Regioselective Head-to-tail Coupling of Allylic Trialkylstannanes with Allylic Halides under High Pressure[1]

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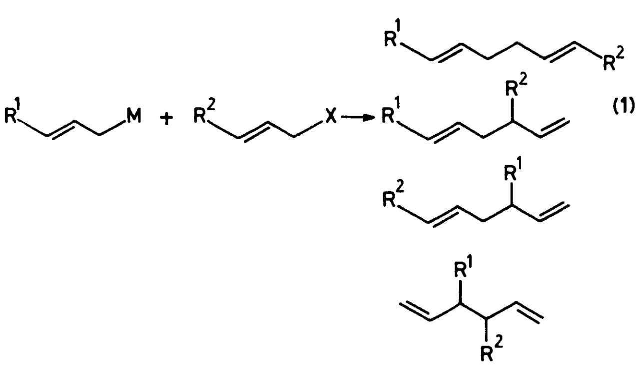
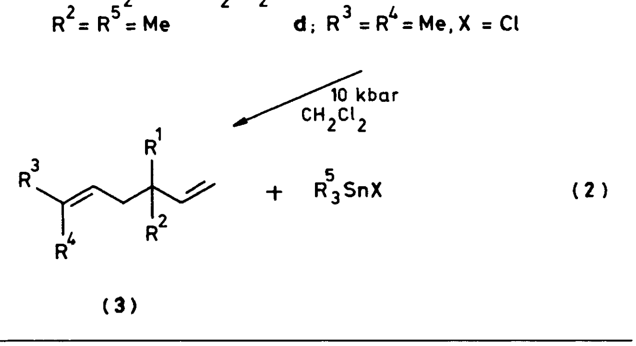
Allylic trialkylstannanes (**1**) regioselectively react with allylic halides (**2**) at room temperature under high pressure (10 kbar) to give head-to-tail coupling products (**3**) in high yields.

In general, the Wurtz-type coupling reaction of allylic organometallics with allylic halides is lacking in regioselectivity: two allylic moieties, one from the allylic organometallic species and the other from the allylic halide, combine randomly to give a mixture of four products (equation 1). To overcome this difficulty, a number of cross coupling methods have been developed.[2] We report that the regioselective head-to-tail coupling of allylic trialkylstannanes (**1**) with allylic halides (**2**) is realized using a high pressure technique (10 kbar) (equation 2). The results are summarized in Table 1.



After the period indicated in Table 1, the pressure was released and the solvent was removed *in vacuo*. ¹H N.m.r.



(**1**)

a; $R^1 = R^2 = H$, $R^5 = Me$

b; $R^1 = Me$, $R^2 = H$, $R^5 = Bu$

c; $R^1 = Me_2C{=}CHCH_2CH_2$, $R^2 = R^5 = Me$

(**2**)

a; $R^3 = Ph$, $R^4 = H$, $X = Cl$

b; $R^3 = Ph$, $R^4 = H$, $X = Br$

c; $R^3 = Me$, $R^4 = H$, $X = Cl$

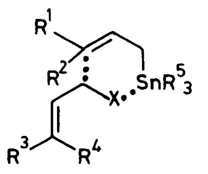
d; $R^3 = R^4 = Me$, $X = Cl$

(**3**)

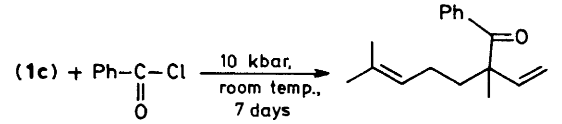
Table 1. Regioselective head-to-tail coupling of (**1**) with (**2**) under high pressure.[a]

Entry	Stannane	Halide	Time/day[b]	Temp./°C[b]	% Yield of (**3**)[c]
1	(**1a**)	(**2a**)	7	50	81
2	(**1b**)	(**2a**)	7	50	88
3	(**1b**)	(**2b**)	7	50	88
4	(**1c**)	(**2b**)	5	Room temp.	85
5	(**1c**)	(**2c**)	5	Room temp.	81
6	(**1c**)	(**2d**)	5	Room temp.	85
7	(**1c**)	$CH_2{=}CHCH(Cl)Me$	5	Room temp.	[d]

[a] In a Teflon capsule (1.5 ml capacity) were placed the halide (1 mmol), the allylic stannane (1 mmol), and dry CH_2Cl_2 (*ca.* 1 ml) as the solvent. High pressure (10 kbar) experiments were performed in a stainless steel die and compressed at room temperature *via* a piston, and then the die was kept at 50 °C if necessary. [b] Reaction conditions are not optimized. The reaction may be complete in a shorter reaction period. [c] Isolated yield. [d] (**1c**) was recovered without change.

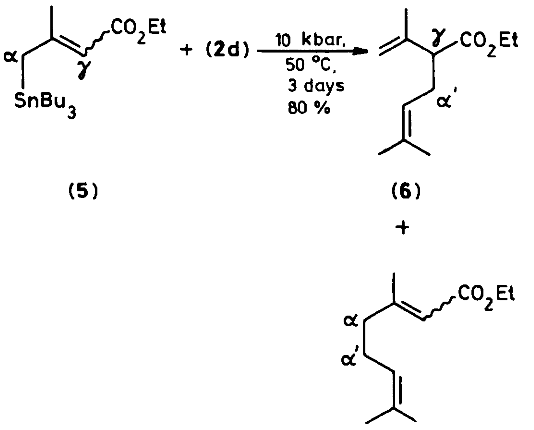


(A)



(4)

(3)



(5)

(6)

(7)

(4)

(6) : (7)
80 : 20

analysis of the reaction mixture indicated that the reaction proceeded quantitatively. Gas–liquid partition chromatographic analysis revealed that the coupling occurred regioselectively in a head-to-tail manner (γ–α′ coupling) (entries 2—6).[3] Quite interestingly (**1c**) did not react with 3-chlorobut-1-ene (entry 7). Presumably, the reaction proceeds through the 6-membered cyclic transition state (A) and hence the steric crowding at the α′ position of (**2**) prevents the coupling reaction.

The reaction with other organic halides was also examined. Primary, secondary, and tertiary alkyl halides, phenyl iodide, and β-bromostyrene did not react with (**1a**), but benzyl bromide gave 1-phenylbut-3-ene in 78% yield. Benzoyl chloride reacted with (**1c**) at room temperature to produce (**4**) in 60% yield (equation 3). The functional group substituted allylic stannane (**5**), which was prepared from the reaction of the corresponding lithium dienolate with tributyltin chloride,[4] was treated with (**2d**). Here again, the γ–α′ coupling product (**6**) was obtained as a major product along with small amounts of (**7**) (α–α′ coupling) (equation 4). In conclusion, the high pressure induced reaction between the relatively unreactive allylic organometallic compound and the relatively reactive halide may provide a new type of regioselective coupling mode.[5]

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References

1 For Part 3 in the series 'Organometallic High Pressure Reactions' see: Y. Yamamoto, K. Maruyama, and K. Matsumoto, *Tetrahedron Lett.*, 1984, in the press.

2 *E.g.* Y. Yamamoto, H. Yatagai, and K. Maruyama, *J. Am. Chem. Soc.*, 1981, **103**, 1969, and references cited therein.

3 For recent papers on the reaction of allylic stannanes with allylic halides and related compounds see: J. P. Godschalx and J. K. Stille, *Tetrahedron Lett.*, 1980, 2599; *ibid.*, 1983, 1905; B. M. Trost and E. Keinan, *ibid.*, 1980, 2595. For the reaction with alkyl halides see: G. E. Keck and J. B. Yates, *J. Am. Chem. Soc.*, 1982, **104**, 5829.

4 The formation of (**5**) is in marked contrast with the formation of the corresponding *O*-silylated dienolate from the reaction of the lithium dienolate with trimethylsilyl chloride; I. Fleming, J. Goldhill, and I. Paterson, *Tetrahedron Lett.*, 1979, 3205; T. Mukaiyama and A. Ishida, *Chem. Lett.*, 1975, 319.

5 For a description of the high pressure equipment employed in this study, see K. Matsumoto, A. Sera, and T. Uchida, *Synthesis*, in the press.