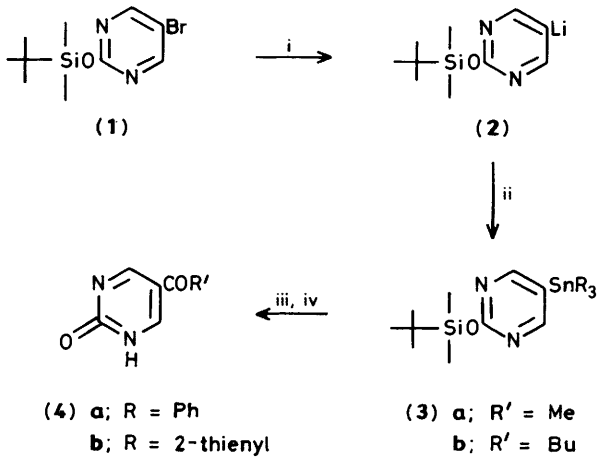
Synthesis of 5-Stannylpyrimidines and their Use in Pd-Catalysed Ketone Formation

Joseph Arukwe, Tore Benneche, and Kjell Undheim *
Department of Chemistry, University of Oslo, N-0315 Oslo 3, Norway

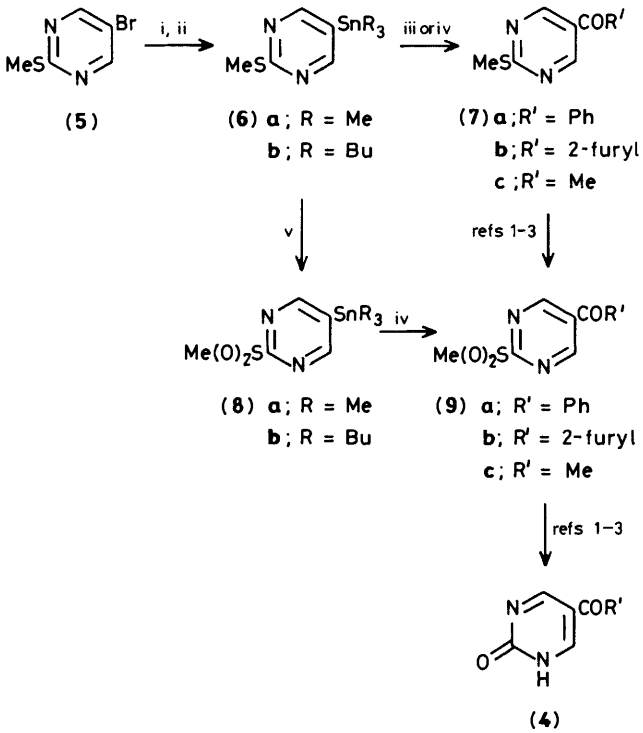
2-(Dimethyl-t-butylsiloxy)-5-stannylpyrimidines have been prepared from the lithiated pyrimidine precursor. 2-Methylthio-5-stannylpyrimidines were prepared similarly and oxidized chemoselectively to the corresponding sulphones. 5-Stannylpyrimidin-2(1*H*)-ones can be prepared by fluoride-induced removal of the silyl group in 2-(dimethyl-t-butylsiloxy)-5-stannylpyrimidines, and the 5-stannylated pyrimidinones can be *N*-alkylated. The stannylated pyrimidines are stable compounds which react readily with acid chlorides in Pd-catalysed reactions with formation of 5-pyrimidinyl ketones.

Ready access to 5-acylpyrimidines is of general interest for making this class of derivatives available for biological evaluations. When we started our studies of pyrimidin-5-yl ketones, only a few 5-acylpyrimidines were known and all had been prepared by pyrimidine cyclization reactions.[1] Starting from pyrimidines we have shown that an *ortho*-lithiated pyrimidine-4-carboxylic acid can react with acid chlorides to yield ketones which are readily decarboxylated,[2] and that the acid chloride of a pyrimidine-5-carboxylic acid reacts with organomanganese(II) reagents to form ketones.[3] In this report we describe ketone syntheses by means of organotin chemistry. Organotin reagents are important in palladium-catalysed cross-coupling reactions.[4] Recently pyridines have been stannylated and coupled with acid chlorides to furnish ketones.[5] The stannylpyridine substrates were prepared by nucleophilic substitution reactions between trimethylstannylsodium and 2- or 4-halogenopyridines.[6] Since the 5-position in pyrimidines is not especially activated for nucleophilic substitution, the 5-stannyl group in our pyrimidines was introduced *via* lithiation. Previous work had shown that 5-halogenopyrimidines can be lithiated at −95 °C without complications from nucleophilic additions and the lithiated species react well with electrophiles.[7] In this work the lithiated pyrimidine was quenched by the addition of either trimethyl- or tributyl-stannyl chloride to form the 5-stannylated pyrimidine in good yields.

The hydroxy group in the starting material 5-bromopyrimidin-2(1*H*)-one was protected as a dimethyl-t-butylsilyl (TBDMS) ether and the protected species (**1**) was lithiated to furnish compound (**2**) as previously described.[7] Treatment



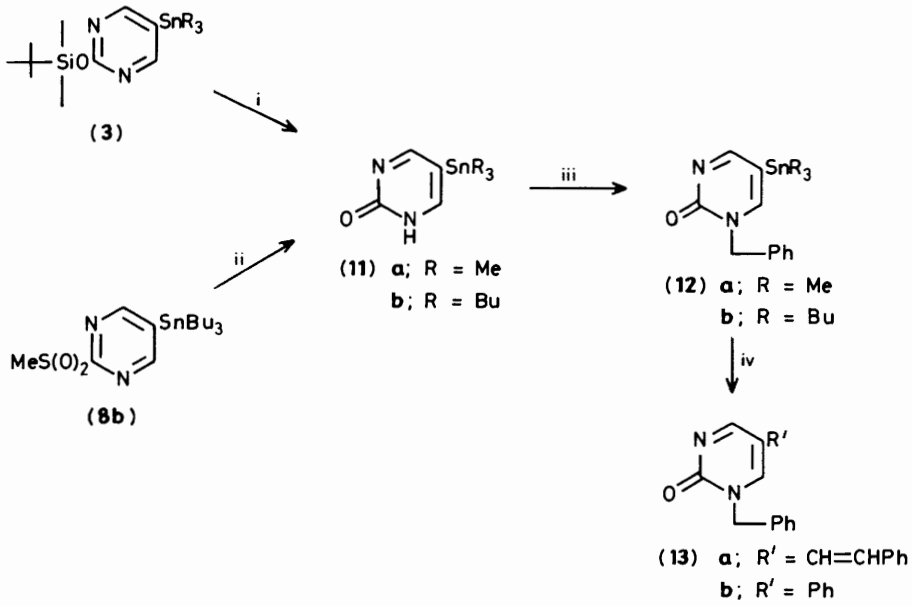
Scheme 1. *Reagents and conditions:* i, BuLi, THF, −95 °C; ii, R_3SnCl; iii, $(Ph_3P)_2PdCl_2$, R'COCl, $ClCH_2CH_2Cl$; iv, AcOH



Scheme 2. *Reagents and conditions:* i, BuLi, THF, −95 °C; ii, R_3SnCl; iii, $(Ph_3P)_2PdCl_2$, R'COCl, $ClCH_2CH_2Cl$; iv, $(Ph_3P)_2PdCl_2$, R'COCl, THF; v, MCPBA, CH_2Cl_2

of compound (**2**) with the trialkylstannyl chlorides gave the stannylated pyrimidines (**3**). The latter were obtained in high yields and could be purified either by chromatography or by distillation. By analogy to coupling reactions with arenes,[8,9] bis(triphenylphosphine)palladium(II) dichloride was used as catalyst in the coupling reactions of compounds (**3**) with acid chlorides. The TBDMS group is cleaved during the reactions in boiling 1,2-dichloroethane; 5-acylpyrimidinones (**4**) were isolated (Scheme 1). Presumably it is the stannyl chloride, which is generated during the coupling reaction, which leads to the cleavage of the silyl–oxygen bond.

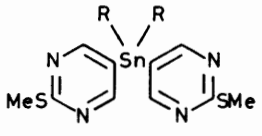
In order to have a 2-substituent which is not affected by the coupling conditions, 5-bromo-2-methylthiopyrimidine (**5**) was used as starting material. Compound (**5**) was lithiated using butyl-lithium at −95 °C and the intermediate was allowed to react with trimethyl- or tributyl-stannyl chloride. Both stannylated pyrimidines (**6**) are stable to normal purification procedures. In both reactions a by-product was isolated by



Scheme 3. *Reagents and conditions:* i, Bu_4NF, BzBr, THF; ii, 1M NaOH, THF; iii, NaH, BzBr, DME; iv, $(Ph_3P)_2PdCl_2$, R'X, $ClCH_2CH_2Cl$

chromatography and identified as the dipyrimidinyltin derivative (**10**). Presumably, compounds (**10**) are formed from dialkyldichlorotin present as an impurity in the commercially obtained trialkylchlorotin reagents.

The stannylpyrimidines (**6**) coupled readily with acid chlorides to yield the 5-acylated products (**7**) under Pd^{II} catalysis. The products (**7**) are readily oxidized to sulfones (**9**) which can be hydrolysed to the 5-acylpyrimidinones (**4**) as previously described[1-3] (see Scheme 2). If the acyl group should contain substituents sensitive to oxidation, the reaction sequence can be reversed. In the reverse route the sulphides (**6**) were oxidized chemoselectively to the corresponding sulphones (**8**) in high yields by *m*-chloroperbenzoic acid (MCPBA). The 2-sulphonyl-5-stannylpyrimidines (**8**) could be purified by recrystallization or by chromatography. They undergo the Pd^{II}-catalysed coupling reaction with acid chlorides under fairly mild conditions; reflux in tetrahydrofuran (THF) was used. The relatively mild conditions required for the coupling of compounds (**8**) suggest that the sulphonyl group in the *para* position exerts an activating effect with respect to the stannyl function.



(**10**) a; R = Me
b; R = Bu

Finally, a method for the preparation of 5-stannylpyrimidinones (**11**) was developed (Scheme 3). The 2-TBDMSoxy-5-stannylpyrimidines (**3**) were desilylated by treatment with anhydrous tetrabutylammonium fluoride in THF to furnish the ammonium salt of the 5-stannylpyrimidin-2(1*H*)-ones (**11**). The stannyl function was not cleaved during *N*-benzylation of compounds (**11**), as the ammonium salt, to form compounds (**12**). Also hydrolysis of the sulphone (**8b**) to furnish (**11b**), using 1M NaOH in THF, did not affect the pyrimidine–tin bond. The stannylated pyrimidinones (**12**) readily undergo Pd^{II}-catalysed reactions with acid chlorides, but the highly π-electron-deficient 5-acylated pyrimidinones were involved in additional reactions to give unidentified product mixtures. The best route for the preparation of such derivatives therefore consists of the hydrolysis of the 5-acylated sulphone (**9**) or the silyl ether of (**4**), and subsequent *N*-alkylation as previously described.[2]

The high reactivity of the 5-stannylated pyrimidinones (**12**) in Pd^{II}-catalysed reactions was verified in reactions with β-bromostyrene and iodobenzene when the coupling products (**13**) were formed.

Experimental

The ^1H n.m.r. spectra were recorded in $CDCl_3$ solutions on a JEOL PMX60SI spectrometer at 60 or Varian XL-3OO at 300 MHz, the ^{13}C n.m.r. spectra at 75 MHz. The mass spectra were recorded at 70 eV on a Micromass 70F spectrometer. Isobutane was used for chemical ionization (c.i.).

The THF used in the organometallic reactions was dried by refluxing and distillation over sodium–benzophenone; 1,2-dichloroethane was distilled over P_2O_5. Light petroleum refers to the fraction boiling in the range 40—60 °C.

2-(Dimethyl-t-butylsiloxy)-5-trimethylstannylpyrimidine (**3a**).—1.6M Butyl-lithium (4.4 ml, 7.0 mmol) was added dropwise from a syringe to a stirred solution of 5-bromo-2-(dimethyl-t-butylsiloxy)pyrimidine (**1**) (2.00 g, 7.00 mmol) in dry THF (40 ml) under N_2 at −95 °C, the pale yellow solution was stirred at −85 °C for 60 min, a solution of chlorotrimethyltin (1.40 g, 7.0 mmol) in dry THF (10 ml) was added dropwise at −90 °C, the mixture was stirred at −85 °C for 30 min, then at 0 °C for 20 h, then poured into 10% aqueous ammonium chloride (30 ml); the mixture was stirred vigorously for 10 min, the two phases were separated, the aqueous phase was extracted with chloroform (3 × 50 ml), and the combined organic phases were washed, dried ($MgSO_4$), and evaporated, and the product was purified by flash chromatography [silica gel; light petroleum–EtOAc (7:3)] to give *compound* (**3a**) (2.11 g, 81%) (Found: C, 47.0; H, 7.0. $C_{13}H_{26}N_2OSiSn$ requires C, 47.18; H, 6.97%); δ_H 0.7 (SnMe and SiMe), 1.40 (Bu^t), and 8.80 (4- and 6-H); *m/z* (c.i.)

379/377/375/374/373/372/371 [(M + H), 3/3/17/7/13/4/8%], 265/263/261/260/259/258/257 (15/11/100/31/76/18/38).

2-(*Dimethyl-t-butylsiloxy*)-5-*tributylstannylpyrimidine* (**3b**).—5-Bromo-2-(dimethyl-t-butylsiloxy)pyrimidine was lithiated as above and treated in the above manner with chlorotributyltin. The reaction mixture was worked up as above and the crude product was distilled (Kugelrohr); oven temp. 200 °C/0.02 mmHg, to give compound (**3b**) (2.83 g, 81%) (Found: C, 53.35; H, 8.7. $C_{22}H_{44}N_2OSiSn$ requires C, 52.90; H, 8.82%); δ_H 0.40 (SiMe), 0.6—1.7 (Bu and Bu^t), and 8.35 (4- and 6-H); m/z (c.i.) 505/503/501/500/499/498/497 [(M + H), 17/19/99/43/71/33/39%], 391/389/387/386/385/384/382 (14/16/83/35/70/2/43), and 293/292/291/290/289/287 (4/4/31/11/22/14).

5-*Benzoylpyrimidin*-2(1H)-*one*[2] (**4a**).—Bis(triphenylphosphine)palladium(II) dichloride (70 mg, 0.10 mmol) was added to a solution of 2-(dimethyl-t-butylsiloxy)-5-trimethylstannylpyrimidine (**3a**) (1.01 g, 2.7 mmol) and benzoyl chloride (0.41 g, 2.9 mmol) in dry 1,2-dichloroethane (20 ml), the mixture was heated under reflux for 20 h, then filtered hot, and acetic acid (0.6 ml) was added to the cold filtrate, the solution was stirred at ambient temperature for 1 h, the solvent was evaporated off, the residue was triturated with diethyl ether (30 ml), and the title product was purified by recrystallization from methanol (0.25 g, 47%), m.p. 244 °C. In an analogous reaction using 2-(dimethyl-t-butylsiloxy)-5-tributylstannylpyrimidine (**3b**) the yield of compound (**4a**) was 30%.

5-(2-*Thenoyl*)*pyrimidin*-2(1H)-*one*[2] (**4b**).—Compound (**4b**) was prepared in the above manner from thenoyl chloride and 2-(dimethyl-t-butylsiloxy)-5-trimethylstannylpyrimidine. The product was recrystallized from water to give compound (**4b**) (0.20 g, 36%), m.p. 252 °C. In an analogous reaction using 2-(dimethyl-t-butylsiloxy)-5-tributylstannylpyrimidine (**3b**) the yield of compound (**4b**) was 27%.

2-*Methylthio*-5-*trimethylstannylpyrimidine* (**6a**).—1.5M-Butyllithium in hexane (7.0 ml, 11.2 mmol) was added dropwise from a syringe to a stirred solution of 5-bromo-2-methylthiopyrimidine (**5**) (2.00 g, 9.8 mmol) in dry THF (130 ml) under N_2 at −95 °C, the pale yellow solution was stirred at −85 °C for 60 min, a solution of chlorotrimethyltin (2.23 g, 11.2 mmol) in dry THF (15 ml) was added dropwise at −90 °C, the greenish yellow solution was stirred at −85 °C for 30 min, left at 0 °C for 20 h, and poured into 10% aqueous ammonium chloride (30 ml), and the mixture was stirred for 10 min before the phases were separated. The aqueous phase was extracted with chloroform (3 × 50 ml), the combined organic phases were washed and dried ($MgSO_4$), the solvents were evaporated off, and the residue was subjected to flash chromatography on silica gel with light petroleum–EtOAc (7:3). The title compound was eluted first (2.30 g, 82%), the second fraction was 2-methylthiopyrimidine (0.20 g, 7%), and the final fraction contained dimethylbis-(2-methylthiopyrimidin-5-yl)tin (**10a**) (0.23 g, 8%). *Title compound* (**6a**) was an oily material (Found: C, 33.3; H, 4.85. $C_8H_{14}N_2SSn$ requires C, 33.22; H, 4.84%); ν(film) 2 970w, 2 910w, 1 540, 1 390, and 1 190 cm^{-1}; δ_H 0.40 (SnMe), 2.60 (SMe), and 8.50 (4- and 6-H, $J_{Sn,4\text{-},6\text{-}H}$ 20 Hz); m/z 279/277/276/275/274/273/272/271 (17/19/8/100/32/73/29/42%), 249/247/245/244/243/242/241 (5/6/22/8/18/6/11).

Dimethylbis-(2-*methylthiopyrimidin*-5-*yl*)*tin* (**10a**) had m.p. 100 °C (from EtOH) (Found: C, 36.6; H, 4.1. $C_{12}H_{16}N_4S_2Sn$ requires C, 36.09; H, 4.01%); δ_H 0.70 (SnMe), 2.60 (SMe), 8.50 (4- and 6-H, $J_{Sn,4\text{-},6\text{-}H}$ 24 Hz); m/z 404/402/400/399/398/-397/396 (M^+, 4/5/26/10/21/7/10), 389/387/385/384/383/382/381 (14/18/100/32/60/24/36), 355/353 (7/5), and 249/247/245/244/243/242/241 (2/2/16/6/12/4/7).

2-*Methylthio*-5-*tributylstannylpyrimidine* (**6b**) was prepared as previously described;[10] ν(film) 2 940, 2 900, 2 840, 1 540, 1 380, and 1 190 cm^{-1}.

5-*Benzoyl*-2-*methylthiopyrimidine*[2] (**7a**).—Bis(triphenylphosphine)palladium(II) dichloride (0.17 g, 0.24 mmol) was added to a solution of benzoyl chloride (0.56 g, 4.0 mmol) and 2-methylthio-5-trimethylstannylpyrimidine (**6a**) (1.01 g, 3.5 mmol) in dry 1,2-dichloroethane (10 ml). The mixture was heated under reflux until t.l.c. (silica gel; EtOAc) showed the reaction to be complete (4 h). Diethyl ether (45 ml) was added to the cold reaction mixture followed by saturated aqueous KF (20 ml), the mixture was stirred vigorously for 60 min, and precipitated fluorotrimethyltin was removed by filtration. The two phases were separated, the washed and dried ($MgSO_4$) organic solution was evaporated, and the residual product was recrystallized from methanol to yield the title compound (0.78 g, 97%), m.p. 100 °C.

5-(2-*Furoyl*)-2-*methylthiopyrimidine*[2] (**7b**).—Furoyl chloride was treated with 2-methylthio-5-trimethylstannylpyrimidine (**6a**) as above in THF under reflux for 3 h. The crude product was recrystallized from dilute ethanol to give compound (**7b**) (0.55 g, 71%), m.p. 76 °C.

5-*Acetyl*-2-*methylthiopyrimidine*[3] (**7c**).—Acetyl chloride was treated with 2-methylthio-5-trimethylstannylpyrimidine (**6a**) as above. The reaction was run in refluxing THF for 2 h. The crude product was recrystallized from methanol to give compound (**7c**) (0.56 g, 96%), m.p. 129 °C.

2-*Methylsulphonyl*-5-*trimethylstannylpyrimidine* (**8a**).—A solution of 2-methylthio-5-trimethylstannylpyrimidine (**6a**) (0.49 g, 1.7 mmol) and MCPBA (0.76 g, 4.4 mmol) in dichloromethane (40 ml) was stirred at ambient temperature until t.l.c. showed that the reaction was complete (2 h). The mixture was shaken with saturated aqueous sodium hydrogen sulphite (2 × 20 ml), the organic solution was dried ($MgSO_4$) and evaporated and the *product* was crystallized from propan-2-ol as white plates, m.p. 108 °C (0.33 g, 96%) (Found: C, 30.0; H, 4.4. $C_8H_{14}N_2O_2SSn$ requires C, 29.91; H, 4.36%); ν(KBr) 2 990w, 2 910w, 1 520, 1 390, 1 300, and 1 120 cm^{-1}; δ_H 0.60 (SnMe), 3.50 (SO_2Me), and 9.10 (4- and 6-H, $J_{Sn,4\text{-},6\text{-}H}$ 20 Hz); m/z 326/324/323/322/321/320/319/318 (M^+, 1/1/1/9/3/8/2/3%), 311/309/307/306/305/304/303 (17/18/100/31/72/26/41), and 292/291/290/289/288 (10/2/7/2/4).

2-*Methylsulphonyl*-5-*tributylstannylpyrimidine* (**8b**).—Compound (**8b**) (0.71 g, 93%) was prepared in the same manner from 2-methylthio-5-tributylstannylpyrimidine; and was a viscous oil (Found: C, 45.6; H, 7.0. $C_{16}H_{32}O_2SSn$ requires C, 45.64; H, 7.16%); ν(KBr) 2 940, 2 900, 2 840, 1 540, 1 390, 1 310, and 1 130 cm^{-1}; δ_H 0.6—1.8 (SnBu), 3.30 (SO_2Me), and 8.90 (4- and 6-H, $J_{Sn,4\text{-},6\text{-}H}$ 16 Hz); m/z (c.i.) 453/451/450/449/448/447/446/445 (15/19/20/100/36/74/27/40%), 393/392/391/390/389/388/387 (5/3/10/4/7/2/4), 371 (4), 291 (5), and 159 (29).

5-*Benzoyl*-2-*methylsulphonylpyrimidine*[2] (**9a**).—*Method A.* Bis(triphenylphosphine)palladium(II) dichloride (0.10 g, 0.14 mmol) was added to a solution of benzoyl chloride (0.25 g, 1.8 mmol) and 2-methylsulphonyl-5-trimethylstannylpyrimidine (**8a**) (0.32 g, 1 mmol) in dry THF (10 ml), the mixture was heated under reflux for 90 min, when t.l.c. showed the reaction to be complete. Diethyl ether (50 ml) was added to the cold reaction mixture, followed by saturated aqueous KF, the mixture was stirred vigorously for 60 min, the fluorotrimethyltin

precipitate was removed by filtration, the two phases were separated, then washed and dried ($MgSO_4$) organic solution was evaporated, and the product was purified by recrystallization from ethanol to give compound (**9a**) (0.19 g, 71%), m.p. *132* °C.

Method B. 2-Methylsulphonyl-5-tributylstannylpyrimidine (**8b**) was used instead of compound (**8a**). The reaction conditions were the same as under method A: yield 61%.

5-(2-*Furoyl*)-2-*methylsulphonylpyrimidine*[2] (**9b**).—*Method A.* 2-Furoyl chloride was treated with 2-methylsulphonyl-5-trimethylstannylpyrimidine as above. The reaction was complete after 2 h. The product crystallized out from the cold solution, when diethyl ether (60 ml) was added as compound (**9b**) (0.18 g, 72%), m.p. 150 °C (from Pr^iOH).

Method B. The yield was 62% when the tributylstannylpyrimidine (**8b**) was used.

5-*Acetyl*-2-*methylsulphonylpyrimidine*[2] (**9c**).—*Method A.* Acetyl chloride was treated with 2-methylsulphonyl-5-trimethylstannylpyrimidine (**8a**) as above. The reaction was complete after 6 h. The product was purified by crystallization from ethanol, and gave compound (**9c**) (0.14 g, 71%), m.p. 132 °C.

Method B. The yield was 52% when the tributylstannylpyrimidine (**8b**) was used.

5-*Tributylstannylpyrimidin*-2(1H)-*one* (**11b**).—*Method A.* Tetrabutylammonium fluoride (6 ml; 1 M solution in THF) was added to a solution of 2-(dimethyl-t-butylsiloxy)-5-tributylstannylpyrimidine (**3b**) (2.99 g, 6.0 mmol) in dry THF (5 ml) under N_2 at 0°C. The mixture was stirred at 0 °C for 2 h and then at ambient temperature for 1 h before a mixture of chloroform and 10% aqueous ammonium chloride was added. The organic phase was separated, and washed with saturated aqueous sodium chloride, dried ($MgSO_4$), and evaporated. The crude product was purified by flash chromatography [silica gel; MeOH–CH_2Cl_2 (1:15)] to give *compound* (**11b**) (652 mg, 71%), m.p. 105—110 °C; ν(film) 2 940, 2 900, 2 840, 1 640br, 1 580, 1 490, 1 450, 1 360, and 1 320 cm^{-1}; δ_H 0.8—2.0 ($SnBu_3$) and 8.21 (4- and 6-H, $J_{Sn,4-,6-H}$ 18 Hz) (Found: C, 49.6; H, 7.9. $C_{16}H_{30}N_2OSn$ requires C, 49.95; H, 7.88%); *m/z* 333/331/329/328/327/326/325 (1/1/6/2/5/3/3%), 313 (7), 272/269/268/267/266/265 (27/10/67/22/50/15), 213 (18), and 177 (34).

Method B. Aqueous sodium hydroxide (2 ml; 1 M) was added to 2-methylsulphonyl-5-tributylstannylpyrimidine (**8b**) (415 mg, 0.93 mmol) and a catalytic amount of benzyltriethylammonium chloride in THF (3 ml) and water (1 ml). The mixture was stirred at ambient temperature for 18 h, chloroform was added, and the solution was washed successively with 10% aqueous ammonium chloride and saturated aqueous sodium chloride. The dried ($MgSO_4$) solution was evaporated to give the title compound (315 mg, 88%).

1-*Benzyl*-5-*tributylstannylpyrimidin*-2(1H)-*one* (**12b**).—*Method A.* Tetrabutylammonium fluoride (4 ml; 1 M solution in THF) was added to a mixture of 2-(dimethyl-t-butylsiloxy)-5-tributylstannylpyrimidine (**3b**) (2.00 g, 4 mmol) and benzyl bromide (0.50 ml, 4.2 mmol) in THF (4 ml) under N_2 at 0 °C. The mixture was stirred for 18 h while reaching ambient temperature before chloroform (20 ml) was added. The solution was washed successively with 10% aqueous ammonium chloride and saturated aqueous sodium chloride (2 ×), dried ($MgSO_4$), and evaporated. The residue was triturated twice with hexane and the solid was purified on a silica gel column (6 cm) with chloroform as eluant to give compound (**12b**) (1.03 g, 54%), m.p. 30—35 °C, ν(film) 2 940, 2 900, 2 840, 1 650br, 1 490, 1 450, and 1 400 cm^{-1}; δ_H 0.8—2.0 ($SnBu_3$), 5.10 (CH_2Ph), 7.29—7.37 (Ph), 7.43 (6-H, d, *J* 2.7 Hz), and 8.47 (4-H, d, *J* 3.7 Hz); *m/z* 476 (M^+, 0.1), 419/418/417/416/415 (78/29/58/24/33), 305 (4), 304 (1), 303 (2), 292 (3), 276 (6), 186 (12), 144 (17), and 91 (100).

Method B. Sodium hydride (25 mg, 0.84 mmol; 80% in mineral oil) was added to a solution of 5-tributylstannylpyrimidin-2(1*H*)-one (**11b**) (324 mg, 0.84 mmol) in 1,2-dimethoxyethane (2 ml). The mixture was stirred for 15 min before benzyl bromide (0.126 ml, 1.06 mmol) was added and the mixture was stirred for 18 h at ambient temperature. Chloroform was added and the solution was washed with saturated aqueous sodium chloride, dried ($MgSO_4$), and evaporated. The crude product was purified by flash chromatography (silica gel; 2% MeOH in $CHCl_3$) to give compound (**12b**) (177 mg, 44%).

1-*Benzyl*-5-*trimethylstannylpyrimidin*-2(1H)-*one* (**12a**).—Compound (**12a**) was prepared as (**12b**) above from 2-(dimethyl-t-butylsiloxy)-5-trimethylpyrimidine (556 mg, 1.49 mmol), benzyl bromide (0.18 ml, 1.51 mmol). and tetrabutylammonium fluoride (1.5 ml; 1 M solution in THF); work-up gave the required *product* (**12a**) (220 mg, 42%), m.p. 101—103 °C (Found: C, 48.8; H, 5.0. $C_{14}H_{18}N_2OSn$ requires C, 48.17; H, 5.21%); ν(KBr) 3 000w,br, 1 650br, 1 500, 1 450, 1 400, and 1 320 cm^{-1}; δ_H 0.30 ($SnMe_3$), 5.09 (2 H), 7.33 (5 H), 7.44 (6-H, d, *J* 3 Hz), and 8.4—8.5 (4-H, br; *m/z* 354/352/350/349/348/347/346 (M^+, 2/1/14/6/10/4/7), 339/337/335/334/333/332/331 (6/6/36/15/29/10/18), 192 (16), 190 (13), 165 (7), 142 (12), and 91 (100).

1-*Benzyl*-5-*styrylpyrimidin*-2(1H)-*one* (**13a**).—β-Bromostyrene (110 mg, 0.6 mmol) was added to a mixture of 1-benzyl-5-tributylstannylpyrimidin-2-(1*H*)-one (**12b**) (238 mg, 0.50 mmol) and bis(triphenylphosphine)palladium(II) dichloride (18 mg, 0.025 mmol) in dichloroethane (2 ml). The mixture was heated under reflux for 12 h, the solvent was evaporated off, and the crude product washed with diethyl ether (2 ×). Insoluble material was dissolved in dichloromethane, the solution was filtered, and the title compound (120 mg, 81%) was precipitated with diethyl ether. The product was identical with an authentic sample.[10]

1-*Benzyl*-5-*phenylpyrmidin*-2(1H)-*one* (**13b**).—*Method A.* Iodobenzene (122 mg, 0.60 mmol) was added to a mixture of 1-benzyl-5-tributylstannylpyrimidin-2(1*H*)-one (**12b**) (248 mg, 0.52 mmol) and bis-(triphenylphosphine)palladium(II) dichloride (18 mg, 0.025 mmol) in 1,2-dichloroethane (2 ml). The mixture was heated at 80 °C for 12 h, chloroform was added, and the mixture was filtered to remove the precipitated palladium black. The solution was evaporated, and the residue was washed with diethyl ether (2 ×) to give the title compound as a solid (114 mg, 87%), m.p. 144—146 °C (Found: C, 78.0; H, 5.3. $C_{17}H_{14}N_2O$ requires C, 77.82; H, 5.39%); δ_H 5.24 (CH_2Ph), 7.1—7.5 (2 Ph), 7.88 (6-H, d, *J* 3 Hz), and 8.89 (4-H, d, *J* 3 Hz); *m/z* 262 (M^+, 44), 233 (2), 221 (2), 220 (12), 207 (2), 206 (2), 171 (6), 156 (6), 116 (7), and 91 (100).

Method B. When 1-benzyl-5-trimethylstannylpyrimidin-2(1*H*)-one (**12a**) was used instead of compound (**12b**) under the same reaction conditions as for method A, compound (**13b**) was obtained in 61% yield.

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