Tetrahedron Vol 46, No. 7, pp. 2623-2632, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00

SYNTHESIS OF 3-SUBSTITUTED FURANS BY DIRECTED LITHIATION AND PALLADIUM CATALYSED COUPLING[1]

David S. Ennis and Thomas L. Gilchrist*

The Robert Robinson Laboratories, University of Liverpool, P.O. Box 147,
Liverpool L69 3BX, U.K.

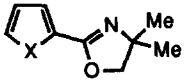
(*Received in UK* 10 *January* 1990)

Abstract: *The 5-position of the furan ring of 4,4-dimethyl-2-(2-furyl)oxazoline (**1a**) was protected by a trimethylsilyl group. The product, compound (**2a**), was then lithiated at the 3-position with sec-butyllithium and converted to the bromozinc species (**2d**) with zinc bromide. Coupling reactions with a range of aryl-, acyl-, and vinyl halides were performed with $Pd(PPh_3)_4$ as catalyst. The reaction with (1-bromoethenyl)-trimethylsilane is abnormal in that it gives a mixture of two products (**2l**) and (**2m**). The origin of the abnormal product (**2l**) is discussed. The coupling reactions of this silane with 2-thienyl-, 2-furyl-, and phenyl-zinc bromide have also been carried out: in each case, a mixture of the expected coupling product and an isomer, the ethen-2-yltrimethylsilane, was obtained. The ratio of products is shown to depend upon the temperature at which the coupling is carried out. 4,4-Dimethyl-2-(2-thienyl)oxazoline (**1b**) was lithiated at the 3-position of the thiophene ring and coupled to iodobenzene without protection of the 5-position.*

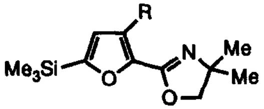
The use of the 4,4-dimethyloxazoline substituent as a directing group for lithiation in the furan and thiophene series has been investigated by Chadwick and his co-workers.[2] They have shown that this substituent in the 2-position of thiophene or furan directs lithiation mainly or exclusively to the 3-position when *sec*-butyllithium is used at low temperature. In the furan series a minor product is derived from lithiation at the 5-position. This position can, however, be protected by a trimethylsilyl substituent, which is introduced by reaction of the furyloxazoline with LDA and chlorotrimethylsilane. The work described here is an investigation of the use of the 3-furyllithium intermediate for the preparation of new 3-substituted furans and thiophenes by palladium(0) catalysed coupling reactions with electrophiles. A related sequence of directed lithiation of benzamides followed by palladium coupling has been used recently as a means of selective carbon-carbon bond formation.[3]

2-Furoic acid was converted into the oxazoline (**1a**) by a literature procedure[2] and the trimethylsilyl group was introduced into the 5-position, giving the furan (**2a**). Lithiation at the 3-position was then achieved by reaction with *sec*-butyllithium at -78°C for 0.5 h. The position of lithiation was established by quenching the reaction mixture with iodomethane and with deuterium oxide, which gave the furans (**2b**) and (**2c**), respectively, in high yield.

The bromozinc species (**2d**) was selected as the organometallic partner in the coupling reactions. This was prepared from the 3-furyllithium compound (**2e**) by reaction with zinc bromide in THF at -20°C. Coupling was first attempted with iodobenzene in the presence of 4 mol% tetrakis(triphenylphosphine)palladium(0). After 24 h at room temperature only 10% of the coupled product was formed. The reaction was therefore repeated and the mixture was heated under reflux and its progress monitored by t.l.c. After 16 h the reaction appeared to be complete. The coupled product, the 3-phenylfuran (**2f**), was then isolated by flash chromatography.

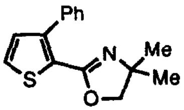


(**1**) **a**; X = O
b; X = S

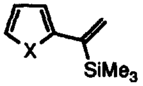


(**2**) **a**; R = H
b; R = Me
c; R = D
d; R = ZnBr
e; R = Li
f; R = Ph
g; R = $CH_2CH=CH_2$
h; R = CH_2Ph
i; R = $C(Ph)=CH_2$
j; R = CH=CHPh
k; R = $4\text{-}C_6H_4CO_2Et$
l; R = $CH=CHSiMe_3$
m; R = $C(SiMe_3)=CH_2$
n; R = COPh

A series of other electrophiles was then coupled in the same way, giving the 3-substituted furans (**2g**) to (**2n**) (Table). With the exception of the reaction with benzoyl bromide, which gave the 3-benzoylfuran (**2n**) in only 32% yield, all the coupling reactions went in good yield. All gave the products expected from regioselective and stereoselective coupling of the halide to (**2d**), with the exception of (1-bromoethenyl)trimethylsilane. This gave a mixture of the expected coupling product the silane (**2m**), and its isomer, the 2-ethenylsilane (**2l**), in a ratio of 55:45, from which the major isomer (**2m**) was isolated in 50% yield. This coupling reaction is discussed below in more detail. A single coupling reaction was also carried out with the thienyloxazoline (**1b**). This compound was selectively lithiated at C-3 by butyllithium without the necessity of protecting the 5-position. Coupling was carried out with iodobenzene in the same way as for the furan (**2a**) and the expected 3-phenylthiophene (**3**) was isolated in good yield.



(**3**)

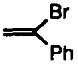
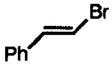
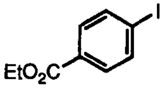
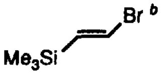
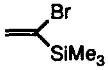


(**4**) **a**; X = S
b; X = O

(**5**) **a**; X = S
b; X = O

TABLE

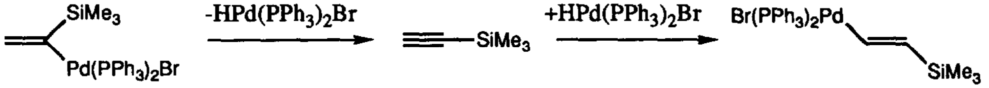
Products of coupling of 3-furylzinc bromide (2d) with halides

Halide	Products and yield (%) [a]
PhI	(2f) (83)
	(2g) (79)
$PhCH_2Br$	(2h) (73)
	(2i) (89)
	(2j) (85)
	(2k) (86)
 [b]	(2l) (86)
	(2m) (50) (2l) (40)
PhCOBr	(2n) (32)

[a] Yields are for isolated products. [b] Contains ca. 8% (Z)-isomer.

The anomalous coupling reaction observed with (1-bromoethenyl)trimethylsilane was investigated further. The silane was unaffected by heating with zinc bromide and $Pd(PPh_3)_4$ in THF under reflux for 12 h. The possibility that the steric bulk of the organozinc species was responsible for the abnormal coupling was investigated by carrying out reactions with 2-thienyl-, 2-furyl-, and phenyl-zinc bromides. In each case coupling reactions gave mixtures of the 1- and 2-(trimethylsilyl)ethenes in approximately the same ratio as before. Thus, 2-thienylzinc bromide gave a 56:44 mixture of the silanes (**4a**) and (**5a**) as estimated by n.m.r. and by g.l.c. The two silanes could not be separated by column chromatography, but they were identified by comparison with specimens prepared independently. The silane (**4a**) was prepared by a coupling carried out in the inverse manner; that is, by reaction of 2-bromothiophene with 1-(trimethylsilyl)ethenylzinc bromide. There was no evidence for the formation of an isomeric product in this coupling reaction. Silane (**5a**) was prepared from (2-bromoethenyl)trimethylsilane and 2-thienylzinc bromide: again, only a single regioisomer was formed in the coupling reaction. Coupling reactions of (2-bromoethenyl)trimethylsilane have been shown to take place selectively with the (E) isomer.[4] Analogous results were obtained when 2-furylzinc bromide and phenylzinc bromide were coupled with (1-bromoethenyl)trimethylsilane. A mixture of the furans (**4b**) and (**5b**) was obtained from 2-furylzinc bromide, the ratio of the two in the product mixture being 52:48. Compound (**5b**) was prepared independently. The silanes $\mathrm{PhC(SiMe_3)=CH_2}$ (**6**) and $\mathrm{PhCH=CHSiMe_3}$ (**7**) were isolated (80%) as an inseparable mixture (55:45) from the reaction with phenylzinc bromide. Specimens of each of these silanes were prepared independently. The compounds were identified by comparison of their n.m.r. spectra with those in the literature.[5]

There are literature precedents for the palladium catalysed coupling of (1-bromoethenyl)trimethylsilane to organometallic species. Huynh and Linstrumelle reported coupling to octylmagnesium bromide[6]; Kumada and his co-workers described coupling reactions with several heterocyclic Grignard reagents, including 2-thienylmagnesium bromide.[7] There was no evidence for the formation of regioisomeric products in these reports. Subsequently Gore and his co-workers, in a study of the catalytic carbopalladation of allenes by this silane, noted the formation of regioisomeric vinylsilanes as minor products in the reaction.[8] Carpita, Rossi, and Scamuzzi also reported the formation of regioisomers in the palladium catalysed coupling of (1-bromoethenyl)trimethylsilane with trimethylstannyl phenyl sulphide.[9] Both groups suggested that the regioisomers were formed by an elimination-addition sequence involving the intermediate organopalladium species (**8**). Gore and co-workers proposed that steric crowding in this intermediate promoted the β-elimination. This mechanism requires competition between nucleophilic attack on (**8**) by the organometallic species and β-elimination from (**8**) to give trimethylsilylacetylene. Our results show that the steric bulk of the organometallic partner has very little effect on the product ratio. If the intermediate (**8**) was undergoing competitive elimination and attack by the organozinc species the ratio of products should vary with the nature of the organometallic reagent, but it does not do so. We found that the ratio of products did vary with the reaction temperature, however. A coupling reaction was carried out at room temperature between (1-bromoethenyl)trimethylsilane and 2-thienylzinc bromide. The reaction was slow and was not complete after 48 h, but the mixture of products was isolated and the isomer ratio was determined by n.m.r. and by g.l.c. The vinylsillanes (**4a**) and (**5a**) were formed in a ratio of 65:35. Thus, the amount of rearrangement is less at a lower temperature.



(**8**)

In the preliminary communication we suggested a mechanism for the formation of regioisomers based on the formation of a transient 5-coordinate palladium species.[1] We have no direct evidence to support this mechanism but extensive work by Stille and his group has shown that palladium(IV) species can participate in coupling reactions.[10] Our results do seem to favour a mechanism in which rearrangement takes place after attack by the organozinc species on the intermediate (**8**); otherwise, it is difficult to account for the almost constant ratio of normal to rearranged products in the reactions. The precise role of the trimethylsilyl group in promoting the rearrangement remains to be established.

EXPERIMENTAL

General. ^{1}H N.m.r. spectra were recorded on a Perkin-Elmer R34 spectrometer operating at 220 MHz; signals are singlets where no multiplicity is shown. G.l.c. analyses were performed on a Perkin-Elmer F33 Gas Chromatograph using a 25m x 0.3 mm OV1 capillary column at 250°C with N_2 as carrier gas. Ether and THF were distilled from sodium-benzophenone before use. M.p.'s were recorded on a Reichert hot stage apparatus and are uncorrected.

4,4-Dimethyl-2-(2-furyl)oxazoline **(1a)**.
The oxazoline was prepared from 2-furoic acid (20 g, 0.18 mol) by the method of Chadwick et al.,[2] and was isolated (25.5 g, 86%) as a colourless waxy solid, m.p. 36-37°C (lit.,[2] 36-37°C); m/z 165.0787 (M^+, 20%; calc. for $C_9H_{11}NO_2$ 165.0789); $\nu_{max.}$ (film) 3 100, 2 950, 1 655, and 1 305 cm^{-1}; δ ($CDCl_3$) 7.52 (1 H, dd, *J* 0.7 and 1.0 Hz, 5-H of furan), 6.91 (1 H, dd, *J* 0.7 and 2.8 Hz, 3-H of furan), 6.47 (1 H, dd, *J* 1.0 and 2.8Hz, 4-H of furan), 4.07 (2 H, OCH_2), and1.36 (6 H).

4,4-Dimethyl-2-(5-trimethylsilyl-2-furyl)oxazoline **(2a)**.
To a solution of LDA (13.33 mmol) and TMEDA (2.01 ml, 13.33 mmol) in tetrahydrofuran (50ml) at -78°C was added the furan **(1a)** (2.00 g, 12.12 mmol). The solution was stirred at -78°C for 1 h then chlorotrimethylsilane (1.54 ml, 12.12 mmol) was added. After the reaction mixture had been stirred for a further 0.5 h methanol (5 ml) was added and the solvent was then removed under reduced pressure. The product was extracted from the residue with ethyl acetate (200 ml). The solution was washed with water (3 x 20 ml), dried, and evaporated. Distillation of the residue by kugelrohr gave the furan **(2a)** (2.53 g, 88%) m.p. 68-70°C (Found: C, 60.25; H, 7.70; N, 5.42. $C_{12}H_{19}NO_2Si$ requires C, 60.72; H, 8.07; N, 5.90%); $\nu_{max.}$ (CCl_4) 1 660 cm^{-1} (C=O); δ ($CDCl_3$) 6.94 (1 H, d, *J* 3.85 Hz, 3-H of furan), 6.68 (1 H, d, *J* 3.85 Hz, 4-H of furan), 4.06 (2 H), 1.38 (6 H), and 0.32 (9 H); m/z 237 (M^+, 14%) and 222 (100).

4,4-Dimethyl-2-(3-methyl-5-trimethylsilyl-2-furyl)oxazoline **(2b)**.
To the furyloxazoline **(2a)** (0.50 g, 2.11 mmol) in THF (30 ml) at -78°C was added sec-butyllithium (1.04 M, 2.74 mmol) and the reaction mixture was stirred for 0.5 h. Iodomethane (0.35 ml, 5.62 mmol) was added and the reaction mixture was stirred for a further 0.5 h at -78°C then for 2 h at room temperature. The solvent was distilled off under reduced pressure and the residue was dissolved in ethyl acetate (200 ml). The solution was washed with water, dried, and evaporated to leave an oil. This was distilled (kugelrohr) at 180oC (bath) and 0.3 mmHg to give the furan **(2d)** (0.49 g, 92%) as an oil [Found: m/z 251.1336 (M^+, 41%). $C_{13}H_{21}NO_2Si$ requires m/z 251.1341]; $\nu_{max.}$ (film) 1 640 cm^{-1} (C=O); δ ($CDCl_3$) 6.53 (1 H, 4-H of furan), 2.28 (3 H, 3-Me), 1.37 (6 H), and 0.30 (9 H).

2-(3-Deuterio-5-trimethylsilyl-2-furyl)-4,4-dimethyloxazoline **(2c)**.
By a procedure analogous to that described for the preparation of furan **(2d)**, compound **(2a)** and deuterium oxide gave the 3-deuteriofuran **(2e)** (94%) [Found: m/z 238.1244 (M^+, 12%). $C_{12}H_{18}DNO_2Si$ requires m/z 238.1248]; δ ($CDCl_3$) 6.74 (1 H), 4.06 (2 H), 1.38 (6 H), and 0.32 (9 H).

Palladium Catalysed Coupling Reactions of The Furyloxazoline (**2a**). General Procedure.
A solution of anhydrous zinc bromide was prepared from zinc powder (0.21 g, 3.16 mmol, freshly washed with acid and dried) and 1,2-dibromoethane (0.27 ml, 3.16 mmol) in THF (20 ml) under reflux for 3.5 h. The furyloxazoline (**2a**) (0.50 g, 2.11 mmol) was converted into its 3-lithio derivative by reaction with *sec*-butyllithium (1.04 M, 2.74 mmol) at -78°C for 0.5 h. The zinc bromide solution was then added and the mixture was stirred at -20°C for 1 h, in order to effect the formation of the bromozinc intermediate (**2d**). Tetrakis(triphenylphosphine)palladium(0) (90 mg, 4 mol %) and the appropriate electrophile (2.11 mmol) were then added together in THF (25 ml). The reaction mixture was allowed to warm to room temperature and it was then heated under reflux with stirring for 16 h. Aqueous ammonium chloride was added, the organic layer was separated off, and the aqueous layer was washed with ether. The combined organic solutions were dried and evaporated to leave the crude product. The product was isolated from this residue by flash column chromatography (silica; light petroleum: ethyl acetate 2:1).

The following furans were prepared by this method:

4,4-Dimethyl-2-(3-phenyl-5-trimethylsilyl-2-furyl)oxazoline (**2f**).
A reaction with iodobenzene as the electrophile gave the furan (**2f**) (0.55 g, 83%) m.p. 64-65°C (Found: C, 69.01; H, 7.41; N, 4.30. $C_{18}H_{23}NO_2Si$ requires C, 69.00; H, 7.35; N, 4.47%); $\nu_{max.}$ (nujol) 1 640 cm-1 (C=O); δ ($CDCl_3$) 7.65 (2 H, m), 7.46 (3 H, m), 6.87 (1 H, 4-H of furan), 4.05 (2 H), 1.43 (6 H), and 0.36 (9 H); m/z 298 (82%, M$^+$) and 270 (27).

4,4-Dimethyl-2-(3-prop-2-en-1-yl-5-trimethylsilyl-2-furyl)oxazoline (**2g**).
Reaction with 3-bromopropene gave the furan (**2g**) (0.46 g, 79%) as an oil (Found: C, 64.94; H, 8.45; N, 4.80. $C_{15}H_{23}NO_2Si$ requires C, 64.98; H, 8.30; N, 5.05%); $\nu_{max.}$ (film) 3 080, 1 664, and 1 645 cm^{-1}; δ ($CDCl_3$) 6.61 (1 H), 5.97 (1 H, m), 5.12 (2 H, m), 4.07 (2 H), 3.56 (2 H, d, *J* 4.9 Hz), 1.40 (6 H), and 0.31 (9 H); m/z 277 (M$^+$, 80%) and 262 (100).

2-(3-Benzyl-5-trimethylsilyl-2-furyl)-4,4-dimethyloxazoline (**2h**).
Reaction with benzyl bromide gave the furan (**2h**) (0.50 g, 73%), m.p. 56-58°C (Found: C, 69.95; H, 7.60; N, 3.98. $C_{19}H_{25}NO_2Si$ requires C, 69.72; H, 7.65; N, 4.28%); $\nu_{max.}$ (nujol) 1 640 cm^{-1} (C=O); δ ($CDCl_3$) 7.18 (5 H, m), 6.35 (1 H), 4.05 (2 H), 3.97 (2 H), 1.29 (6 H), and 0.33 (9 H); m/z 327 (M$^+$, 100%) and 312 (24).

4,4-Dimethyl-2-[3-(1-phenylethenyl)-5-trimethylsilyl-2-furyl]oxazoline (**2i**).
Reaction with 1-bromo-1-phenylethene gave the furan (**2i**) (0.64 g, 89%), m.p. 69-71°C (Found: C, 70.59; H, 7.39; N, 3.93. $C_{20}H_{25}NO_2Si$ requires C, 70.80; H, 7.37; N, 3.63%); $\nu_{max.}$ (nujol) 1 650 cm^{-1} (C=O); δ ($CDCl_3$) 7.29 (5 H, m), 6.66 (1 H), 5.64 (1 H), 5.43 (1 H), 3.63 (2 H), 1.19 (6 H), and 0.31 (9 H); m/z 339 (M$^+$, 50%) and 338 (100).

4,4-Dimethyl-2-[3-(2-phenylethenyl)-5-trimethylsilyl-2-furyl]oxazoline (**2j**).
Reaction with (E)-1-bromo-2-phenylethene gave the furan (**2j**) (0.61 g, 85%), m.p. 84-85°C (Found: C, 70.50; H, 7.39; N, 3.96. $C_{20}H_{25}NO_2Si$ requires C, 70.80; H, 7.37; N, 3.63%); $\nu_{max.}$ (nujol) 1 640 cm^{-1} (C=O); δ ($CDCl_3$) 7.74 (1 H, d, *J* 16.1 Hz), 7.56 (2 H, m), 7.01 (1 H), 6.98 (1 H, d, *J* 16.1 Hz), 4.13 (2 H), 1.43(6 H), and 0.34 (9 H); m/z 339 (M$^+$, 15%) and 262 (100).

4,4-Dimethyl-2-[3-(4-ethoxycarbonylphenyl)-5-trimethylsilyl-2-furyl]oxazoline (**2k**).
Reaction with ethyl 4-iodobenzoate gave the furan (**2k**) (0.63 g, 78%) m.p. 86-87°C (Found: C, 65.77; H, 7.11; N, 3.37. $C_{21}H_{27}NO_4Si$ requires C, 65.45; H, 7.00; N, 3.64%); $\nu_{max.}$ (nujol) 1 705 and1 640 cm^{-1} (C=O); δ ($CDCl_3$) 8.26 (2 H, d, *J* 7.8 Hz), 7.84 (2 H, d, *J* 7.8 Hz), 6.97 (1 H), 4.50 (2 H, q), 4.07 (2 H), 1.44 (3 H, t), 1.41 (6 H), and 0.35 (9 H); m/z 385 ($M^{+\cdot}$ 32%), 384 (100), and 370 (30).

4,4-Dimethyl-2-[5-trimethylsilyl-3-(2-trimethylsilylethenyl)-2-furyl]oxazoline (**2l**).
Reaction with (E)-(2-bromoethenyl)trimethylsilane gave the furan (**2l**) (0.60 g, 86%), m.p. 76-77°C (Found: C, 60.70; H, 8.86; N, 3.95. $C_{17}H_{29}NO_2Si_2$ requires C, 60.90; H, 8.66; N, 4.18%); $\nu_{max.}$ (nujol) 1 640 cm^{-1} (C=O); δ ($CDCl_3$) 7.65 (1 H, d, *J* 22.0 Hz), 7.56 (2 H, m), 7.07 (1 H), 6.48 (1 H, d, *J* 22.0 Hz), 4.13 (2 H), 1.41 (6 H), and 0.32 (9 H); m/z 335 (M^+, 1%) and 262 (100).

4,4-Dimethyl-2-[5-trimethylsilyl-3-(1-trimethylsilylethenyl)-2-furyl]oxazoline (**2m**).
Reaction with (1-bromoethenyl)trimethylsilane gave (by t.l.c, n.m.r., and g.l.c.) a mixture containing the furans (**2l**) and (**2m**) (ratio 45:55 by n.m.r. and g.l.c.). Flash chromatography allowed separation of the furan (**2m**) (0.35 g, 50%) as an oil (Found: C, 60.75; H, 8.83; N, 4.01. $C_{17}H_{29}NO_2Si_2$ requires C, 60.90; H, 8.66; N, 4.18%); $\nu_{max.}$ (nujol) 1 640 cm^{-1} (C=O); δ ($CDCl_3$) 6.59 (1 H), 5.97 (1 H, d, *J* 3.9 Hz), 5.85 (1 H, d, *J* 3.9 Hz), 4.17 (2 H), 1.56 (6 H), and 0.28 (9 H); m/z 335 (M^+, 44%), 334 (100), and 262 (84). Furan (**2l**) (0.28 g, 40%) was also isolated and was identified by comparison with an authentic specimen.

2-(3-Benzoyl-5-trimethylsilyl-2-furyl)-4,4-dimethyloxazoline (**2n**).
Reaction with benzoyl bromide gave the furan (**2n**) (0.23 g, 32%) as an oil [Found: m/z 341.1445 (M^+,18%). $C_{19}H_{23}NO_3Si$ requires m/z 341.1447]; $\nu_{max.}$ (nujol) 1 674 and 1 640 cm^{-1} (C=O); δ ($CDCl_3$) 7.82 (2 H, m), 7.53 (1 H, m), 7.45 (2 H, m), 7.25 (1 H), 3.69 (2 H), 3.97 (2 H), 1.23 (6 H), and 0.32 (9 H); m/z 341 (M^+, 18%) and 312 (100).

4,4-Dimethyl-2-(3-phenyl-2-thienyl)oxazoline (**3**).
4,4-Dimethyl-2-(2-thienyl)oxazoline (**1b**) (0.38 g, 2.11 mmol) was treated with butyllithium (1.52 M, 2.15 mmol) in ether (30 ml) under the conditions described for 3-lithiation by Della Vecchia and Vlattas,[11] i.e., at -78°C for 0.25 h then at 0°C for 0.5 h. The solution was then cooled to -20°C and zinc bromide solution (3.16 mmol) was added. The reaction mixture was stirred at -20°C for 1 h and a solution of $Pd(PPh_3)_4$ (0.1 g, 4 mol %) and iodobenzene (0.14 ml, 2.11 mmol) in THF (25 ml) was then added. The reaction mixture was allowed to warm to room temperature and it was then heated under reflux for 16 h. Isolation of the crude product by the standard procedure followed by flash chromatography and distillation (kugelrohr) at 185°C (bath) and 0.1 mmHg gave the thiophene (**3**) (0.44 g, 81%) as an oil which crystallised to a solid m.p. 48-49°C (Found: C, 69.69; H, 5.83; N, 5.37. $C_{15}H_{15}NOS$ requires C, 70.04; H, 5.84; N, 5.45%); $\nu_{max.}$ (nujol) 1 640 cm^{-1} (C=O); δ ($CDCl_3$) 7.38 (6 H, m Ph and 5-H of thiophene), 7.19(1 H, d, *J* 5.15 Hz, 4-H of thiophene), 3.96 (2 H), and 1.36 (6 H); m/z 257 (M^+, 21%) and 256 (100).

[1-(2-Thienyl)ethenyl]trimethylsilane (**4a**).

(1-Bromoethenyl)trimethylsilane (1.50 g, 8.37 mmol) in THF (30 ml) was allowed to react with butyllithium (9.21 mmol) at -78°C for 1 h. Zinc bromide (12.5 mmol) in THF (30 ml) was added and the reaction mixture was stirred at -20°C for 1.5 h. A solution containing Pd(PPh$_3$)$_4$ (0.39 g, 4 mol %) and 2-bromothiophene (0.81 ml, 8.37 mmol) in THF (25 ml) was added, the mixture was allowed to warm to room temperature, and it was then heated under reflux and stirred for 1 h. After the reaction mixture had been quenched the product was isolated by flash chromatography followed by distillation (kugelrohr). This gave *the thiophene* (**4a**) (1.34 g, 88%), b.p. 105°C (bath) and 0.2 mmHg [Found: *m/z* 182.0586 (*M*$^+$). $C_9H_{14}SSi$ requires *m/z* 182.0584]; δ (CDCl$_3$) 7.18 (1 H, dd *J* 3.0 and 2.0 Hz, 5-H), 7.00 (2 H, m, 3-H and 4-H), 6.09 (1 H, d, *J* 2.0 Hz), 5.51 (1 H, d, *J* 2.0 Hz), and 0.24 (9 H); *m/z* 182 (*M*$^+$, 45%), 141 (45), and 73 (100).

[2-(2-Thienyl)ethenyl]trimethylsilane (**5a**).

Thiophene (1.0 ml, 12.5 mmol) was converted into 2-thienyllithium by reaction with butyllithium (12.5 mmol) and TMEDA (12.5 mmol) in ether (30 ml) at 20°C for 0.3 h. A solution of zinc bromide (15.6 mmol) in THF (30 ml) was added and the reaction mixture was stirred at -20°C for 1 h. A solution of Pd(PPh$_3$)$_4$ (0.58 g, 4 mol %) and (2-bromoethenyl)trimethylsilane (1.92 ml, 12.5 mmol) in THF (25 ml) was then added. The reaction mixture was allowed to warm to room temperature and it was then heated under reflux for 1 h. The reaction mixture was quenched and the product isolated by flash chromatography followed by distillation (kugelrohr). This gave *the thiophene* (**5a**) (2.02 g, 89%) as an oil, b.p. 105°C (bath) at 2 mmHg (Found: C, 59.48; H, 7.89. $C_9H_{14}SSi$ requires C, 59.34; H, 7.69%); δ (CDCl$_3$) 7.19 (1 H, m, 5-H), 7.04 (1 H, d, *J* 19.0 Hz), 7.04 (2 H, m, 3-H and 4-H), 6.29 (1 H, d, *J* 19.0 Hz), and 0.14 (9 H); *m/z* 182 (*M*$^+$, 54%) and 167 (100).

Reaction of (1-Bromoethenyl)trimethylsilane with 2-Thienylzinc bromide

This experiment was carried out under identical conditions to those described above for the preparation of (**5a**), except that (1-bromoethenyl)trimethylsilane was used in place of the 2-bromosilane. The crude reaction product was analysed by n.m.r., which showed the presence of (**4a**) and (**5a**) in a 56:44 ratio as estimated from the integrals of the signals for the vinylic hydrogens. The product ratio and the identity of the products was supported by g.l.c. analytical comparison with authentic specimens.

An experiment was also carried out in which identical reagents were used but the reaction temperature was reduced. The reaction mixture was not heated, but instead was stirred at room temperature for 48 h. Analysis of the reaction products showed that (**4a**) and (**5a**) were formed under these conditions in a ratio of 65:35.

[2-(2-Furyl)ethenyl]trimethylsilane (**5b**)

This compound was prepared by the procedure described for the thiophene (**5a**) from furan (1.0 ml, 13.7 mmol). Kugelrohr distillation gave the furan (**5b**) (1.96 g, 86%) as an oil, b.p. 110°C (bath) at 2 mmHg (Found: C, 64.88; H, 8.58. $C_9H_{14}OSi$ requires C, 65.06; H, 8.43%); δ (CDCl$_3$) 7.38 (1 H, d, *J* 2.0 Hz, showing further small coupling, 5-H), 6.71 (1 H, d, *J* 19.6 Hz), 6.40 (1 H, dd, *J* 3.5 and 2.0 Hz, 4-H), 6.39 (1 H, d, *J* 19.6 Hz), 6.30 (1 H, d, J 3.5 Hz, showing further small coupling, 3-H), and 0.13 (9 H); *m/z* 166 (*M*$^+$, 30%) and 151 (100).

Reaction of (1-Bromoethenyl)trimethylsilane with 2-Furylzinc bromide

This experiment was carried out under identical conditions to those described above for the preparation of (**5b**), except that (1-bromoethenyl)trimethylsilane was used in place of the 2-bromosilane. The crude reaction product was analysed by g.l.c. and by n.m.r., which showed the presence of (**4b**) and (**5b**) in a 52:48 ratio by g.l.c. and as estimated from the integrals of the signals for the vinylic hydrogens [signals for (**4b**) at δ 6.22 (1 H, d, *J* 3.4 Hz), 5.46 (1 H, d, *J* 3.4 Hz), and 0.22 (9 H)]. The isomers were isolated by flash chromatography as an inseparable mixture [Found: m/z 166.0814 (M$^+$). $C_9H_{14}OSi$ requires m/z 166.0817].

(1-Phenylethenyl)trimethylsilane (**6**).

This compound was prepared from (1-bromoethenyl)trimethylsilane (8.37 mmol) and iodobenzene (8.37 mmol) by a method analogous to that used for the preparation of the thiophene (**4a**). It was isolated (1.28 g, 87%) by kugelrohr distillation as an oil, b.p. 102°C (bath) at 2 mmHg [Found: m/z 176.1024 (M$^+$, 56%). Calc. for $C_{11}H_{16}Si$: m/z 176.1021]. The ^1H n.m.r. spectrum was in accord with that reported earlier*: δ ($CDCl_3$) 7.24 (5 H, m), 5.83 (1 H, d, *J* 4.0 Hz), 5.62 (1 H, d, *J* 4.0 Hz), and 0.15 (9 H).

(2-Phenylethenyl)trimethylsilane (**7**).

This compound was prepared from phenyllithium (8.37 mmol) and (2-bromoethenyl)trimethylsilane (8.37 mmol) by a method analogous to that used for the preparation of the thiophene (**5a**). It was isolated (1.13 g, 77%) by kugelrohr distillation as an oil, b.p. 102°C (bath) at 2 mmHg [Found: m/z 176.1020 (M$^+$, 31%). Calc. for $C_{11}H_{16}Si$: m/z 176.1021]. The ^1H n.m.r. spectrum was in accord with that reported earlier*: δ ($CDCl_3$) 7.53 (2 H, m), 7.42 (3 H, m), 6.88 (1 H, d, *J* 19.5 Hz), 6.47 (1 H, d, *J* 19.5 Hz), and 0.16 (9 H).

Reaction of (1-bromoethenyl)trimethylsilane with Phenylzinc bromide

This reaction was carried out under the conditions described for the preparation of (**5a**) but with phenyllithium in place of 2-thienyllithium. This gave a mixture (80%) of (**6**) and (**7**) in a ratio of 55:45 as determined by g.l.c. and by n.m.r. comparison with the authentic materials.

Acknowledgements: We thank Drs D. Bethell and D. J. Chadwick for discussion and the S.E.R.C. for a Studentship (to D. S. E.).

REFERENCES

[1] Part of this work has appeared as a preliminary communication: Ennis, D.S.; Gilchrist, T. L. *Tetrahedron Lett.*, 1989, **30**, 3735-3736.

[2] Chadwick, D. J.; McKnight, M. V.; Ngochindo, R. I. *J. Chem. Soc., Perkin Trans. 1*, 1982, 1343-1347.

[3] Fu, J.-m.; Sharp, M. J.; Snieckus, V. *Tetrahedron Lett.*, 1988, **29**, 5459-5462; Siddiqui, M. A.; Snieckus, V. *Tetrahedron Lett.*, 1988, **29**, 5463-5466; Salituro, F. G.; McDonald, I. A. *J. Org. Chem.*, 1988, **53**, 6138.

[4] Andreini, B. P.; Carpita, A.; Rossi, R.; Scamuzzi, B. *Tetrahedron*, 1989, **45**, 5621-5640.

[5] Liepins, E.; Goldberg, Y.; Lorel, I.; Lukevics, E. *J. Organometal. Chem.*, 1987, **335**, 301-311.

[6] Huynh, C.; Linstrumelle, G. *Tetrahedron Lett.*, 1979, 1073-1076.

[7] Minato, A.; Suzuki, K.; Tamao, K.; Kumada M. *Tetrahedron Lett.*, 1984, **25**, 83-86.

[8] Cazes B.; Colovray V.; Gore J. *Tetrahedron Lett.*, 1988, **29**, 627-630.

[9] Carpita A.; Rozzi R.; Scamuzzi B. *Tetrahedron Lett.*, 1989, **30**, 2699-2702.

[10] Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.*, 1980, **102**, 4933-4941, and references therein.

[11] Della Vecchia, L.; Vlattas, I. *J. Org. Chem.*, 1977, **42**, 2649-2650.