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PALLADIUM-CATALYSED VINYLATION OF ENOL TRIFLATES

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Abstract: Enol triflates react with olefinic products in the presence of triethylamine and a palladium acetate-triphenylphosphine catalyst to give conjugated dienes in good yield and under mild conditions.

Since their introduction in 1969, enol trifluoromethanesulphonates (enol triflates) have primarily and widely been used for the direct solvolytic generation of vinyl cations and, via α-elimination, for the generation of unsaturated carbenes.[1]

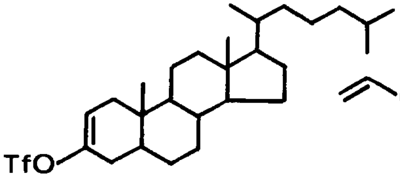
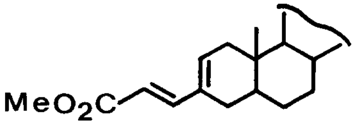
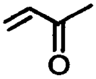
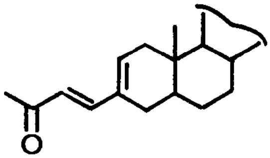
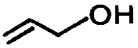
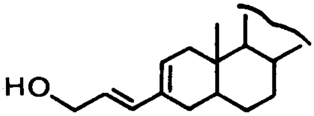
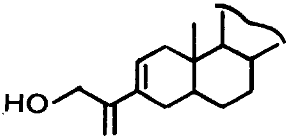
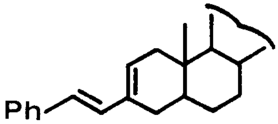
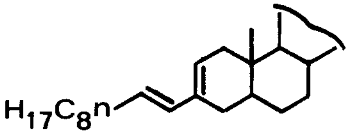
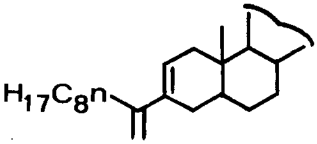
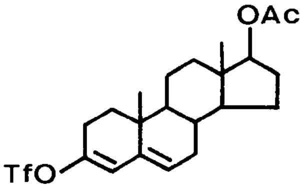
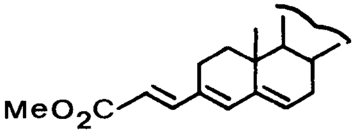
More recently, the coupling with lithium dialkylcuprates[2] and hydrogenolysis to hydrocarbons[3] have extended the usefulness of these readily accessible intermediates[4] in preparative organic chemistry.

We have now found that enol triflates, with similarity to the behaviour of vinyl halides,[5] undergo an efficient palladium-catalysed coupling with a variety of olefinic compounds, thus broadening existing methodologies in the area commonly referred to as vinylic substitution.

The representative results are listed in the Table.

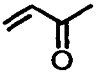
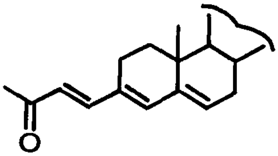
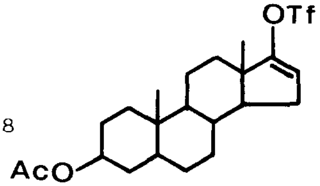
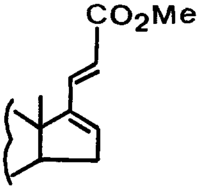
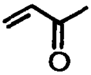
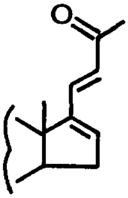
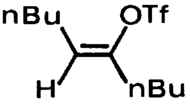
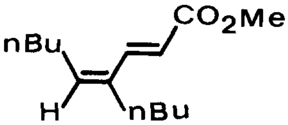
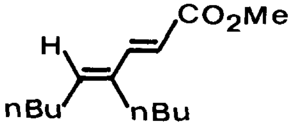
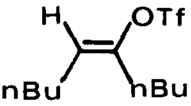
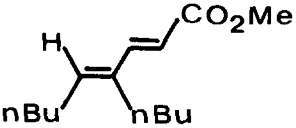
In a typical procedure (entry 1), a mixture of cholest-2-en-3-yl triflate (0.52 g, 1 mmol),[4] methyl acrylate (0.14 ml; 1.5 mmol), triethylamine (0.28 ml, 2 mmol), palladium acetate (4 mg, 0.02 mmol), and triphenylphosphine (10 mg, 0.04 mmol) in DMF (4 ml) was stirred at 60 °C for 5 hr, under nitrogen. The reaction was then diluted with water, extracted with ether, washed with water until neutral, dried (Na_2SO_4), and evaporated. Chromatography of the residue (0.45 g) on silica gel (15 g, hexane/benzene = 3/2 as eluant) provided pure methyl (E)-3-(3-cholest-2-enyl)-2-propenoate (0.39 g, 86%): mp 150.5-151.5 °C (from AcOEt); $[\alpha]_D$($CHCl_3$, 1%), +93°; IR (KBr), 1713, 1631 cm^{-1};

Table. Palladium-Catalysed Vinylation of Enol Triflates[a]

Entry	Enol Triflate[b]	Olefin	Reaction time(hr)	Product[b]	Yield[c] (%)
1			5		86
2	"		6		82
3	"		5		50
					14
4	"		3		77
5	"		43		60^{d}
					18^{d}
6			14		82

(continued)

Table (continued).

Entry	Enol Triflate[b]	Olefin	Reaction time(hr)	Product[b]	Yield[c] (%)
7	"		39		64
8			6		82
9	"		7		70
10			4[e]		20
					5
11		"	24[e]		27

[a] All reactions were carried out at 60 °C in DMF under N_2 with a molar ratio enol triflate:olefin:Et_3N:$Pd(OAc)_2$:PPh_3= 1:1.5:2:0.02:0.04, unless otherwise specified. Disappearance of starting material was monitored by TLC. [b] All new compounds were fully characterized spectroscopically and by combustion analyses. [c] Yields of pure isolated material, except entry 5. [d] Relative yields determined from ^{1}H NMR analysis of the inseparable mixture of the two dienes. [e] 3 mol% of $Pd(OAc)_2$ with 6 mol% of PPh_3 as catalyst and MeCN as solvent were used.

^{1}H NMR ($CDCl_3$), δ 0.65 (s, 3H), 0.71 (s, 3H), 3.74 (s, 3H), 5.80 (d, J = 16 Hz, 1H), 6.10 (m, 1H), 7.33 (d, J = 16 Hz, 1H). Anal. Calcd for $C_{31}H_{50}O_2$: C, 81.88; H, 11.08. Found: C, 81.90; H, 11.02.

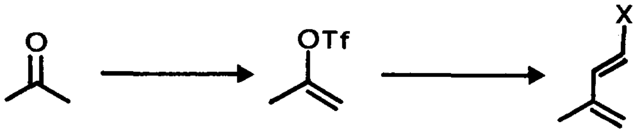
In the absence of triphenylphosphine, only a 6% of the coupling product was obtained under identical conditions.

Employing enol acetates instead of enol triflates met with failure. Thus, cholest-2-en-3-yl acetate,[6] when reacted with methyl acrylate at 80 °C overnight, was completely unchanged.

In contrast to vinyl halides,[5] vinylations of enol triflates were free from complications arising from the conjugated diene products undergoing Diels-Alder reaction with starting olefins.

That the coupling reaction occurs with satisfactory stereoselectivity was exemplified by the treatment of pure (Z)- and (E)-5-decen-5-yl triflates[4] with methyl acrylate (entries 10 and 11).

In conclusion, the ready availability of enol triflates coupled with the simplicity and mildness of the reaction conditions should foster future recourse to our procedure to solve, for instance, the challenging problem of transforming a carbonyl group into a functionalised diene:



(X = COR, CO_2R)

Further work along this line is in progress.

References and Notes

1. P. J. Stang, M. Hanack, and L. R. Subramanian, Synthesis, 85 (1982).
2. J. E. McMurry and W. J. Scott, Tetrahedron Lett., 4313 (1980).
3. V. B. Jigajinni and R. H. Wightman, Tetrahedron Lett., 117 (1982).
4. The steroidal enol triflates used in this work were prepared from the corresponding ketones using 2,6-di-t-butyl-4-methyl pyridine and triflic anhydride in dichloromethane solution according to the general procedure of Stang: P. J. Stang and W. Treptow, Synthesis, 283 (1980); P. J. Stang and T. E. Fisk, Synthesis, 438 (1979); J. R. Hassdenteufel and M. Hanack, Tetrahedron Lett., 503 (1980). Cholestan-3-one afforded an inseparable mixture of isomeric Δ^2- and Δ^3-3-triflates in a 83:17 ratio. Equilibration in dichloromethane containing 1 drop of triflic acid and 0.1 ml of triflic anhydride/mmole of substrate furnished Δ^2-isomer $\geqslant$95% pure after 4 days at room temperature. (Z)- and (E)-5-decen-5-yl triflates (entries 10 and 11) were prepared according to ref. 2 (note 7).
5. R. F. Heck, Org. React., **27**, 345 (1982) and references therein; L. C. Kao, F. G. Stakem, B. A. Patel, and R. Heck, J. Org. Chem., **47**, 1267 (1982).
6. W. G. Dauben, R. A. Micheli, and J. F. Eastham, J. Am. Chem. Soc., **74**, 3852 (1952).

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