



Bistrifluoromethanesulfonimide in the Catalytic Conjugate Allylation of α,β -Unsaturated Carbonyl Compounds

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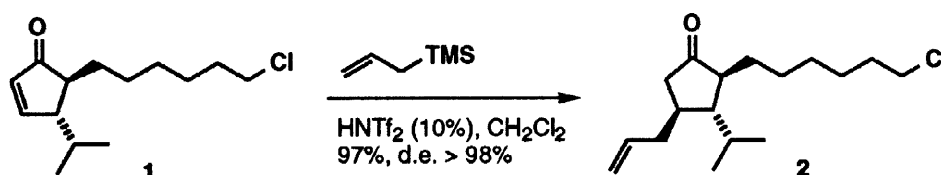
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Abstract: Bistrifluoromethanesulfonimide may be used directly to initiate the catalytic conjugate allylation of α,β -unsaturated carbonyl compounds with allyltrimethylsilane; high yields of either silyl enol ethers or δ,ϵ -unsaturated ketones and esters may be obtained under mild conditions.

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During attempts to prepare substituted bicyclo[10.2.1]decenone intermediates¹ we were faced with the apparently straightforward task of introducing an allyl side chain onto enone **1**. Allylcuprate² and allylbarium reagents,³ have been successful for this type of transformation but the Sakurai reaction⁴ was considered likely to effect the most practical and diastereoselective allylation. However, in our hands, the standard protocol [TiCl₄, allyltrimethylsilane, CH₂Cl₂, -78°C → r.t., 2 → 24h] gave none of the desired product and the copper catalysed addition of allylmagnesium chloride returned ketone **2** in only 25% yield.

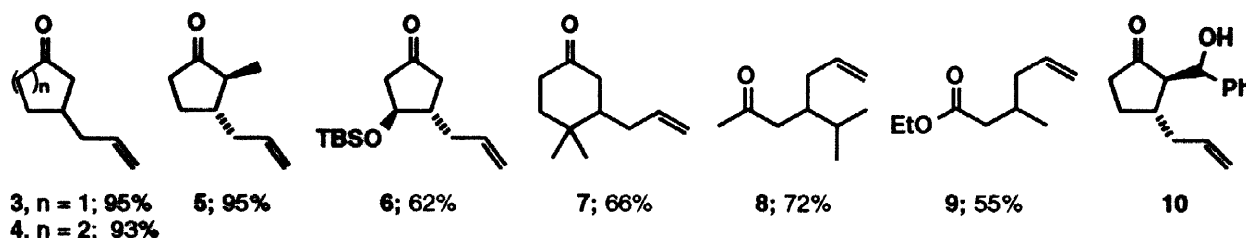
Whilst TMSOTf is known *not* to catalyse enone allylation with allylsilanes⁵ Ghosez has recently highlighted the much more powerful carbonyl-activating properties of TMSNTf₂⁶ and we chose to evaluate this catalyst in the allylation of enone **1**. However, TMSNTf₂ is moisture-sensitive but since it may be readily prepared from commercially available HNTf₂ and allyltrimethylsilane we considered generating the catalyst *in situ*. Although the reported conditions for preparing TMSNTf₂ (neat, rt, distillation)⁶ were rather different from those we employed (dilute solution in CH₂Cl₂, -78°C) this proposal proved successful to provide, after hydrolysis of the intermediate silyl enol ether, ketone **2** in 97% yield (d.e. > 98%).



An n.m.r. experiment⁸ confirmed that propene and TMSNTf₂ formed rapidly when allyltrimethylsilane was added to a solution of HNTf₂ in CD₂Cl₂ at -78°C. Interestingly the liberated propene was partially consumed, presumably by HNTf₂,⁹ over a period of 5h at 20°C to give a new component assigned as *i*-PrNTf₂ on the basis of the ¹H n.m.r. spectrum.¹⁰ A pK_a of 1.7 has been reported for HNTf₂ in water¹¹ so electrophilic hydroamination of propene is quite possible; the only precedent for this is in its addition to *fluoroolefins*.¹²

Using cyclopentenone as a test case we found that allylation generally initiates at temperatures above ca. -40°C as suggested both by t.l.c. analysis and a red colouration in the reaction mixture. Whilst as little as 0.5% of HNTf₂ could be used without a decrease in yield there was an associated increase in reaction time from ca. 1h to 18h. To enable convenient reaction times, between 5 and 10% of HNTf₂ was used in the allylation of a small range of enones and enoates to generate allylated compounds **3–9** in good to excellent isolated yields.¹³

By omitting the aqueous work-up and evaporating the solvent after disappearance of the enone (t.l.c.) the intermediate silyl enol ethers could be obtained. Additionally, sequential allylation–aldol reaction with cyclopentenone and benzaldehyde was possible to give adduct 10 although the yield was low (*ca.* 30%).¹⁴



It is significant that allylation of 4-(*tert*-butyldimethylsilyloxy)cyclopent-2-enone provided the product (6) of *anti*- allylation (d.e. > 96%) because this is the *opposite* stereochemical outcome to that obtained under the classical Sakurai conditions.¹⁵ The allylation of ethyl crotonate to give δ,ϵ -unsaturated ester 9 is also of interest since this is a process known to be ineffective using titanium (IV) chloride as an activator.¹⁶

In summary, we have presented an efficient and practical method for the allylation of α,β -unsaturated carbonyl compounds to generate either silyl enol ethers or free carbonyl products under mild conditions. Not only does this catalytic procedure provide products unavailable by the conventional method, it avoids the use of toxic and/or air-sensitive organometallic and metal halide reagents. Since the system is also tolerant of small amounts of moisture⁹ industrial applications may be possible.

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References and Notes

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- The *syn,anti*- diastereomer was not observed by either GCMS or ¹H n.m.r. spectroscopy (500 MHz).
- Propene: δ_{H} (200 MHz; CD₂Cl₂) 1.74 (3H, dt, *J* 6.4, 1.5), 4.95 (1H, br d, *J* 11.8), 5.03 (1H, br d, *J* 17.6), 5.73 (1H, ddq, *J* 17.6, 11.8, 6.4); TMSNTf₂: δ_{H} (200 MHz; CD₂Cl₂) 0.62 (9H, s) (lit.¹¹ δ_{H} (60 MHz) 0.57 (9H, s)).
- Hydrolysis of TMSNTf₂ to HNTf₂ occurs in solvents that have not been specially dried. This does not affect enone allylation since any water present is converted into TMS₂O and the so-formed HNTf₂ reacts rapidly with excess allyltrimethylsilane to regenerate TMSNTf₂; i.e. the system is self-drying.
- i*-PrNTf₂: δ_{H} (200 MHz, CD₂Cl₂) 1.62 (6H, d, *J* 6.8), 4.74 (1H, sept, *J* 6.8).
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- General experimental procedure:** To a stirred solution of the enone (1 mmol) and allyltrimethylsilane (175 μ l, 1.1 mmol) in dry CH₂Cl₂ (2 mL) at –78°C under a nitrogen atmosphere was added HNTf₂ (28 mg, 0.1 mmol) as a solution in dry CH₂Cl₂ (1 mL). The mixture was allowed to warm to 20°C over 1 h and saturated NH₄Cl solution (3 mL) was added. The separated aqueous phase was extracted with ether (2 \times 10 mL), the combined organic portions dried (MgSO₄), and the solvents removed *in vacuo*. The allylated ketones were obtained as colourless oils after purification by either short-path distillation or column chromatography.
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