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ABNORMAL PRODUCTS OF PALLADIUM CATALYSED COUPLING REACTIONS OF (1-BROMOVINYL)TRIMETHYLSILANE

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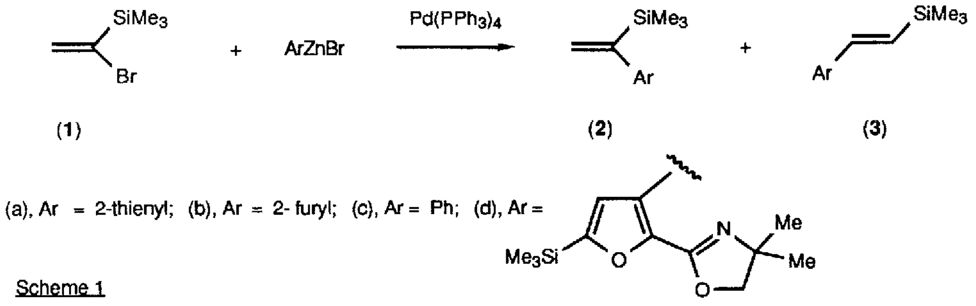
Summary: Coupling reactions of (1-bromovinyl)trimethylsilane (**1**) with organozinc bromides catalyzed by tetrakis(triphenylphosphine)palladium(0) give not only the expected 1-substituted vinylsilanes (**2**) but also the isomeric 2-substituted vinylsilanes (**3**).

As part of an investigation into the synthesis of new furan and thiophene derivatives we have been studying the palladium(0) catalyzed coupling reactions of various furyl- and thienyl- zinc bromides with vinyl and aryl halides. Many literature precedents indicate that such reactions generally proceed in good yield, regioselectively, and with retention of the stereochemistry of the vinylic halide.[1] Exceptionally, however, we find that (1-bromovinyl)trimethylsilane (**1**), when reacted with several organozinc bromides under standard coupling conditions,[2] gives a mixture of two vinylsilanes (**2**) and (**3**), in a ratio of approximately 55:45 in each case (Scheme 1). The structures of the vinylsilanes (**3**) were established by comparison with authentic samples obtained from coupling reactions of (2-bromovinyl)trimethylsilane: the reactions of this bromovinylsilane proceeded normally.[3]

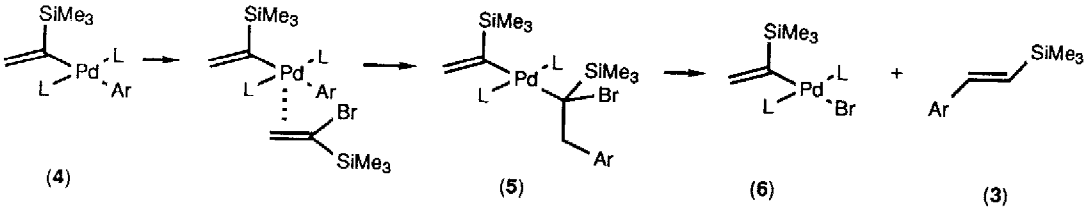


Scheme 1

The vinylsilanes (**2**) are the expected coupling products but the presence of the isomers (**3**) as products is, as far as we are aware, without analogy. We know of two literature reports of coupling reactions in which (1-bromovinyl)trimethylsilane has been used as the electrophilic component,[4] but in both cases the couplings proceeded as expected, apparently without the formation of isomeric products.

Some preliminary experiments have been carried out in an attempt to discover the origin of the rearranged vinylsilanes (**3**). These experiments have ruled out some possible sources of the isomeric products. (1-Bromovinyl)trimethylsilane is unaffected by heating with zinc bromide and Pd(Ph_3)$_4$ in THF under reflux for 12 h: none of the isomeric E-(2-bromovinyl)trimethylsilane could be detected by g.l.c. No reaction occurs between 2-thienylzinc bromide and the bromovinylsilane (**1**) in the absence of the palladium catalyst, thus ruling out uncatalysed conjugate addition to the vinylsilane or elimination of hydrogen bromide. An inverse coupling reaction which was carried out between 2-bromothiophene and (1-trimethylsilyl)vinylzinc bromide in the presence of Pd(PPh_3)$_4$ proceeded normally and gave exclusively the vinylsilane (**2a**).

The commonly accepted mechanism for coupling reactions of this type involves the formation of a trans-disubstituted palladium(II) complex as an intermediate. Coupling takes place by rearrangement to a cis complex followed by elimination. There is evidence that the final elimination step is sometimes preceded by oxidative addition of a further molecule of the halide to give a transient, hexacoordinate palladium(IV) species.[5] It therefore seems possible that in these reactions the bromovinylsilane present in the reaction mixture coordinates to the complexes (**4**) and that the pentacoordinate species so formed undergo a rearrangement, analogous to the Heck reaction[6] (Scheme 2). The resulting complexes (**5**) then decompose to regenerate the initially formed bromovinylsilane adduct (**6**), which is then available for further reaction with the arylzinc bromide, and the vinylsilanes (**3**). The α-trimethylsilyl group clearly has a crucial influence in diverting the coupling reaction from its normal pathway.



(**4**) (**5**) (**6**) (**3**)

Scheme 2

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[1] M. Kumada, Pure Appl. Chem., 1980, **52**, 669; E. I. Negishi, Acc. Chem. Res., 1982, **15**, 340.

[2] To the arylzinc bromide in THF the silane (**1**) (1 mol) and Pd(PPh_3)$_4$ (0.04 mol) in THF were added at -20°C. The reaction mixture was allowed to warm to 20°C then the solution was heated under reflux for 1 to 12 h. The mixtures of vinylsilanes were isolated in high yield (80-89%).

[3] Commercial available (2-bromovinyl)trimethylsilane was used ; this contains ca. 13% of the Z-isomer. Coupling gave similar E/Z mixtures from which the E-isomers were isolated by chromatography.

[4] C. Huynh and G. Linstrumelle, Tetrahedron Lett., 1979, 1073; A. Minato, K. Suzuki, K. Tamao, and M. Kumada, Tetrahedron Lett., 1984, **25**, 83.

[5] A. Gillie and J. K. Stille, J. Am. Chem. Soc., 1980, **102**, 4933; M. K. Loar and J. K. Stille, J. Am. Chem. Soc., 1981, **103**, 4174.

[6] R F. Heck, Org. React., 1982, **27**, 345.

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