Reductive Solvolysis of Dimethylindenylsilane: Evidence for a Two-step Mechanism

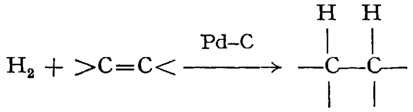
By Philip E. Rakita* and (Miss) Fong-Ying Wang

(*William Rand Kenan, Jr., Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina* 27514)

Summary The reductive solvolysis of dimethylindenylsilane (I) to alkoxydimethylindanylsilane (IV) in alcohols catalysed by Pd–C proceeds in a stepwise manner.

It was recently reported[1] that polymethylhydrosiloxane in alcohol solution with Pd–C catalyst is a versatile reagent for the hydrogenation (in high yield) of *cis* and terminal olefins, aromatic nitro-compounds, and aromatic aldehydes. The lack of solvolysis of the Si–H bond with alcohol and catalyst in the presence of *trans*-olefins (which are not hydrogenated under these conditions) led to the conclusion that the reduction does not proceed by the known[2] stepwise Pd–C-catalysed solvolysis of silyl hydride, followed by olefin hydrogenation [reactions (1) and (2)]. We have used[3] a variation of this sequence in the preparation of a series of siloxy-ethers and we report here some preliminary kinetic studies on the mechanism.

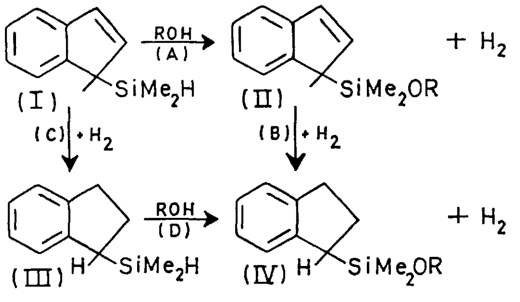
$$\text{Si-H} + \text{ROH} \xrightarrow{\text{Pd–C}} \text{SiOR} + \mathrm{H_2} \qquad (1)$$



$$\mathrm{H_2} + {>}\mathrm{C{=}C}{<} \xrightarrow{\text{Pd–C}} -\underset{|}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}-\underset{|}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}- \qquad (2)$$

Dimethylindenylsilane (I) reacts with methanol, ethanol, and propan-2-ol under hydrogen in the presence of catalytic amounts of 10% Pd–C to give the corresponding alkoxydimethylindanylsilane. Provided that the catalyst is pretreated with hydrogen, no net consumption of hydrogen is observed when the reaction is carried out under hydrogen, in agreement with the Scheme. The reaction can be followed by monitoring the volume of the system (at 1 atm.). The reaction proceeds with an initial increase in volume to a maximum, followed by a decrease to the initial volume.

The time for complete reaction as well as the maximum volume of gas evolved during the course of the reaction depends on the alcohol used. For equivalent reaction conditions, the time required for complete reaction increases in the order $\mathrm{MeOH} < \mathrm{EtOH} < \mathrm{Pr^{i}OH}$ and the maximum volume of gas evolved during the reaction is $\mathrm{MeOH} > \mathrm{EtOH} > \mathrm{Pr^{i}OH}$. In each case, the net volume change after complete reaction was essentially zero.



SCHEME. R = Me, Et, *or* Pr^{i}.

In ethanol under nitrogen, complete solvolysis occurs with only partial reduction of the double bond. Notably, the maximum volume of gas evolved corresponds with the value predicted for complete solvolysis. Subsequent partial reduction by the liberated H_2 yields a mixture of dimethylethoxysilyl-indene (II) and -indane (IV).

If the hydrogen produced in the solvolysis step is removed from the reaction mixture by continuous purging with nitrogen, (IV) is not formed and dimethylethoxysilylindene (II) is produced in high yield.[4]†

The Scheme summarizes the results. Steps A and D produce one mol of H_2 per mol of reactant (I) or (III). Steps B and C consume one mol of H_2 per mol of reactant (I) or (II), and the final product, compound (IV), is obtained by a combination of paths A + B and C + D. Initially, only starting material (I) is present, and only reactions A and C can occur. From the observed volume increase during the early stages it is clear that reaction A occurs more readily than reaction C even under H_2. Moreover, the evolution of H_2 is nearly as rapid as it is when the reaction is carried out under nitrogen where, in the early stages, reaction C is negligible. By continuously removing the H_2 produced in reaction A, steps B and C can be eliminated and compound (II) is formed in high yield.

It is evident that in this case the reductive solvolysis of unsaturated silanes occurs in a stepwise manner, as verified by the isolation of (II). Hydrogen evolution observed in our reactions contrasts sharply with the results in ref. 1. The reported[1] unreactivity of *trans*-olefins cannot easily be accommodated by the stepwise mechanism proposed above.

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† All new compounds were characterized by i.r., n.m.r., mass spectral, and elemental analysis.

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