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The allylation reactions of aromatic aldehydes and ketones with tin dichloride in water

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ABSTRACT

The allylation reactions of aromatic aldehydes and ketones were carried out in 31–86% yield using $SnCl_2$–H_2O system under ultrasound irradiation at r.t. for 5 h. The reactions in the same system gave homoallyl alcohols in 21–84% yield with stirring at r.t. for 24 h. Compared with traditional stirring methods, ultrasonic irradiation is more convenient and efficient.

1. Introduction

Carbon–carbon bond formation is the essence of organic synthesis. One of the most powerful methods for constructing carbon–carbon bond is the allylation reaction between an allyl halide and carbonyl compounds [1]. Metals such as tin [2–6], indium [7], samarium [8], gallium [9], ytterbium [10], manganese [11], magnesium [12], zinc [13–18], have been found to be effective for such transformations. However, there were always some troubles due to long reaction time or the critical reduction. Recently, the chemists have been pursuing the simple and efficient synthetic method and searching for safe and harmless reaction solvent. In this area, organic reactions in aqueous media have been attracted considerable interests because water is considered to be a safe and environmentally benign solvent.

Ultrasound has increasingly been used in organic synthesis. Sonochemistry is also becoming more and more important for a variety of synthetic organic reactions as an energy source to generate radicals and initiate the electron-transfer process. Many metal-mediated organic reactions have been accelerated under ultrasound [19]. Ultrasound irradiation can activate the surface of metal and reduce the particle size, and bring about an effective surface modification. Recently, we reported that ultrasonic irradiation can promote the allylation reactions of aromatic aldehydes by using Zn [20], Sn [21], La [22], Nd [23] and Li [24] in aqueous media. This prompted us to study the possibility of the allylation reactions of aromatic aldehydes and ketones using tin dichloride in water under ultrasound irradiation.

A search of the literature revealed that no report has appeared the results of the allylation reactions using tin dichloride under ultrasound irradiation in water to date. Herein, we wish to report the results of the allylation reactions of aromatic aldehydes and ketones by tin dichloride in water with stirring or under ultrasound irradiation, respectively (Scheme 1).

2. Method

2.1. Apparatus and analysis

Liquid substrates were distilled before use. IR spectra were recorded on Bio-Rad FTS-40 spectrometer (KBr). MS spectra were measured on an AEI MS-50 SD90 spectrometer (EI, 70 eV). ^1H NMR spectra were measured on VXR-300S spectrometer (300 MHz) with $CDCl_3$ as solvent and TMS as internal standard. Sonication was performed in a Shanghai SK8200LH ultrasonic cleaner (with a frequency of 40 kHz and a nominal power 500 W; Shanghai Kudos ultrasonic instrument Co., Ltd.). The reaction flask was located at the maximum energy area in the cleaner, the surface of reactants is slightly lower than the level of the water. The reaction temperature was controlled by bath water.

2.2. General procedure

A 50 ml Pyrex flask was charged with the desired aldehyde or ketone (1 mmol), allyl bromide (3 mmol), tin dichloride (0.2 g,

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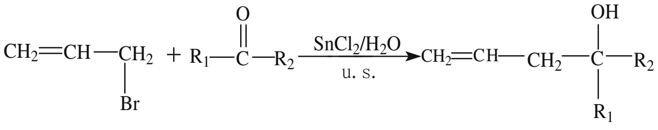

$$CH_2{=}CH{-}\underset{\displaystyle Br}{CH_2} + R_1{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R_2 \xrightarrow[\text{u. s.}]{SnCl_2/H_2O} CH_2{=}CH{-}CH_2{-}\underset{\displaystyle R_1}{\overset{\displaystyle OH}{C}}{-}R_2$$

1 (a-h) **2 (a-h)**

Scheme 1.

1 mmol) and H_2O (4 mL). The mixture was irradiated in the water bath of an ultrasonic cleaner under an air conditions at 25–30 °C for 5 h or stirring 24 h (monitored by TLC). After the completion of the reaction, the resulting suspension was filtered. The filtrate was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution and brine, dried over anhydrous magnesium sulfate for 12 h and filtered. Ethyl acetate was evaporated under reduced pressure to give the crude product, which was separated by column chromatography on silica (200–300 mesh), eluted with petroleum ether or a mixture of petroleum ether and diethyl ether. All the products were confirmed by IR, MS, ^{1}H NMR, spectral data.

2a ^{1}H NMR: δ_H2.40 (t, J = 6.6 Hz, 2H), 2.90–2.98 (br, 1H), 4.58 (t, J = 6.6 Hz, 1H), 5.02–5.05 (m, 1H), 5.04–5.06 (m, 1H), 5.64–5.70 (m, 1H), 7.25–7.68 (m, 5H). MS m/z (%): 148 (M$^+$). IR (KBr) ν: 3405, 1191, 990 cm^{-1}.

2b ^{1}H NMR: δ_H2.41 (t, J = 6.6 Hz, 2H), 3.03–3.10 (br, 1H), 4.57 (t, J = 6.6 Hz, 1H), 5.05–5.08 (m, 1H), 5.10 (m, 1H), 5.68–5.72 (m, 1H), 7.18 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H). MS m/z (%): 182 (M$^+$). IR (KBr) ν: 3406, 1195, 985 cm^{-1}.

2c ^{1}H NMR: δ_H 1.90–2.15 (br, 1H), 2.63 (q, J = 7.1 Hz, 2H), 4.72 (t, J = 7.1 Hz, 1H), 5.15–5.18 (m, 1H), 5.15–5.20 (m, 1H), 5.76–5.82 (m, 1H), 6.28–6.36 (m, J = 3.3 Hz, 1H), 7.26–7.40 (m, J = 3.3 Hz, 1H). MS m/z (%): 138 (M$^+$). IR (KBr) ν: 3401, 1192, 992 cm^{-1}.

2d ^{1}H NMR: δ_H 2.02 (1H, s), 2.40–2.50 (2H, m), 4.32–4.44 (1H, t), 5.14–5.26 (2H, m), 5.78–5.88 (1H, m), 6.60–6.72 (1H, m), 7.18–7.40 (5H, m). MS m/z (%): 174 (M$^+$). IR (KBr) *ν:* 3400, 1642, 988 cm^{-1}.

2e ^{1}H NMR: δ_H 2.40 (t, J=6.4 Hz, 2H), 2.49–2.60 (br, 1H), 4.56 (t, J = 6.4 Hz, 1H), 5.08 (m, 1H), 5.10 (m, 1H), 5.68–5.76 (m, 1H), 5.90 (s, 2H), 6.68–6.74 (m, 2H), 6.80 (s, 1H). MS m/z (%): 192 (M$^+$). IR (KBr) ν: 3420, 1192, 990 cm^{-1}.

2f ^{1}H NMR: δ_H 2.43 (q, J = 6.6 Hz, 2H), 2.79–2.86 (br, 1H), 3.76 (s, 3H), 4.61 (t, J = 6.6, 1H), 5.04–5.09 (m, 1H), 5.08–5.12 (m, 1H), 5.72–5.82 (m, 1H), 6.82 (d, J = 8.8, 2H), 7.21(d, J = 8.8, 2H). MS m/z (%): 178 (M$^+$). IR (KBr) *ν:* 3410, 1191, 991.

2h ^{1}H NMR: δ_H 1.23–1.42 (s, 3H), 1.48–1.73 (s, 1H), 2.26–2.60 (d, 2H), 4.62–5.08 (d, 2H), 5.16–5.69 (m, 1H), 6.86–7.39 (m, 5H). MS m/z (%): 162 (M$^+$). IR (KBr) *ν:* 3430, 1192, 990.

3. Result and discussion

With our optimized the conditions, we screened the reaction of benzaldehyde with allyl bromide in a variety of $SnCl_2$–H_2O reaction system (Table 1). From the result in Table 1, the optimized reaction conditions are: benzaldehyde:allyl bromide:$SnCl_2$ = 1:3:1, time: 5 h.

In order to demonstrate the positive effect of ultrasound irradiation on the reaction, the same reaction in Entries(a–h) (Table 2) also has been researched under stirring.

As shown in Scheme 1 and Table 2, the allylation reaction was carried out under ultrasonic irradiation or stirring giving higher yield. For example, benzaldehyde (**1a**), *p-Cl*-benzaldehyde (**1b**), Cinnamaldehyde (**1d**), Piperonal (**1e**) and *p-CH₃O*-benzaldehyde (**1f**) reacted with allyl bromide in $SnCl_2$–H_2O system giving 86%, 76%, 73%, 79% and 84% yield of the corresponding homoallylic alcohols (**2a**, **2b, 2d, 2e, 2f**) under ultrasonic irradiation for 5 h. Whereas in case with stirring for 24 h, the yield of the corresponding homoallylic alcohols(**2a**, **2b, 2d, 2e, 2f**) was only 84%, 77%, 71%, 77% and 84%, respectively. The data indicates that the reaction time gets reduced remarkably under ultrasound irradiation condition. In order to expose the effects of carbonyl group of ketone, we choose benzophenone (**1g**) and acetophenone (**1h**) as substrates. It is found that there were no products with benzophenone as substrate. While acetophenone as substrate the corresponding products were obtained only in 31% and 21% yield under ultrasound irradiation or stirring respectively. We can infer that the steric hindrance around the carbonyl group may inhibit the allylation reactions.

Table 1
Optimization of the allylation reaction of C_6H_5CHO mediated by $SnCl_2$ in water under ultrasonic irradiation with various conditions.

Entry	Reaction system	Time/h	Isolated yield/%
1	benzaldehyde:allyl bromide:$SnCl_2$ = 1:1:1	1	38
2	benzaldehyde:allyl bromide:$SnCl_2$ = 1:1:1	2	45
3	benzaldehyde:allyl bromide:$SnCl_2$ = 1:1:1	3	60
4	benzaldehyde:allyl bromide:$SnCl_2$ = 1:1:1	4	72
5	benzaldehyde:allyl bromide:$SnCl_2$ = 1:1:1	5	76
6	benzaldehyde:allyl bromide:$SnCl_2$ = 1:1:1	6	77
7	benzaldehyde:allyl bromide:$SnCl_2$ = 1:1:1	5	75
8	benzaldehyde:allyl bromide:$SnCl_2$ = 1:2:1	5	80
9	benzaldehyde:allyl bromide:$SnCl_2$ = 1:3:1	5	86
10	benzaldehyde:allyl bromide:$SnCl_2$ = 1:4:1	5	85
11	benzaldehyde:allyl bromide:$SnCl_2$ = 1:3:1	5	86
12	benzaldehyde:allyl bromide:$SnCl_2$ = 1:3:2	5	85

Isolated yield based on the substrate; H_2O: 4 ml; Ultrasound irradiation: 40 kHZ.

Table 2
The allylation reactions of aromatic aldehydes and ketones mediated in $SnCl_2$–H_2O system under ultrasound irradiation or stirring.

Entry	Substrate	Isolated yield (%)	
		Stirring (24 h)	Ultrasound (5 h)
1a	C_6H_5CHO	84	86
1b	$4\text{-}ClC_6H_4CHO$	77	76
1c	furfural	58	59
1d	cinnamaldehyde	71	73
1e	$3,4\text{-}(OCH_2O)C_6H_3CHO$	77	79
1f	$4\text{-}CH_3OC_6H_4CHO$	84	84
1g	$C_6H_5COC_6H_5$	–	–
1h	$C_6H_5COCH_3$	21	31

Ultrasound irradiation time for 5 h and stirring for 24 h.

4. Conclusion

Based on those results, we demonstrated that ultrasound irradiation can speed up markedly the allylation reaction of aromatic aldehydes and ketones with $SnCl_2$–H_2O system. Compared with traditional stirring methods, ultrasonic irradiation is more convenient and efficient. More importantly, the allylation reaction was carried out in water, so the environmental concerns were improved.

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