VINYL TRIFLUOROSULFONATES IN THE CARBOPALLADATION OF ALLENIC HYDROCARBONS

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<u>Summary</u>: The palladium-catalyzed reaction of an enol triflate, an allenic hydrocarbon, and the anion of dimethyl malonate leads to conjugated dienes <u>1</u> in good yield. No isomerisation is observed when this reaction is run with both triflates of 2-methylcyclohexanone.

We have recently shown that functionalized 1,3-dienes of general formulae $\underline{1}$ can be obtained in fairly good yields by a palladium-catalyzed reaction involving a vinyl halide, an allenic hydrocarbon and a delocalized anion issued from a malonate (Z=Z'=CO₂Me), a β -keto-ester (Z=CO₂Me, Z'=COMe), a sulforyl ester (Z=CO₂Me, Z'=SO₂Ø) etc... (1). The same process involving a functionalized allenic compound $\underline{2}$ leads principally to dienes of type $\underline{3}$ by an intramolecular trapping of the intermediately formed π -allyl complex (2).



Both kinds of compounds $\underline{1}$ and $\underline{3}$ could be interesting substrates for the synthesis of polycyclic systems by using ultimately a Diels-Alder reaction.

A severe limitation to the synthetic application of this carbopalladation of allenic compounds lies in the lack of good methods for the preparation of vinyl halides, substituted or functionalized in a definite position. This point led us to consider the possibility of using, in this process, enol triflates which can be easily prepared by trapping, with triflic anhydride or N-phenyl triflimide, regiospecifically generated enolates (3). These enol triflates have been recently used as synthons for the formation of carbon-carbon bonds in palladium-catalyzed reactions (4-6).

Thus the cyclohexanone enol triflate 4a was treated in a stainless-steel bomb with 1,2-propadiene 5a and methyl sodiomalonate in the conditions previously used for cyclohexenyl bromide [THF, 65° C, 48 hours, 4% Pd(dba)₂ + 4 PPh₃] (1) with a slight modification : addition of 2.5 molar equivalents of lithium chloride known to increase, probably by a ligand exchange, the reactivity of the initially-formed vinyl palladium species (5a). The conjugated diene <u>la</u> was then isolated (flash-chromatography) with a 55% yield, increased to 85% by using dimethylsulfoxide in place of tetrahydrofuran.

Subsequently, these conditions were used with enol triflates 4b and 4c and the catalytic process was demonstrated to be efficient for the synthesis of monocyclic 1,3-dienes 1 starting either from 1,2-propadiene 5a or 1,2-decadiene 5b (Table). With this last hydrocarbon the reaction in tetrahydrofuran gives a poor yield (10% in the case of 4a), but all the results are fairly good when the solvent is dimethylsulfoxide. As in the case of cyclohexenyl bromide, the reaction is regiospecific and highly stereoselective giving the (E)-1 diene as the major stereoisomer (ratio E/Z = 85-90/15-10) as shown both by GC-MS experiments and ¹H and ¹³C NMR spectroscopy.

Another point of this study was dealing with a possible isomerisation of the starting triflate and (or) of the vinyl organopalladium species in the experimental conditions. For this purpose, 6-methylcyclohex-1-enyl triflate $\underline{4d}$ (3a) and 2-methylcyclohex-1-enyl triflate $\underline{4e}$ (7) were regioselectively prepared according to the literature and submitted to the reaction with 1,2-propadiene and dimethyl sodiomalonate following the general procedure. Both triflates $\underline{6a}$ and $\underline{6b}$ were specifically converted to dienes $\underline{1g}$ (74%) and $\underline{1h}$ (65%) without any migration of the double hond.



In conclusion, the use of vinyl triflates increases greatly the synthetic potential of the carbopalladation of allenic compounds, several applications of which are currently undertaken and will be described in the future.

General procedure :

2 mmol of 1,2-decadiene 5b and 2 mmol of the vinyl triflate 4 are added to the solution in dimethylsulfoxide (20 ml) of dimethyl sodiomalonate (2.6 mmol, prepared by using sodium hydride), 5 mmol of lithium chloride and 0.08 mmol of the catalyst Pd(PPh₃)₄, generated <u>in situ</u> by adding 4 equivalents of triphenylphosphine to the bis(dibenzylideneacetone)palladium complex Pd(dba)₂ (1). The resulting solution is then heated under argon at 65°C during 48 hours.

The reactions using 1,2-propadiene $\underline{5a}$ are run in a stainless-steel autoclave with 7.5 mmol of this diene and 2 mmol of the triflate $\underline{4}$.

Table :



starting triflate		Allene	Diene <u>1</u> (E/Z)	Yield *
OTF		59	C0 ₂ Me <u>la</u> R ≈ H	85%
	<u>4a</u>	<u>5</u> b	R = nC7H ₁₅ (90/10)	80%
Me UTf		<u>5a</u>	$ \begin{array}{c} \text{Me} \\ \downarrow \\ \downarrow$	53%
	<u>4b</u>	<u>5b</u>	$\frac{1}{R} = nC7H_{15}$ (83/17)	65%
OTF		<u>5a</u>	$C0_2 Me = H$ $C0_2 Me$	75%
	<u>4c</u>	<u>5b</u>	R ≈ nC7H15 (85/15)	75%

* The yield is calculated from quantities of pure diene 1 isolated by flash-chromatography (8,9) and refers to diene 5b or, in the case of the reactions of the gaseous 1,2-propadiene 5a, to the triflate 4.

REFERENCES

- 1. M. AHMAR, J.J. BARIEUX, B. CAZES and J. GORE, Tetrahedron, 1987, 43, 513.
- 2. M. AHMAR, B. CAZES and J. GORE, Tetrahedron, 1987, <u>43</u>, 3453.
- 3 a. P.J. STANG, M. HANACK and L.R. SUBRAMANIAN, Synthesis, 1982, 85.
- b. J.E. Mc MURRY and W.J. SCOTT, Tetrahedron Lett., 1983, 979.
- 4. For a review on the synthesis and the organometallic coupling reactions of enol triflates see :

W.J. SCOTT and J.E. Mc MURRY, Acc. Chem. Res., 1988, 21, 47.

- 5. Palladium-catalyzed olefination (Heck reaction) of vinyl triflates :
 - a. S. CACCHI, E. MORERA and G. ORTAR, Tetrahedron Lett., 1984, 25, 2271.
 - b. W.J. SCOTT, M.R. PENA, K. SWÄRD, S.J. STOESSEL and J.K. STILLE, J.Org.Chem., 1985, <u>50</u>, 2302.
- Palladium-catalyzed carbonylative couplings of enol triflates :
 G.T. CRISP, W.J. SCOTT and J.K. STILLE, J.Amer.Chem.Soc., 1984, <u>106</u>, 7500.
- 7. G.T. CRISP and W.J. SCOTT, Synthesis, 1985, 335.
- 8. W.C. STILL, M. KAHN and A. MITRA, J.Org.Chem., 1978, 43, 2923.
- 9. Compounds <u>la</u> and <u>lb</u> have been previously described (1); their spectra were used as reference for the identification of the other dienes <u>lc</u>, <u>ld</u>, <u>lg</u>, <u>lh</u> having a cyclohexenyl structure.

Cyclopentenyl dienes <u>le</u> and <u>lf</u> have the following ^lH NMR spectra (CDCl₃ - 300 MHz) :

<u>le</u>: 1.88 (quint , J = 7.6 Hz , 2H), 2.43 (t , J = 7.6 Hz , 4H), 2.89 (part B_2 of an AB_2 system, roughly a doublet, J \sim 7.5 Hz , 2H), 3.66 (part A of an AB_2 system, roughly a triplet, J \sim 7.5 Hz , 1H), 3.71 (s , 6H), 4.92 and 4.93 (2s , 2H), 5.8 (s , 1H).

<u>lf</u> (E-isomer) : 0.88 (t, J = 6.3 Hz, 3 H), 1.27 (m, 10H), 1.89 (quint, J = 7.3 Hz, 2H), 2.1 (quart, J = 7.3 Hz, 2H), 2.42 (t, J = 7.3 Hz, 4H), 2.94 (part B₂ of an AB₂ system, roughly a doublet, $J \sim 7.5 \text{ Hz}$, 2H), 3.7 (part A of an AB₂ system, roughly a triplet, $J \sim 7.5 \text{ Hz}$, 1H), 3.74 (s, 6H), 5.48 (t, J = 7.3 Hz, 1H), 5.64 (s, 1H).

In the spectrum of the Z-isomer, the two last signals are located at 5.29 and 5.36 ppm.

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