

FLUORIDE ION INDUCED ALLYLATION OF ACTIVATED ALKENES

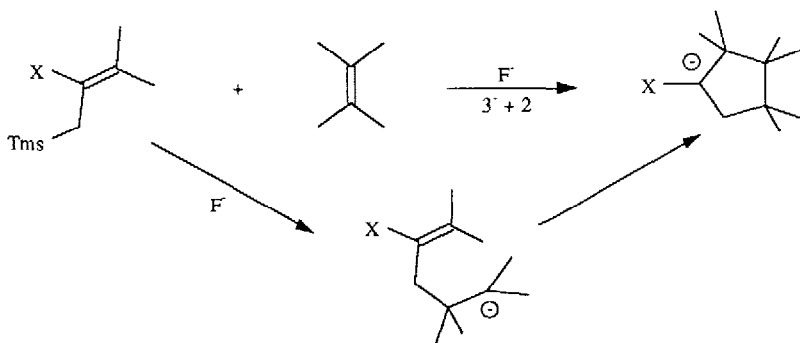
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Summary : In the presence of fluoride anions, β -substituted allylsilanes behave as nucleophiles and not as anionic 1,3 dipoles.

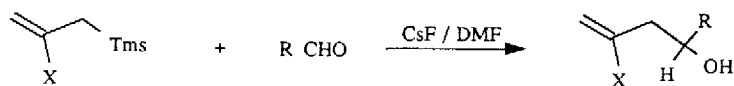
Sakurai et al. have shown that allylsilane reacts with aldehydes in the presence of catalytic amounts of $\text{Bu}_4\text{N}^{\oplus} \text{F}^{\ominus}$ to give alcohols and they suggested the intermediacy of an allylic anion^{1,2}. When our work was underway, Ishikawa et al.³ reported the addition of $\text{CH}_2=\text{C}(\text{CF}_3)\text{CH}_2\text{TMS}$ to carbonylated compounds in the same way. More recently Majetich et al.⁴ extended this reaction of allylsilane with activated alkenes and showed that this allylation procedure was more efficient than those using lithium dialkyl cuprates or allylsilane in the presence of Lewis acids.

In connexion with our previous work^{5,6} related to $[3^{\ominus} + 2]$ cycloaddition of imine anions, we were interested by the reactivity of "allylic anions" towards activated alkenes in order to synthesize cyclopentanes either by $[3^{\ominus} + 2]$ cycloaddition or by a two step process (Scheme 1).



Scheme 1

We choose allylsilanes bearing in β position an X substituent able to stabilize a cyclopentylanion. First of all we checked the reaction with aldehydes in the presence of catalytic amounts of dry CsF (10 %) in DMF.



1 : X = Ph

2 : X = Tms

3 : X = CO₂Me

4 : X = Ph ; R = Ph

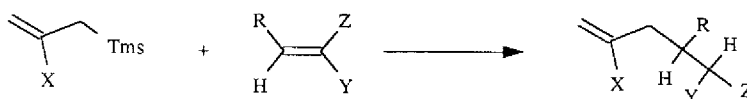
5 : X = Tms ; R = Ph

6 : X = Ph ; R = PhCH=CH-

7 : X = Tms ; R = Ph-CH=CH-

The addition proceeds at room temperature (16 hours) and after hydrolysis with HCl in MeOH, we got the alcohols 4 to 7 in a nearly quantitative yield. These compounds are characterized by ¹H NMR and Mass spectrometry⁷. 3 is not reacting with aldehydes and decomposes in the reaction conditions.

In the same way, 1 and 2 react with activated alkenes in the presence of an equivalent of CsF to give allylation products in good yields (70 to 85 %).



1 : X = Ph

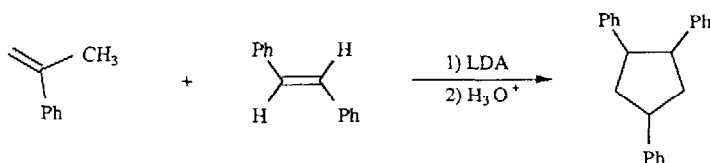
2 : X = Tms

1 : $\begin{cases} \underline{8} : R = \text{Ph} ; Y = Z ; \text{CO}_2\text{Me} \\ \underline{9} : R = \text{Ph} ; Z = \text{H} ; Y = \text{CO}_2\text{Me} \\ \underline{10} : R = \text{CO}_2\text{Me} ; Z = \text{CO}_2\text{Me} ; Y = \text{H} \\ \underline{11a}, \underline{11b} : R = \text{Ph} ; Z = \text{CN} ; Y = \text{CO}_2\text{Me} \end{cases}$

2 : 12, 13, 14, 15a, 15b, R, Y, Z, as for 8, 9, 10, 11a, 11b, respectively.

In the case of methylbenzylidene cyanoacetate two diastereomers are formed : 11a, 11b (X = Ph; 63/37) and 15a, 15b (X = Tms, 63/37). All these compounds are isolated in good yields (65 to 85 %), and characterized by ¹H NMR and Mass spectrometry⁸. These allylic compounds (8 to 15) could not be cyclized in basic medium, according to Baldwin rules "5 endo trig" ring closure is not favoured although some examples of this type are known⁹.

If an allylic anion intermediate was formed according to Sakurai^{1,2}, 1 should add to trans stilbene in the presence of one equivalent of CsF to give triphenylcyclopentane as was shown by Kauffman¹⁰ in the reaction of α -methylstyrene anion (generated with LDA) with trans stilbene.



In fact 1, in the presence of CsF and trans stilbene in DMF leads to α -methylstyrene resulting from complete desilylation of 1 and unreacted stilbene. 1 and 2 in the presence of F⁻ and activated alkenes behave like nucleophiles leading to allylation products and not like an anionic 1,3 dipole. It seems, in agreement with Majetich results ⁴ that there is no allylic anion but a nucleophilic intermediate of hypervalent silicon resulting from the addition of F⁻ to the silicon atom, giving rise to a conjugated 1,4 addition process.

References and Notes

1. A. Hosami, A. Shirahato and H. Sakurai, *Tetrahedron Letters*, 1978, 3043.
2. id, *Chem. Letters*, 1978, 901.
3. T. Yamazaki and N. Ishikawa, *Chem. Letters*, 1984, 521.
4. G. Majetich, A. Casares, D. Chapman and M. Behrike, *J. Org. Chem.*, 1986, 51, 1745.
5. S. Sinbandhit and J. Hamelin, *J.C.S. Chem. Commun*, 1977, 768.
6. M. Joucla B. Fouchet and J. Hamelin, *Tetrahedron*, 1985, 41, 2707.
7. As an example, the main features of 4 and 6 are given below :
4 b.p./0.04 = 125° (82 % yield). Mass spectrometry : C₁₆H₁₆O calculated 224.1201, found 224.1183. ¹H NMR (CDCl₃) : 2.10 (s, 1H, OH) ; 2.97 (B) and 3.08 (A) (J_{AB} = 14 Hz, ³J_(A-H) = 5 Hz, ³J_(B-H) = 8 Hz, ⁴J_(B-H) = 8.1 Hz, ⁴J_(A-H) = 1 Hz, ⁴J_(B-H) = 1.3 Hz =C-CH₂) ; 4.8 (m, 1H, CHOH) ; 5.2 (m, 1H, ²J_(H-H) = 1.4 Hz, H-C=) ; 5.47 (m, 1H, ²J_(H-H) = 1.4 Hz, HC=) ; 7.1-7.55 (m, 10H, C₆H₅).
6 b.p./0.04 = 150° (70 % yield). Mass spectrometry : C₁₈H₁₈O calculated 250.1357, found 250.1324.
8. For instance the characteristics of 8, 10 and 12, 14 are following :
8. b.p./0.04 = 130° (80 % yield). Mass spectrometry : C₂₁H₂₂O₄ (M⁺-OMe)⁺ C₂₀H₁₉O₃ calculated 307.1334, found 307.1331. ¹H NMR (CDCl₃) : 2.7 (A), 3.10 (B) (m, 2H, J_(A-B) = 13.8 Hz, ³J_(A-H) = 10 Hz, ³J_(B-H) = 3.5 Hz, =C-CH₂) ; 3.12 (s, 3H, CO₂Me) ; 3.77 (s, 3H, CO₂Me) ; 3.53 to 3.80 (m, 2H, -CHPh-CH(CO₂Me)) ; 4.77 (m, 1H, ²J = 1.4 Hz, ⁴J = 0.5 Hz, CH=) ; 5.07 (m, 1H, ²J = 1.4 Hz, =CH) ; 6.9 to 7.6 (m, 10H, C₆H₅).
10 b.p./0.04 = 100° (80 % yield). Mass spectrometry : C₁₅H₁₈O₄, calculated 262.1205, found 262.1201. ¹H NMR (CDCl₃) : 2.74 to 3.16 (m, 3H, =C-CH₂- and CHCO₂Me) ; 2.60 (A), 2.78 (B)(m, 2H, J_(AB) = 16.8 Hz, ³J_(AH) = 4.8 Hz, ³J_(BH) = 8.9 Hz, -CH₂-CO₂Me) ; 5.21 (m, 1H, ²J =

1.4 Hz, $^4J = 1$ Hz, $\underline{\text{CH}}=$) ; 5.45 (m, 1H, $^2J = 1.4$ Hz) ; 3.74 (s, 6H, 2 CO_2Me) ; 7.37 to 7.54 (m, 5H, C_6H_5).

12 b.p./0.04 = 120° (83 % yield). Mass spectrometry $\text{C}_{18}\text{H}_{26}\text{O}_4\text{Si}$. ($\text{M}^+ - \text{CH}_3$)⁺ $\text{C}_{17}\text{H}_{23}\text{O}_4\text{Si}$ calculated 319.1365, found 319.1355. ^1H NMR (CDCl_3) : 0.12 (s, 9H, Tms) ; 2.50 (m, 2H, =C- $\underline{\text{CH}}_2$) ; 3.40 to 3.90 (m, 2H, $\underline{\text{CH}}\text{Ph}$ and $\underline{\text{CH}}(\text{CO}_2\text{Me})_2$) ; 3.43 (s, 3H, CO_2Me) ; 3.77 (s, 3H, CO_2Me) ; 5.25 (m, 1H, $^2J = 2.7$ Hz, $^4J = 0.7$ Hz, $\underline{\text{CH}}=$) ; 5.35 (m, 1H, $^2J = 2.7$ Hz, $^4J = 1.3$ Hz, $\underline{\text{CH}}=$) ; 7.15 to 7.7 (m, 5H, C_6H_5).

14 : b.p./0.04 = 100° (81 % yield). Mass spectrometry : $\text{C}_{12}\text{H}_{22}\text{O}_4\text{Si}$, M^+ is weak and $\text{M}^+ - \text{CH}_3$ is measured : $\text{C}_{11}\text{H}_{19}\text{O}_4\text{Si}$, calculated 243.1052, found 243.1047. ^1H NMR (CDCl_3) : 0.19 (s, 9H, Tms) ; 2.26 (A)-2.62 (B) (m, 2H, $J_{\text{AB}} = 14$ Hz, $^3J_{\text{AB}} = 8.8$ Hz, $^3J_{\text{BH}} = 6.4$ Hz, =C- $\underline{\text{CH}}_2$ -); 2.51 (A) - 2.66 (B) (m, 2H, $J_{\text{AB}} = 16.8$ Hz, $^3J_{\text{AH}} = 4.9$ Hz, $^3J_{\text{BH}} = 9.4$ Hz, $\underline{\text{CH}}_2\text{CO}_2\text{Me}$) ; 3.04 (m, 1H, $\underline{\text{CH}}\text{CO}_2\text{Me}$) ; 3.70 (s, 3H, CO_2Me) ; 3.72 (s, 3H, CO_2Me) ; 5.45 (m, 1H, $^2J = 2.6$ Hz, $^4J = 0.8$ Hz, $\underline{\text{CH}}=$) ; 5.61 (m, 1H, $^2J = 2.6$ Hz, $^4J = 1.3$ Hz, = $\underline{\text{CH}}$).

9. P. Auvray, P. Knochel and J.F. Normant, Tetrahedron Letters, 1985, 26, 4455.
10. R. Eidenschink and T.R. Kauffman, Angew. Chem. Int. Ed., 1972, 11, 292.

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