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Allylation Reactions of Aromatic Aldehydes with Antimony in Aqueous Media Under Ultrasonic Irradiation

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Abstract: The allylation reactions of aromatic aldehydes with allyl bromide were carried out in 89–98% yield with Sb-H_2O-KF-CH_3OH under ultrasound irradiation at rt for 2.5 h. The reactions in the same system gave allylic alcohols in 30–69% yield with stirring for 24 h. The main advantages of the present procedure are shorter reaction time, better yield, and environmental friendliness.

Keywords: Allylation, antimony, ultrasound irradiation

Carbon–carbon bond formation is the essence of organic synthesis. One of the most powerful methods for constructing carbon–carbon bonds is the allylation reaction between an allyl halide and carbonyl compounds.[1] Metals such as tin,[2–6] indium,[7] samarium,[8] gallium,[9] yetterbium,[10] manganese,[11] magnesium,[12] and zinc,[13–18] have been found to be effective for such transformations. However, there were always some troubles because of long reaction time or critical reduction.

Ultrasound has been increasingly used in organic synthesis. Many metal-mediated organic reactions have been accelerated with ultrasound.[19–23] A search of the literature revealed that no report has appeared on the results of allylation reactions using antimony under

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Table 1. Optimization of the allylation reaction of C_6H_5CHO mediated by Sb in aqueous media under ultrasonic irradiation with various conditions

Entry	Reaction system	CH_3OH (mL)	Time (h)	Isolated yield (%)
1	Benzaldehyde/allyl bromide/Sb = 1:2.5:5	2	1	43
2	Benzaldehyde/allyl bromide/Sb = 1:2.5:5	2	1.5	62
3	Benzaldehyde/allyl bromide/Sb = 1:2.5:5	2	2	86
4	Benzaldehyde/allyl bromide/Sb = 1:2.5:5	2	2.5	93
5	Benzaldehyde/allyl bromide/Sb = 1:2.5:5	2	3	93
6	Benzaldehyde/allyl bromide/Sb = 1:2.5:5	1	2.5	81
7	Benzaldehyde/allyl bromide/Sb = 1:2.5:5	2	2.5	93
8	Benzaldehyde/allyl bromide/Sb = 1:2.5:5	3	2.5	93

Notes. Isolated yield based on the substrate. KF (aqueous): 4 mL. Ultrasound irradiation: 40 KHz. Temperature: rt.

ultrasound irradiation to date. Herein, we report the results of the allylation reactions of aromatic aldehydes by antimony (Sb) with stirring or ultrasound irradiation.

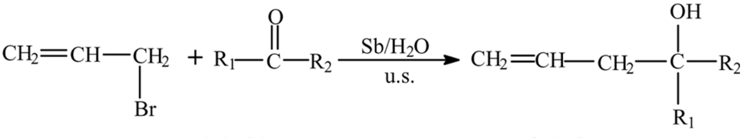
To optimize the conditions, we screened the reaction of benzaldehyde with allyl bromide in a variety of Sb-H_2O-KF-CH_3OH reaction systems (Table 1). From the results in Table 1, the optimized reaction conditions are benzaldehyde/allyl bromide/Sb 1:2.5:5 and time of 2.5 h. To demonstrate the positive effect of ultrasound irradiation on the reaction, the same reaction in entries a–f, Table 2 also has been researched using stirring.

Table 2. Allylation reactions of aromatic aldehydes using Sb-H_2O-KF-CH_3OH system under ultrasound irradiation or stirring

Entry	Substrate	Isolated yield (%)		R_f[a]
		Stirring (24 h)	Ultrasound (2.5 h)	
1a	C_6H_5CHO	60	93	0.61
1b	4-ClC_6H_4CHO	66	89	0.59
1c	Furfural	30	97	0.52
1d	Cinnamaldehyde	61	98	0.68
1e	3,4-$(OCH_2O)C_6H_3CHO$	69	94	0.53
1f	4-$CH_3OC_6H_4CHO$	65	96	0.50
1g	$C_6H_5COC_6H_5$	—	—	—
1h	$C_6H_5COCH_3$	—	—	—

Notes. Isolated yield based on the substrate. Ultrasound irradiation time: 2.5 h. Stirring time: 24 h.

[a] Eluent: petroleum ether/diethyl ether (v/v) = 1:1.

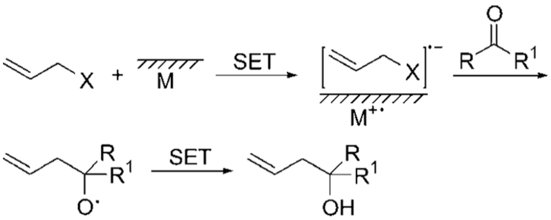


1 (a-h) **2 (a-h)**

Scheme 1.

As shown in Table 2, the allylation reaction was carried out under ultrasonic irradiation, giving great yield. For example, benzaldehyde (**1a**), 4-ClC_6H_4CHO (**1b**), furfural (**1c**), cinnamaldehyde (**1d**), piperonal (**1e**), and 4-$CH_3OC_6H_4CHO$ (**1f**) reacted with allyl bromide in a Sb-H_2O-KF-CH_3OH system to give a nearly quantitative yield of the corresponding homoallylic alcohols (**2a, 2b, 2c, 2d, 2e, 2f**) under ultrasonic irradiation for 2.5 h, whereas with stirring for 24 h, the yields of the corresponding homoallylic alcohols were only 60, 66, 30, 61, 69, and 65% respectively. The data indicate that the reaction time is reduced and yields improved under ultrasound irradiation. To expose the effects of the carbonyl group of ketone, we choose benzophenone (**1g**) and acetophenone (**1h**) as substrates. It is found that no the corresponding products were obtained under ultrasound irradiation or stirring, respectively. We can infer that the steric hindrance around the carbonyl group may inhibit the allylation reactions.

It was reported that the allylation reaction proceeded via a single electron-transfer mechanism[24] (Scheme 2). In the present process, homoallylic alcohols were be obtained by forming an allyl radical anion, which nucleophilically attacks a carbonyl group, leading to homoallylic radical formation while proceeding via a single electron-transfer. This can be protonated by H^+ to give homoallylic alcohols as the product. Accordingly, sonication promotes generation of the radicals and initiates the electron-transfer process. Ultrasound irradiation favors the reaction



Scheme 2.

via single electron-transfer mechanism. Aromatic aldehydes exhibited greater reactivity than aromatic ketones; perhaps the steric hinderance around the carbonyl group of aromatic ketones inhibits the addition reaction.

Based on these results, we demonstrated that ultrasound irradiation can speed up markedly the allylation reaction of aromatic aldehydes with the Sb-H_2O-KF-CH_3OH system. The main advantages of the present procedure are the greater yield and the shorter reaction time. This new approach shows considerable practical value because of its efficiency and simplicity.

EXPERIMENTAL

Liquid substrates were distilled before use. Infrared (IR) spectra were recorded on a Bio-Rad FTS-40 spectrometer (KBr). Mass spectra (MS) were determined on an AEI MS-50 SD90 spectrometer (EI, 70 eV). ^1H NMR spectra were measured on a VXR-300S spectrometer (300 MHz) by using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Sonication was performed in a Shanghai SK8200LH ultrasonic cleaner (with a frequency of 40 kHz and a nominal power of 500 W; Shanghai Kudos Ultrasonic Instrument Co., Ltd.). The reaction flask was located at the maximum energy area in the cleaner, where the surface of reactants is slightly less than the level of the water. (Observation of the surface of the reaction solution during vertical adjustment of vessel depth showed the optimum position by the point at which maximum surface disturbance occurred.) The reaction temperature was controlled by addition or removal of water from the ultrasonic bath. The calorimetric transfer efficiency of ultrasonic bath is 1.26. (The calorimetric power measurements were carried out as the literature.[26]

A 50-ml Pyrex flask was charged with the desired aldehyde (1 mmol), allyl bromide (2.5 mmol), antimony (5 mmol), KF (aqueous) (4 mL), and CH_3OH (2 mL). The mixture was irradiated in the water bath of an ultrasonic cleaner under air conditions at 25–30°C for 2.5 h (or stirring for 24 h). After the completion of the reaction, the resulting suspension was filtered to remove the Sb. The filtrate was extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution and brine, then dried over anhydrous magnesium sulfate for 12 h. Ethyl acetate was evaporated under reduced pressure to give the crude product, which was separated by column chromatography on silica (200–300 mesh) and eluted with a mixture of petroleum ether and diethyl ether. All the products were confirmed their IR, MS, ^1H NMR, and spectral data.

Data

Compound **2a**[25]

Oil; ^{1}H NMR: δ_H 2.40 (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}.

Compound **2b**[25]

Oil; ^{1}H NMR: δ_H 2.41 (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}.

Compound **2c**[25]

Oil; ^{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}.

Compound **2d**[25]

Oil; ^{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}.

Compound **2e**[25]

Oil; ^{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}.

Compound **2f**[25]

Oil; ^{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.

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