Pergamon

Tetrahedron Letters 39 (1998) 3215-3216

TETRAHEDRON
LETTERS

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

Nikolai Kuhnert, Jonathan Peverley, and Jeremy Robertson*

Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY, U.K.

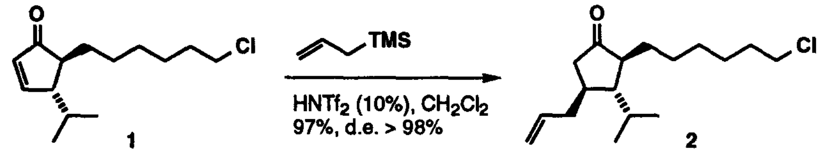
Received 23 December 1997; revised 17 February 1998; accepted 19 February 1998

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.

© 1998 Elsevier Science Ltd. All rights reserved.

During attempts to prepare substituted bicyclo[10.2.1]decenone intermediates[1] we were faced with the apparently straightforward task of introducing an allyl side chain onto enone **1**. Allylcuprate[2] and allylbarium reagents,[3] have been successful for this type of transformation but the Sakurai reaction[4] was considered likely to effect the most practical and diastereoselective allylation. However, in our hands, the standard protocol [$TiCl_4$, allyltrimethylsilane, CH_2Cl_2, –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 allylsilanes[5] Ghosez has recently highlighted the much more powerful carbonyl-activating properties of $TMSNTf_2$[6] and we chose to evaluate this catalyst in the allylation of enone **1**. However, $TMSNTf_2$ is moisture-sensitive but since it may be readily prepared from commercially available $HNTf_2$ and allyltrimethylsilane we considered generating the catalyst *in situ*. Although the reported conditions for preparing $TMSNTf_2$ (neat, rt, distillation)[6] were rather different from those we employed (dilute solution in CH_2Cl_2, –78°C) this proposal proved successful to provide, after hydrolysis of the intermediate silyl enol ether, ketone **2** in 97% yield (d.e. > 98%[7]).

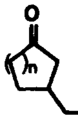


An n.m.r. experiment[8] confirmed that propene and $TMSNTf_2$ formed rapidly when allyltrimethylsilane was added to a solution of $HNTf_2$ in CD_2Cl_2 at –78°C. Interestingly the liberated propene was partially consumed, presumably by $HNTf_2$,[9] over a period of 5h at 20°C to give a new component assigned as *i*-$PrNTf_2$ on the basis of the ^1H n.m.r. spectrum.[10] A pK_a of 1.7 has been reported for $HNTf_2$ in water[11] so electrophilic hydroamination of propene is quite possible; the only precedent for this is in its addition to *fluoro*olefins.[12]

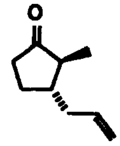
Using cyclopentenone as a test case we found that allylation generally initiates at temperatures above *ca.* –40°C as suggested both by t.l.c. analysis and a red colouration in the reaction mixture. Whilst as little as 0.5% of $HNTf_2$ could be used without a decrease in yield there was an associated increase in reaction time from *ca.* 1h to 18h. To enable convenient reaction times, between 5 and 10% of $HNTf_2$ 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]

0040-4039/98/$19.00 © 1998 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(98)00394-3

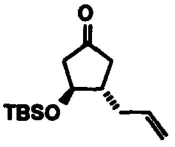
By omitting the aqueous work-up and evaporating the solvent after disappearance of the enone (t.l.c.) the intermediate silyl enol ethers could be obtained. Additionally, sequential allylation–aldol reaction with cyclopentenone and benzaldehyde was possible to give adduct **10** although the yield was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



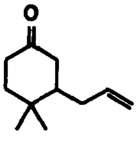
3, n = 1; 95%
4, n = 2; 93%



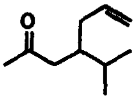
5; 95%



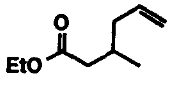
6; 62%



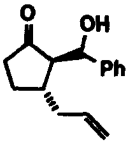
7; 66%



8; 72%



9; 55%



10

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 moisture[9] industrial applications may be possible.

Acknowledgments: We thank the EPSRC for a post doctoral research fellowship (GR/K88354) and both Zeneca (Strategic Research Fund) and Pfizer for unrestricted research grants.

References and Notes

1. Robertson, J.; Burrows, J. N.; Stupple, P. A. *Tetrahedron*, **1997**, *53*, 14807–14820; Robertson, J.; Burrows, J. N. *Synthesis*, **1998**, 63–66.
2. E.g.: Lipshutz, B. H.; Ellsworth, E. L.; Dimock, S. H.; Smith, R. A. J. *J. Am. Chem. Soc.*, **1990**, *112*, 4404–4410; Lipshutz, B. H.; Hackmann, C. *J. Org. Chem.*, **1994**, *59*, 7437–7444
3. Yanagisawa, A.; Habaue, S.; Yasue, K.; Yamamoto, H. *J. Am. Chem. Soc.*, **1994**, *116*, 6130–6141.
4. Hosomi, A.; Sakurai, H. *J. Am. Chem. Soc.*, **1977**, *99*, 1673–1675.
5. Kim, S.; Lee, J. M. *Synth. Commun.*, **1991**, *21*, 25–29.
6. Mathieu, B.; Ghosez, L. *Tetrahedron Lett.*, **1997**, *38*, 5497–5500; see also Ishii, A.; Kotera, O.; Saeki, T.; Mikami, K. *Synlett*, **1997**, 1145–1146.
7. The *syn,anti*- diastereomer was not observed by either GCMS or ^{1}H n.m.r. spectroscopy (500 MHz).
8. Propene: δ_H (200 MHz; CD_2Cl_2) 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); $TMSNTf_2$: δ_H (200 MHz; CD_2Cl_2) 0.62 (9H, s) {lit.[11] δ_H (60 MHz) 0.57 (9H, s)}.
9. Hydrolysis of $TMSNTf_2$ to $HNTf_2$ occurs in solvents that have not been specially dried. This does not affect enone allylation since any water present is converted into TMS_2O and the so-formed $HNTf_2$ reacts rapidly with excess allyltrimethylsilane to regenerate $TMSNTf_2$; i.e. the system is self-drying.
10. *i*-$PrNTf_2$: δ_H (200 MHz, CD_2Cl_2) 1.62 (6H, d, *J* 6.8), 4.74 (1H, sept, *J* 6.8).
11. Foropoulos, J., Jr.; DesMarteau, D. D. *Inorg. Chem.*, **1984**, *23*, 3720–3723.
12. Vij, A.; Zheng, Y. Y.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.*, **1994**, *33*, 3281–3288.
13. *General experimental procedure:* To a stirred solution of the enone (1 mmol) and allyltrimethylsilane (175 µl, 1.1 mmol) in dry CH_2Cl_2 (2 mL) at –78°C under a nitrogen atmosphere was added $HNTf_2$ (28 mg, 0.1 mmol) as a solution in dry CH_2Cl_2 (1 mL). The mixture was allowed to warm to 20°C over 1h and saturated NH_4Cl solution (3 mL) was added. The separated aqueous phase was extracted with ether (2 × 10 mL), the combined organic portions dried ($MgSO_4$), and the solvents removed *in vacuo*. The allylated ketones were obtained as colourless oils after purification by either short-path distillation or column chromatography.
14. A similar sequence has been reported using trityl perchlorate: Hayashi, M.; Mukaiyama, T. *Chem. Lett.*, **1987**, 289–292.
15. Jeroncic, L. O.; Cabal, M.-P.; Danishefsky, S. J.; Shulte, G. M. *J. Org. Chem.*, **1991**, *56*, 387–395.
16. For a discussion see Fleming, I.; Dunoguès, J.; Smithers, R. *Org. React.*, **1989**, *37*, 57–575.