SYNTHESIS OF SILVLATED 1,3-DIENES VIA THE CARBOPALLADATION OF ALLENES.

Bernard CAZES, Véronique COLOVRAY and Jacques GORE .

Laboratoire de Chimie Organique I , associé au CNRS , Université Claude Bernard ESCIL - 43 Bd du 11 Novembre 1918, 69622 VILLEURBANNE, France .

Summary: Catalytic carbopalladation of allenes 1 or 2 with silylated vinyl bromides 3 gives π -allyl palladium complexes 5 which are trapped by stabilized enolates and lead to β -difunctionalized silylated dienes 7 - 2.

Unsaturated organosilicon compounds have been extensively studied in the last decade because of their interesting potential in selective organic synthesis (1). Thus vinyl and allylsilanes have received much attention and their synthetic utility has been used in numerous electrophilic carbon-carbon bond forming reactions (1,2).

The synthetic use of silylated 1,3-dienes belonging to the four following classes I-IV (eventually substituted) has been recognized as well (3-6):



Featuring the reactivity pattern of vinyl (3c) or allylsilanes (4, 6a), they may furthermore be involved in [4+2] cycloaddition processes which broaden their utility as synthetic intermediates (3a,b ; 4d ; 6b,c). However these applications seems to remain limited because of the few procedures for their preparation.

We devised a new way to synthesize functionalized silvated 1,3-dienes $\mathbf{I} - \mathbf{2}$ which is based on the carbopalladation of allenes, a palladium-catalyzed procedure we described recently and used for the stereoselective synthesis of styrenes and conjugated dienes $\mathbf{6}$ (7).



The use of silylated vinyl bromides \mathbf{J} (R' or R" = SiMe₃ or CH₂-SiMe₃) in this reaction should lead to silicon dienic compounds $\mathbf{J} - \mathbf{2}$ (R' or R" = SiMe₃ or CH₂-SiMe₃) of the classes I-IV according to the nature of the silylated vinyl precursor \mathbf{J} , some of which are now commercially available. Thus, allenic hydrocarbons \mathbf{J} or $\mathbf{2}$ were treated for 24 h at 65°C in THF or DMSO with 1.1 eq. of a silylated vinyl bromide \mathbf{J} and the sodium enolate of dimethyl malonate or ethyl acetylacetate in the presence of the catalytic system bis(dibenzylideneacetone)palladium -1,2-bis(diphenylphosphino)ethane [Pd(dba)₂ + 1 eq. dppe ; 4% molar]. Our preliminary results are compiled in the table.

Silylated vinyl bromides **3a** and **3b** give the expected 1,3-dienes **7** and **8** as the major products. The yields are fairly good in the majority of the cases and especially in the reaction of 1,2-propadiene **1** (64 - 85 %). In the case of allene **2**, minor coproducts could be isolated by flash chromatography as the regioisomer **10** in the case of the reaction of vinyl bromide **3a** or as the desilylated dienic malonate **11** in the case of **3b**. The stereoisomeric ratio E/Z of the dienes **7b** (E/Z = 60/40) and **8b** (E/Z = 95/5) is in good agreement with our previous mechanistic proposal (7) : carbopalladation of allene **2** leads kinetically to the π -allyl complex anti-**5**, the isomerisation of which to the syn-**5** complex is mainly dependent of steric factors, this isomerisation being favoured only when R' = H (complex **5** leads then to E/Z = 60/40 **7b**).



1- Trimethylsilyl vinylbromide 3c leads to more complex reaction products since with both allenes 1 and 2 two silylated dienes are obtained, one of which (Za, Zb respectively) corresponding to a transposition of the silylated vinyl moiety. The formation of these two dienes Za and Zb can be rationalized by the rearrangement of the intermediate 6-vinylic palladium complex Ac which carbometallates the allenic unit.

This rearrangement of $\underline{4c}$ to the more stable complex $\underline{4a}$, which might proceed through &-elimination of H-Pd-Br followed by its reversed addition to trimethylsilylacetylen, would be the consequence of steric hindrance around the 6-vinyl C-Pd bond. This intermediate $\underline{4c}$ might be desilylated to vinyl palladium bromide, leading to diene $\underline{12}$. The fact that desilylation occurred either at the stage of $\underline{4c}$ (by an unclear mechanism) or more likely from the assumed intermediate trimethylsilylacetylen (perhaps via acetylen) can be deduced from the fact that $\underline{3c}$ and the silylated dienes $\underline{7b}$ and $\underline{9b}$ are recovered unchanged when submitted to the reaction conditions.



Table



Z = COOMe Z' = COOMe or CO-Me

Yields correspond to pure compounds isolated by flash chromatography.

All new compounds obtained in this work gave correct elemental analysis and spectral data.

Synthetic applications of these silylated functionalized dienes ${\it 7}$, ${\it 8}$ and ${\it 2}$ through Diels-Alder cycloaddition and/or cyclisation are currently being studied. For example, diene 8a' was stereospecifically transformed to the cis-B-hydroxyester 13 under the action of titanium tetrachloride at low temperature (1,2,8), giving easy access to derivatives of 1.2-dimethylenecyclohexane which are useful synthetic intermediates. Analogous cyclisations were very recently disclosed with allylsilanes (9) and dienylsilanes (10).



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