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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-dihalogeno-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-diarylethanes 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 $\underline{1}$ to aryl-substituted ethenes $\underline{3}$ or to aryl-substituted 1,2-dichloroethanes $\underline{4}$ and dehalogenation of 1,2-dichloro- and 1,2-dibromo-1,2-diphenylethane to trans-stilbene $\underline{3}$(Ar=Ph), using sym-dichlorotetramethyldisilane $\underline{2}$, formally tetra-valent silicon species.⁷⁾

$$\underset{\underline{1}}{\mathrm{ArCHCl_2}} + \underset{\underline{2}}{\mathrm{(ClMe_2Si)_2}} \xrightarrow{\mathrm{Pd(0)}} 1/2\ \underset{\underline{3}}{\mathrm{ArCH{=}CHAr}} + 2\ \mathrm{Me_2SiCl_2} \qquad (1)$$

$$\mathrm{ArCHCl_2} + 1/2\ \mathrm{(ClMe_2Si)_2} \xrightarrow{\mathrm{Pd(0)}} 1/2\ \underset{\underline{4}}{\mathrm{ArCHClCHClAr}} + \mathrm{Me_2SiCl_2} \qquad (2)$$

$$\underset{\underline{5}\ (X=\ Cl,\ Br)}{\mathrm{PhCHXCHXPh}} + \mathrm{(ClMe_2Si)_2} \xrightarrow{\mathrm{Pd(0)}} \mathrm{PhCH{=}CHPh} + 2\ \mathrm{Me_2SiClX} \qquad (3)$$

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]

$$\mathrm{ArCHCl_2} + \mathrm{(ClMe_2Si)_2} \xrightarrow{\mathrm{Pd(0)}} \underset{\underline{6}}{\mathrm{ArCHClSiMe_2Cl}} + \mathrm{Me_2SiCl_2} \qquad (4)$$

$$\underline{6} + \mathrm{ArCHCl_2} \xrightarrow{\mathrm{Pd(0)}} \mathrm{ArCHClCHClAr} + \mathrm{Me_2SiCl_2} \qquad (5)$$

$$\mathrm{CH_2{=}CHCH_2SiMe_3} + \mathrm{CH_2{=}CHCH_2Br} \xrightarrow{\mathrm{Pd(0)}} \mathrm{(CH_2{=}CHCH_2{-})_2} + \mathrm{Me_3SiBr} \qquad (6)$$

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-elimination[10] 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 $(ClMe_2Si)_2$

Run[a]	Halide	Conditions	Product[b]	Yield(%)[c]
1	$C_6H_5CHCl_2$	130°C, 2.5 h	$(C_6H_5CH=)_2$	78
2	$C_6H_5CHCl_2$	" , 1.0 h	$(C_6H_5CHCl-)_2$[d]	90[e]
3	$o-ClC_6H_4CHCl_2$	" , 0.5 h	$(o-ClC_6H_4CH=)_2$	94(75)
4	$p-ClC_6H_4CHCl_2$	" , 0.5 h	$(p-ClC_6H_4CH=)_2$	100(81)
5	$2,4-Cl_2C_6H_3CHCl_2$	" , 0.5 h	$(2,4-Cl_2C_6H_3CH=)_2$	94(76)
6	$(C_6H_5CHCl-)_2$[d]	" , 5.0 h	$(C_6H_5CH=)_2$	99
7	$(C_6H_5CHBr-)_2$[d]	" , 5.0 h	$(C_6H_5CH=)_2$	100
8[f]	$C_6H_5CHCl_2$	reflux, 12.0 h	$(C_6H_5CH=)_2$	40
			$(C_6H_5CHCl-)_2$	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.

$$PhCHXCHXPh + (ClMe_2Si)_2 \xrightarrow{Pd(0)} PhCHXCH(SiMe_2Cl)Ph + Me_2SiClX \quad (7)$$

$$PhCHXCH(SiMe_2Cl)Ph \xrightarrow[\beta\text{-Elimination}]{} PhCH=CHPh + Me_2SiClX \quad (8)$$

X= Cl, Br

large quantities[11)] 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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