

THE PALLADIUM(0)-CATALYZED REDUCTIVE COUPLING OF HALIDES USING
sym-DICHLOROTETRAMETHYLDISILANE AS A REDUCING AGENT

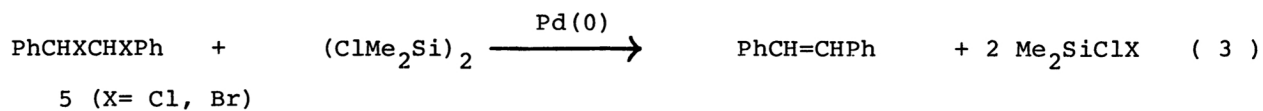
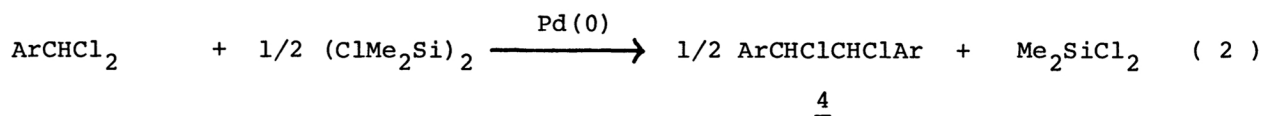
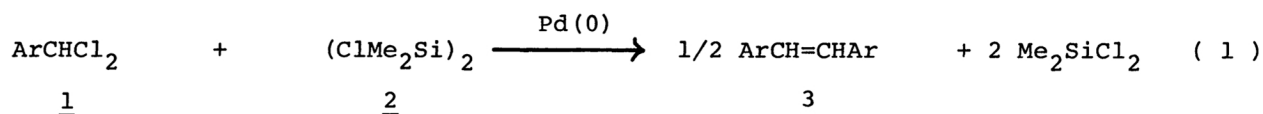
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The reaction of benzylidene chlorides as well as 1,2-dihalo-
geno-1,2-diphenylethanes with sym-dichlorotetramethyldisilane in
the presence of a catalytic amount of tetrakis(triphenylphosphine)-
palladium(0) gave aryl-substituted ethenes in good yields.

The reductive coupling of benzylidene chlorides yielding 1,2-dichloro-1,2-di-
arylethanes and stilbenes usually employs active metal agents in low oxidation
state such as various zero-valent metals¹⁾ as well as Cr(II),²⁾ Cu(I),³⁾ V(II),⁴⁾
Ti(II),⁵⁾ and Co(I)⁶⁾ species.

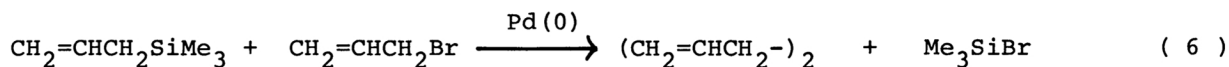
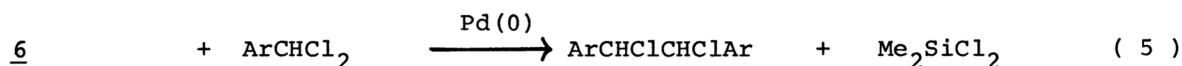
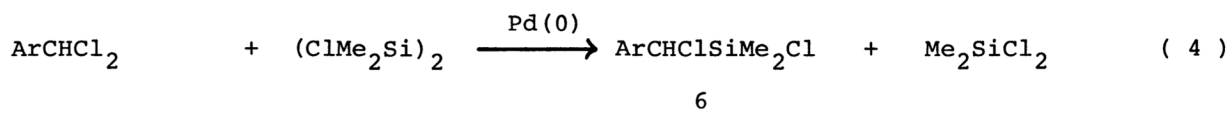
We report herein our results on reductive coupling of benzylidene chlorides
1 to aryl-substituted ethenes 3 or to aryl-substituted 1,2-dichloroethanes 4 and
dehalogenation of 1,2-dichloro- and 1,2-dibromo-1,2-diphenylethane to trans-stil-
bene 3 (Ar=Ph), using sym-dichlorotetramethyldisilane 2, formally tetra-valent
silicon species.⁷⁾



A typical experiment is as follows. A mixture of benzylidene chloride (1.16g, 10 mmol), sym-dichlorotetramethyldisilane (2.8g, 15 mmol), tetrakis(triphenylphosphine)palladium(0) (50mg, 0.08 mmol) and mesitylene (3 ml) was stirred at 130°C for 2.5 h under argon. GLC analysis of the resulting mixture disclosed that the trans-stilbene had been produced in 78% yield. Results were summarized in the Table.

Hexamethyldisilane was found to work as well for the coupling reaction. In this case, however, the yield of trans-stilbene from benzylidene chloride was slightly low (40%) and the reaction required prolonged heating.

The use of slight excess of the disilane is sufficient to promote reaction (1), while the use of a half mole of the disilane relative to benzylidene chloride gives the dichlorodiphenylethane 4 (Ar=Ph). Reaction (2) can be rationalized in terms of the palladium(0)-catalyzed metathesis (eqn 5) between a benzylidene chloride and a rather unstable intermediate, α -chlorobenzylchlorodimethylsilane 6 which would be produced by reaction (4). The formation of 6 is reasonably anticipated, since it has been reported by Eaborn and coworkers that the Pd(0)-catalyzed reaction of benzyl chlorides with hexamethyldisilane gives benzyltrimethylsilanes in variable yields.⁸⁾ Reaction (5) is reminiscent of the Pd(0)-catalyzed reaction of allyltrimethylsilane with allyl bromide that gives 1,5-hexadiene together with trimethylbromosilane (eqn 6).⁹⁾



1,2-Dichloro- and 1,2-dibromo-1,2-diphenylethane gave trans-stilbene in quantitative yield. This reaction can be similarly elucidated by the metathesis of 5 with 2 giving 1,2-diphenyl-1-halogeno-2-(chlorodimethylsilyl)ethanes (eqn 7), which release spontaneously chlorohalogenodimethylsilane via the well-known β -elimination¹⁰⁾ resulting in the formation of trans-stilbene (eqn 8).

The reported reactions are all clean and homogeneous and good yields of aryl-substituted alkenes are generally obtained. Disilanes are available in

Table The Palladium(0)-Catalyzed Reductive Coupling Reaction of Benzylic Halides with $(\text{ClMe}_2\text{Si})_2$

Run ^{a)}	Halide	Conditions	Product ^{b)}	Yield(%) ^{c)}
1	$\text{C}_6\text{H}_5\text{CHCl}_2$	130°C, 2.5 h	$(\text{C}_6\text{H}_5\text{CH=})_2$	78
2	$\text{C}_6\text{H}_5\text{CHCl}_2$	" , 1.0 h	$(\text{C}_6\text{H}_5\text{CHCl-})_2^{\text{d)}$	90 ^{e)}
3	$\text{o-ClC}_6\text{H}_4\text{CHCl}_2$	" , 0.5 h	$(\text{o-ClC}_6\text{H}_4\text{CH=})_2$	94 (75)
4	$\text{p-ClC}_6\text{H}_4\text{CHCl}_2$	" , 0.5 h	$(\text{p-ClC}_6\text{H}_4\text{CH=})_2$	100 (81)
5	$2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{CHCl}_2$	" , 0.5 h	$(2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{CH=})_2$	94 (76)
6	$(\text{C}_6\text{H}_5\text{CHCl-})_2^{\text{d)}$	" , 5.0 h	$(\text{C}_6\text{H}_5\text{CH=})_2$	99
7	$(\text{C}_6\text{H}_5\text{CHBr-})_2^{\text{d)}$	" , 5.0 h	$(\text{C}_6\text{H}_5\text{CH=})_2$	100
8 ^{f)}	$\text{C}_6\text{H}_5\text{CHCl}_2$	reflux, 12.0 h	$(\text{C}_6\text{H}_5\text{CH=})_2$	40
			$(\text{C}_6\text{H}_5\text{CHCl-})_2$	39

a) Conditions (molar ratio). Run 1,6,7,8; Halide/Disilane/Pd(0)=1.00/1.50/0.005.

Run 2; " " " =1.00/0.50/0.005.

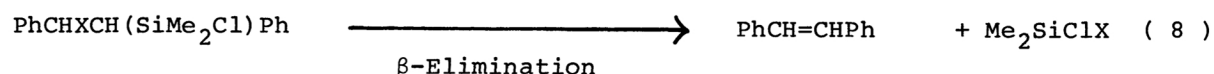
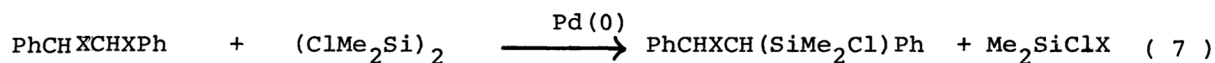
Run 3,4,5; " " " =1.00/2.00/0.01.

b) Only trans-isomer was obtained. Analyses and physical properties are consistent with the assigned structures.

c) GLC yields based on the halide charged. In parentheses are given isolated yields.

d) meso-Form. e) Yield is based on the halide consumed (Conversion;50%).

f) Hexamethyldisilane was used as a reducing agent.



X= Cl, Br

large quantities¹¹⁾ and removal of the counter product, dichlorodimethylsilane (bp. 70°C), from the reaction mixture can be most easily achieved by evaporation.

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