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A Highly Efficient Addition of Allylic Bromides to Carbonyl Compounds Promoted by Cp_2TiCl_2(cat.)/Zn System

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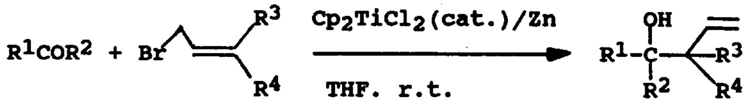
Abstract: Aldehydes or ketones reacted with allylic bromides in the presence of Cp_2TiCl_2(cat.)/Zn system at room temperature to give homoallylic alcohols in high yields.

Allylation of carbonyl compounds is one of the most useful carbon-carbon forming reactions in organic synthesis. Various allylic metal reagents have been exploited extensively.[1] Among them Zn-prompted allylation of carbonyl compounds has been improved by means of various efficient preactivation of Zn[2-4] or powerful solvents.[1] However, these methods need an excess of zinc dust.[5-6] Herein, we wish to report a new efficient and convenient allylation method of aldehydes or ketones with allylic bromides promoted by Cp_2TiCl_2(cat.)/Zn system in THF or diethyl ether with high yield and regioselectivity.



R^3=H, CH_3
R^4=H, CH_3, Ph.

General procedure is as follows: To a solution of carbonyl compound (20 mmol) in THF (A.R.20ml) was added allylic bromide(24mmol), Cp_2TiCl_2 (0.2-0.4 mmol), and zinc dust (10-20mmol). The mixture was stirred at r.t. for 2-5 min, the original red suspension turned to green. After 10 min, the unreacted zinc dust was removed by filtration and the filtrate afforded, after the usual work-up, homoallylic alcohols in excellent yields with good regioselectivity.

As shown in Table, the reaction proceeded smoothly. The reaction of substituted allylic bromides took place exclusively at γ-position of the bromides. We found that allylic chloride did not react in the same conditions. The addition was sluggish or did not react at all without catalyst Cp_2TiCl_2. Chemical outcome of this reaction is quite contrary to $TiCl_4/Zn$ system which gave only the coupling product of carbonyl compounds.

Table. Allylation of aldehydes or ketones in Cp_2TiCl_2(cat.)/Zn system.

Entry	Aldehyde/ketone	Allylic bromide	Time(min.)	Yield(%)[a,b]
1	n-C_3H_7CHO	$CH_2{=}CHCH_2Br$(1a)	3	80
2	i-C_3H_7CHO	1a	3	90
3	PhCHO	1a	5	75
4	p-HO-C_6H_4CHO	1a	5	81
5	Cyclopentanone	1a	5	98
6	Cyclohexanone	1a	5	95
7	$PhCH_2CH_2COCH_3$	1a	5	96
8	$CH_3COCH_2COOC_2H_5$	1a	11	75
9	trans-$CH_3CH{=}CHCHO$	1a	5	75
10	$(CH_3)_2C{=}CHCOCH_3$	1a	6	76
11	n-$C_5H_{11}CHO$	$(CH_3)_2C{=}CHCH_2Br$	5	80
12	Cyclohexanone	trans-$CH_3CH{=}CHCH_2Br$	6	87
13	n-$C_5H_{11}CHO$	trans-$CH_3CH{=}CHCH_2Br$	6	86 (54:46 threo/erythro)[c]
14	n-$C_5H_{11}CHO$	trans-$PhCH{=}CHCH_2Br$	8	85 (58:42 threo/erythro)[c]
15	p-$CH_3C_6H_4CHO$	trans-$CH_3CH{=}CHCH_2Br$	7	78 (67:33 threo/erythro)[c]

(a) Satisfactory IR, ^{1}HNMR, MS and elemental analyses are obtained.

(b) Isolated yield after flash column chromatography or distillation.

(c) Determined by ^{1}HNMR (600MHz).

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