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LETTERS

1,4-Conjugate addition of allyltrimethylsilane to α,β-unsaturated ketones

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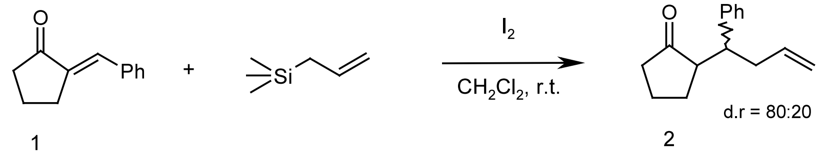
Abstract—α,β-Unsaturated ketones smoothly undergo conjugate addition with allyltrimethylsilane in the presence of a catalytic amount of elemental iodine under very mild and convenient conditions to afford the corresponding Michael adducts in high yields with high selectivity. © 2002 Elsevier Science Ltd. All rights reserved.

The conjugate addition of allylsilanes to electrophilic alkenes, referred to as the Sakurai–Hosomi reaction has been recognized as a particularly efficient method of carbon–carbon bond formation and has been extensively applied in organic synthesis, especially in natural product synthesis.[1] Lewis acids such as $TiCl_4$, $AlCl_3$, and $BF_3 \cdot OEt_2$ have been employed as the most effective promoters for these conjugate allylations.[2] Subsequently, modified reagents such as allylbarium[3] and allylcopper[4] and allylindium[5] reagents have been developed to avoid strongly acidic conditions. With these modified reagents the allylation of acyclic enones is far more difficult than that of cyclic ketones. Recently, organotantalum reagents have also been developed for the allylation of enones by transmetalation of organotin compounds.[6] However, many of these methods involve the use of highly toxic tin compounds, expensive reagents and require a stoichiometric amount or even an excess amount of the Lewis acid to obtain reasonable reaction rates and acceptable yields of products. Thus, there is still scope to develop a simple and efficient method for the conjugate allylation of α,β-unsaturated ketones. Furthermore, the development of new reagents, which are more efficient and lead to convenient procedures with improved yields, is well appreciated.

In continuation of our interest on catalytic applications of elemental iodine for various organic transformations,[7] we report herein a mild and convenient method for the conjugate allylation of both cyclic and acyclic enones with allyltrimethylsilane using elemental iodine as an efficient catalyst. Thus, treatment of 2-benzylidenecyclopentanone with allyltrimethylsilane in the presence of 5 mol% of elemental iodine in dichloromethane afforded the corresponding 2-(1-phenyl-3-butenyl)cyclopentanone in 90% yield with 80:20 diastereoselectivity (Scheme 1).

Similarly, 2-benzylidenecyclohexanone, 2-benzylidene-1-tetralone and benzylideneacetone reacted well to give the corresponding 1,4-adducts in excellent yields. Cyclic enones such as 2-cyclohexenone, 2-cyclopentenone and acyclic enones such as chalcones afforded the corresponding Michael adducts in excellent yields. In all cases the reactions proceeded smoothly at ambient temperature with high selectivity. No 1,2-adduct was



Scheme 1.

Keywords: Michael addition; α,β-unsaturated ketones; iodine catalysis; 1,4-adducts.

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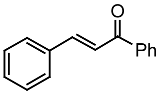
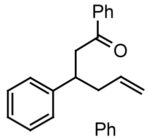
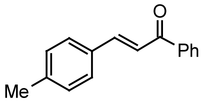
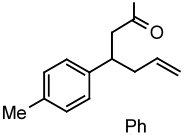
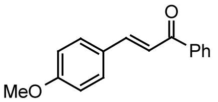
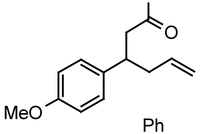
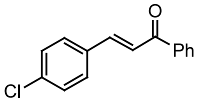
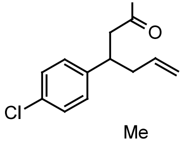
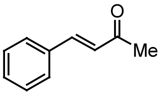
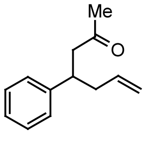
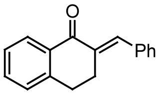
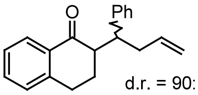
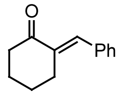
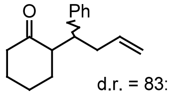
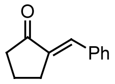
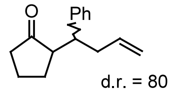
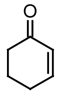
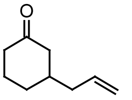
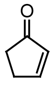
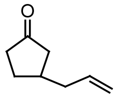
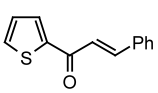
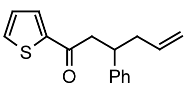
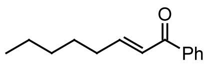
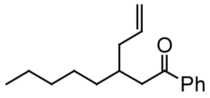
obtained under these reaction conditions. The products were characterized by ^{1}H NMR, IR, and mass spectroscopy and also by comparison with authentic compounds.[3,5] Dichloromethane is the solvent of choice giving the best results. This method is equally effective for the allylation of both cyclic and acyclic enones. The results of the conjugate allylation of enones, both cyclic and acyclic substrates, are presented in Table 1. Inter-

Table 1. Iodine-catalyzed conjugate allylation of α,β-unsaturated ketones[8]

Entry	Enone **1**	Product[a] **2**	Reaction Time (h)	Yield [b] (%)
a			3.5	90
b			3.0	89
c			3.5	87
d			4.5	90
e			2.5	88
f		 d.r. = 90:10	5.5	85[c]
g		 d.r. = 83:17	4.5	90[c]
h		 d.r. = 80: 20	4.0	87[c]
i			4.0	82
j			3.5	80
k			3.0	85
l			5.0	75

a: All products were characterized by ^{1}H NMR, IR and mass spectroscopy

b: Isolated and unoptimized yields

c:Diastereomeric ratio (d.r.) wasdetermined from the ^{1}H NMR spectra of the products estingly, a catalytic amount of TMSI was also found to be equally effective for this conversion. However, the use of allyltri-*n*-butyltin in place of allyltrimethylsilane did not yield any product under these reaction conditions, perhaps because iodine does not interact with allyltri-*n*-butyltin. Furthermore, the reactions of enones, with allylsilane in the presence of metal triflates such as scandium or ytterbium triflate afforded 1,2-adducts predominantly. In addition, attempted allylation with allylsilane and solid acids such as K10 clay and Amberlyst-15 gave only 1,2-adducts. Thus, the combination of allyltrimethylsilane and iodine could be the method of choice for conjugate allylation of enones. There are many advantages in the use of elemental iodine as catalyst for this transformation, which include high yields of products, mild reaction conditions, greater selectivity, cleaner reaction profiles and operational simplicity. No additives or acidic promoters are required for the reaction to proceed. The catalyst is readily available at low cost and is highly efficient in promoting conjugate allylations.

In summary, this paper describes a simple and efficient method for the conjugate allylation of α,β-unsaturated ketones using the cheap and readily available elemental iodine as catalyst. In addition to its efficiency, simplicity and mild reaction conditions, this method provides high yields of products with high selectivity, which makes it a useful and attractive process for the synthesis of δ,ε-unsaturated ketones of synthetic importance.

Acknowledgements

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References

1. (a) Colvin, E. *Silicon in Organic Synthesis*; Butterworth: London, 1981; p. 97; (b) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200; (c) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375.
2. (a) Hosomi, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 1673; (b) Fleming, I.; Dunogues, J.; Smithers, R. *Org. React.* **1989**, *37*, 57–575.
3. Yanagisawa, A.; Habaue, S.; Yasue, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1994**, *116*, 6130.
4. (a) Lipshutz, B. H.; Ellsworth, E. L.; Dimock, S. H.; Smith, R. A. J. *J. Am. Chem. Soc.* **1990**, *112*, 4404; (b) Lipshutz, B. H.; Hackmann, C. *J. Org. Chem.* **1994**, *59*, 7437.
5. (a) Lee, P. H.; Ahn, H.; Lee, K.; Sung, S.-Y.; Kim, S. *Tetrahedron Lett.* **2001**, *42*, 37; (b) Lee, P. H.; Lee, K.; Sung, S.-Y.; Chang, S. *J. Org. Chem.* **2001**, *66*, 8646.
6. Shibata, I.; Kano, T.; Kanazawa, N.; Fukuoka, S.; Baba, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1389.
7. (a) Yadav, J. S.; Reddy, B. V. S.; Hashim, S. R. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3025; (b) Yadav, J. S.; Reddy, B. V. S.; Sabitha, G.; Reddy, G. S. K. K. *Synthesis* **2000**, 1532; (c) Kumar, H. M. S.; Reddy, B. V. S.; Reddy, E. J.; Yadav, J. S. *Chem. Lett.* **1999**, 857; (d) Yadav, J. S.; Reddy, B. V. S.; Rao, C. V.; Chand, P. K.; Prasad, A. R. *Synlett* **2001**, 1638.
8. *General procedure*: To a stirred solution of the α,β-unsaturated ketone (1 mmol), and iodine (0.2 mmol) in dichloromethane (10 mL), allyltrimethylsilane (1.5 mmol) was added slowly at 0°C and the mixture stirred at rt for the appropriate time (Table 1). After complete conversion as indicated by TLC, the reaction mixture was quenched with water (15 mL) and extracted with dichloromethane (2×15 mL). The combined extracts were washed with a 15% solution of sodium thiosulphate, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting product was purified by column chromatography on silica gel (Merck, 100–200 mesh, ethyl acetate–hexane, 1:9) to afford the pure product.
   Spectral data for selected products: **2e**: ^{1}H NMR ($CDCl_3$) δ: 2.0 (s, 3H), 2.30–2.35 (dd, 2H, $J=5.5$, 7.0, 12.5 Hz), 2.70–2.75 (dd, 2H, $J=6.0$, 12.5 Hz), 3.25–3.30 (m, 1H), 4.97–5.0 (2d, 2H, $J=17.0$, 10.2 Hz), 5.58–5.65 (ddt, 1H, $J=17.0$, 10.2, 7.0 Hz), 7.20–7.35 (m, 5H). ^{13}C NMR ($CDCl_3$, proton decoupled, 50 MHz) δ: 30.7, 40.6, 40.8, 49.5, 116.7, 126.4, 127.5, 128.4, 136.2, 144.1, 207.8. EIMS: m/z: 188 $M^{\bullet+}$ IR (KBr) ν: 3015, 2951, 1705, 1440, 1398, 1108, 963, 770.
   2i: ^{1}H NMR ($CDCl_3$) δ: 1.35–1.40 (m, 1H), 1.60–1.64 (m, 1H), 1.82–2.75 (m, 6H), 2.25–2.41 (m, 3H), 5.05 (2d, 2H, $J=17.8$, 10.7 Hz), 5.75 (ddt, 1H, $J=17.8$, 10.7, 7.0 Hz). ^{13}C NMR ($CDCl_3$, proton decoupled, 50 MHz) δ: 25.0, 30.7, 38.6, 40.7, 41.3, 47.5, 116.7, 135.6, 211.4. EIMS: m/z: 138 $M^{\bullet+}$ IR (KBr) ν: 3025, 2950, 1690, 1443, 1390, 1108, 970, 763.