trimethylvinylsilane (40 mg, 0.40 mmol) and allylpalladium chloride dimer (2.7 mg, 0.0075 mmol) dissolved in hexamethylphosphoric triamide (HMPA) (0.3 mL) at 0 °C under an argon atmosphere. 1-Iodonaphthalene (76 mg, 0.30 mmol) was injected to the resulting solution, and the mixture was stirred at 50 °C for 2 h. After completion of the reaction, the bulk of the solvent was removed by passing the reaction mixture through a silica gel column with pentane as the eluent. Evaporation of the pentane under reduced pressure gave pure 1-vinylnaphthalene (42 mg, 98% yield). The results obtained by application to various organosilicon compounds and organic halides are summarized in Table I.

A slight excess of TASF over the substrate is essential for the reaction, as use of an equimolar amount or less of the reagent lowered the yields of coupled products, and no reaction took place in the absence of TASF. The reaction was quite sensitive to the nature of the F^- reagent used. Tetrabutylammonium fluoride (TBAF)[15] was inferior to TASF; CsF and KF afforded only a trace amount of the desired products. The low activity of these inorganic salts may be attributed to insolubility in the reaction media.

The success of the coupling reaction is ascribed to the following: (1) attack of F^- to organosilicon compounds to

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(1) (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1987. (b) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: New York, 1985. (c) Davies, S. G. *Organotransition Metal Chemistry. Application to Organic Syntheses*; Pergamon Press: Oxford, 1982.

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(15) For TBAF-catalyzed carbonyl addition of allylsilane, see: (a) Hosomi, A.; Shirahata, A.; Sakurai, H. *Tetrahedron Lett.* **1978**, 3043. (b) Hosomi, A.; Araki, Y.; Sakurai, H. *J. Org. Chem.* **1983**, *48*, 3122. They assume that a naked allyl anion is generated rather than a pentacoordinate silicate intermediate. In contrast, a recent report by Sakurai and Kira suggests the latter possibility: Kira, M.; Kobayashi, M.; Sakurai, H. *Tetrahedron Lett.* **1987**, *28*, 4081.

0022-3263/88/1953-0918$01.50/0

Table I. TASF/Pd Catalyst Mediated Cross-Coupling of Organosilanes with Organic Halides

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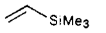
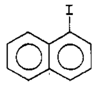
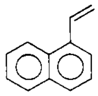
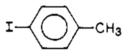
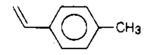
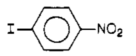
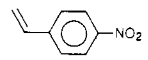
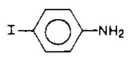
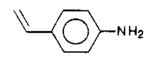
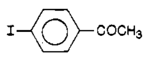
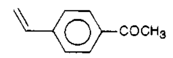
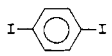
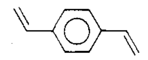
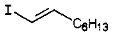
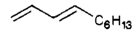
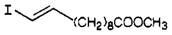
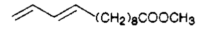
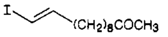
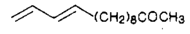
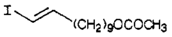
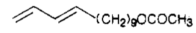
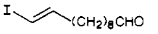
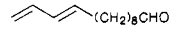
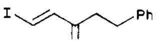
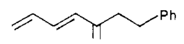
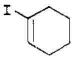
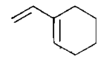
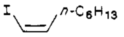
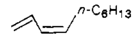
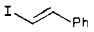
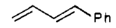
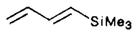
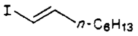
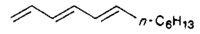
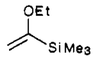
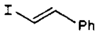
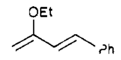
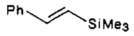
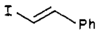
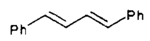
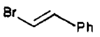
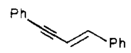
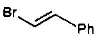
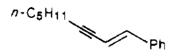
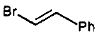
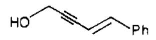
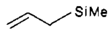
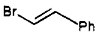
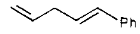
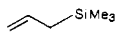
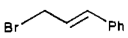
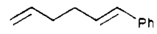
1			A		98
2			A		89
3			A		83
4			A		85
5			A		86
6			A[d]		84
7			B		(100)[e]
8			B		88
9			B		67
10			B		70
11			B		52
12			B		85
13			B		(100)[e]
14			B		76
15			B		93
16			B		78
17			B		45
18			B		32
19	Ph—≡—SiMe$_3$		C		83
20	n-C$_5$H$_{11}$—≡—SiMe$_3$		C		86
21	HOCH$_2$—≡—SiMe$_3$		C		84
22			C		28
23			C		83

[a] Reactions were carried out with 0.3 mmol of halides and 0.4 mmol of organosilanes in the presence of TASF (0.4 mmol) and 2.5 mol % of (η^3-C$_3$H$_5$PdCl)$_2$ under the following conditions: (A) HMPA (0.3 mL), 50 °C; (B) P(OEt)$_3$ (0.015 mmol), THF (0.3 mL), 50 °C; (C) THF (0.3 mL), room temperature. [b] Isolated yields unless otherwise noted. [c] All products gave satisfactory spectral data in addition to elemental analysis for new compounds. [d] The reaction was carried out by using 2.2 equiv of trimethylvinylsilane and TASF. [e] Yield determined by GLC.

generate pentacoordinated silicates,[14,15] (2) the anionic nature of the organic groups in organosilicon compounds is remarkably enhanced, and (3) the transfer of the organic group from silicon to palladium catalyst in the transmetalation step is extremely facilitated.

The highest yields of products from the F$^-$-promoted coupling reactions of aryl halides with trimethylvinylsilane were obtained by using HMPA as the solvent, allylpalladium chloride dimer as the catalyst (entries 1–6), and iodides as the substrate.[16] Under similar conditions, however, coupling of vinyl halides with trimethylvinylsilane gave unsatisfactory yields of the desired conjugated dienes. To overcome the drawback, we surveyed the catalytic activity of various palladium complexes and the effect of additives, and found that triethyl phosphite cocatalyst employed in THF remarkably accelerated the reaction rate and improved the yields of coupled products (entries 7–18). The reaction with tetrakis(triphenylphosphine)palladium or bis(triphenylphosphine)palladium dichloride in THF or HMPA resulted in low conversion of the organic halides.

The following points deserve particular comments.

First, in contrast to conventional transition-metal-catalyzed coupling reactions,[1] undesirable side reactions are hardly detected, and thus the coupling products such as 1,3-dienes, conjugated enynes, and styrene derivatives are obtained uniformly in moderate to high yields. In this respect, the silicon-based coupling reactions disclosed

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[16] Aryl bromides were less effective as the substrate: the conversion of the reaction was low even after prolonged reaction time.

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herein contrast sharply to the copper-promoted cross-coupling reactions[3b] wherein homo coupling often results considerably. Also, vinylation of aryl compounds catalyzed by transition-metal complexes frequently lacks regiospecificity and is accompanied by considerable homo coupling products of both substrates.[17]

Second, reaction conditions are so mild that, unlike many other similar reactions, the fluoride ion promoted cross-coupling using organosilanes is tolerant of a wide variety of organic functionality on both substrates: ester (entries 8 and 10) or ketone (entries 5 and 9) carbonyls, ethoxy (entry 17), hydroxy (entry 21), and even aldehyde carbonyl (entry 11). Thus, without protection of these groups, functionalized styrene, conjugated diene, and enyne derivatives are readily accessible by the one-pot reaction.

Third, stereospecificity and regioselectivity of the reaction is noteworthy. The reaction proceeds with retention of the double-bond geometry of the vinyl halides (entries 7 and 14). Further, the coupling reaction of allylsilane with cinnamyl bromide took place selectively at the primary allylic carbon of the bromide (entry 23).

In conclusion, the TASF/Pd catalyst promoted cross-coupling of organosilanes with organic halides has the advantage of stereospecificity and chemoselectivity in addition to commercial availability of organosilicon compounds and provides a facile method for the construction of the conjugated carbon systems.

Registry No. TASF, 59201-86-4; $H_2C{=}CHTMS$, 754-05-2; $H_2C{=}CHCH{=}CHTMS$, 1798-76-1; $H_2C{=}C(TMS)OEt$, 81177-92-6; (*E*)-PhCH=CHTMS, 19372-00-0; PhC≡CTMS, 2170-06-1; TMSC≡C-*n*-C_5H_{11}, 15719-56-9; $HOCH_2C{\equiv}CTMS$, 5272-36-6; $H_2C{=}CHCH_2TMS$, 762-72-1; *p*-IC_6H_4Me, 624-31-7; *p*-$IC_6H_4NO_2$, 636-98-6; *p*-$IC_6H_4NH_2$, 540-37-4; *p*-IC_6H_4Ac, 13329-40-3; *p*-IC_6H_4I, 624-38-4; (*E*)-$ICH{=}CHC_6H_{13}$, 42599-17-7; (*E*)-$ICH{=}CH(CH_2)_8CO_2Me$, 78461-59-3; (*E*)-$ICH{=}CH(CH_2)_8Ac$, 104761-38-8; (*E*)-$ICH{=}CH(CH_2)_9OAc$, 111468-58-7; (*E*)-$ICH{=}CH(CH_2)_8CHO$, 111468-59-8; (*E*)-$ICH{=}CHC({=}CH_2)(CH_2)_2Ph$, 111468-60-1; (*Z*)-ICH=CH-*n*-C_6H_{13}, 52356-93-1; (*E*)-ICH=CHPh, 42599-24-6; $BrCH_2CH{=}CHPh$, 4392-24-9; *p*-$MeC_6H_4CH{=}CH_2$, 622-97-9; *p*-$NO_2C_6H_4CH{=}CH_2$, 100-13-0; *p*-$NH_2C_6H_4CH{=}CH_2$, 1520-21-4; *p*-$AcC_6H_4CH{=}CH_2$, 10537-63-0; *p*-$(CH_2{=}CH)_2C_6H_4$, 105-06-6; (*E*)-$H_2C{=}CHCH{=}CHC_6H_{13}$, 58396-45-5; (*E*)-$H_2C{=}CHCH{=}CH(CH_2)_8CO_2Me$, 80625-41-8; (*E*)-$H_2C{=}CHCH{=}CH(CH_2)_8Ac$, 111468-61-2; (*E*)-$H_2C{=}CHCH{=}CH(CH_2)_9OAc$, 80625-42-9; (*E*)-$H_2C{=}CHCH{=}CH(CH_2)_8CHO$, 111468-62-3; (*E*)-$H_2C{=}CHCH{=}CHC({=}CH_2)(CH_2)_2Ph$, 111468-63-4; (*Z*)-$H_2C{=}CHCH{=}CH$-*n*-$C_6H_{13}$, 66717-33-7; (*E*)-$H_2C{=}CHCH{=}CHPh$, 16939-57-4; $H_2C{=}CHCH{=}CHCH{=}CH$-*n*-C_6H_{13}, 72084-21-0; (*E*)-$H_2C{=}C(OEt)CH{=}CHPh$, 1902-98-3; (*E*,*E*)-PhCH=CHCH=CHPh, 538-81-8; (*E*)-PhC≡CCH=CHPh, 13343-79-8; (*E*)-*n*-$C_5H_{11}C{\equiv}CCH{=}CHPh$, 111468-65-6; (*E*)-$HOCH_2C{\equiv}CCH{=}CHPh$, 103606-73-1; (*E*)-$H_2C{=}CHCH_2CH{=}CHPh$, 55666-17-6; (*E*)-$H_2C{=}CH(CH_2)_2CH{=}CHPh$, 56644-04-3; $(\eta^3\text{-}C_3H_5PdCl)_2$, 12012-95-2; 1-iodonaphthalene, 90-14-2; 1-iodocyclohexene, 17497-53-9; 1-vinylnaphthalene, 826-74-4; 1-ethenylcyclohexene, 2622-21-1.

Supplementary Material Available: Physical and spectroscopic data for new compounds (4 pages). Ordering information is given on any current masthead page.

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[17] (a) Heck, R. F. *Org. React.* (*N.Y.*) **1982**, *27*, 345. (b) Plevyak, J. E.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2454. (c) Kikukawa, K.; Ikenaga, K.; Kono, K.; Toritani, K. *J. Organomet. Chem.* **1984**, *270*, 277.

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Silyl Enol Ethers Bearing Stereogenic Silicon Atoms and Chiral Alkoxy Groups: The Effect of These Groups upon the Facial Selectivity of the Epoxidation of an Enol Double Bond[1]

Summary: Silyl enol ethers having stereogenic silicon atoms which bear chiral alkoxy groups on the silicon were prepared and found to induce modest stereoselectivity in MCPBA epoxidations of the enol double bond by virtue of the alkoxy group.

Sir: We recently reported that the lithium enolate of pinacolone reacted with dichlorodimethylsilane to form chlorosilyl enol ether **1** which underwent displacement reactions with alcohols and amines to yield alkoxysilyl and aminosilyl enol ethers (e.g. **2** and **3**, Scheme I).[2] We are interested in silyl enol ethers bearing non-alkyl ligands on the silicon because such ligands may electronically or sterically affect the reactivity of the enol ether, relative to that of the better-known trialkylsilyl ethers,[3] in a synthetically useful manner. A chiral alkoxy or amino group on the silicon may direct the approach of a reagent preferentially to one face of the prochiral enol ligand, and a stereogenic silicon atom in the silyl enol ether may also affect the stereoselectivity of such additions.[4] To our knowledge, only one report of silyl enol ethers bearing stereogenic silicon atoms—a series of β-dicarbonyl-derived enol ethers bearing the well-known chiral methylphenyl-α-naphthylsilyl group—is in the literature.[5] Our methodology is well-suited to the synthesis of a great variety of chiral enol ethers, as the reaction of a lithium enolate with a dichlorosilane bearing any two different alkyl groups will form a chlorosilyl enol ether which would react with a chiral alcohol or amine to form diastereomeric enol ethers epimeric at the silicon. We now report the first syntheses of alkoxysilyl enol ethers which are chiral at the silicon center and results of a study of the effects of a chiral alkoxy group and a stereogenic silicon atom upon the stereofacial selectivity of a peracid epoxidation of one of these silyl enol ethers.

A list of enol ethers that we have prepared is given in Table I. When lithium enolates were exposed to dichloromethylphenylsilane followed by (*S*)-methyl mandelate, alkoxysilyl enol ethers **4a**,**b**, **5a**,**b**, and **6a**,**b** were formed in high yields.[6] The diastereomers could be separated by using preparative HPLC to yield enantiomerically pure silyl ethers. Varying the chiral alcohol to (*S*)-ethyl lactate or (*S*)-ethyl 3-hydroxybutanoate gave the enol ethers **7a**,**b** and **8a**,**b**, and varying the dichlorosilane to dichloromethylvinylsilane gave the enol ethers **9a**,**b**.

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[1] Silicon-Functionalized Silyl Enol Ethers. 2. For 1, see ref 2.

[2] Walkup, R. D. *Tetrahedron Lett.* **1987**, *28*, 511.

[3] Brownbridge, P. *Synthesis* **1983**, 1; 85.

[4] For examples (leading references) of enolate addition reactions featuring stereoselectivity due to a chiral group on the enolate, see: (a) Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top. Stereochem.* **1982**, *13*, 1. (b) Heathcock, C. H. In *Asymmetric Synthesis*, Vol. 2; Morrison, J. D., Ed.; Academic Press: New York, 1983; Chapter 2. (c) Davies, S. G.; Walker, J. C. *J. Chem. Soc., Chem. Commun.* **1986**, 495. (d) Helmchen, G.; Schmierer, R.; Grotemeier, G., Selim, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 207. (e) Nagao, Y., Hagiwara, Y., Kumagai, T., Ochiai, M., Inoue, T., Hashimoto, K., Fujita, E. *J. Org. Chem.* **1986**, *51*, 2391. (f) Braun, M.; Devant, R. *Tetrahedron Lett.* **1984**, *25*, 5031. (g) Masamune, S.; Sato, T.; Kim, B.-M.; Wollmann, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 8279.

[5] Kusnezowa, I. K.; Ruhlmann, K.; Grundemann, I. *J. Organomet. Chem.* **1973**, *47*, 53.

[6] All of the alkoxysilyl enol ethers were synthesized as described in ref 2. Complete spectroscopic data for 4–14 and 16 is given in the supplementary material. Due to the reactive nature of these compounds, samples of a purity adequate for elemental analyses could not be obtained.

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