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An efficient method for allylation of ketones with tetra-allylstannane

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Abstract—A variety of ketones undergo an allylation reaction with tetra-allyltin in the presence of a catalytic amount of $Cu(OTf)_2$ or $Sn(OTf)_2$. The method was found to be superior to most of the known methods, which are efficient only with aldehydes.

The allylation of carbonyl compounds using various allylating reagents is very important in organic synthesis as it gives homoallylic alcohols with the formation of a new carbon–carbon bond.[1] One important application of this reaction is the synthesis of δ-lactones, for example via acylation and Grubb's cyclization.[2] The allylation reaction with tetra-allyltin has been studied mostly for aldehydes[3] but rarely for ketones[4] because of the reactivity difference in these carbonyl groups. Recently, it was reported that a combination of zinc triflate and a base such as 2,6-lutidine and pyridine catalyzed the allylation of ketones.[5] However, zinc triflate alone was ineffective as only a 16% yield was obtained in case of acetophenone. While working on $Cu(OTf)_2$- and $Sn(OTf)_2$-catalyzed reactions,[6] we observed that allylation of acetophenone using tetra-allyltin is efficiently catalyzed by these Lewis acids. Since the reaction did not require any base and it can be extended to the enantioselective version, we explored it further and our results are described in this paper.

In a typical procedure, acetophenone (1 mmol) was treated with tetra-allyltin (1 mmol) in the presence of $Cu(OTf)_2$ (10 mol%) in dry CH_2Cl_2 (5 mL) at rt overnight (10–12 h). The reaction mixture was concentrated and the residue was taken up in EtOAc (10 mL). It was washed with aq $NaHCO_3$, water and brine then dried. Solvent removal and purification over silica gel gave the pure product (72% yield). In a similar fashion, the reaction was attempted in the presence of $Sn(OTf)_2$, which also gave a clean reaction and similar yield. Since the former Lewis acid is cheaper than the latter, it was preferred for other substrates. Dichloromethane was later found to have been a good choice as other solvents such as MeCN, ether, THF, toluene, and DMSO were inferior. It was observed that the addition of a base such as collidine reduced the yield to 5%. The reaction was extended to several ketones with various steric and electronic natures, and results are summarized in Table 1. In most of the cases, we obtained a high yield in the allylation reaction. In the case of 4-*t*-butylcyclohexanone (entry 21), a mixture of axial and equatorial alcohols (79:21) was obtained; the ratio was established by ^{1}H NMR by comparison with a sample prepared by a different method.[7] In the case of (−)-menthone, the selectivity was reversed due to the equatorial nature of the isopropyl group. In order to ascertain how many allyl groups are transferred, 1, 0.5, and 0.25 equiv. of tetra-allyl tin was used in three separate experiments by taking an example of a simple ketone such as cyclododecanone. It was observed that 1 and 0.5 equiv. of the reagent gave the same yield (98%) of the allylated product (entry 23). However, on use of 0.25 equiv. of the tetra-allyltin, only 60% yield of the product was obtained even after 24 h at rt. Similar experiments were carried out with the less reactive ketone 3-trifluoromethyl benzophenone (entry 17), and the yield of allylated product dropped from 91 to 74% when only 0.5 equiv. of the reagent was used in the reaction. The yield dropped further to 60% when 0.25 equiv. of reagent was used in the reaction. Thus, it was concluded that two allyl groups are readily transferred in case of reactive ketones such as cyclododecanone. But, the transfer of second allyl group is slow in the case of less reactive ketone.

In conclusion, we have shown that $Cu(OTf)_2$ is an efficient catalyst for the allylation of ketones. The reac-

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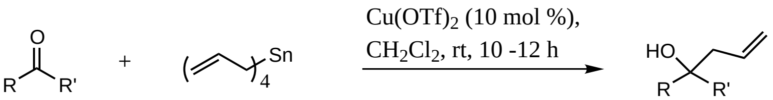
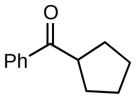
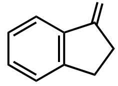
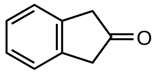
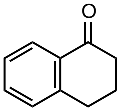
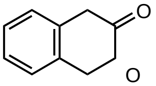
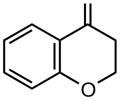
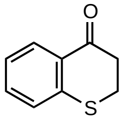
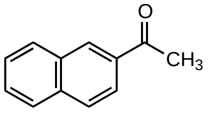
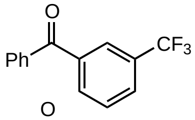
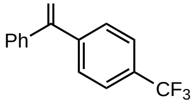
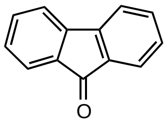
Table 1. Cu(OTf)$_2$-catalyzed allylation of ketones using tetra-allylstannane



S.N.	Substrate	Yield (%)
1.	PhCOCH$_3$	72
2.	PhCOCH$_2$CH$_3$	84
3.	PhCOCH$_2$CH$_2$CH$_3$	82
4.	PhCOCH$_2$Cl	62
5.	PhCOPh	81
6.	*p*-Br-C$_6$H$_4$COCH$_3$	98
7.	*p*-OH-C$_6$H$_4$COCH$_3$	73
8.	p-OMe-C$_6$H$_4$COCH$_3$	85
9.		90
10.		86
11.		93
12.		71
13.		91
14.		98
15.		84
16.		74
17.		91
18.		86
19.		95
20.	Cyclohexanone	82
21.	4-*t*-butyl cyclohexanone	84[a]
22.	Cycloheptanone	88
23.	Cyclododecanone	98
24.	Cyclohexylmethyl ketone	81
25.	(-)-Menthone	80[b]

[a] A mixture of axial and equatorial alcohols in a ratio of 79:21 (^{1}H NMR). [b] A mixture of axial and equatorial alcohols in a ratio of 28:72 (^{1}H NMR).

tion does not require any base as an additive. Further work on the enantioselective version of this reaction is in progress.

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